PLASTICS DESIGN LIBRARY (PDL)
PDL HANDBOOK SERIES
Series Editor: Sina Ebnesajjad, PhD (sina@FluoroConsultants.com)
President, FluoroConsultants Group, LLC
Chadds Ford, PA, USA
www.FluoroConsultants.com

The **PDL Handbook Series** is aimed at a wide range of engineers and other professionals working in the plastics industry, and related sectors using plastics and adhesives.

PDL is a series of data books, reference works and practical guides covering plastics engineering, applications, processing, and manufacturing, and applied aspects of polymer science, elastomers and adhesives.

Recent titles in the series

Biopolymers: Processing and Products, Michael Niaounakis (ISBN: 9780323266987)
Biopolymers: Reuse, Recycling, and Disposal, Michael Niaounakis (ISBN: 9781455731459)
Carbon Nanotube Reinforced Composites, Marcio Loos (ISBN: 9781455731954)
Extrusion, 2e, John Wagner & Eldridge Mount (ISBN: 9781437734812)
Fluoroplastics, Volume 1, 2e, Sina Ebnesajjad (ISBN: 9781455731992)
Handbook of Biopolymers and Biodegradable Plastics, Sina Ebnesajjad (ISBN: 9781455728343)
Handbook of Molded Part Shrinkage and Warpage, Jerry Fischer (ISBN: 9781455725977)
Handbook of Polymer Applications in Medicine and Medical Devices, Kayvon Modjarrad & Sina Ebnesajjad (ISBN: 9780323228053)
Handbook of Thermoplastic Elastomers, Jiri G Drobny (ISBN: 9780323221368)
Handbook of Thermoset Plastics, 2e, Hanna Dodiuk & Sidney Goodman (ISBN: 9781455731077)
High Performance Polymers, 2e, Johannes Karl Fink (ISBN: 9780323312226)
Introduction to Fluoropolymers, Sina Ebnesajjad (ISBN: 9781455774425)
Ionizing Radiation and Polymers, Jiri G Drobny (ISBN: 9781455778812)
Manufacturing Flexible Packaging, Thomas Dunn (ISBN: 9780323264365)
Plastic Films in Food Packaging, Sina Ebnesajjad (ISBN: 9781455731121)
Plastics in Medical Devices, 2e, Vinny Sastri (ISBN: 9781455732012)
Polylactic Acid, Rahmat et al. (ISBN: 9781437744590)
Polyvinyl Fluoride, Sina Ebnesajjad (ISBN: 9781455778850)
Reactive Polymers, 2e, Johannes Karl Fink (ISBN: 9781455731497)
The Effect of Creep and Other Time Related Factors on Plastics and Elastomers, 3e, Laurence McKeen (ISBN: 9780323353137)
The Effect of Long Term Thermal Exposure on Plastics and Elastomers, Laurence McKeen (ISBN: 9780323221085)
The Effect of Sterilization on Plastics and Elastomers, 3e, Laurence McKeen (ISBN: 9781455725984)
The Effect of Temperature and Other Factors on Plastics and Elastomers, 3e, Laurence McKeen (ISBN: 9780323310161)
The Effect of UV Light and Weather on Plastics and Elastomers, 3e, Laurence McKeen (ISBN: 9781455728510)
Thermoforming of Single and Multilayer Laminates, Ali Ashter (ISBN: 9781455731725)
Thermoplastics and Thermoplastic Composites, 2e, Michel Biron (ISBN: 9781455778980)
Thermosets and Composites, 2e, Michel Biron (ISBN: 9781455731244)

To submit a new book proposal for the series, or place an order, please contact David Jackson, Acquisitions Editor
david.jackson@elsevier.com
or
Sina Ebnesajjad, Series Editor sina@fluoroconsultants.com

Biopolymers: Processing and Products

Michael Niaounakis

AMSTERDAM • BOSTON • HEIDELBERG • LONDON • NEW YORK • OXFORD • PARIS
SAN DIEGO • SAN FRANCISCO • SINGAPORE • SYDNEY • TOKYO

William Andrew is an imprint of Elsevier

William Andrew is an imprint of Elsevier
The Boulevard, Langford Lane, Kidlington, Oxford, OX5 1GB, UK
225 Wyman Street, Waltham, MA 02451, USA

Copyright © 2015 Elsevier Inc. All rights reserved.

No part of this publication may be reproduced or transmitted in any form or by any means, electronic or mechanical, including photocopying, recording, or any information storage and retrieval system, without permission in writing from the publisher. Details on how to seek permission, further information about the Publisher's permissions policies and our arrangement with organizations such as the Copyright Clearance Center and the Copyright Licensing Agency, can be found at our website: www.elsevier.com/permissions

This book and the individual contributions contained in it are protected under copyright by the Publisher (other than as may be noted herein).

Notices

Knowledge and best practice in this field are constantly changing. As new research and experience broaden our understanding, changes in research methods, professional practices, or medical treatment may become necessary.

Practitioners and researchers must always rely on their own experience and knowledge in evaluating and using any information, methods, compounds, or experiments described herein. In using such information or methods they should be mindful of their own safety and the safety of others, including parties for whom they have a professional responsibility.

To the fullest extent of the law, neither the Publisher nor the authors, contributors, or editors, assume any liability for any injury and/or damage to persons or property as a matter of products liability, negligence or otherwise, or from any use or operation of any methods, products, instructions, or ideas contained in the material herein.

Statement

The views and opinions expressed in this book are those of the author and do not represent the views of the European Patent Office (EPO).

ISBN: 978-0-323-26698-7

British Library Cataloguing in Publication Data
A catalogue record for this book is available from the British Library

Library of Congress Cataloging in Publication Data
A catalog record for this book is available from the Library of Congress

For information on all William Andrew publications
visit our website at http://store.elsevier.com/

Typeset by TNQ Books and Journals
www.tnq.co.in

Printed in the United States of America

ELSEVIER
Book Aid International
Working together
to grow libraries in
developing countries

www.elsevier.com • www.bookaid.org

Foreword

The present book forms the second part of a trilogy dedicated to biopolymers. The book "Biopolymers: Reuse, Recycling and Disposal" formed the first part, and the book "Applications and Trends"—to appear in spring 2015—will form the third part. All three books cover every aspect of biopolymers, from feedstocks for the production of biopolymers to the disposal and/or recycling.

In the present study the term "biopolymers" is interpreted as including both polymers derived from renewable resources (bio-based), which are either biodegradable or nonbiodegradable, and polymers derived from fossil fuel resources, which are biodegradable. Biopolymers can be produced by biological systems such as microorganisms, plants, or animals, or obtained by chemical synthesis.

Emphasis is given to patents, which despite their industrial and economical importance are still underrepresented in scientific literature. Although a substantial number of patents has been cited and critically commented, the book does not pretend to cover the whole range of available patents. Undoubtedly, important patents were left out, but taken into account the extent of the coverage, this was unavoidable. In any case, a genuine effort was made to cover the most represented patents in each technical field.

The patents were retrieved from the patent server "espacenet" (www.espacenet.com) of the European Patent Office (EPO). EPO's worldwide collection of published patent applications contains not only patents from the major patent offices (EPO, WIPO, USA, JPO), but also patents from over 90 national offices. This server has certain advantages compared to other free patent servers, as it covers not only patents in English, but also patents in German and French. In addition, espacenet contains bibliographic data and abstracts of all Japanese, Korean, Chinese and Russian patents, as well as patents in several other languages, and provides machine translations of most of these patents. It is firmly believed that the appeal of the book will increase by the retrieval and analysis of patent information in so many languages.

The book consists of 16 chapters. The first 2 chapters provide basic information on biopolymers, while the remaining 14 chapters are focusing on processing and products. Few parts of the present book, and especially Chapter 1: Introduction, and Chapter 16: Recycling, are coming inevitably from the previous book, "Biopolymers: Disposal, Reuse and Recycling," Elsevier, 2006, albeit in an extended and updated form.

Chapter 1, introduction, constitutes of three parts. The first part presents and compares the various terms used to describe biopolymers, namely "degradable," "biodegradable," "bio-based," "compostable," and "biopolymer," which appear to have multiple and overlapping meanings. The second part gives an extensive introduction to most of the existing and newly developed biopolymers and provides updated lists of their commercial products and current applications. The third part investigates the possible sources of biopolymers, including first, second, and third generation feedstocks.

Chapter 2 presents the main properties of biopolymers and constitutes of three parts. The first part relates to intrinsic properties, which refer to the polymer itself. The second part relates to processing properties, which refer to the behavior of the polymer during forming. The third part relates to product properties, which refer to the properties of the polymer as an entity. Among the intrinsic properties are: density, transition temperatures and crystallinity, solubility, gas barrier properties, transparency, and electromagnetic properties. Among the product properties are: mechanical behavior, heat resistance, water resistance, antistatic properties, aesthetic properties, and environmental behavior of biopolymers. The chapter contains several comparative tables, tables of selected properties, and schemes of (bio) degradation mechanisms.

Chapter 3 relates to blending of biopolymers with other polymers, and constitutes mainly of two parts. The first part examines blends of biopolymers with other biopolymers. The second part examines blends of biopolymers with synthetic nonbiodegradable polymers, where the biopolymers are either in majority or minority. The chapter is accompanied by several tables that summarize a large number of blend formulations of biopolymers and their miscibilities with other (bio)polymers.

Chapter 4 relates to emulsions, dispersions, solutions, and gels of biopolymers made by other methods than by emulsion, suspension, or solution polymerization. The various techniques described in the prior art for the preparation of polymer emulsions, dispersions and lattices are divided roughly into three main groups: solvent-based, thermomechanical, and solvent-free destructuring methods. The solvent-based methods in turn include the emulsification–evaporation, (nano)precipitation, salting, and emulsification-diffusion techniques.

Chapter 5 investigates the various techniques employed for the compounding of biopolymers with additives categorized in two main groups: (1) compounding by shear and heat, and (2) compounding in liquid or solution. In both groups the additives are added to the biopolymer as powders, dispersions, solutions or masterbatches. A separate section reviews the various types of additives and modifiers which are used to protect the biopolymers during processing and/or service life, including also some other additives which can accelerate the degradation of the biopolymer after disposal. The chapter is accompanied by several tables summarizing representative compounding techniques and formulations of biopolymers, as well as lists of selected additives in biopolymer systems.

Chapter 6 relates to methods of preparing particles from preformed biopolymers and constitutes of six parts: (1) pelletization (e.g., by melt kneading), (2) pulverization (e.g., by mechanical crushing, grinding, or shredding), (3) dissolution–deposition, (4) emulsion-precipitation, (5) coagulation and (6) supercritical fluid technology.

Chapter 7 relates to chemical treatment or chemical modification of biopolymers, and constitutes of four parts. The first part examines the various techniques of introducing functional groups in a polymer chain and includes the cases of: (1) incorporation of functional monomers during the polymerization process; (2) modification of the terminal groups; and (3) grafting/block copolymerization. The second part examines the techniques for modifying the molecular weight of a biopolymer by either controlled degradation or increase of the molecular weight through coupling. The third part relates to radiation treatment of biopolymers in the bulk, which is distinguished from the radiation on the surface of biopolymers of Chapter 8. The fourth part relates to the various techniques of crosslinking including the special case of interpenetrating network (IPN).

Chapter 8 examines the various techniques of altering the surface nature of biopolymers categorized into three groups: (1) physical treatment, (2) chemical treatment, and (3) coating or printing, which can include a pretreatment step by any of the techniques of (1) and (2). The physical methods (1) include (a) treatment with solvents/swelling agents, (b) roughening (e.g., mechanical abrasion) and (c) heat treatment (e.g., annealing). The chemical methods (2) used to modify the surface properties of biopolymers are divided in the following subgroups: (a) hydrolysis/aminolysis/solvolysis; (b) incorporation of functional groups by chemical means, flame treatment, radiation, plasma, corona treatment, or any method that can introduce functional groups to the surface of the biopolymer; and (c) grafting of polymerizable monomers or preformed polymers. Coating or printing (3) includes single coating and multiple coatings, coating with inorganic or low molecular weight organic compounds, and coating with polymer(s).

Chapter 9 relates to foams and constitutes of five parts. The first part examines foams made of various types of biopolymers, namely polyesters and starch. The second part examines physical and chemical foaming agents, as well as compounding ingredients. The third part examines expandable particles. The fourth part examines composite foams and crosslinking; and the fifth part examines the after treatment of foams including heat treatment and coating.

Chapter 10 relates to films and constitutes of two parts. The first part examines free standing films made of various types of biopolymers. Two special types of films are the shrinkable films and the porous films. The second part examines laminates that are multilayered structures composed at least in part of biopolymers.

Chapter 11 relates to fibers made of biopolymers and constitutes of three parts. The first part examines fibers made of various types of biopolymers. The second part examines fiber structures, namely nonwoven webs including carpets and woven/knitted fabrics. The third part examines selected properties of fibers made of biopolymers including wearing resistance and antistatic properties. A separate section is dedicated to nanofibers.

Chapter 12 relates to biocomposites and constitutes of two parts. The first part examines the various types of biocomposites including biopolymers reinforced with inorganic or organic fillers in the form of loose or coherent particles or fibers. A special category of biocomposites is the nanobiocomposites that are biopolymers reinforced with nanofillers and/or nanofibers. Another category is the prepregs that are fiber structures that have been impregnated with resins prior to curing the composition. The second part examines the various techniques of bonding a preformed biopolymer to the same or other solid material by means of adhesives, heat and surface treatment.

Chapter 13 relates to coating compositions based on biopolymers applied to any type of substrates. The chapter is distinguished from the coating compositions of Chapter 8: Surface treatment, wherein any type of material, including biopolymers, is applied to a biopolymer substrate. The chapter constitutes of two parts. The first part examines coating compositions made of various types of biopolymers. The second part examines powder coatings and temporary or strippable coatings. The various types of biopolymer-based coating compositions are summarized in a comprehensive table.

Chapter 14 relates to inks made of biopolymers. Various types of inks are examined including jet printing inks such as hot melt inks, flexographic inks, gravure inks, screen inks, electrophotographic toners, color changing inks, and writing inks.

Chapter 15 relates to adhesives made of biopolymers and constitutes of two parts. The first part examines nonreactive adhesives including drying adhesives, water-based adhesives, solvent-based adhesives, pressure-sensitive adhesives, and hot melt adhesives. The second part relates to reactive adhesives including one-component reactive adhesives and multicomponent reactive adhesives.

Chapter 16 relates to the recycling of biopolymers and constitutes of three parts. The first part examines all the possible ways of reusing discarded biopolymers. The second part examines the various methods for the physical or mechanical recycling of biopolymers including techniques for identifying and sorting materials by polymer type. A separate section reviews the various marker systems including the Resin Identification Codes (RIC) and fluorescent additives. A distinction is made between reuse and physical or mechanical recycling. The third part examines the various methods for the chemical recycling of biopolymers including hydrolysis/alcoholysis, dry heat depolymerization, hydrothermal depolymerization, and enzymatic depolymerization.

I wish to thank Dr Sina Ebnesajjad, Series Editor of Plastics Design Library (PDL), published by Elsevier, for giving me the opportunity to author this book. I am also greatly indebted to David Jackson, Acquisitions Editor at Elsevier, and Peter Gane, Editorial Project Manager at Elsevier, for their continuous guidance and support during the writing of this book.

Michael Niaounakis
May 2014, Rijswijk

Abbreviations of Biopolymers

γ-PGA	poly(γ-glutamic acid)
ε-PL	poly(ε-lysine)
CA	cellulose acetate
CAB	cellulose acetate butyrate
CAP	cellulose acetate propionate
CMC	carboxymethylcellulose
CN	cellulose nitrate
HEC	hydroxyethylcellulose
P2HB	poly(2-hydroxybutyrate)
P3DD	poly(3-hydroxydodecanoate)
P3HB	poly(3-hydroxybutyrate) (or PHB or β-PHB)
P3HB4HB	poly(3-hydroxybutyrate-*co*-4-hydroxybutyrate)
P3HBHHx	poly(3-hydroxybutyrate-*co*-3-hydroxyhexanoate) or poly(hydroxybutyrate-*co*-hydroxyhexanoate)
P3HD	poly(3-hydroxydecanoate) (or PHD)
P3HN	poly(3-hydroxynonanoate) (or PHN)
P3HO	poly(3-hydroxyoctanoate)
P3HP	poly(3-hydroxypropionate)
P3HV	poly(3-hydroxyvalerate)
P3UD	poly(3-hydroxyundecanoate)
P4HB	poly(4-hydroxybutyrate)
P4HB2HB	poly(4-hydroxybutyrate-*co*-2-hydroxybutyrate)
P4HP	poly(4-hydroxypropionate)
P4HV	poly(4-hydroxyvalerate)
P5HB	poly(5-hydroxybutyrate)
P5HV	poly(5-hydroxyvalerate)
P6HH	poly(6-hydroxyhexanoate)
PA 1010	polyamide 1010
PA 1012	polyamide 1012
PA 11	polyamide 11
PA 410	polyamide 410
PA 610	polyamide 610
PAA	poly(alkylene alkanoate)
PADC	poly(alkylene dicarboxylate)
PBA	poly(butylene adipate)
PBAT	poly(butylene adipate-*co*-terephthalate)
PBT	poly(butylene carbonate)
PBP	poly(butylene pimelate)
PBS	poly(butylene succinate); see also poly(tetramethylene succinate) (PTMS); (different CAS)
PBSA	poly(butylene succinate-*co*-adipate)
PBSC	poly(butylene succinate-*co*-carbonate)
PBSE	poly(butylene sebacate)
PBSeT	poly(butylene sebacate-*co*-terephthalate)
PBSL	poly(butylene succinate-*co*-lactate)
PBST	poly(butylene succinate-*co*-terephthalate)
PCHC	poly(cyclohexene carbonate)
PCL	poly(ε-caprolactone)
PDLA	poly(D-lactide), poly(D-lactic acid)
PDLLA	poly(D-lactic-*co*-L-lactic acid) or poly(D,L-lactide) or poly(D,L-lactic acid)
PDLGA	poly(D,L-lactide-*co*-glycolide), poly(D,L-lactic-*co*-glycolic acid)
PDO	polydioxanone (or PDS)
PE	polyethylene (bio-based)
PEA	poly(ethylene adipate)
PEAM	poly(ester amide)
PEAz	poly(ethylene azelate)
PEC	poly(ethylene carbonate)
PEDe	poly(ethylene decamethylate)
PEF	poly(ethylene furanoate)
PEOx	poly(ethylene oxalate)
PES	poly(ethylene succinate)
PESA	poly(ethylene succinate-*co*-adipate)
PESE	poly(ethylene sebacate)
PEST	poly(ethylene succinate-*co*-terephthalate)
PESu	poly(ethylene suberate)
PET	poly(ethylene terephthalate) (bio-based)
PEUU	poly(ester urethane urea) (biodegradable)
PGA	polyglycolide, poly(glycolic acid)
PGCL	poly(glycolide-*co*-caprolactone)
PHA	polyhydroxyalkanoate
PHBHD	poly(3-hydroxybutryrate-*co*-3-hydroxydecanoate)
PHBHP	poly(3-hydroxybutyrate-*co*-3-hydroxypropionate)
PHBO	poly(3-hydroxybutyrate-*co*-3-hydroxyoctanoate)
PHBHV	poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate)
PHD	polyhydroxydecanoate (or P3HD)
PHHp	poly(3-hydroxyheptanoate)
PHHx	poly(3-hydroxyhexanoate) or poly(3-hydroxycaproate)
PHN	polyhydroxynonanoate (or P3HN)
PHP	poly(3-hydroxypropionate) (or P3HP)
PHSE	poly(hexamethylene sebacate)
PLA	polylactide, poly(lactic acid)
PLCL	poly(lactide-*co*-caprolactone)
PLGA	poly(lactide-*co*-glycolide)
PLLA	poly(L-lactide), poly(L-lactic acid)
PLLCL	poly(L-lactide-*co*-ε-caprolactone)
PLLGA	poly(L-lactide-*co*-glycolide)
PM	polymandelide
PMLA	Poly(β-malic acid)
POE I	poly(ortho ester) I
POE II	poly(ortho ester) II
POE III	poly(ortho ester) IIII

POE IV	poly(ortho ester) IV
PPA	polyphthalamide
PPHOS	polyphosphazene
PPF	poly(propylene fumarate)
PPL	poly(β-propiolactone) (or β-PPL)
PPS	poly(propylene succinate)
PPT	poly(propylene terephthalate) (bio-based); see also PTT
PTeMAT	poly(tetramethylene adipate-*co*-terephthalate)
PTeMC	poly(tetramethylene carbonate)
PTMC	poly(trimethylene carbonate)
PTMS/PTeMC	poly[(tetramethylene succinate)-*co*-(tetramethylene carbonate)]
PTMA	poly(trimethylene adipate)
PTMAT	poly(methylene adipate-*co*-terephthalate)
PTeMA	poly(tetramethylene adipate)
PTMG	poly(tetramethyl glycolide)
PTeMS	poly(tetramethylene succinate); see also poly(butylene succinate) (PBS) (different CAS)
PTT	poly(trimethylene terephthalate) (bio-based); see also PPT
PU	polyurethane (bio-based)
PVOH	poly(vinyl alcohol)
scPLA	stereocomplex PLA
TPS	thermoplastic starch

Chapter 1

Introduction

1.1 DEFINITION OF TERMS

In recent years, interest in protecting the environment by not only using products made from natural renewable resources but also products that decompose into environmentally friendly constituents has been steadily and rapidly increasing. Green movements, initiatives, and regulations have sprung up in almost every developed country to reduce the volume of solid polymers waste generated by consumers each year. Consumers have also expressed their desire for products that are environmentally friendly while providing the same results with products made from synthetic materials. However, consumer preferences for environmentally friendly products can be hindered by the higher cost and inferior properties of these products as compared to synthetically derived products.

In literature and patents there is no consensus over the exact definition of the generic terms *degradable*, *biodegradable*, *bio-based*, *compostable*, and *biopolymer*, which appear to have multiple and overlapping meanings.

Degradable is a broad term applied to polymers or plastics that disintegrate by a number of processes, including physical disintegration, chemical degradation, and biodegradation by biological mechanisms. As a result of this definition, a polymer may be degradable but not biodegradable.

Biodegradable is a term focused on the functionality of a polymer, "biodegradability," and it is applied to polymers that will degrade under the action of microorganisms such as molds, fungi, and bacteria within a specific period of time and environment. On its own, the term biodegradable has no clear meaning and creates confusion. According to the withdrawn standard ASTM D5488-94de1, biodegradable polymers refer to polymers that are "capable of undergoing decomposition into carbon dioxide, methane, water, inorganic compounds, or biomass in which the predominant mechanism is the enzymatic action of microorganisms that can be measured by standard tests, over a specific period of time, reflecting available disposal conditions."

The Japan Bioplastics Association (JBPA) defines the term *biodegradability* as the characteristics of material that can be microbiologically degraded to the final products of carbon dioxide and water, which, in turn, are recycled in nature. Biodegradation should be distinguished from disintegration, which simply means the material is broken into small and separate pieces. Biodegradability of plastics is determined by the International Organization for Standardization (ISO) methods and evaluated based upon the preestablished criteria. Only biodegradable plastics that meet the rigorous criteria such as contents of heavy metals and safe intermediate reaction products may be classified as GreenPla® [1].

Biodegradable polymers are certified according to any of the following legally binding international standards [2]:

ISO 17088:2012
EN 13432:2000, EN 14995:2006
ASTM D6400-12

Bio-based is a term focused on the raw materials basis, and it is applied to polymers derived from renewable resources. Raw materials are defined as renewable if they are replenished by natural procedures at rates comparable or faster than their rate of consumption [3].

Bio-based products as defined by the Farm Security and Rural Investment Act of 2002 (FSRIA) [4] are products determined by the U.S. Secretary of Agriculture to be "commercial or industrial goods—other than food or feed—composed in whole or in significant part of biological products, forestry materials or renewable domestic agricultural materials, including plant, animal or marine materials" [5]. ASTM defines a bio-based material as "an organic material in which carbon is derived from a renewable resource via biological processes. Bio-based materials include all plant and animal mass derived from carbon dioxide (CO_2) recently fixed via photosynthesis, per definition of a renewable resource." In practical terms, a bio-based polymer is not per se a sustainable polymer; this depends on a variety of issues, including the source material, production process, and how the material is managed at the end of its useful life. Not every bio-based polymer is biodegradable, e.g., bio-based polyethylene or polyamide 11; and not every biodegradable polymer is bio-based, e.g., poly(ε-caprolactone) or poly(glycolic acid); although some fall into both categories, such as polyhydroxyalkanoates (PHA)s.

Currently, there are no standards on what can be called "bio-based product." However, there are objective ways to quantify the bio-based content of a product. The ASTM and ISO have developed standards for measuring the bio-based content of materials via carbon isotope analysis. Relevant standards include:

ASTM D6866-12
ASTM D7026-04

Biopolymers: Processing and Products. http://dx.doi.org/10.1016/B978-0-323-26698-7.00001-5

The bio-based content of a biopolymer can be determined by calculating the number of carbon atoms that come from the short CO_2 cycle, that is, from biomass as raw material. It is known in the art that carbon-14 (^{14}C), which has a half-life of about 5700 years, is found in bio-based materials but not in fossil fuels. Thus, "bio-based materials" refer to organic materials in which the carbon comes from nonfossil biological sources. The detection of ^{14}C is indicative of a bio-based material. ^{14}C levels can be determined by measuring its decay process (disintegrations per minute per gram carbon or dpm/gC) through liquid scintillation counting. A bio-based PET comprises at least about 0.1 dpm/gC (disintegrations per minute per gram carbon) of ^{14}C [6].

"Compostable" polymer was defined by ASTM D6002 as "a plastic which is capable of undergoing biological decomposition in a compost site as part of an available program, such that the plastic is not visually distinguishable and breaks down to carbon dioxide, water, inorganic compounds, and biomass at a rate consistent with known compostable materials (e.g., cellulose) and leave no toxic residue." However, this definition drew much criticism, and in January 2011, the ASTM withdrew standard ASTM D6002 [7].

In order for a polymer to be called compostable, it should meet any of the following international standards:

ASTM Standard D6400 (for compostable plastics) or D6868 (for compostable packaging)

CEN standard EN 14995:2006 (for compostable plastics) or EN 13432:2000 (for compostable packaging)

ISO 17088:2012

The standards ISO 17088:2012 and ASTM D6400 describe the same check scheme as EN 13432:2000. The ISO-Standard not only refers to plastic packaging but to plastics in general.

A polymer that meets the requirements of any of the above standards: (1) disintegrate rapidly during the composting; (2) biodegrade quickly under the composting conditions; (3) not reduce the value or utility of the finished compost and the compost can support plant life; (4) not contain high amounts of regulated metals or any toxic materials.

The difference between biodegradable polymers and compostable polymers is determined by the rate of biodegradation, disintegration, and toxicity. All compostable polymers are by default biodegradable but not vice versa.

Two different criteria underline the definition of a "biopolymer" (or "bioplastic"): (1) the source of the raw materials, and (2) the biodegradability of the polymer. Here, a differentiation is made between:

A. biopolymers made from renewable raw materials (bio-based), and being biodegradable;
B. biopolymers made from renewable raw materials (bio-based), and not being biodegradable;
C. biopolymers made from fossil fuels, and being biodegradable.

The biopolymers of (A) can be produced by biological systems (microorganisms, plants, and animals), or chemically synthesized from biological starting materials (e.g., corn, sugar, starch, etc.). Biodegradable bio-based biopolymers include: (1) synthetic polymers from renewable resources such as poly(lactic acid) (PLA); (2) biopolymers produced by microorganisms, such as PHAs; (3) natural occurring biopolymers, such as starch or proteins—natural polymers are by definition those that are biosynthesized by various routes in the biosphere. The most used bio-based biodegradable polymers are starch and PHAs.

The biopolymers of (B) can be produced from biomass or renewable resources and are nonbiodegradable. Nonbiodegradable bio-based biopolymers include: (1) synthetic polymers from renewable resources such as specific polyamides from castor oil (polyamide 11), specific polyesters based on biopropanediol, biopolyethylene (bio-LDPE, bio-HDPE), biopolypropylene (bio-PP) or biopoly (vinyl chloride) (bio-PVC) based on bio-ethanol (e.g., from sugar cane), etc.; (2) natural occurring biopolymers such as natural rubber or amber.

The biopolymers of (C) are produced from fossil fuel, such as synthetic aliphatic polyesters made from crude oil or natural gas, and are certified biodegradable and compostable. Poly(ε-caprolactone) (PCL), poly(butylene succinate) (PBS), and certain "aliphatic-aromatic" copolyesters are at least partly fossil fuel–based polymers, but they can be degraded by microorganisms.

According to European Bioplastics a plastic material is defined as a bioplastic if it is either bio-based, biodegradable, or features both properties [8]. On the basis of this definition, biopolymers or bioplastics consist of either biodegradable polymers (e.g., polymers of type A or C) or bio-based polymers (e.g., polymers of type A or B). Therefore, a biopolyethylene derived from sugarcane, nicknamed "green polyethylene," is nonbiodegradable, but emits less greenhouse gases when compared to fossil-based polyethylene, and is classified as biopolymer. The interrelationship between biodegradable polymers and bio-based polymers is shown in Table 1.1. To summarize:

"Biopolymers are defined as polymers that are derived from renewable resources, as well as biological and fossil-based biodegradable polymers."

1.2 CLASSIFICATION OF BIOPOLYMERS

Biopolymers can be divided also into two broad groups, namely biodegradable and nonbiodegradable biopolymers. Alternatively, biopolymers can be classified on their origin as being either bio-based or fossil fuel-based. The bio-based biopolymers can be produced from plants, animals, or microorganisms. There are many more nondegradable bio-based biopolymers than there are biodegradable bio-based biopolymers [3].

Table 1.2 presents the main categories for distinguishing between the different types of biopolymers. This is not meant to be a comprehensive and all-inclusive list. Several

TABLE 1.1 Biodegradable versus Bio-Based Polymers

Origin	Biodegradable	Nonbiodegradable
Bio-based	CA, CAB, CAP, CN, P3HB, PHBHV, PLA, starch, chitosan	PE (LDPE), PA 11, PA 12, PET, PTT
Partially bio-based	PBS, PBAT, PLA blends, starch blends	PBT, PET, PTT, PVC, SBR, ABS, PU, epoxy resin
Fossil fuel-based	PBS, PBSA, PBSL, PBST, PCL, PGA, PTMAT, PVOH	PE (LDPE, HDPE), PP, PS, PVC, ABS, PBT, PET, PS, PA 6, PA 6.6, PU, epoxy resin, synthetic rubber

ABS, acrylonitrile-butadiene-styrene; CA, cellulose acetate; CAB, cellulose acetate butyrate; CAP, cellulose acetate propionate; CN, cellulose nitrate; HDPE, high density polyethylene; LDPE, low density polyethylene; PA 6, polyamide 6; PA 6.6, polyamide 6.6; PA 11, aminoundecanoic acid-derived polyamide; PA 12, laurolactam-derived polyamide; PBAT, poly(butylene adipate-*co*-terephthalate); PBS, poly(butylene succinate); PBSA, poly(butylene succinate-*co*-adipate); PBSL, poly(butylene succinate-*co*-lactide); PBST, poly(butylene succinate-*co*-terephthalate); PBT, poly(butylene terephthalate); PCL, poly(ε-caprolactone); PE, polyethylene; PET, poly(ethylene terephthalate); PGA, poly(glycolic acid), polyglycolide; P3HB, poly(3-ydroxybutyrate); PHBHV, poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate); PLA, poly(lactic acid), polylactide; PP, polypropylene; PS, polystyrene; PTMAT, poly(methylene adipate-*co*-terephthalate); PTT, poly(trimethylene terephthalate); PVOH, poly(vinyl alcohol); PVC, poly(vinyl chloride); PU, polyurethane; SBR, styrene-butadiene rubber.

TABLE 1.2 Classification of Biopolymers

Biodegradable				Nonbiodegradable
Bio-Based			Fossil-Based	Bio-Based
Plants	Microorganisms	Animals		
Cellulose and its derivatives[1] (polysaccharide)	PHAs (e.g., P3HB, P4HB, PHBHV, $P3HBHH_x$)	Chitin (polysaccharide)	Poly(alkylene dicarboxylate)s (e.g., PBA, PBS, PBSA, PBSE, PEA, PES, PESE, PESA, PPF, PPS, PTA, PTMS, PTSE, PTT)	PE (LDPE, HDPE), PP, PVC
Lignin	PHF	Chitosan (polysaccharide)	PGA	PET, PPT
Starch and its derivatives (monosaccharide)	Bacterial cellulose	Hyaluronan (polysaccharide)	PCL	PU
Alginate (polysaccharide)	Hyaluronan (polysaccharide)	Casein (protein)	PVOH	PC
Lipids (triglycerides)	Xanthan (polysaccharide)	Whey (protein)	POE	Poly(ether-ester)s
Wheat, corn, pea, potato, soy, potato (protein)	Curdlan (polysaccharide)	Collagen (protein)	Polyanhydrides	Polyamides (PA 11, PA 410, PA 610, PA 1010, PA 1012)
Gums (e.g. *cis*-1, 4-polyisoprene)	Pullulan (polysaccharide)	Albumin (protein)	PPHOS	Polyester amides
Carrageenan	Silk (protein)	Keratin, PFF (protein)		Unsaturated polyesters
PLA (from starch or sugar cane)		Leather (protein)		Epoxy
				Phenolic resins

HDPE, high density polyethylene; LDPE, low density polyethylene; P3HB, poly(3-hydroxybutyrate); $P3HBHH_X$, poly(3-hydroxybutyrate-*co*-3-hydroxyhexanoate); P4HB, poly(4-hydroxybutyrate; PBA, poly(butylene adipate); PBS, poly(butylene succinate); PBSA, poly(butylene succinate-*co*-adipate); PBSE, poly(butylene sebacate); PC, polycarbonate; PCL, poly(ε-caprolactone); PE, polyethylene; PEA, poly(ethylene adipate); PES, poly(ethylene succinate); PESA, poly(ethylene succinate-*co*-adipate); PESE, poly(ethylene sebacate); PET, poly(ethylene terephthalate); PFF, poultry feather fiber; PGA, poly(glycolic acid), polyglycolide; PHA, polyhydroxyalkanoate; PHBHV, poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate); PHF, polyhydroxy fatty acid; PHH, poly(3-hydroxyhexanoate); PLA, poly(lactic acid), polylactide; POE, poly(ortho ester); PP, polypropylene; PPF, poly(propylene fumarate); PPHOS, polyphosphazenes; PPS, poly(propylene succinate); PTA, poly(tetramethylene adipate); PTMS, poly(tetramethylene succinate); PTSE, poly(tetramethylene sebacate); PTT, poly(trimethylene terephthalate); PVC, poly(vinyl chloride); PVOH, poly(vinyl alcohol); PU, polyurethane.

[1] *Acetyl cellulose (AcC) is either biodegradable or nonbiodegradable, depending on the degree of acetylation. AcCs with a low acetylation can be degraded, while those with high substitution ratios are nonbiodegradable.*

of the mentioned biopolymers can be derived from both bio-based and fuel-based resources, such as PLA, PBS, PTT, etc. Although PLA is largely produced by fermentation from renewable resources such as starch and sugar cane, it can be synthesized also from fossil fuels.

Biopolymers can also be classified based on the ways in which they respond to heat as thermoplastics, thermosets [9], or elastomers. Nowadays, the volume of bio-based thermoset biopolymers exceeds the volume of bio-based thermoplastic biopolymers [3].

Biopolymers are classified also on their composition as blends, composites, or laminates. Biopolymer blends are mixtures of polymers from different origins such as the commercial product Ecovio® (BASF AG), which is a blend of PLA and poly(butylene adipate-*co*-terephthalate) (PBAT) (Ecoflex®, BASF AG). Another group is the biocomposites, which are biopolymers or synthetic polymers reinforced with natural fibers, such as sisal, flax, hemp, jute, banana, wood, and various grasses, and/or fillers and additives. Novel biocomposites are based on a biodegradable matrix polymer reinforced with natural fibers.

In the following Section 1.3: Types of chemistry of biopolymers, the biopolymers are classified according to the chemical nature of their backbone.

1.3 TYPES AND CHEMISTRY OF BIOPOLYMERS

The biopolymers can be classified into a chemical synthesis type, a microorganism production type, and natural type, which are derived from the biomass, i.e., materials derived from plants. The chemical synthesis type may include PLA, e.g., LACEA® (Mitsui Chemicals, Inc.), obtained by polymerizing lactic acid, which is produced by fermenting saccharides and starch derived from corn, potato, and sugarcane; poly(butylene succinate) type resins, e.g., GS-Pla® (Mitsubishi Chemical Corporation), produced from succinic acid derived from starch and 1,4-butane diol as a raw material; and polyamide 11, e.g., Rilsan® B (ARKEMA), produced from castor oil as a raw material. The microorganism production type may include poly-3-hydroxybutyrate type resins such as poly(3-hydroxybutyrate), e.g., Biogreen® (Mitsubishi Gas Chemical Company, Inc.), and copolymers of 3-hydroxybutyrate and 3-hydroxyhexanoate, e.g. PHBHHx (Kaneka Corp.). The natural type may include cellulose acetate (e.g., CELGREEN PCA, manufactured by Daicel Chemical Industries, Ltd.); esterified starch (e.g., Cornpole, manufactured by Nihon Cornstarch Corporation), chitosan-cellulose-starch (e.g., Dolon CC, manufactured by Aicello Chemical Co., Ltd.); starch-modified polyvinyl alcohol (e.g., Mater-Bi, manufactured by Novamont).

PLA and P3HB are biodegradable bio-based biopolymers, aimed to production of ecologically friendly polymeric materials with excellent ultimate properties, especially strength and stiffness. On the other hand, both polymers are brittle, possessing small deformability. This behavior is limiting regarding a number of potential applications.

1.4 POLYESTERS

Polyesters, and especially the aliphatic ones, are the most extensively studied class of biopolymers [10]. Polyesters can be classified into two groups according to the bonding of the constituent monomers [11]. The first group consists of the poly(hydroxy acid)s. These are polyesters synthesized from hydroxy acids and/or esters or by ring opening polymerization of cyclic esters. The second group consists of the poly(alkylene dicarboxylate)s (PADC)s. These are polyesters prepared by polycondensation of diols and dicarboxylic acids.

The condensation reaction of an hydroxy acid and/or ester, and the ring opening polymerization of a cyclic ester provides a polymer having a repeat unit with a head-tail-head-tail configuration of the general structure: $–[(CR''_2)_y–CO–O]–$. In contrast, the condensation of a diol and a dicarboxylic acid provides a polymer having a repeat unit with a head-tail-tail-head configuration of the general formula: $–[(CR_2)_x–O–CO–(CR'_2)_y–CO–O]–$ (1999, **WO9950345** A1, CARGILL INC).

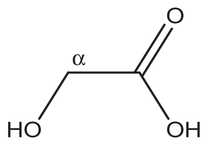
1.4.1 Poly(hydroxy acid)s

A series of hydroxy acids are the hydroxyalkanoic acids, which are distinguished by the position of the hydroxyl group in relation to the carboxyl group (e.g. from position α, β, γ, δ, ε, or ω). The poly(hydroxy acid)s derived from β-, γ-, δ-, ε- and ω-hydroxyalkanoic acids are usually termed *polyhydroxyalkanoates*.

1.4.1.1 Poly(α-hydroxyalkanoic acid)s

Poly(α-hydroxyalkanoic acid)s are poly(α-ester)s derived from α-hydroxyalkanoic acids (see Scheme 1.1). A list of common α-hydroxyalkanoic acids is shown in Table 1.3.

Common α-hydroxyalkanoic acids include lactic acid, glycolic acid, tartaric acid, malic acid, mandelic acid, benzylic acid, α-hydroxyvaleric acid, α-hydroxybutyric acid, α-hydroxycaprylic acid, α-hydroxystearic acid, and



SCHEME 1.1 Typical example of an α-hydroxyalkanoic acid: glycolic acid.

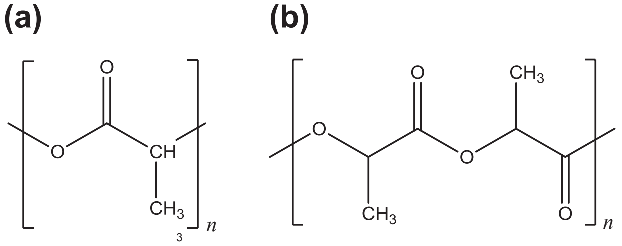
TABLE 1.3 List of α-Hydroxyalkanoic Acids

α-Hydroxyalkanoic Acids	
α-Hydroxyethanoic acid (glycolic acid)	α-Hydroxydecanoic acid (α-hydroxycapric acid)
α-Hydroxypropanoic acid (lactic acid)	α-Hydroxyundecanonic acid (α-hydroxyhendecanoic acid)
(2,3-Dihydroxybutanedioic acid) (tartaric acid)	α-Hydroxydodecanoic acid (α-hydroxylauric acid)
α-Hydroxybutanedioic acid (malic acid)	α-Hydroxytridecanoic acid
2-Hydroxy-2-phenylacetic acid (mandelic acid)	α-Hydroxytetradecanoic acid (α-hydroxymyristic acid)
2-Hydroxy-2,2-di(phenyl)acetic acid (benzylic acid)	α-Hydroxypentadecanonic acid
	α-Hydroxyhexadecanoic acid (α-hydroxypalmitic acid)
1-Hydroxy-1-cyclohexane carboxylic acid	α-Hydroxyheptadecanoic acid
2-Hydroxy-2-(2-tetrahydrofuranyl) ethanoic acid	α-Hydroxynonadecanoic acid
2-Hydroxy-2-(2-furanyl) ethanoic acid	α-Hydroxystearic acid
2-Hydroxy-2-phenylpropanoic acid	α-Hydroxyarachidic acid
2-Hydroxy-2-methylpropanoic acid	α-Hydroxybehenic acid
2-Hydroxy-2-methylbutanoic acid	α-Hydroxylignoceric acid
2-Hydroxy-2-ethylhexylcarboxylic acid	α-Hydroxycerotic acid
α-Hydroxybutanoic acid (α-hydroxybutyric acid)	α-Hydroxyoleic acid
α-Hydroxypentanoic acid (α-hydroxyvaleric acid)	α-Hydroxylinoleic acid
α-Hydroxyhexanoic acid (α-hydroxycaproic acid)	α-Hydroxylinolenic acid
α-Hydroxyheptanoic acid (α-hydroxyenanthoic acid)	α-Hydroxyarachidonic acid
α-Hydroxyoctanoic acid (α-hydroxycaprylic acid)	α-Hydroxynonanoic acid (α-hydroxypelargonic acid)

mixtures thereof. Most used α-hydroxyalkanoic acids are lactic acid, glycolic acid, and mixtures thereof; the corresponding polymers, poly(lactic acid) and poly(glycolic acid) and copolymers thereof have been known for years, since they were synthesized in the 1930s and 1940s, respectively (1935, **US1995970** A; 1944, **US2362511** A, DU PONT).

1.4.1.1.1 Poly(lactic acid)

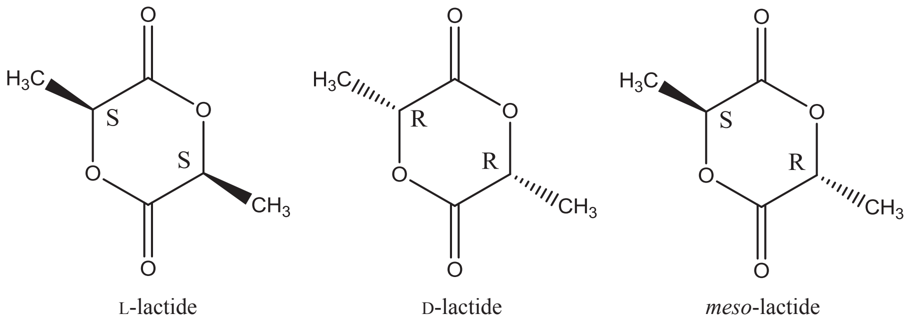
Poly(lactic acid) or polylactide, hereinafter also referred to as PLA, is a linear aliphatic poly(α-ester) or α–hydroxyalkanoic acid-derived polyester; see Scheme 1.2.



SCHEME 1.2 (a) Poly(lactic acid) or (b) polylactide (PLA).

PLA is obtainable primarily by the ionic polymerization of lactide, a cyclic compound formed by the dehydration-condensation of two lactic acid molecules. At temperatures between 140°C and 180 °C and under the action of catalytic tin compounds (such as tin oxide), a ring opening polymerization takes place. Lactide itself can be made through lactic acid fermentation from renewable resources such as starch by means of various bacteria. PLA can also be produced directly from lactic acid by polycondensation. However, this process yields low molecular weight polymers, and the disposal of the solvent is a problem in the industrial production. Some representative procedures for synthesizing, purifying, and polymerizing lactide on an industrial scale are disclosed in **US4057537** A (1977, GULF OIL CORP), **EP0261572** A (1988, BOEHRINGER INGELHEIM KG; BOEHRINGER INGELHEIM INT) and described in literature [12–14]. Currently, the most used method for producing L-lactide includes a two-stage polycondensation of lactic acid to form an oligomer followed by a depolymerization (2010, **WO2010022966** A, UHDE INVENTA FISCHER GMBH; UHDE GMBH).

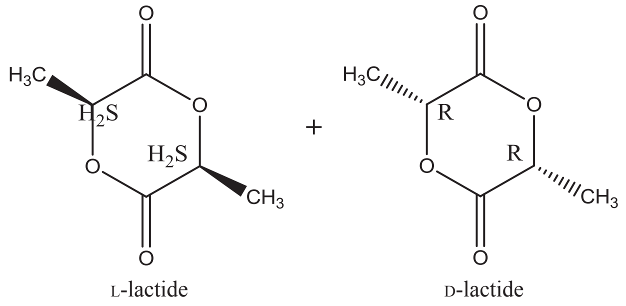
Each lactic acid molecule has one asymmetric carbon, and there are two optically active forms of lactic



SCHEME 1.3 Stereoisomeric forms of lactide.

TABLE 1.4 Melting Temperatures of Lactides (2010, WO2010022966 A2, UHDE INVENTA FISCHER GMBH; UHDE GMBH)

	L-Lactide	D-Lactide	*meso*-Lactide	*rac*-Lactide
T_m (°C)	97	97	54	129



SCHEME 1.4 LD-Lactide (rac-lactide): equimolar mixture of L-lactide and D-lactide.

acid: L-lactic acid and D-lactic acid. Therefore, in lactide, the cyclic diester of lactic acid, there are three isomeric forms (see Scheme 1.3) depending on whether they consist of:

1. two L-lactic acid molecules: L-lactide;
2. two D-lactic acid molecules: D-lactide;
3. one L-lactic acid molecule and one D-lactic acid molecule: *meso*-lactide.

Meso-lactide, like L-lactide, is a cyclic diester with two optically active carbon atoms in the ring. It has an optical R- and an S-center and is therefore optically inactive. *Meso*-lactide is characterized by a melting temperature (T_m) of around 54 °C, whereas the T_m of L- and D-lactide isomers is 97 °C (see Table 1.4).

An equimolar mixture of L - and D-lactide results in LD-lactide (*rac*-lactide) (see Scheme 1.4). *rac*-lactide has been obtained to date from equal quantities of D- and L,L-lactide by melting.

Four different stereoisomers of PLA can be distinguished (see Scheme 1.5):

1. Isotatic PLA is formed from either pure D- or L-lactide, and the sequential stereogenic carbons have the same configuration;
2. Syndiotactic PLA has alternating configurations of the sequential stereocenters;
3. Tactic PLA has a random distribution of configurations about the stereocenters, while its heterotactic counterpart has regions of stereohomogeneity;
4. Isotactic stereoblock PLA is similar to isotactic PLA but differs in that *rac*-lactide is used instead of pure L- or D-lactide

The various types of PLA are classified into:

1. poly(L-lactide) (PLLA)
2. poly(D-lactide) (PDLA)
3. syndiotactic poly(D,L-lactide) (syndiotactic PDLLA)
4. attactic poly(D,L-lactide) (attactic PDLLA)
5. isotactic stereocomplex PLA (csPLA)
6. stereoblock copolymer PLA (sbcPLA)
7. copolymers with other polymers, depending on the type of constitutive monomer (see Scheme 1.5).

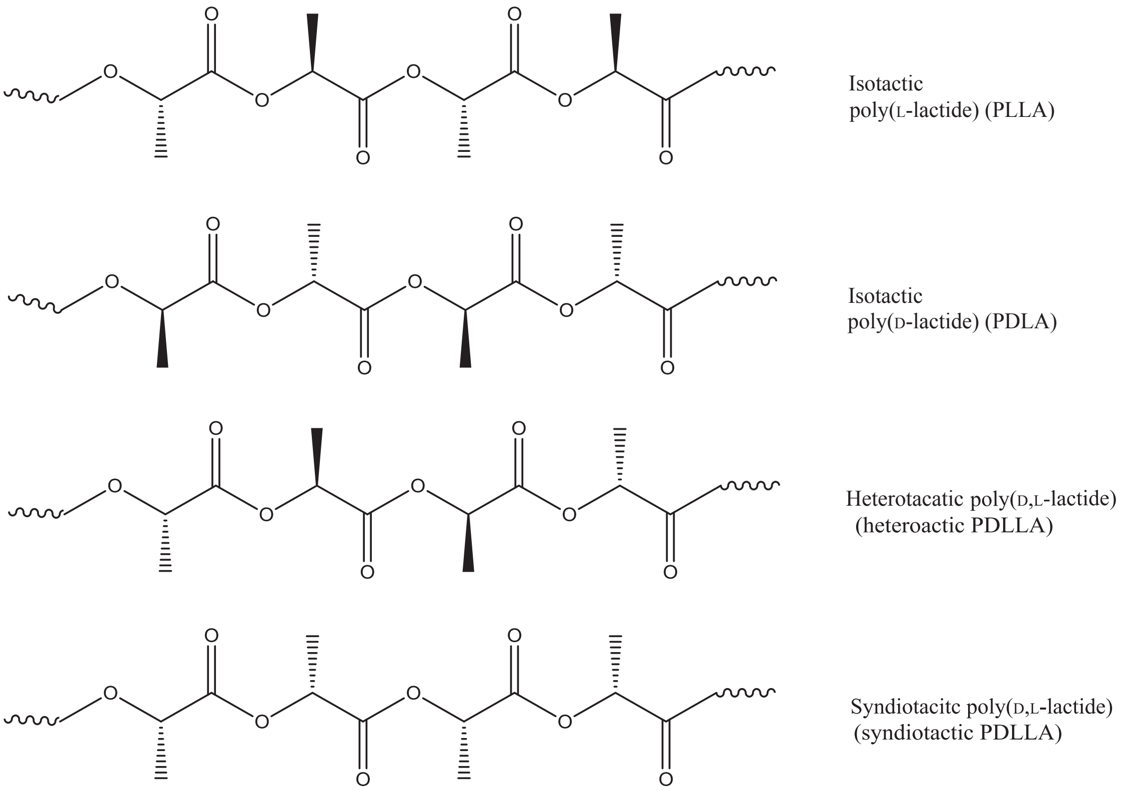
The mechanical properties of all these types of PLA are different as are their degradation times [15]. Thus, a regular PLLA is a hard, transparent polymer; it has a T_m of 160–185 °C, a T_g of 53–63 °C, and a crystallization temperature (T_c) of 100–120 °C (see Table 1.5).

Syndiotactic PLA can be produced from the polymerization of *meso*-lactide using a stereoselective catalyst (isopropoxide) [16], the thermal properties of which are, however, poorer than those of PLLA.

On the other hand, atactic PLA has no T_m, a T_g of 50–55 °C, and it shows much lower tensile strength [17]. Atactic PLA derived from *rac*-lactide (i.e., a 1:1 mixture of D- and L-lactide) yields amorphous polymers with T_g near room temperature [18].

PDLA is available only in small quantities and is very expensive.

There is also another form of PLA known as isotactic stereocomplex (scPLA) prepared from *rac*-lactide using a



SCHEME 1.5 Stereoisomeric forms of PLA.

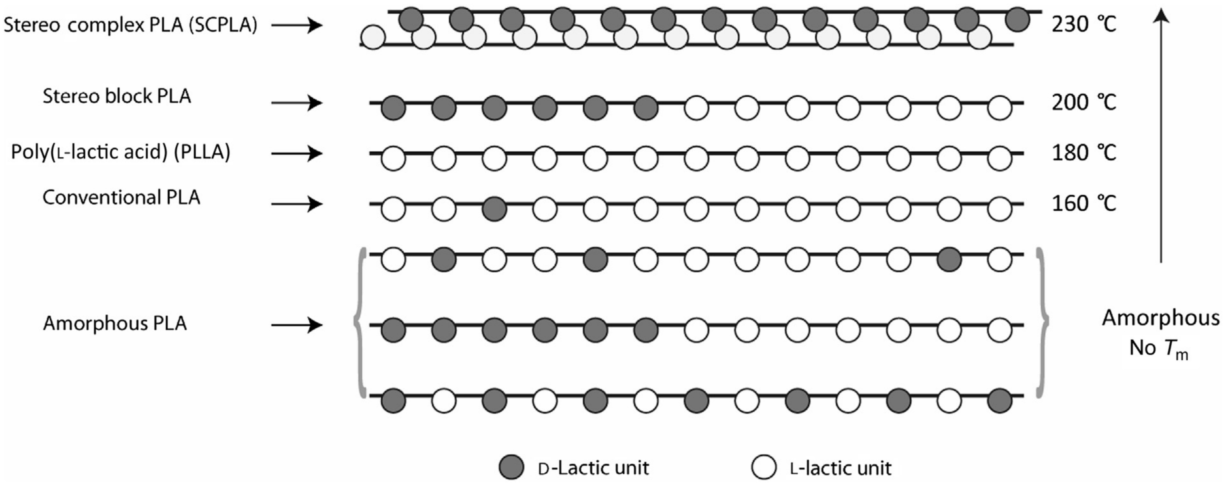
TABLE 1.5 Transition Temperatures of the Various Types of PLA

Transition Temperatures	PLLA	*rac*PLA	*meso*PLA	*sc*PLA	*sbc*PLA
T_g (°C)	53–63	50–55	40–45/34	80–90	50–55
T_m (°C)	160–185	–	–/153	201–230	185–195

*meso*PLA, *meso*-poly(lactic acid), *meso*-poly(lactide); PDLA, poly(D-lactic acid), poly(D-lactide); PLLA, poly(L-lactic acid), pol(L-lactide); sbcPLA, stereoblock copolymer PLA; scPLA, stereocomplex PLA

racemic catalyst (isopropoxide). The term *stereocomplex* means a crystal structure that PLLA and PDLA form alternating helices. The stereocomplex is formed by interaction between PLLA and PDLA, which is stronger than interaction between L-units or interaction between D-units (see also Chapter 3: Blending; Section 3.2.1.1.1: Blending optical isomers of PLA). scPLA has a T_m>50°C than the T_m of either PLLA or PDLA alone [18], (1986, **JPS6136321** A, DAICEL CHEM; BIO MATERIAL UNIVERS), (1988, **US4719246** A, DU PONT). A schematic representation of scPLA, in comparison to other stereoisomeric forms of PLA is given in Scheme 1.6.

scPLA is produced by mixing PLLA and PDLA in a solution state [19,20] or in a molten state (2003, **JP2003192884** A; 2003, **WO03057781** A, ASAHI DENKA KOGYO KK; TOYOTA MOTOR CORP). In order to prepare a csPLA having a high stereocomplex content from the combination of high molecular weight PLAs, it is necessary to keep the mixed solution in a solution state for a long period of time in the case of mixing them in a solution state, or it is necessary to knead for a long period of time in the case of mixing them in a molten state. However, these procedures cause a problem such that the molecular weights are decreased, and thereby the molecular weights of the PLLA and PDLA, which are constituent materials, cannot be kept (2011, **WO2011002004** A1, MITSUI CHEMICALS INC). Furthermore, the solution process has the additional problem that it is necessary to evaporate the solvent after mixing, which increases manufacturing costs. In order to solve these problems, several methods have been proposed with the purpose of increasing the molecular weight of PLA. **WO2011002004** A1 (2011, MITSUI CHEMICALS INC) discloses a method of preparing scPLA by reacting



SCHEME 1.6 Schematic representation of the various stereoisomeric forms of PLA (*Source: Corbion Purac, NL*).

a mixture of PLLA and PDLA having carboxyl terminal groups with a polyisocyanate compound in the presence of an amidation catalyst.

The properties of PLA depend primarily on the molecular weight the degree of crystallinity, and possibly the proportion of comonomers. A higher molecular weight raises T_g, as well as T_m, tensile strength, elastic modulus, and lowers the elongation at break. Due to the $–CH_3$ side group (see Scheme 1.2), the material has water-repellent or hydrophobic behavior. PLA is soluble in many organic solvents, such as dichloromethane or the like. PLA has higher transparency than other biodegradable polymers, and is superior in weather resistance, and workability.

Commercially available PLA at present is mostly PLLA. In order to synthesize crystalline PLLA, the optical purity of L-lactide to be used as starting material is crucial. PLLA acquires a crystalline structure in which the PPLA molecules are regularly arranged. However, it is known that PLA synthesized from L-lactide with ≥8% of D-lactide and/or *meso*-lactide is amorphous because the PLA molecules cannot be regularly arranged (2013, **WO2013039266** A1, HITACHI SHIPBUILDING ENG CO; TOHOKU ELECTRIC POWER CO; UNIV NAGOYA NAT UNIV CORP; NATUREWORKS LLC).

PLA has low melt viscosity required for the shaping of a molding. PLA is, however, slow in the crystallization rate with long molding cycle and has poor gas properties; further, it has inferior thermal resistance and mechanical characteristics (toughness, impact resistance, and the like) compared with those of existing synthetic resin-molded articles. To solve these problems, there were generally given many countermeasures, including blending PLA with other polymers, and compounding various kinds of substances as filler, thus the PLA products have been entering practical applications.

PLA is gaining a lot of interest due to its biodegradability, biocompatibility, and renewable resource–based origin. It can be said that PLA is a low environment load polymer, which does not cause a direct increase in the total amount of carbon dioxide gas, even if the polymer is finally biodegraded or burned up. The (bio)degradability of PLA, though, has both negative and positive aspects. The positive aspects are: (1) the ability of PLA to form nonhazardous products when PLA polymers or articles are discarded or composted after completing their useful life; (2) the slow degradation of PLA—over a period of several weeks up to about one year—is advantageous for some other applications as it leads to a relatively good shelf life. The negative aspects are: (1) the thermal degradation of PLA during processing causes deterioration of properties; (2) the degradation rate of PLA is still low as compared to the waste accumulation rate, meaning that a large amount of PLA left untreated outdoors may cause a new environmental problem. Thus, the same properties that make PLA polymers desirable as replacements for nondegradable fossil fuel–based polymers also create undesirable effects that must be overcome. PLA has a considerably lower biodegradability than poly(ε-caprolactone) (PCL) or poly(3-hydroxybutyrate) (P3HB).

PLA is the most common biopolymer currently on the market. As such, it has a variety of brand names associated with it (see Table 1.6).

1.4.1.1.2 Polymandelide

Polymandelide (PM) is an aryl analogue of PLLA and can be synthesized by the ring-opening polymerization of mandelide, the cyclic dimer of mandelic acid [21]. As shown in Scheme 1.7, the structure of PM differs from PLLA in that the methyl groups of the monomer units are replaced with phenyl groups.

PM is a glassy amorphous polymer with a T_g of 100 °C, with rheological properties comparable to polystyrene. Thermal gravimetric analyses under nitrogen show that the

TABLE 1.6 Commercial α–Hydroxycarboxylic Acid-Derived Polyesters

Biopolymer	Commercial Name	Manufacturer	Application
PLA	Related Ingeo™ Biopolymer grades NatureWorks® 2000 series: 2003D TDS NatureWorks® 3000 series: 3001D SDS 3052D SDS 3251D SDS 3801X SDS NatureWorks® 4000 series: 4032D TDS 4043D TDS 4060D TDS NatureWorks® 6000 series: 6060D TDS 6201D TDS 6202D TDS 6204D TDS 6400D TDS 6251D TDS 6252D TDS 6302D TDS 6751D TDS 6752D TDS NatureWorks® 7000 series: 7001D TDS 7032D TDS	NatureWorks LLC (USA)	2003D TDS: food packaging; 2003D TDS, 3001D TDS, 3052D TDS, 3251D TDS: service ware; 3001D SDS, 3052D SDS, 3251D SDS, 3801X SDS: durable goods; 4032D TDS, 4043D TDS, 4060D TDS: films, cards, folded cartons; 6201D TDS, 6204D TDS: apparel; 6201D TDS, 6202D TDS, 6204D TDS, 6400D TDS: home textiles (woven and knitted); 6060D TDS, 6202D TDS, 6251D TDS, 6252D TDS, 6302D TDS, 6751D TDS, 6752D TDS: nonwovens; 7001D TDS, 7032D TDS: bottles
PLA	Econstrong®	Far Eastern Textiles (TW)	Catering products (cups, trays, cutlery)
PLA	Eco plastic®	Toyota (JP)	Floor mats in cars
PLA	Heplon	Chronopol (USA)	Bags
PLA	Lacea® H-100 Lacea® H-280 Lacea® H-400 Lacea® H-440	Mitsui Chemicals (JP)	Bags, containers, films, nonwovens, packaging (stationeries, cosmetic containers, pots for seedlings)
PLA	Lacty® 5000 series Lacty® 9000 series Lacty® 9800 series	Shimadzu Corp (JP)	Injection molding, fibers, films, sheets
PLA	Terramac®	Unitika Ltd (JP)	
	TE-2000 TE-1030 TE-1070		Injection: smaller goods, containers, various plastic parts, etc.
	TE-7000 TE-7307 TE-7300 TE-8210 TE-8300		Injection: containers, table wear, chassis, etc.
	TP-4000 TP-4030 HV-6250H		Extrusion, blown, and foam: containers, bottles, pipes, foam sheet, etc.
PLA	Ecoloju® S series	Mitsubishi Plastics, Inc. (JP)	Films, sheets
PLA, recycled	LOOPLA® Galacid®	Galactic (BE) Futerro Total/Galactic (BE)	Recycled PLA grades are not suitable for food-grade applications

Continued

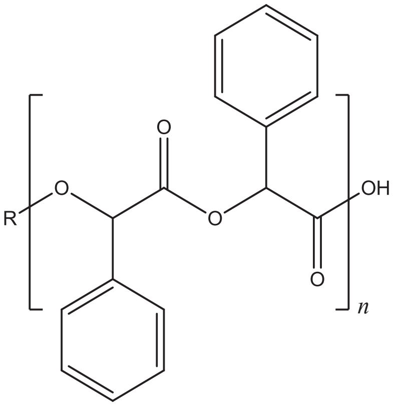
TABLE 1.6 Commercial α–Hydroxycarboxylic Acid-Derived Polyesters—cont'd

Biopolymer	Commercial Name	Manufacturer	Application
PLA	Palgreen®	Mitsui Chemicals Tohcello	Films
PLA	L-PLA D-PLA PDLA® PURALACT®	Purac (NL) & Sulzer Chemtech	Molded plastic parts, fibers, films, foam, heat stable applications
PDLLA	BIOFRONT®	Teijin (JP)	Fibers, injection molding, eyeglass frames; films and sheets
PLA	REVODE 100 series REVODE 200 series	Daishin Pharma-Chem Co, Ltd/Zhejiang Hisun Biomaterials Co, Ltd (CN)	Fixed installations such as bone plates, bone screws, surgical sutures, spinning
PLA/PCL blend	VYLOECOL BE-400[1] VYLOECOL BE-600 VYLOECOL BE-910 VYLOECOL HYD-306 VYLOECOL BE-450 VYLOECOL BE-410 VYLOECOL HYD-006	Toyobo (JP)	Printing ink, adhesive, paint, master batch resin, etc; BE-400 (pellet): general purpose grade, agent for various coating; BE-600 (sheet): anchor coating for vapor deposition film, anchor coating for printing ink; BE-910 (sheet): adhesive for dry lamination
PLA/polyether copolymer	Ecodear® series: Ecodear® V554R10 Ecodear® V554X51 Ecodear® V554X52 Ecodear® V751X52 Ecodear® V751X53 Ecodear® V911X51	Toray Industries (JP)	Electric commodity appliances; film, bags, fibers; food packaging applications (frozen foods, snacks, cookies, cereal and nutrition bars, and confectionery items); packaging for nonfood items (personal care items, fashion accessories, promotional items, toys, office supplies, and other retail goods)
PLA (Nature-Works)/ copolyester blend	BIO-FLEX® series: BIO-FLEX A 4100 CL BIO-FLEX® F 1110 BIO-FLEX® F 1130 BIO-FLEX® F 1137 BIO-FLEX® F 2110 BIO-FLEX® F 2201 CL BIO-FLEX® F 6510 BIO-FLEX® F 6513 BIO-FLEX® F 6611 BIO-FLEX® S 5630 BIO-FLEX® S 6540 BIO-FLEX® S 9533	FKuR Kunststoff GmbH (DE)	Blown film extrusion, flower wrapping, clam shell packaging(BIO-FLEX A 4100 CL); air pillow, carrier bag, waste bag (BIO-FLEX® F 1130); shopping bag (BIO-FLEX® F 1137); deep freeze packaging, netting, waste bag (BIO-FLEX® F 2110); film (BIO-FLEX® F 2201 CL); multilayer film (BIO-FLEX® A 4100 CL/F 2201 CL/A 4100 CL; ball pen, mugs, straws (BIO-FLEX® F 6510); injection molding (BIO-FLEX® F 6513); thermoforming (BIO-FLEX® F 6611); thermoformed inlay (BIO-FLEX® S 5630); cosmetic jar (BIO-FLEX® S 6540); (BIO-FLEX® S 9533)
PGA	Kuredux® Kuresurge®	KUREHA (JP)	Kuredux®: used in multilayer PET bottles for carbonated drinks; Kuresurge®: used for surgical sutures
PGA	PURASORB® PG 20	PURAC (NL)	Medical device and pharmaceutical industry

TABLE 1.6 Commercial α–Hydroxycarboxylic Acid-Derived Polyesters—cont'd

Biopolymer	Commercial Name	Manufacturer	Application
PLGA	PURASORB® PLG 8531 PURASORB® PLG 8523 PURASROB® PLG 8560 PURASORB® PLG 8218 PURASORB® PLG 8055 PURASORB® PLG 1017	PURAC (NL)	Medical device and pharmaceutical industry
PLGA	Coated VICRYL™ RAPIDE (polyglactin 910)	ETHICON INC (USA)	Coated absorbable sutures
PGCL	MONOCRYL™ plus antibacterial (poliglecaprone 25) Suture	ETHICON INC (USA)	Monofilament absorbable sutures

PGA, poly(glycolic acid) PGCL, poly(glycolide-*co*-caprolactone); PLA, poly(lactic acid) PLCL, poly(lactide-*co*-caprolactone); PLGA, poly(lactide-*co*-glycolide).
[1] *VYLOECOL® is made from lactides supplied by PURAC. PURAC markets these lactides, under the brand name PURALACT®.*

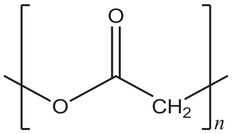


SCHEME 1.7 Polymandelide (PM).

polymer is stable to 300 °C [21]. Degradation of PM in pH 7.4 buffer at 55 °C is consistent with a bulk erosion model and, due to its high T_g, proceeds at 1/100 the rate of PLLA under similar conditions. The higher radiation and thermal stability of PLLA in the polymer formulation is due to the phenyl groups (2011, **US2011065825** A1, ABBOTT CARDIOVASCULAR SYSTEMS INC).

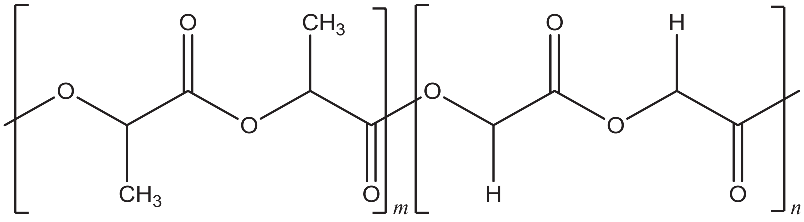
1.4.1.1.3 Poly(glycolic acid)

Poly(glycolic acid) or polyglycolide, hereinafter also referred to as PGA, is the simplest linear aliphatic polyester (see Scheme 1.8). PGA can be produced by a process such as dehydration polycondensation of glycolic acid, dealcoholization polycondensation of an alkyl glycolate, desalting polycondensation of a glycolic acid salt or ring-opening polymerization of glycolide. Glycolide monomer is synthesized from the dimerization of glycolic acid. Among these production processes, the ring-opening polymerization process of glycolide yields high molecular weight materials, with residual monomer of approximately 1–3% (2009, **WO2009107425** A1, KUREHA CORP). PGA is highly crystalline (45–55%), with a high T_m (220–225 °C) and a T_g of 35–40 °C [22]. Because of its high degree of crystallinity, it is not soluble in most organic solvents; the exceptions are highly fluorinated organics such as hexafluoroisopropanol.



SCHEME 1.8 Poly(glycolic acid) or polyglycolide (PGA).

PGA has an extremely high gas-barrier property, as high as c. three times or higher (i.e., c. 1/3 or lower in terms of an oxygen transmission coefficient) as that of PEVOH (ethylene-vinyl alcohol copolymer), which is a representative gas-barrier resin used heretofore, so that a bottle, especially made of PET, with a remarkably improved gas-barrier property can be obtained by including a thin layer of PGA thereof in addition to the principal resin layer, especially bottles made of poly(ethylene terephthalate) (PET). Accordingly, it becomes possible to effectively prevent the degradation of contents due to oxidation or poorer quality due to dissipation of carbon dioxide gas. Furthermore, PGA has a substantial hydrolyzability with alkaline washing liquid, water (particularly, warmed water), or acid water. In contrast thereto, PLA does not exhibit gas-barrier property like that of PGA and can only show a slower hydrolyzation speed with alkaline water, water, or acidic water (2003, **WO03097468** A1, KUREHA CHEM IND CO LTD). Fibers from PGA exhibit high strength and modulus and are too stiff to be used as sutures except in the form of braided material. Sutures of PGA lose about 50% of their strength after 2 weeks and 100% at 4 weeks, and are completely absorbed in 4–6 months. Glycolide has been copolymerized with other monomers to reduce the stiffness of the resulting



SCHEME 1.9 Poly(lactide-*co*-glycolide) (PLGA).

fibers. PGA can be utilized as a packaging material, for example, lightweight PET bottles, as well as for oil recovery and other industrial and medical applications.

1.4.1.1.4 Poly(lactide-*co*-glycolide)

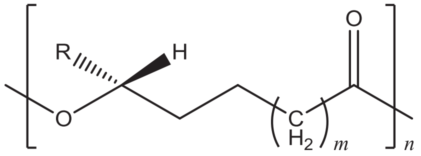
Poly(lactide-*co*-glycolide) (PLGA) is a copolymer of hydrophobic PLA and hydrophilic PGA (see Scheme 1.9). L-lactide and D,L-lactide have been used for copolymerization with glycolide. Amorphous polymers are obtained for a 25 lactide/75 glycolide monomer ratio. A copolymer with a monomer ratio of 80 lactide/20 glycolide is semicrystalline. When the ratio of monomer lactide/glycolide increases, the degradation rate of the copolymer decreases [10].

PLGA is useful in drug delivery and tissue regeneration applications since it degrades into harmless substances. Since polymers of lactic and glycolic acids and their copolymers degrade quickly in the body into nontoxic products, PLGA is used for biodegradable sutures and can potentially be used in implantable screws, intravascular stents, pins, drug delivery devices, and as a temporary scaffold for tissue and bone repair. Additionally, PLGA has good mechanical properties that improve the structural integrity of such devices. However, since PLGA degrades completely by bulk erosion, it loses more than 50% of its mechanical strength in less than two months, which can lead to uncontrollable release rates of drugs and can develop biocompatibility problems, probably due to an accumulation of lactic and glycolic acids during degradation (2000, **US6077916** A, PENN STATE RES FOUND).

1.4.1.2 Poly(β-, γ-, δ-hydroxyalkanoate)s

Polyhydroxyalkanoates (PHAs) are polyesters of β-, γ-, δ-, and ε-hydroxyalkanoic acids (also known as 3-, 4-, 5-, and 6- hydoxyacids or -hydroxycarboxylic acids) the general formula of which is given in Scheme 1.10. The hydroxyalkanoic acids are distinguished mainly by the position of the hydroxyl group in relation to the carboxyl group (see Scheme 1.11(a) and (b)), but also by the length of the side-alkyl chain, by a large variety of substituents in the side chains, and by one additional methyl group at carbon atoms between the hydroxyl and the carboxyl groups [23].

To date, more than 150 hydroxyalkanoic acids have been detected as constituents in bacterial PHAs; these constituents are produced by microorganisms grown on carbon substrates containing different types of chemical structures [23–25]. Beside linear and branched β-, γ-, δ-, and ε-hydroxyalkanoates, various constituents such as PHA containing halogenated or aromatic side chains have been described [26,27]. A list of β-, γ-, and δ-hydroxyalkanoic acids is given in Table 1.7.

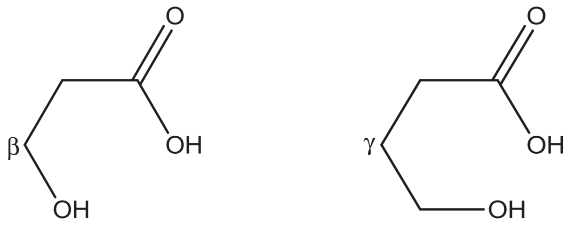


SCHEME 1.10 General formula of polyhydroxyalkanoates; wherein $m \geq 0$, R = H, (un)substituted alkyl.

PHA monomers range from a compound having three carbon atoms (3-hydroxypropionate) to a compound containing 14 carbon atoms (3-hydroxytetradecanoate). In general, PHA polymers composed of short-chain-length monomers, such as poly(3-hydroxybutyrate) (P3HB), are brittle. With increasing monomer chain length, the material gets more flexible. Poly(3-hydroxyoctanoate) (P3HO), for example, is an elastomer [6]. Depending on the number of carbon atoms, PHAs are classified as short-chain-length PHAs (PHA_{SCL}) that contain 3–5 carbon atoms and medium-chain-length PHAs (PHA_{MCL}) that contain 6–14 carbon atoms.

The PHAs are commercially produced by several bacteria as intercellular carbon and energy storage materials [28]. The PHAs may constitute up to 90% of the dry cell weight of bacteria, and are found as discrete granules inside the bacterial cells. Produced naturally by soil bacteria, the PHAs are degraded upon subsequent exposure to these same bacteria in soil, compost, or marine sediment. Biodegradation starts when microorganisms begin growing on the surface of PHA and secrete enzymes that break down the biopolymer into hydroxy acid monomeric units. The hydroxy acids are then taken up by the microorganisms and used as carbon sources for growth. The monomers and polymers can also be produced chemically.

This class of polyesters is attractive as a potential alternative to conventional fossil fuel–based polymers. PHAs can be processed by traditional polymer techniques for use in an enormous variety of applications, including consumer packaging, disposable diaper linings, garbage bags, and food and medical products [28,29]. PHAs have also been extensively studied for use in biomedical applications. These



α. β-Hydroxyalkanoic acid. **β. γ-Hydroxyalkanoic acid.**

SCHEME 1.11 Typical examples of a) a β-hydroxyalkanoic acid: β-hydroxypropanoic acid; and b) a γ-hydroxyalkanoic acid: γ-hydroxybutanoic acid.

TABLE 1.7 List of β-, γ-, and δ-Hydroxyalkanoic Acids

β-Hydroxyalkanoic acids	γ-Hydroxyalkanoic acids	δ-Hydroxyalkanoic acids
β-Hydroxypropanoic acid (hydracrylic acid)		
β-Hydroxybutanoic acid (β-hydroxybutyric acid)	γ-Hydroxybutanoic acid (γ-hydroxybutyric acid)	
3-Hydroxy-2-methylpropanoic acid (β-hydroxyisobutyric acid)		
β-Hydroxypentanoic acid (β-hydroxyvaleric acid)	γ-Hydroxypentanoic acid (γ-hydroxyvaleric acid)	δ-Hydroxypentanoic acid (δ-hydroxyvaleric acid)
3-Hydroxy-3-methylpentanoic acid (3-hydroxy-3-methylvaleric acid)		
β-Hydroxyhexanoic acid (β-hydroxycaproic acid)	γ-Hydroxyhexanoic acid (γ-hydroxycaproic acid)	δ-Hydroxyhexanoic acid (δ-hydroxycaproic acid)
β-Hydroxyheptanoic acid (β-hydroxyenanthoic acid)	γ-Hydroxyheptanoic acid (γ-hydroxyenanthoic acid)	δ-Hydroxyheptanoic acid (δ-hydroxyenanthoic acid)
β-Hydroxyoctanoic acid (β-hydroxycaprylic acid)		
β-Hydroxynonanoic acid	γ-Hydroxynonanoic acid	
	γ-Hydroxydecanoic acid (γ-hydroxycapric acid)	δ-Hydroxydecanoic acid (δ-hydroxycapric acid)
β-Hydroxydodecanoic acid (β-hydroxylauric acid)	γ-Hydroxydodecanoic acid (γ-hydroxylauric acid)	
	γ-Hydroxytridecanoic acid	
	γ-Hydroxyhexadecanoic acid (α-hydroxypalmitic acid)	

studies range from potential uses in controlled release to use in formulation of tablets, surgical sutures, wound dressings, lubricating powders, blood vessels, tissue scaffolds, surgical implants to join tubular body parts, bone fracture fixation plates, and other orthopedic uses (1999, **WO9932536** A1, METABOLIX INC).

Because of their great compositional diversity, PHAs with a range of physical properties can be produced [30]. There are currently several commercially available PHAs including poly(3-hydroxybutyrate) (P3HB), poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate) (PHBHV), poly(3-hydroxybutyrate-*co*-4-hydroxybutyrate) (P3HB4HB), and poly(3-hydroxybutyrate-*co*-3-hydroxyhexanoate) (PHBHHx),which are derived from bacterial fermentations (see Table 1.8).

1.4.1.2.1 Poly(3-hydroxybutyrate)

Poly(3-hydroxybutyrate) (P3HB or PHB) is synthesized and stored within cells as an energy source for various microorganisms [31–33] (see Scheme 1.12). P3HB can be extracted from the microorganisms by various techniques

TABLE 1.8 Commercial Polyhydroxyalkanoates (PHAs)

Biopolymer	Commercial Name	Manufacturer	Applications
P3HB	Biogreen®	Mitsubishi Gas Chemical Co., Inc. (JP)	As a component material for biodegradable polymers; (cast) films, in natural latex gloves
P3HB	Mirel™ 3000 series (“P” and “F” versions)[1] Mirel 400 series (“P” and “F” versions)	Telles (ADM/Metabolix) (US)[2]	Mirel™ 3000: thermoforming Mirel 400: sheet applications
P3HB	Biocycle™ B1000 B18BC-1 B189C-1 B189D-1	PHB Industrial S/A (BR)	Films, disposables, medical applications
PHBHV and P3HB	Biomer® 300 P300E P300F P300F	Biomer Inc. (DE)	P300E: for extrusion, but not for film blowing; P300F: for food contact (EU only); P300F: for extrusion and food contact, not for film blowing
PHBHV, PHBHV/PLA	ENMAT™ Y1000 ENMAT™ Y1010 (with nucleating and stabilizing agent) ENMAT™ Y1000P ENMAT™ Y3000 ENMAT™ Y3000P ENMAT™ F9000P	Tianan Biologic, Ningbo (CH)	Thermoplastics: injection molding, extrusion, thermoforming, blown films; fiber & nonwovens Denitrification: Water treatment
PHBHHx	Nodax™[3]	Meredian (USA)	Packaging, laminates, coatings, nonwoven fibers
PHBHx	Kaneka PHBH	Kaneka Co (JP)	Film, sheets, foam, injection moldings, fibers, etc.; expected to be used in agricultural and construction interior materials, automotive interior materials, electrical devices, packaging, etc.
P3HB4HB	GreenBio®	Tianjin Green Bio-Science Co. (CN)/DSM (NL)	Fresh film, mulch film, laminating film, wrapping film, heat shrinkable film, etc.; food packaging, shopping bags, garbage bags, gift bags, produce bags, etc.
PHBHHx	AONILEX®	Kaneka (JP)	High-durability molded products: bottles and containers, auto interiors, electrical equipment
PHBHV	BIOPOL®[4]	Metabolix Inc. (USA)	Disposable products used in the food industry (utensils, cups and plates); plastic wrap for packaging, coatings for paper and cardboard, moisture barrier films for hygienic products, disposable containers for shampoo and cosmetics, and disposable items (razors, rubbish bags and disposable nappies); agricultural uses include a carrier for slow release of pesticides, herbicides or fertilizers; medical and pharmaceutical uses (gauzes, sutures, filaments, implants, drug carriers, and coatings for drugs); bicycle helmet with Biopol® fibers and cellulose high performance fibers
P4HB	TephaFLEX®	Tepha, Inc.	Monofilament suture; absorbable surgical film

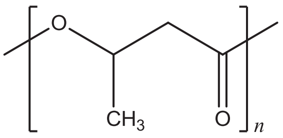
P3HB, poly(3-hydroxybutyrate); PHBHV, poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate); P3HB4HB, poly(3-hydroxybutyrate-*co*-4-hydroxybutyrate); PHBHHx, Poly(3-hydroxybutyrate-*co*-3-hydroxyhexanoate).

[1] *The “P” and “F” versions refer to general-purpose and food contact applications, respectively.*

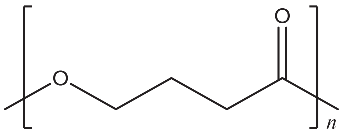
[2] *On January 12, 2012 Metabolix announced that Archer Daniels Midland Company (ADM) has given notice of termination of the Telles, LLC joint venture for PHA biopolymers. Telles was established as a joint venture between Metabolix and ADM in July 2006. The joint venture sells PHA-based biopolymers, including Mirel and Mvera, in the United States, Europe, and other countries.*

[3] *Meredian Inc. bought Nodax PHA™ technology from Procter & Gamble Co.*

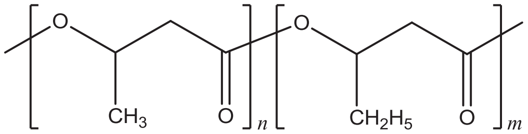
[4] *Monsanto’s rights to BIOPOL® were sold to Metabolix (U.S.) in 2001.*



SCHEME 1.12 Poly(3-hydroxybutyrate) (P3HB or PHB).



SCHEME 1.13 Poly(4-hydroxybutyrate) (P4HB).



SCHEME 1.14 Poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate) (PHBHV).

such as those disclosed in **EP0015123** A1 (1980) and **EP0046335** A2 (1982) of ICI PLC. The basic production process of P3HB consists of two steps: (1) fermentative step, in which the microorganisms metabolize the sugar available in the medium and accumulate the P3HB in the interior of the cell as source of reserve; (2) extracting step, in which the polymer accumulated in the interior of the cell of the microorganism is extracted and purified to get P3HB granules.

P3HB is a homopolymer having stereoregular structure with high crystallinity. The high crystallinity leads to a rather stiff and brittle material. P3HB has low melt viscosity and a narrow processing window. Its inherent brittleness and thermal instability during melt processing impedes its commercial application [34]. Several techniques have been practiced to overcome the brittleness of P3HB. The most common are: (1) plasticization of P3HB or addition of processing additives (e.g., nucleating agents); (2) copolymerization of 3-hydroxybutyrate with 3-hydroxyvalerate or with higher homologs of PHAs (see Section 1.4.1.2.3; (3) adjustment of the processing conditions; (4) calendering the material at temperature above room temperature but below melting temperature; and (5) heating up the shaped material after achieving complete crystallization to temperature around 120°C or more (2012, **WO2012141660**, USTAV POLYMEROV SAV).

P3HB finds uses in a broad range of applications, namely in packaging of disposable items, in agriculture for the prolonged release of fertilizers and agrochemicals, in medical devices for the controlled release of medical substances, as biofiller in nonbiodegradable polymers, for accelerating the degradation of the material, etc.

The commercial products of P3HB are outlined in Table 1.8.

1.4.1.2.2 Poly(4-hydroxybutyrate)

Poly(4-hydroxybutyrate) (P4HB) can be produced using transgenic fermentation methods (2000, **WO0056376** A1, METABOLIX INC). A commercial product of P4HB is TephaFLEX® produced by Tepha, Inc. P4HB is a strong, pliable thermoplastic polyester that, despite its biosynthetic route, has a relatively simple structure (see Scheme 1.13).

Biological production of P4HB has certain advantages over traditional chemical synthetic methods. The chemical synthesis of high molecular weight P4HB (greater than 1×10^5 g/mol) is difficult due to the tendency of the free acid to lactonize to form the relatively unstrained and kinetically favored five-membered ring. Thus, polycondensation of 4-hydroxybutyric acid is difficult to achieve, while the material that results from high pressure ring-opening polymerization reactions of ε-butyrolactone is of very low molecular weight [35] and would have poor mechanical properties. An alternate synthetic strategy for P4HB, the free radical ring-opening polymerization of 2-methylene-1,3-dioxolane, results in a copolymer containing ring opened and unopened units [36].

P4HB and its copolymers are used in medical applications, for example, in implantable medical devices and or for the controlled release of bioactive substances (2013, **US2013085185** A1, TEPHA INC).

1.4.1.2.3 Poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate)

Poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate) (PHBHV) is a copolymer in which 3-hydroxyvalerate (HV) units are incorporated in the P3HB backbone during the fermentation process (see Scheme 1.14). Microbiologically produced PHBHV can be made, for example, by the techniques described in **EP0052459** A1 (1982) and **EP0069497** A2 (1983) of ICI PLC.

PHBHV has improved flexibility and toughness and lower processing temperature over P3HB. The use of copolymers, for example, containing 10–25, particularly 15–20 mol% of HV units may in some cases be advantageous to lower the modulus of the P3HB since then bags made from a film of such copolymers are less liable to make rustling noises upon movement of the wearer. Presently, PHBHV having an HV content below 15 mol% are commercially available, while large-scale production of PHBHV having higher HV content is presently not commercially viable due to the surprisingly high production cost [37]. The available PHBHV (having an HV content of less than 15 mol%) has a low toughness and elongation at break. In general, lowering the HV content results in an increase of T_m (which can be in the temperature range of 120–180°C), water permeability, T_g and tensile strength; on the other hand, impact resistance and elongation at break are reduced [38,39].

PHBHV has achieved a certain economic importance because of its polypropylene-like material properties, and its commercial products are outlined in Table 1.7.

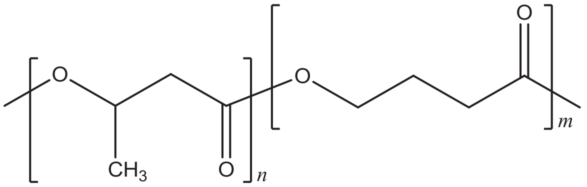
P3HB and PHBHV often have unsatisfactory properties. P3HB tends to be thermally unstable, while P3HB and PHBHV often have slow crystallization rates and flow properties that make processing difficult. For example, PHBHV remains tacky for long periods of time, and may stick to itself when being processed into films.

The commercially available P3HB and PHBHV represent only a small component of the property sets available to the PHAs. For example, the elongation at break of P3HB and PHBHV range from around 4–42%, whereas the same property for P4HB is about 1000%. Similarly, the values of Young's modulus and tensile strength for P3HB and PHBHV are 3.5 to 0.5 GPa and 40 to 16 MPa, respectively (for increasing HV content to 25 mol%), compared to 149 MPa and 104 MPa, respectively, for P4HB [40].

In addition to finding commercial use as a biodegradable replacement for synthetic commodity resins, P3HB and PHBHV have been extensively studied for use in biomedical applications. These studies range from potential uses in controlled release [41,42] to use in formulation of tablets, surgical sutures, wound dressings, lubricating powders, blood vessels, tissue scaffolds, surgical implants to join tubular body parts, bone fracture fixation plates, and other orthopedic uses, as described in **WO9851812** A2 (1998, METABOLIX INC). P3HB and PHBHV are also used for preparing a porous, bioresorbable flexible sheet for tissue separation and stimulation of tissue regeneration in injured soft tissue as disclosed in **EP0349505** A2 (1990, ASTRA MEDITEC AB).

1.4.1.2.4 Poly(3-hydroxybutyrate-*co*-4-hydroxybutyrate)

Poly(3-hydroxybutyrate-*co*-4-hydroxybutyrate) (P3HB4HB) was first found in 1988 from *Ralstonia eutropha* cultivated with 4-hydroxybutyric or 4-chlorobutyric acid as carbon sources. The incorporation of 4-hydroxybutyrate (4HB) units into P3HB improves the material application potential, and the copolymer shows a wide range of physical properties ranging from highly crystalline polymer to elastic rubber, depending on the polymer composition (see Scheme 1.15). Generally, carbon sources structurally related to 4HB are required to generate 4HB-containing PHA, such as 4-hydroxybutyric acid, γ-butyrolactone, and 1,4-butane diol. However, these carbon sources are much more expensive than glucose or other 3HB-generating carbon sources. The high cost of raw material for the copolymer production has become an obstacle for the wide production and application of P3HB4HB. **US2012214213** A1 (2012, TIANJIN GREENBIO MATERIAL CO LTD) discloses methods of producing P3HB4HB with high 4HB monomer content using carbon sources that are structurally unrelated to 4-hydroxybutyrate.



SCHEME 1.15 Poly(3-hydroxybutyrate-*co*-4-hydroxybutyrate) (P3H4BH).

1.4.1.2.5 Poly(3-hydroxybutyrate-*co*-3-hydroxyhexanoate)

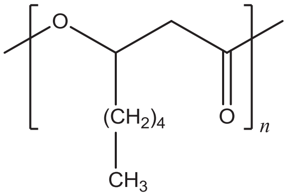
Poly(3-hydroxybutyrate-*co*-3-hydroxyhexanoate) (PHBHHx) can be obtained from either a microorganism or chemical synthesis. PHBHHx produced from a microorganism is preferable from the viewpoint of being fine powder.

Examples of microorganisms that accumulate PHBHHx within their cells are *Alcaligenes* such as *Alcaligenes lipolytica*, *Alcaligenes eutrophus*, and *Alcaligenes latus*, *Pseudomonas*, *Bacillus*, *Azotobacter*, *Nocardia*, and *Aeromonas*. Of these, a strain such as *Aeromonas caviae* and also *A. eutrophus* AC32, in which PHA synthetic enzyme genes are introduced, are preferable in view of productivity of PHBHHx. The method for obtaining PHBHHx from *A. caviae* is disclosed, for example, in **EP0533144** A2 (1993, KANEGAFUCHI CHEMICAL IND). These microorganisms are cultured under suitable conditions to accumulate PHBHHx in the microorganism (2004, **WO2004041936** A1, KANEKA CORP).

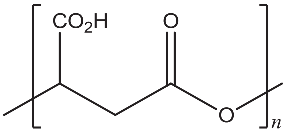
Known biological systems for the production of PHBHHx are inefficient. For example, Shimamura et al. [43] discloses that *A. caviae* synthesizes a PHBHHx composed of 3-hydroxybutyrate and when grown on olive oil or C_{12} to C_{18} fatty acids. The fraction of the 3-hydroxyhexanoate (3HHx) monomer was determined to be dependent on the concentration of the carbon source and the fermentation time and could amount to levels of 25% [44]. As a result of increasing 3HHx substrate levels, the crystallinity, T_m, and T_g of the PHA decrease. These changes in physical properties lead to an increased susceptibility to degradation by P3HB depolymerase from *Alcaligenes faecalis*. Other natural microorganism that incorporate low levels of 3HHx in a P3HB copolymer are *Comamonas testosteroni* and *Bacillus cereus* [45,46]. Recombinant *Pseudomonas putida* GPp104 strains in which the P3HB genes from either *Thiocapsia pfenigii* or *Chromatium vinosum* were introduced also accumulated PHA with 3HH as major constituent (2000, **WO0043523** A2, METABOLIX INC).

1.4.1.2.6 Poly(3-hydroxyoctanoates)

Poly(3-hydroxyoctanoates (P3HOs) are medium-chain-length PHAs (PHA_{MCL}). P3Hos, unlike P3HB or PHBHV,



SCHEME 1.16 Polyhydroxyoctanoate (P3HO).



SCHEME 1.17 Poly(β-malic acid) (PMLA).

are virtually amorphous owing to the recurring pentyl and higher alkyl side chains that are regularly spaced along the backbone groups (see Scheme 1.16). Their crystalline fraction, however, has a very low melting temperature as well as an extremely slow crystallization rate, two major drawbacks that seriously limit their potential as uses.

P3HO homopolymer can be made in substantial amounts using a genetically modified microorganism *Streptomyces lividans* TK64 when grown in a conventional mineral medium containing glycerol (2002, **US2002090687** A1, TRIPATHI GYANENDRA; MAHISHI LATA HANAMANTRAO; RAMACHANDER TURAGA VENKATA NAGA; RAWAL SHUBAN KISHEN; COUNCIL OF SCIENTIFIC & INDUSTRIAL RESEARCH). P3HO homopolymer has also been reported to be produced by *Pseudomonas mendocina* when grown on sodium octanoate as the sole carbon source [47].

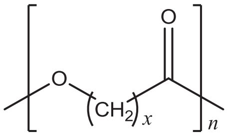
A known P3HO is poly(3-hydroxybutyrate-*co*-3-hydroxyoctanoate) (PHBO).

1.4.1.2.7 Poly(β-malic acid)

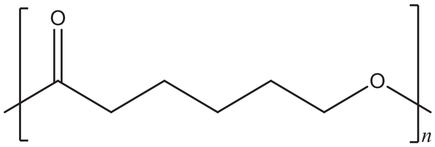
Poly(β-malic acid) (PMLA) is a biodegradable and bioabsorbable water-soluble aliphatic polyester having modifiable pendant carboxyl groups (see Scheme 1.17). PMLA has been reported to be produced by *Penicillium cyclopium*, *Physarum polycephalum*, and *Aureobasidium* [48]. Various representative industrial methods for producing PMLA are described in **CN102002148** A (2001, ZHANGJIAGANG CHAINENG BIOLOG SCIENCE CO LT), **JP2004175999** A (2004) and **JP2005320426** A (2005, NAT INST FOR MATERIALS SCIENCE). PMLA has various important applications in the biomedical field.

1.4.1.3 Poly(ω-hydroxyalkanoate)s

The general formula of poly(ω-hydroxyalkanoate)s is given in Scheme 1.18. A representative example of poly (ω-hydroxyalkanoate)s is poly(ε-caprolactone) (PCL).



SCHEME 1.18 Poly(ω-hydroxyalkanoate)s.



SCHEME 1.19 Poly(ε-caprolactone) (PCL).

1.4.1.3.1 Poly(ε-caprolactone)

Poly(ε-caprolactone) (PCL) is a fossil fuel–based aliphatic polyester, manufactured by ring-opening polymerization (ROP) of ε-caprolactone using homogenous organic metal complex catalysts such as zinc alkoxide [49], aluminum triflate [50], and tin alkoxides [51,52]. Tin(II) bis-(2-ethylhexanoate), also commonly referred to as tin octoate catalyst (stannous $Sn(Oct)_2$) is the most popular catalyst because of low cost, low toxicity, and high efficiency [53]. Scheme 1.19 presents the chemical structure of PCL.

PCL is a tough, flexible, and semicrystalline polymer with a degree of crystallinity of about 50%. It has a rather low T_g (−60 °C) and T_m (60 °C). The slow crystallization rate causes variation in the crystallinity with time. Due to its low T_m, PCL is difficult to process. Nevertheless, its ability to increase the mobility in the polymeric chains makes it a suitable candidate as plasticizer. Its biocompatibility and its in vivo degradation (much slower than other polyesters), also enable its use in the medical field for systems of long periods of time (1–2 years).

Among poly(ω-hydroxyalkanoate)s, PCL is the most thoroughly investigated owing to the possibility of blending this aliphatic polyester with a number of miscible commercial polymers such as PVC, chlorinated polyethylene, styrene-*co*-acrylonitrile copolymers, and bisphenol-A polycarbonate [54]. PCL blends with other biodegradable polymers that are also of potential use in the medical field, for example, the P3HB/PCL blends. Examples of commercially available products of PCL are Capa® polylactones (produced by Perstorp, formerly from Solvay) or Tone® polylactones (produced by Dow Chemicals Co) (see Table 1.9).

A block copolymer of ε-caprolactone with glycolide, poly(glycolide-*co*-ε-caprolactone) (PGCL), offering reduced stiffness compared with pure PGA, is being sold as a monofilament suture by Ethicon Inc., under the trade name MONOCRYL™.

1.4.2 Poly(alkylene dicarboxylate)s

Poly(alkylene dicarboxylate)s (PADCs) are polyesters derived from dicarboxylic acids and dihydroxy compounds.

TABLE 1.9 Commercial Polylactones

Biopolymer	Commercial Name	Manufacturer	Applications
PCL	Tone® series[1]: Tone® P-300, Tone® P-700, Tone® P-767, Tone® P-787 Tone® UC-261	Dow Chemicals Co (ex Union Carbide) (USA)	Coatings, elastomers, agricultural films, drug delivery systems, matrices for the controlled release of pesticides, herbicides and fertilizers
PCL	Capa™ 6000 series: Capa™ 6200 Capa™ 6250 Capa™ 6400 Capa™ 6430 Capa™ 6500 Capa™ 6500C Capa™ 6506 Capa™ 6800 Capa™ FB100 Capa™ 7000 series (copolymers)	Perstorp (UK)	Medical applications: alternative to traditional plaster, orthopedic splints, dental impressions, and oncology immobilization systems; films and laminates: blown films, laminates and packaging (e.g., foamed packaging or wrapping for both direct and indirect food contact); other applications: universal master batches
PCL	Celgreen PH	Daicel Chemical Industries (JP)	Mulch films, loose fill packaging, developing foam products, etc.
PCL, PCL derivatives	Placcel® 200 series Placcel® 300 series Placcel® F series (macro-monomers) Placcel® H1P (M_w 10,000)	Daicel Chemical Industries (JP)	Chemical compounds for use in or as coating materials or polyurethanes; modifiers for plastics; electric insulating materials; ink binders; additives for adhesives
PGCL	MONOCRYL™ Plus Antibacterial (poliglecaprone 25)	Ethicon Inc (USA)	Monofilament absorbable suture

PCL, poly(ε-caprolactone); PGCL, poly(glycolide-*co*-ε-caprolactone).
[1] *The production of Tone® has been stopped or sold.*

These biodegradable polyesters can be characterized as belonging to three general classes: (1) aliphatic polyesters (polyesters derived solely from aliphatic dicarboxylic acids), (2) aliphatic-aromatic polyesters (polyesters derived from a mixture of aliphatic dicarboxylic acids and aromatic dicarboxylic acids), and (3) aromatic polyesters.

1.4.2.1 Poly(alkylene alkanoate)s

The polyesters derived solely from aliphatic dicarboxylic acids, also called poly(alkylene alkanoate)s (PAAs), are polyesters prepared from a dicarboxylic acid containing 4–10 carbon atoms and a diol containing 2–6 carbon atoms, and two or more kinds of each of dicarboxylic acid and diol may be employed. Examples include poly(ethylene adipate) (PEA), poly(ethylene succinate) (PES) and poly(butylene succinate) (PBS). Commercially available industrial PAAs are shown in Table 1.10.

1.4.2.1.1 Poly(ethylene succinate)

Polyethylene succinate (PES) is chemically synthesized either by polycondensation of ethylene glycol and succinic acid or by ring-opening polymerization of succinic anhydride with ethylene oxide [55,56] (**JP9031174** A, 1997, UNITIKA LTD; **CN101628972** A, 2010, QINGDAO INST OF BIOMASS ENERGY) (see Scheme 1.20). PES has a T_m of 103–106 °C and good mechanical properties, especially elongation [57,58]. It has a high oxygen gas barrier property, which is one of advantageous properties taking film utility into consideration, and is excellent in biodegradability (2005, **EP1564235** A1; 2005, **JP2005264155** A, NIPPON CATALYTIC CHEM IND).

1.4.2.1.2 Poly(butylene succinate)

Poly(butylene succinate) (PBS)[1] is chemically synthesized through polycondensation of 1,4-butane diol and succinic acid or its anhydride in the presence of a catalyst [55] (**JP8003302** A, 1996, UNITIKA LTD; **JP9031176** A, 1997, SHOWA HIGHPOLYMER & SHOWA DENKO K.K.; **JP2001098065** A, 2001, MITSUBISHI CHEM CORP;

---

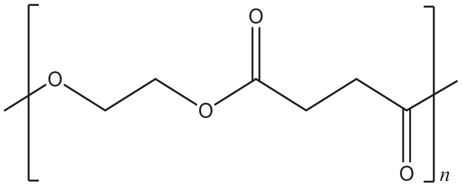
[1] Poly(tetramethylene succinate) (PTeMS) has the same structure with PBS, but different CAS number.

TABLE 1.10 Poly(alkylene alkanoate)s (PAA)s

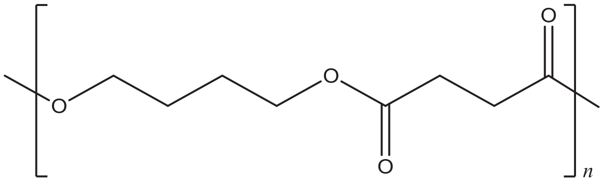
Biopolymer	Commercial Name	Manufacturer	Applications
PBS	Skygreen® SG100	SK Chemicals (KR)	Injection molding, disposable goods, fibers
PBS	EnPol® G4000 series: EnPol® G4560 EnPol® G4560J (>MFI)	IRE Chemical Ltd (KR)	EnPol G4560: disposable goods (fork, spoon, knife, golf tee), horticulture equipment (plant pot, clip), fishing gear
PBS	Bionolle™ 1000 series: Bionolle™ 1001MD[1] Bionolle™ 1020MD Bionolle™ 1903MD	Showa High Polymer Co Ltd (JP)	Bionolle™ 1001MD: blown film (mulch films, compost bags), monofilament, blow molding, sheets, flat yarns; Bionolle™ 1020MD: injection molding, staple fiber; Bionolle™ 1903MD: foamed sheet, extrusion coating, uses for additive
PBSA	Bionolle™ 3000 series: Bionolle 3001 Bionolle™3003 Bionolle™ 3020 Bionolle™ 3900 Bionolle™ 5000	Showa High Polymer Co Ltd (JP)	Bionolle™ 3001MD: blown film (mulch films, compost bags), monofilament, blow molding, sheets, flat yarns; Bionolle™ 3020MD: injection molding, staple fiber
PBSA	Skygreen™ SG200	SK Chemicals (KR)	Extrusion films, sheets, extrusion coating
PBSL	GS Pla® AD92W GS Pla® AZ91T GS Pla® GZ95T	Mitsubishi Chemical (JP)	Biodegradable multifilms for agriculture; disposable table utensils
PES	Lunare SE®	Nippon Shokubai (JP)	Moldings, films, fibers

PBA, poly(butylene adipate); PBS, poly(butylene succinate); PBSA, poly(butylene succinate-adipate); PBSL, poly(butylene succinate-co-lactate); PES, poly(ethylene succinate).

[1] *Bionolle™ 1001 is synthesized from succinic acid and 1,4-butane diol using 1,6-hexamethylene diisocyanate as chain extending agent.*



SCHEME 1.20 Poly(ethylene succinate) (PES).



SCHEME 1.21 Poly(butylene succinate) (PBS).

WO2010123095 A1, 2010, HITACHI PLANT TECHNOLOGIES LTD) (see Scheme 1.21).

The succinic acid can be manufactured by fermentation of a saccharide such as sugarcane or corn (maize) (2005, **JP2005211041** A, NIPPON CATALYTIC CHEM IND). Showa Denko K.K. (SDK) announced that it has succeeded in producing its PBS under the trademark Bionolle™, using bio-based succinic acid. Another company already producing bio-based PBS (containing bio-succinic acid) is Mitsubishi Chemical Company [59].

PBS has a relatively high melting temperature (T_m = 13 °C) and favorable mechanical properties, which are comparable with those of such widely used polymers as polyethylene and polypropylene [60]. PBS has a relatively low biodegradation rate because of its high crystallization rate and high crystallinity. The enzymatic degradability of PBS was reported to be lower than that of PCL [61]. BIONOLLE™ 1001 manufactured by Showa High Polymer (JP) is an example of a commercially available PBS. Other examples of commercially available products of PBS are shown in Table 1.10.

Another form of poly(butylene succinate) is poly(2,3-butylene succinate), which is an amorphous PBS with a relatively low softening point (45–50 °C), which is used in pharmaceutical applications. It has relatively "fast" in vivo bioresorption rates, with samples becoming completely metabolized in 4–6 weeks without any observable untoward effects (1995, **US5439688** A, DEBIO RECH PHARMA SAA DEBIO RECH PHARMA SA).

1.4.2.1.3 Poly(butylene adipate)

Poly(butylene adipate) (PBA) is chemically synthesized through polycondensation of adipic acid or its lower alkyl ester with 1,4-butaediol in the presence of a polymerization catalyst such as a titanium compound (1988, **JP63251424** A, UNITIKA LTD; 1996, **JP8301996** A, KANEBO LTD; 2001, **JP2001098065** A, MITSUBISHI CHEM CORP) (see Scheme 1.22).

1.4.2.1.4 Poly(butylene succinate-*co*-adipate)

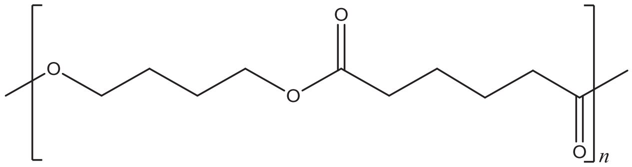
Poly(butylene succinate-*co*-butylene adipate) (PBSA) is a combination of 1,4-butane diol, succinic acid, and adipic acid [55] (see Scheme 1.23). PBSA is prepared by adding adipic acid to source materials during PBS synthesis. Although usually synthesized from fossil fuel, it is also possible for the monomers that make up PBSA to be produced from bio-based feedstock. PBSA degrades faster than PBS. Further, PBS and PBSA are known to biodegrade more slowly than PHAs. Of the two, PBS has higher crystallinity and is better suited for molding, while PBSA has lower crystallinity and is better suited to film applications. Both polymers have a low (subzero) T_g, and their processing temperatures overlap with PHAs.

1.4.2.1.5 Polyoxalates

The synthesis of polyoxalate polymers (see Scheme 1.24) was first reported by Carothers et al. (1930) [62]; they described the ester interchange reaction of diols such as ethylene glycol, 1,3-propane diol, or 1,4-butane diol with diethyl oxalate to yield a mixture of monomer, soluble polymer, and insoluble polymer. The reaction of oxalic acid and an alkylene glycol to form polyester resins is described in **US2111762** A (1938, ELLIS FOSTER CO), while methods for the preparation of polyoxalates of fiber-forming quality and the formation of sutures from filaments made of polyoxalates are described in **US4141087** A (1979) and **GB1590261** A (19810 of ETHIKON INC). The synthesis of poly(ethylene oxalate) (PEOx or polyacetal) is described also in **WO2008038648** A1 (2008, TOYO SEIKAN KAISHA LTD).

1.4.2.1.6 Poly(propylene fumarate)

Poly(propylene fumarate) (PPF) is a biodegradable unsaturated linear polyester, which is synthesized typically via transesterification (see Scheme 1.25). The fumarate double bonds in PPF can be crosslinked at low temperatures to form polymer networks. The high mechanical strength of crosslinked PPF matrices and their ability to be crosslinked in situ make them especially suitable for orthopedic applications. PPF degrades in the presence of water into propylene glycol and fumaric acid, degradation products that are easily cleared from the human body by normal metabolic processes.



SCHEME 1.22 Poly(butylene adipate) (PBA).

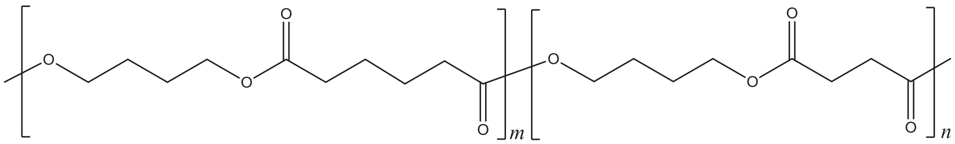
Representative synthesis methods and applications for PPF are described in **WO9529710** A1 (1995, RICE UNIVERSITY), **WO9952469** A1 (1999, UNIV WM MARSH RICE), **WO0062630** A1 (2002, UNIV WM MARSH RICE), and **US2004023028** A1 (2004, MAYO FOUNDATION).

1.4.2.2 *Aliphatic-Aromatic Copolyesters*

Aliphatic-aromatic copolyesters are a general class of biodegradable polymers that can be prepared by condensing aliphatic diols, aliphatic dicarboxylic acids/esters, and aromatic dicarboxylic acids/esters. The polyester repeat units derived from the aliphatic dicarboxylic acids enable enzymatic hydrolysis under biodegradation conditions, such as composting. The presence of the aromatic component in the polyester chain is important to obtain polymers with sufficiently high T_m and with adequate crystallization rates. In commercial products the amount of aromatic acid in the chain is typically lower than 49% since the percentage of biodegradation of the polyesters decreases significantly above said threshold.

Copolyesters containing components such as pol(alkylene ether) glycol are no longer pure copolyesters but instead copolyetheresters. Generally, known aliphatic-aromatic copolyetheresters incorporate high levels of the poly(alkylene ether) glycol component. Aliphatic-aromatic copolyetheresters containing high levels of the poly(alkylene ether) have lowered thermal properties; for example, **WO9615174** A1 (1996), **US5936045** A (1999), and **US6046248** A (2000) of BASF AG disclose aliphatic-aromatic polyetherester compositions that have 20–25 mol% of the poly(alkylene ether) glycol component and are found to have lowered crystalline T_ms in the range of 111–127.5 °C. In addition, the poly(alkylene ether) glycol repeat units can enable a second mode of degradation occurring through their oxidative cleavage in the polymer chains.

Known biodegradable aliphatic-aromatic copolyesters include poly(butylene succinate-*co*-terephthalate) (PBST),

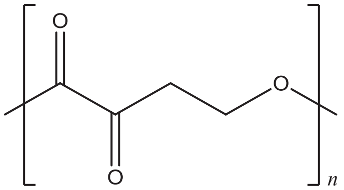


SCHEME 1.23 Poly(butylene succinate adipate) (PBSA).

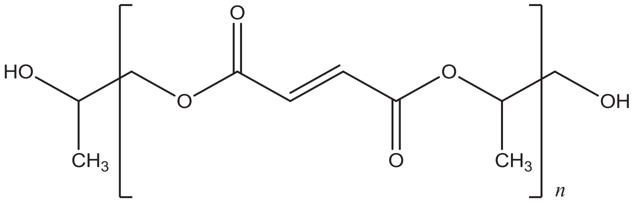
poly(butylene adipate-*co*-terephthalate) (PBAT) and poly(tetramethylene adipate-*co*-terephthalate) (PTeMAT). Various representative industrial methods for producing aliphatic-aromatic copolyesters are described in **US5171308** A (1992) and **WO9514740** A1 (1995) of DUPONT; **WO9625446** A1 (1996, BASF); **US5171308** A (1992), **EP1108737** A2 (2001), and **EP1106640** A2 (2002) of IRE CHEMICAL LTD). The aliphatic-aromatic copolyesters are synthetically polymerized, and they are not entirely renewable. Examples of commercially available aliphatic-aromatic polyesters are shown in Table 1.11.

1.4.2.2.1 Poly(butylene adipate-*co*-terephthalate)

Poly(butylene adipate-*co*-terephthalate) (PBAT) is a random copolymer of butylene adipate and terephthalate prepared by melt polycondensation of 1,4-butanediol, dimethyl terephthalate, and adipic acid, and catalyzed by tetrabutyl-orthotitanate [63] (see Scheme 1.26). PBAT has exhibited useful properties such as high elasticity, wear and fracture resistance, resistance to water and oil, and full biodegradability under composting conditions. It owes its biodegradability to the butylene adipate group and its stability and mechanical properties to the terephthalate group, which results in high elongation (700%) but relatively low tensile strength (32 MPa) [64]. High production costs, dependency on fossil fuel resources as the raw materials, and low modulus have limited broad applications of this polymer.



SCHEME 1.24 Poly(ethylene oxalate) (PEOx).



SCHEME 1.25 Poly(propylene fumarate) (PPF).

Representative commercial products of PBAT are Ecoflex® (BASF AG) and Origo-Bi® (ex Eastar BIO® (Novamont, formerly Eastman Chemical). Ecoflex® is designed to process like low density polyethylene (LDPE) into films, bags, or coatings. It is ideal for trash bags or disposable packaging as it decomposes in compost within a few weeks or in soil without leaving any residues. Other commercial products of PBAT can be seen in Table 1.11.

1.4.2.3 Aromatic Polyesters (Bio-Based)

Bio-based aromatic polyesters are capable of reducing the use of fossil fuel resources and the increase of carbon dioxide, but they are not biodegradable. Examples of commercially available bio-based aromatic polyester are shown in Table 1.12.

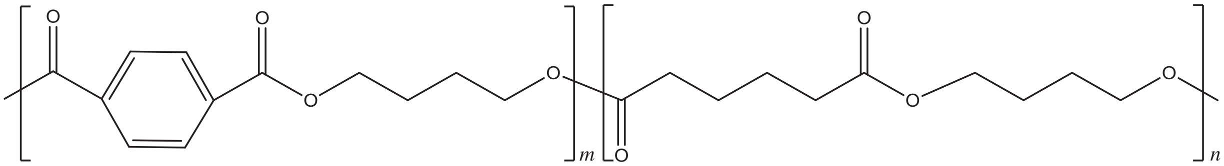
1.4.2.3.1 Poly(ethylene terephthalate) (Bio-Based)

Bio-based poly(ethylene terephthalate) (PET) is made from ethylene glycol and terephthalic acid or its ester-forming derivative, wherein at least one of the diol components and/or

TABLE 1.11 Aliphatic-Aromatic (co)polyesters

Biopolymer	Commercial Name	Manufacturer	Applications
PBAT	EnPol® G8000 series: EnPol® G8002 Enpol G8060 EnPol G8060F (G8060 & biomass)	IRE Chemical Ltd (KR)	Enpol G8060: packaging films, plastic bags, PLA modifier; EnPol G8060F: high quality films
PBAT	Skygreen™ SG300	SK Chemicals (KR)	Extrusion, film, sheet
PBAT	FEPOL® 1000 series FEPOL® 2000 series: FEPOL® 2024	Far Eastern New Century Co. (TW)	Packaging films, agricultural films and compost bags
PBAT	Ecoflex® series: Ecoflex® F 1200 Ecoflex® F BX 7011	BASF (DE)	Packaging films, agricultural films, compost bags, coated applications
PBAT	Origo-Bi® (ex Eastar Bio®[1])	Novamont (IT)	Plastic bags, plastic sacks, plastic envelopes
EST	Green Ecopet (recycled PET fiber/resin)	Teijin (JP)	Fibers

PBAT, poly(butylene adipate-*co*-terephthalate); PBST, poly(butylene succinate-*co*-terephthalate); PEST, poly(ethylene succinate-*co*-terephthalate).
[1] *The Eastman Chemical's Eastar Bio technology was bought in 2004 by Novamont.*

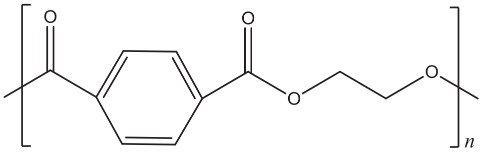


SCHEME 1.26 Poly(butylene adipate-*co*-terephthalate) (PBAT).

TABLE 1.12 Bio-Based Aromatic Polyesters

Biopolymer	Commercial Name	Manufacturer	Applications
PET	Up to 30% bio-based PET (Plantbottle™)	Coca Cola Co (USA)	Containers for packaging food products, soft drinks, alcoholic beverages, detergents, cosmetics, pharmaceutical products, and edible oils
PET (70% terephthalic acid and 30% of mono-ethylene glycol, MEG)	GLOBIO	FKuR Kunststoff GmbH (DE), distributor in Europe	Bottles, films, automotive and other injection-molding applications
PTT	Sorona®	DuPont (USA)	Fibers, multifilament surgical device (suture, mesh, sternal closure device, cable, and tape)
PTT	Biomax® PTT 1100 Biomax® PTT 1002	DuPont (USA)	Biomax® PTT 1002: packaging and industrial applications; Biomax® PTT 1100: injection-molded containers, cosmetic packaging and other parts where polyesters are used

PET, poly(ethylene terephthalate); PTT, poly(trimethylene terephthalate).



SCHEME 1.27 Poly(ethylene terephthalate) (PET).

terephthalate components are derived from at least one bio-based material (see Scheme 1.27).

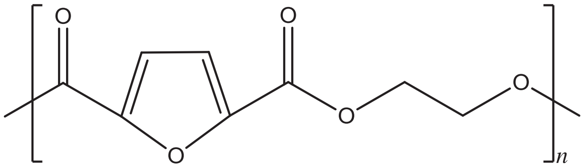
WO2009120457 A2 (2009) and **US2010028512** A1 (2010) of COCA COLA CO disclose such a bio-based PET. The bio-based PET comprises 25–75 wt% of a terephthalate component and 20–50 wt% of a diol component, wherein at least 1 wt%, preferably 10 wt%, of the diol component and/or terephthalate component are derived from at least one bio-based material; e.g., corn and potato. The bio-based PET is useful for making a bio-based container for packaging food products, soft drinks, alcoholic beverages, detergents, cosmetics, pharmaceutical products, and edible oils.

Coca-Cola's current renewable bottle, named PlantBottle™, is made by converting sugarcane into ethylene glycol, which represents 30 wt% of the total composition of PET [65]. But deriving terephthalic acid from nature has been much more difficult. In November 2011, Japanese industrial group Toray announced that it had produced the world's first "fully renewable" bio-based PET fiber with terephthalic acid made from *p*-xylene derived from biomass via isobutanol from Gevo (USA) [66]. Gevo's yeast-based fermentation process converts corn starch–derived sugar into isobutanol, which after subsequent chemical reactions, is transformed into a stream of aromatics containing more than 90% *p*-xylene. Its technology is easily retrofitted into existing ethanol plants.

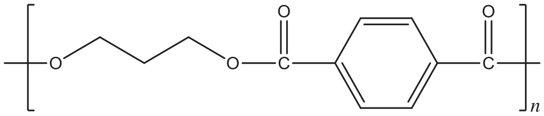
JP2011219736 A (2011, TORAY IND INC) discloses a bio-based poly(alkylene terephthalate) obtained by using, as raw materials, biomass-resource-derived glycol and biomass-resource-derived terephthalic acid and/or its ester-forming derivative, and a phosphorus compound.

1.4.2.3.2 Poly(ethylene furanoate)

Poly(ethylene furanoate) (PEF) is made from ethylene glycol and 2,5-furan dicarboxylic acid (FDCA) (see Scheme 1.28). Avantium (NL) developed a process using catalytic reactions to create FDCA, which reacts with ethylene glycol to make PEF. PEF is abio-based alternative to PET; the main component of PET is terephthalic acid, which could be replaced by bio-based FDCA. According to Avantium, PEF exceeds PET in terms of oxygen barrier and temperature performance.



SCHEME 1.28 Poly(ethylene furanoate) (PEF).



SCHEME 1.29 Poly (trimethylene terephthalate) (PTT).

Even though the PEF production process is still under development, it has been estimated that the complete substitution of PET by PEF is likely to offer savings between 43% and 51% of fossil fuel, and reduction between 46% and 54% of CO_2 emissions for the system "cradle to grave" [67].

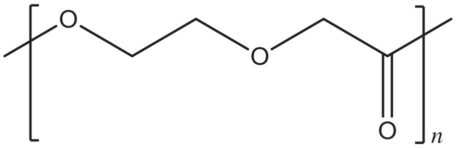
1.4.2.3.3 Poly(trimethylene terephthalate) (Bio-Based)

Poly(trimethylene terephthalate) (PTT) or poly(propylene terephthalate) (PPT) belongs to the group of linear aromatic polyesters next to PET and poly(butylene terephthalate) (PBT) with three methylene groups in the glycol repeating units (see Scheme 1.29). The odd number of methylene units affects the physical and chemical structure of PTT, resulting in several excellent properties as the high elastic recovery and dyeing ability [68]. Initially, PTT was intended for the carpeting market, but due to its processability like spinning and dyeing properties, it was also found to be suitable for the fiber market in the fields of sportswear and active wear [68,69].

PTT is made by polycondensation of 1,3-propane diol and either terephthalic acid or dimethyl terephthalate. This polymer has attracted the attention in the recent years after the development of production of 1,3-propane diol from starch-derived glucose, a renewable resource (2001, **WO0112833** A2, DU PONT). As disclosed in **WO0111070** A2 (2001, DU PONT) and **US6428767** B1 (2002, DU PONT; GENENCOR INT) bio-based 1,3-propanediol and polymers derived therefrom can be distinguished from their petrochemical derived counterparts on the basis of ^{14}C and dual carbon-isotopic fingerprinting.

Bio-based PTT is marketed by DuPont Company as Sorona® fibers, and the polymer is additionally used in many other end-use applications for films, filaments, and engineering plastics. DuPont™ Sorona® EP thermoplastic polymers contain 20–37 wt% renewably sourced material derived from corn sugar 1,3-propane diol. The new material exhibits performance and molding characteristics similar to high performance PBT.

DuPont Packaging & Industrial Polymers introduced Biomax® PTT, which contains up to 37% renewably sourced content for packaging applications, where chemical resistance and durability are essential features. Biomax® PTT 1100 is especially suitable for use in injection-molded containers, cosmetic packaging, and other parts where polyesters are used.



SCHEME 1.30 Polydioxanone (PDO).

1.5 POLY(ETHER-ESTER)S (BIO-BASED)

Bio-based poly(ether ester)s are thermoplastic elastomers prepared by a two-stage melt transesterification process from readily available starting materials such as alkylene terephthalate, an alkane diol, and a poly(alkylene glycol ether) derived from renewable resources. The resulting poly(ether ester)s consist of crystallizable alkylene terephthalate sequences (hard segments) and elastomeric poly(alkylene oxide) sequences (soft segments). These materials show a wide range of properties depending upon the content of alkylene terephthalate segments and the length of poly(alkylene oxide) [70–72]. Several commercially available bio-based block poly(ether ester)s, based on PBT and poly(tetramethylene oxide) are known, such as Hytrel® RS (DuPont) and Arnitel® Eco (DSM). These block copolyesters combine many interesting properties, including a high temperature T_m, a low T_g, and high yield stress, elongation at break, and elasticity along with ease of processing [72]. Hytrel® RS grades contain rubbery soft blocks made from CERENOL™, a polyether diol containing 50–100 wt% renewably sourced 1,3-propanediol derived from corn. According to DuPont, Hytrel® RS thermoplastic elastomers have many applications including hoses and tubing for automotive and industrial uses, boots for CV joints, air bag doors, and energy dampers. According to DSM, Arnitel® Eco is suitable for applications in consumer electronics, sports and leisure, automotive interiors and exteriors, furniture, alternative energy, and specialty packaging. The material is designed for a long service lifetime under extreme conditions.

1.5.1 Polydioxanone

Polydioxanone (PDO, PDS) is a colorless, crystalline, biodegradable synthetic polymer of multiple repeating ether-ester units. Referred to as poly(oxyethylene glycoate) and poly(ether ester), the ring-opening polymerization of *p*-dioxanone results in a synthetic suture, known as PDS or polydioxanone (1984, **US4490326** A, 1984, ETHICON INC) (see Scheme 1.30). The polymer is processed at the lowest possible temperature to prevent depolymerization back to monomer. The monofilament loses 50% of its initial breaking strength after 3 weeks and is absorbed within 6 months, providing an advantage over other products for slow-healing wounds. A commercial product of poly (*p*-dioxanone) is PDS™ Plus Antibacterial Suture of ETHICON, which is a monofilament synthetic absorbable suture.

1.6 ALIPHATIC POLYCARBONATES

The synthesis of high molecular weight poly(alkylene carbonate)s was first reported by Inoue et al. in the late 1960s [73,74]. These rather new polymers are derived from carbon dioxide and are produced through the copolymerization of CO_2 with one or more epoxy compounds (ethylene oxide or propylene oxide). They can contain up to 50 wt% CO_2 or CO and sequester this harmful greenhouse gas permanently from the environment.

Aliphatic polycarbonates (APCs), as another important class of biodegradable polymers, are widely used in the areas of packaging materials, drug carriers, and tissue engineering for their favorable biodegradability, biocompatibility, and nontoxicity [75].

1.6.1 Poly(ethylene carbonate)

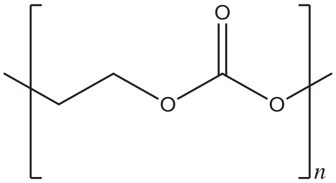
Poly(ethylene carbonate) (PEC) is the product of alternating copolymerization of ethylene oxide and CO_2 (see Scheme 1.31). PEC is a biodegradable amorphous polymer with a T_g of 15–25 °C, and it exhibits elastomeric characteristics at ambient temperature. Extruded films of PEC have high oxygen barrier properties that make it useful as a barrier layer for food packaging applications. PEC has also been found to decompose more cleanly at lower temperatures both in nitrogen and in air than most other commercial polymers.

Empower Materials Inc. commercializes QPAC® 25, a PEC, which is used as binder or sacrificial material.

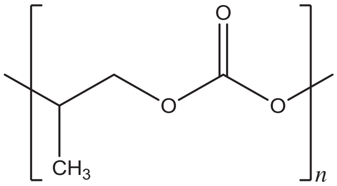
Novomer also commercializes PEC in two application markets: as a traditional polymer for packaging and as a clean burning sacrificial material for high-end processing, including ceramic and electronic processing.

1.6.2 Poly(propylene carbonate)

Poly(propylene carbonate) (PPC) is the product of alternating copolymerization of propylene oxide and CO_2 (see Scheme 1.32). PPC is a biodegradable amorphous polymer because of the aliphatic polycarbonate ester structure on its backbone [76]. High-molecular-weight PPC has been predominantly synthesized using zinc carboxylate catalysts to copolymerize propylene oxide and CO_2. Transition metal complexes have been developed for the copolymerization of carbon dioxide and epoxides (2002, **US2002082363** A1, CHANGCHUN INSTITUTE OF APPLIED CHEMISTRY CHINESE ACADEMY OF SCIENCES; 2003, **CN1436803** A, CHANGCHUN APPLIED CHEMISTRY); but such complexes have not been fully exploited and/or optimized in the preparation of improved PPC materials.



SCHEME 1.31 Poly(ethylene carbonate) (PEC).



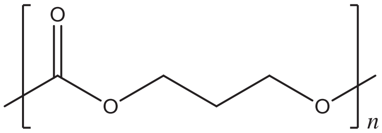
SCHEME 1.32 Poly(propylene carbonate) (PPC).

PPC was the focus of intense investigation, and several companies have explored applications for the material as a commodity thermoplastic. To date, PPC has been commercialized only as a sacrificial polymer in applications where the clean thermal decomposition of PPC is advantageous. PPC has good properties such as compatibility and impact resistance, and can be melt processed like commercial polyethylene [77]. However, its commercialization for thermoplastic applications has been complicated by poor thermal and processing properties. PPC has a relatively low T_g (37–41 °C); furthermore, its terminal groups are hydroxyl groups, therefore PPC has shortcomings such as viscous flow at room temperature and a relatively large brittleness at low temperature. An end-capped PPC can prevent the occurrence of unzipping reaction from its terminal, so that its heat stability is improved (2007, **US2007117908** A1, CHANGCHUN APPLIED CHEMISTRY). The thermal and mechanical properties of PPC can be improved by blending PPC with another polymer (see Chapter 3: Blending; Section 3.2.3: Blending aliphatic polycarbonates with aliphatic polyesters).

Empower Materials Inc. commercializes QPAC® 40, a PPC, which, like QPAC® 25, is used in binder and sacrificial structure applications.

In addition to PEC and PPC, Empower Materials Inc. commercializes several other QPAC® polymers that have been successfully synthesized on pilot scale including: QPAC® 130 (poly(cyclohexene carbonate); PCHC) and QPAC® 100 (PPC/PCHC).

Novomer Inc (USA) and SK Energy Co., Ltd. (SK) are also commercializing PPC. SK is creating its 44% $C0_2$-based Greenpol™ PPC using a proprietary catalyst and a continuous polymerization process. PPC has potential uses for packaging materials, competing with commodity polymers such as polyolefins.



SCHEME 1.33 Poly(trimethylene carbonate) (PTMC).

Novomer is working with Eastman Kodak to develop PPC for packaging applications. Novomer plans to make enough PPC resins and films so that potential customers can test them in packaging applications. Novomer targets its first PPC product, NB-180, as a temporary binder for electronics. Because it breaks down into carbon dioxide and water when exposed to high temperatures, it can be burned off without a trace. Both NB-180 and the new PPC polymer are made by polymerizing propylene oxide with carbon dioxide using a proprietary catalyst. As a packaging polymer, PPC is touted as offering unique impact resistance, stiffness, and oxygen barrier properties.

WO2011005664 A2 (2011, NOVOMER INC) discloses PPC films as parts of a multilayer film. In certain embodiments, PPC acts as a tie layer in a laminate film. In some embodiments, a PPC composition provides a structural layer in a multilayer film. In certain other embodiments, the films comprise a PPC composition in combination with one or more other degradable polymers as PLA, P3HB, poly(3-hydroxypropionate) (P3HP or PHP), starch, or modified cellulose. In still other embodiments, the layer containing the PPC composition acts as a barrier layer to retard the transmission of oxygen, water vapor, carbon dioxide, or organic molecules.

1.6.3 Poly(trimethylene carbonate)

Poly(trimethylene carbonate) (PTMC) is a biodegradable polycarbonate with rubber-like properties. PTMC is obtained by ring-opening polymerization of trimethylene carbonate (TMC), catalyzed with diethyl zinc [10] (see Scheme 1.33). A high-molecular-weight flexible polymer was prepared, but displays poor mechanical performance [78]. Due to this property, its applications are limited and copolymers are more often used. Copolymers with glycolide and dioxanone have also been prepared [22].

Mitsubishi Gas Chemical Co. has marketed a copolyester carbonate, namely poly[oligo(tetramethylene succinate)-*co*-(tetramethylene carbonate)] (PTMS/PTeMC). The copolyester carbonate is composed of a polyester part and a polycarbonate part. The content of carbonate inside the copolymer is variable. The T_m of the copolymer is about 100–110 °C. Introducing poly(tetramethylene carbonate) (PTeMC) into poly(tetramethylene succinate) (PTMS) probably causes disorder in the crystal structure, thus lowering its T_m and increasing its susceptibility to enzymatic and microbial attacks [10]. The microbial degradability of copolyester carbonate was confirmed to be higher than those of both of its constituents [79].

1.6.4 Poly(butylene carbonate)

Poly(butylene carbonate) (PBC), which is a very important member of the APC family, is a semicrystalline polymer with a T_m around 60 °C, as well as a T_g of −38 °C [75]. Due to the flexibility of the polymer chains and its crystallizability, PBC possesses excellent impact resistance and satisfactory tensile strength.

Empower Materials Inc. synthesized PBC on pilot scale under the name QPAC® 60 to be used as a binder or sacrificial material.

1.7 POLYAMIDES

Polyamides are polymers with amide groups (R–CO–NH–R′) as integral parts of the main polymer chain. Bio-polyamides are basically formed from polycondensation of: (1) diamines and dicarboxylic acids, (2) ω-amino carboxylic acids as bifunctional monomers, and (3) α-amino carboxylic acids as bifunctional monomers [80]. Bio-polyamides include both bio-based polyamides and biodegradable fossil fuel–based polyamides. The commercially available bio-polyamides are shown in Table 1.13.

1.7.1 Polycondensation of Diamines and Dicarboxylic Acids

The dicarboxylic acid can be derived from renewable resources such as castor oil. The diamines are mainly derived from fossil fuel [80]. Commercial bio-polyamides produced by the polycondensation of diamines and dicarboxylic acids include polyamide 1010 (PA 1010), polyamide 410 (PA 410), polyamide 610 (PA 610), and polyphthalamides (PPA).

1.7.2 Polycondensation of ω-Amino Carboxylic Acids or Lactams

An example of a bio-polyamide produced by the ring-opening polymerization of ε-caprolactam is polyamide 11 (PA 11).

1.7.3 Poly(α-amino acids)

Synthetic polymers of α-amino acids contain peptide bonds in the main chain and can be composed of the same structural units (α-amino acids) as the poly(amino acid)s of natural origin, such as polypeptides and proteins. In this regard they may be considered as being protein analogues. Two amino acid homopolymers comprising a single type of amino acid are known in nature [81]: poly(γ-glutamic acid) (γ-PGA) and ε-poly(L-lysine) (ε-PL).

TABLE 1.13 Commercially Available Bio-Polyamides

Biopolymer	Commercial Name	Manufacturer	Applications
PA 11	Rilsan®	ARKEMA (FR)	Electrical cables, automotive, pneumatic, and hydraulic hose
PA	Rilsan® Clear G830 Rnew	ARKEMA (FR)	Molding applications, ideally suited for optics as high-end eyewear frames
co-PA	Platamid® Rnew	ARKEMA (FR)	Hot melt adhesive
PA 1010	Grilamid 1S	EMS-GRIVORY (DE)	Reinforced Grilamid 1S: Manufacture of stiff covers; Nonreinforced, amorphous grades: injection-molding processes for overmolding metal sheets
PA 1010	VESTAMID® Terra DS	EVONIK (DE); FKuR Kunststoff GmbH (DE), distributor worldwide	Injection molding, fibers, powder, extrusion, and films
PA 1010	Zytel® RS LC1000 BK385 Zytel® RS LC1200 BK385 Zytel® RS LC1600 BK385	DUPONT (USA)	Multiple extrusion applications
PA 1010	Hiprolon® 200 series	Suzhou Hipro Polymers (CN)	Gear, electronics housing parts, rigid technical tubing, technical film, powder coating
PA 1012	Hiprolon® 400 series	Suzhou Hipro Polymers (CN)	Automotive tubing systems, oil and gas pipe, technical decorative films
PA 1012	VESTAMID® Terra DD	EVONIK (DE); FKuR Kunststoff GmbH (DE), distributor worldwide	Injection molding, fibers, powder, extrusion, and films
PA 410	EcoPaXX™	DSM (NL)	Automotive and electrical applications: engine cover, cooling circuit components, sensors
PA 610	VESTAMID® Terra HS	Evonik (DE); FKuR Kunststoff GmbH (DE), distributor worldwide	Injection molding, fibers, powder, extrusion, and films
PA 610	Grilamid® 2S	EMS-GRIVORY (DE)	Injection molding, extrusion (tubes for automotive industry)
PA (amorphous)	Grilamid® BTR	EMS-GRIVORY (DE)	Used to make windows
PA 610	Ultramid® S Balance	BASF (DE)	Overmolding metal and electronic components, plug-in connectors, pipes, and reservoirs in cooling circuits
PA 610	Zytel® RS LS3030 NC010 Zytel® RS LC3060 NC010 Zytel® RS LC3090 NC010	DUPONT (USA)	Zytel® RS LS3030 NC010: Injection applications; Zytel® RS LC3060 NC010: Injection and extrusion applications; Zytel® RS LC3090 NC010: Extrusion applications
PA 610	Hiprolon® 70 series	Suzhou Hipro Polymers (CN)	Monofilament, industrial parts with high heat resistance and extrusion tubing product
PA 612	Hiprolon® 90 series	Suzhou Hipro Polymers (CN)	Monofilament and other industrial parts with different compounding process
Long chain PA	Hiprolon® 11	Suzhou Hipro Polymers (CN)	Auto fuel lines, air brake tubing, cable sheathing
Long chain PA	Hiprolon® 211	Suzhou Hipro Polymers (CN)	Auto fuel lines, air brake tubing, cable sheathing
PPA	Rilsan® HT	ARKEMA (FR)	Flexible tubing, injection molding
PPA	Grivory HT3	EMS-GRIVORY (DE)	Electronic connector applications

TABLE 1.13 Commercially Available Bio-Polyamides—cont'd

Biopolymer	Commercial Name	Manufacturer	Applications
PPA	VESTAMID® HT plus	EVONIK (DE)	Material for housings of pumps and filter systems or for use in vehicles in the vicinity of the engine, as in the charge air duct

PA 1010, polyamide 1010—produced from 1,10-decamethylene diamine (castor oil derivative) and sebasic acid (both derived from castor oil); PA 11, polyamide 11—produced from 11-aminodecanoic acid (derived from castor oil); PA 1012, polyamide 1012—produced from 1,10-decamethylene diamine and 1,12-dodecanedioic acid (both derived from plant oil, e.g., palm kernel oil); PA 410, polyamide 410—produced from tetramethylene diamine and sebasic acid (derived from castor oil); PA 610, polyamide 610—produced from hexamethylene diamine and sebasic acid (derived from castor oil); PPA, polyphthalamide produced from decamethylene diamine, terephthalic acid, and amino acid.

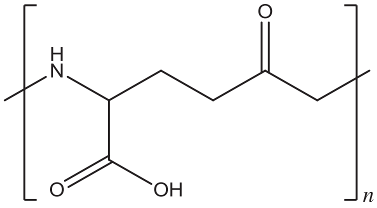
Poly(α-amino acids) are mainly used to create high-purity materials needed for biomedical applications. To date, commercial applications of protein polymers, such as poly(D-Lysine) and poly(L-lysine), are limited to use as adhesives/substrates for cell culture. Copolymers of α-amino acids (such as serine) with other biodegradable polymers (such as PLA) are synthesized as drug delivery systems (1998, **WO9828357** A1, CONNAUGHT LAB). In addition to drug delivery and targeting, poly(amino acids) are being investigated for applications such as biodegradable sutures and artificial skins.

Three kinds of poly(amino acid)s—poly(γ-glutamic acid), poly(α-aspartic acid), and ε-poly(L-lysine)—attracted more attention because of their unique properties and various applications.

1.7.3.1 Poly(γ-glutamic acid)

Poly(γ-glutamic acid) (also known as polyglutamate and γ-PGA) is a water-soluble, anionic, biodegradable polyamide consisting of D- and L-glutamic acid monomers connected by amide linkages between α-amino and γ-carboxyl groups (see Scheme 1.34). γ-PGA is synthesized by several bacteria, and its molecular weight can vary anywhere from 20,000 to over 2 million Da depending on the method of production. A major advantage of using γ-PGA is its low cost and relative abundance [82,83]. γ-PGA has several environmental/industrial, agricultural, food, and pharmaceutical applications. One environmental application of γ-PGA is its use as a flocculent. Another newer environmental application of γ-PGA is in removing heavy metal contaminants, such as those used by the plating industry. γ-PGA has a very large anionic charge density. Contaminants such as copper, lead, mercury, and other positively charged metal ions associate very strongly with γ-PGA and can then be concentrated and removed from the waste stream.

Since γ-PGA is comprised of an amino acid, it is an excellent source of nitrogen. This suggests an application in agriculture as a fertilizer. For analogous reasons it is good for drug delivery. A polymer mixture can be packed with nutrients for a particular crop. Once the fertilizer is applied, it has a longer residence time in the soil since the fertilizer nutrients are protected from the natural environment by the γ-PGA.



SCHEME 1.34 Poly(γ-glutamic acid).

In the food industry, work has been done that shows PGA functions as a cryoprotectant. γ-PGA has been shown to have antifreeze activity significantly higher than glucose, a common cryoprotectant. In the medical field, PGA is being studied as a biological adhesive and a drug delivery system (2005, **US2005095679** A1, CRESCENT INNOVATIONS INC).

PGA is degraded by a class of extracellular enzymes called γ-glutamyl hydrolases and, as a polyamide, is more resistant than synthetic polyesters to random chain hydrolysis. In biological systems γ-PGA undergoes enzymatic degradation from the surface, rather than bulk hydrolysis. Thus, γ-PGA provides benefits for use as a scaffold material, preventing rapid deterioration in scaffold strength. In addition, due to the presence of the carboxyl group (–COOH) on the side chain, γ-PGA exhibits unique advantages over other materials in terms of scaffold applications (2012, **WO2012004402** A1, IMP INNOVATIONS LTD).

US2005095679 A1 (2005, CRESCENT INNOVATIONS INC) discloses a method for producing high molecular weight γ-PGA via the fermentation of a nonpathogenic organism. Organisms may include *Bacillus subtilus*, or recombinant *Escherichia coli*, though *Bacillus licheniformis* ATCC 9945a is preferred. This PGA may be isolated and purified via a series of membrane filtration steps and/or pH adjustment and centrifugation. Inclusion of all steps results in a medical-grade product capable of being used in vivo without any immune response from the body. If lower levels of purity are required, they may be achieved by selectively eliminating various purification steps. Purification is accomplished by buffer exchange via diafiltration using a filter with a molecular weight cutoff of less than about 100 kDa, and preferably at least about 30 kDa. Typically, in order to produce agricultural-grade PGA, viable cells are removed by filtration at about 0.22 µm. For a food-grade product, this would be followed by filtration at about 0.1 µm, which clarifies the product. Any medical use requires the diafiltration steps.

US4450150 A (1984, LITTLE INC A) and **FR2786098** A1 (2000, FLAMEL TECH SA) disclose copolymers of poly(glutamic acid) and polyglutamate, which are pharmaceutically acceptable matrices for drugs or other active substances wherein the copolymer controls the rate of drug release.

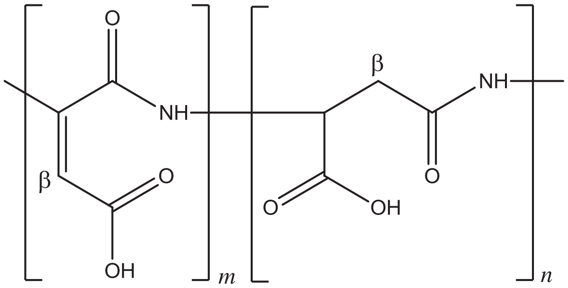
1.7.3.2 Poly(α-aspartic acid)

Poly(α-aspartic acid) (also called polyaspartate) is a biodegradable polyamide synthesized from L-aspartic acid, a natural amino acid (see Scheme 1.35). Poly(α-aspartic acid) has similar properties to the polyacrylate, and so it is used as antifouling agent, dispersant, antiscalant, or superabsorber.

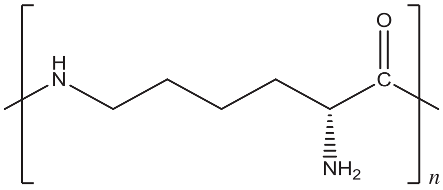
US5315010 A (1994, DONLAR CORP) discloses a method for producing poly(α-aspartic acid) that has been produced by hydrolysis of polysuccinimide (anhydropolyaspartic acid). The polysuccinimide is produced by thermal condensation polymerization of L-aspartic acid comprising the steps of: (1) heating powdered L-aspartic acid to at least 188 °C (370 °F) to initiate the condensation reaction and produce a reaction mixture, then (2) raising the reaction mixture temperature to at least 227 °C (440 °F), and (3) maintaining at least the 227 °C (440 °F) temperature for the reaction mixture until at least 80% conversion has occurred.

NanoChem, which bought the Donlar assets, produces polyaspartates for industrial and consumer applications. NanoChem polyaspartates have a wide range of molecular weights:

1. Low-molecular-weight polyaspartate A-2C, A-3C, and A-5D have application as general-purpose anti-scalants in hard water environments, corrosion inhibitor, function as dispersants for mineral slurries, and control redeposition of soil in laundry and hard surface cleaners.
2. High-molecular-weight polyaspartate C-5D and C-10D have applications as general-purpose dispersants, clay-soil removal, inorganic scale removal, anti-scalant in hard water environments, mineral slurry dispersant and anti-redeposition of soil in laundry, and hard surface cleaner applications.
3. Low-color-polyaspartate C-LC, C-LC/SD, and C-LC/GC are low color polyaspartates with application as general-purpose anti-scalants in hard-water environments, function as dispersant for mineral slurries and control redeposition of soil in laundry, and hard surface cleaners. Because of their low color, these polymers are specifically designed for applications where color affects the end use.



SCHEME 1.35 Thermal poly(α,β-D,L-aspartate).



SCHEME 1.36 ε-Poly(L-lysine) (ε-PL).

1.7.3.3 ε-Poly(L-lysine)

ε-Poly(L-lysine) (ε-PL) is a biodegradable water-soluble natural homopolymer of the essential amino acid L-lysine that is produced by bacterial fermentation (see Scheme 1.36). ε-PL consists of 25–35 L-lysine residues with linkages between α-carboxyl groups and ε-amino groups produced by *Streptomyces albulus*, giving a high selective antimicrobial activity. This biopolymer is widely used as a food additive. It has also been used for preparation of biodegradable hydrogels by γ-irradiation of microbial ε-poly(L-lysine) aqueous solutions [84].

Ajinomoto and Toray have entered into an agreement to begin joint research for manufacturing the nylon raw material 1,5-pentanediamine (1,5-PD) from the amino acid lysine produced from plant materials by Ajinomoto using fermentation technology and commercializing a bio-based nylon made from this substance. The bio-based nylon that Ajinomoto and Toray will research and develop is produced from plant materials by decarbonating the amino acid lysine through an enzyme reaction to make 1,5-PD, which Toray then polymerizes with dicarboxylic acid. This bio-based nylon fiber made from 1,5-PD is not only sustainable because it is plant based but it also shows promise for development into highly comfortable clothing. For example, PA 56 (nylon 56) fiber manufactured using 1,5-PD is pleasing to the touch, yet has the same strength and heat resistance as conventional nylon fiber made from the petrochemical derivative hexamethylenediamine. It also absorbs and desorbs moisture nearly as well as cotton [85].

1.8 POLY(ESTER AMIDES)

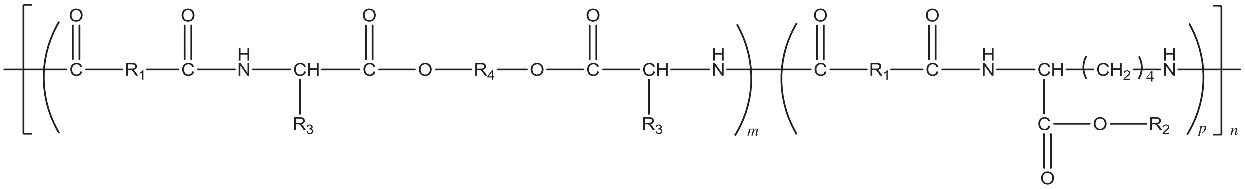
Poly(ester amide)s constitute a promising family of biodegradable materials since they combine a degradable character, afforded by the easily hydrolyzable ester groups (–COO–), with relatively good thermal and mechanical properties given by the strong intermolecular hydrogen bonding interactions that can be established between their amide groups (–NHCO–) [86].

Poly(ester amide)s, which can be easily produced and are also completely biodegradable, are known from **DE4327024** A1 (1995, BAYER AG). In 1995, Bayer AG introduced a series of biodegradable poly(ester-amide)s for film and molding applications under the name BAK®. In 2001, Bayer stopped the production of BAK®. The poly(ester amide)s of Bayer are based on the following combinations of monomers: (1) adipic acid, 1,4-butane diol, and ε-caprolactam; (2) adipic acid, 1,4-butane diol, diethylene glycol and hexamethylene diamine. The various commercial products that result from the combination of monomers (1) are based on polyamide 6 and named BAK® 404, BAK® 401, and BAK® 1095. The products that result from the combination of monomers (2) are based on polyamide 6,6 and named BAK® 402 and BAK 2195® [87] (1999, **DE19754418** A1, BAYER AG).

Hyperbranched poly(ester amide)s are produced on an industrial scale and commercialized by DSM (Hybrane®). These poly(ester amide)s are intrinsically biodegradable and synthesized from cyclic anhydride (e.g., succinic anhydride) and a diisopropanol amine. Hyperbranched poly(ester amide)s are used as performance additive in many applications such as oil field chemicals, demulsifiers, drug carriers, paper coatings, etc.

Alpha-amino acid-based poly(ester amide)s are being developed by DSM as a new biomaterial for sustained-release drug delivery. Their physical and mechanical properties can be adjusted by varying the three components in the building blocks during their synthesis: α-amino acids, aliphatic dicarboxylic acids, and aliphatic α-ω diols. These amino acid–based poly(ester amide)s are currently in human clinical studies as biodegradable coatings for drug eluting stents and ocular drug delivery.

WO0218477 A2 (2002, CORNELL RES FOUNDATION INC) discloses elastomeric functional copolyester amides (see Scheme 1.37) and elastomeric copolyester urethanes based on α-amino acids. In contrast to conventional poly(α-amino acids), the disclosed elastomeric functional copolyester amides and copolyester urethanes possess advantageous physical, chemical, and biodegradation properties, and can be obtained in high yields. The polymers are useful as carriers of drugs or other bioactive substances.

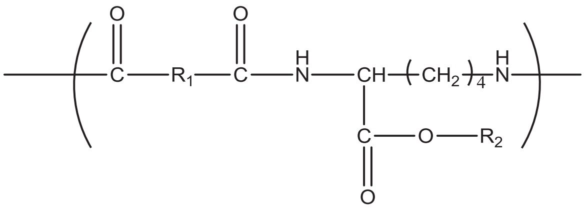


$$\left[\left(-\overset{O}{\overset{\|}{C}}-R_1-\overset{O}{\overset{\|}{C}}-\overset{H}{N}-\underset{R_3}{\underset{|}{CH}}-\overset{O}{\overset{\|}{C}}-O-R_4-O-\overset{O}{\overset{\|}{C}}-\underset{R_3}{\underset{|}{CH}}-\overset{H}{N}-\right)_m\left(-\overset{O}{\overset{\|}{C}}-R_1-\overset{O}{\overset{\|}{C}}-\overset{H}{N}-\underset{\underset{\underset{O}{\|}}{C}-O-R_2}{\underset{|}{CH}}-(CH_2)_4-\overset{H}{N}-\right)_p\right]_n$$

SCHEME 1.37 Chemical formula of α-amino acid-based poly(ester amide) (2002, **WO0218477** A2, CORNELL RES FOUNDATION INC).

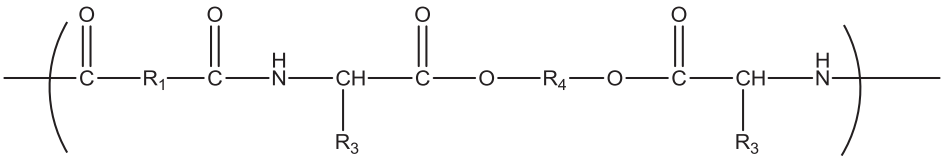
wherein:

m: is about 0.1 to about 0.9;
p: is about 0.9 to about 0.1;
n is about 50 to about 150;
R_1 is independently (C_2-C_{20})alkylene;
R_2 is independently hydrogen, or (C_6-C_{10})aryl(C_1-C_6) alkyl;
R_3 is independently hydrogen, (C_1-C_6)alkyl, (C_2-C_6)alkenyl, (C_2-C_6)alkynyl, or (C_6-C_{10})aryl(C1-C_6)alkyl; and
R_4 is independently (C_2-C_{20})alkylene; comprising one or more subunits of the formula (I):



$$\left(-\overset{O}{\overset{\|}{C}}-R_1-\overset{O}{\overset{\|}{C}}-\overset{H}{N}-\underset{\underset{\underset{O}{\|}}{C}-O-R_2}{\underset{|}{CH}}-(CH_2)_4-\overset{H}{N}-\right) \quad \text{(I)}$$

and one or more subunits of the formula (II):



$$\left(-\overset{O}{\overset{\|}{C}}-R_1-\overset{O}{\overset{\|}{C}}-\overset{H}{N}-\underset{R_3}{\underset{|}{CH}}-\overset{O}{\overset{\|}{C}}-O-R_4-O-\overset{O}{\overset{\|}{C}}-\underset{R_3}{\underset{|}{CH}}-\overset{H}{N}-\right) \quad \text{(II)}$$

wherein the combined number of subunits (I) and (II) is about 50 to about 150. Specifically,

R_1 can independently be $(CH_2)_4$, $(CH_2)_8$, or $(CH_2)_{12}$;
R_2 can independently be hydrogen or benzyl;
each R_3 can independently be iso-butyl or benzyl; and
R_4 can independently be $(CH_2)_4$, $(CH_2)_6$, $(CH_2)_8$, or $(CH_2)_{12}$.

WO2013087903 A1 (2013, DSM IP ASSETS BV) discloses an alternative amino acid–based poly(ester amide), which is used for the manufacturing of a drug delivery system in ophthalmology, cardiovascular, pain management, musculoskeletal, cancer treatment or in the delivery of vaccines.

1.9 POLY(ETHER AMIDE)S

Poly(ether amide)s are thermoplastic elastomers (TPE)s that can be processed by injection molding and profile or film extrusion. A commercially available product of bio-based poly(ether amide)s is the Pebax® Rnew (Arkema). Pebax® Rnew is a plasticizer-free poly(ether-*b*-amide) TPE from renewable sources (up to 90% derived from castor oil), made up of a block copolymer consisting of a sequence of polyamide 11 (PA 11) and polyether segments.

1.10 POLYURETHANES (BIO-BASED PU)

The term *polyurethane* (PU) includes all polymers incorporating more than one urethane group (–NH–CO–O–) in the polymer backbone. Polyurethanes are commonly formed by the polyaddition reaction of a polyisocyanate such as a diisocyanate with a polyol such as a diol, resulting in the formation of linear, branched, or crosslinked polymers. Other low-molecular-weight reagents such as chain extenders or crosslinking agents may be added during the polyaddition process.

As polyol components used as raw materials of bio-based PUs, there are used polyether and polyester polyols derived from natural resources. Polyether polyols are produced from sucrose, glucose, fructose, and glycerol. Polyester polyols are made from diacids and di- or trifunctional polyols. Suitable diacids include adipic acid, succinic acid, azelaic acid, and glutaric acid, etc. Suitable polyols include ethylene glycol, glycerol, 1,4-butane diol, 1,2-propanediol, 1,6-hexane diol, 1,10-dodecane diol, etc. Most of bio-based polyols for bio-based PUs are synthesized from vegetable oils. Vegetable oils include castor, soy, sunflower, rapeseed, and linseed oils. Chain extenders that break down to compounds such as amino acids have been used for formulating biodegradable PUs. The commercially available polyols derived from renewable resources are summarized in Table 1.14.

The isocyanate component is not produced from renewable resources. Aliphatic polyisocyanates, such as hexamethylene diisocyanate (HDI), butane diisocyanate (BDI), lysine diisocyanate ethyl ester, and lysine diisocyanate methyl ester, are used for the production of bio-based PUs.

The poly(ester-urethane)s are more liable to biodegradation than the poly(ether-urethane)s. Polyester polyols such as polycaprolactone, polylactide, and polyglycolide are the most widely used polyols in biodegradable polyurethanes. In a thermoplastic elastomer polyurethane (TPU), the polyester polyol forms the “soft” segment of the polymer while the diisocyanate and the chain extender form the hard segment. The hard segment forms ordered domains due to hydrogen bonding and imparts high mechanical strength to the material. The soft domains are formed mainly by the polyester polyol and provides elastic properties to the polymer. The biodegradation of these polymers occur largely due to the hydrolytic degradation of the ester, urethane, and urea linkages of the polymer. The urethane or urea linkages in the hard segment degrade by hydrolysis at a significantly slower rate than ester linkages. Because of the relatively slow degradation rates of these linkages compared with ester linkages, the polymer degradation may lead to oligomers containing mainly hard segments. The soft segment of the TPU degrades significantly faster than the hard segment as a result of the presence of relatively easily hydrolysable ester linkages and the amorphous nature of the soft segment (2007, **WO2007033418**, POLYNOVO BIOMATERIALS PTY LTD; GUNATILLAKE P).

Numerous industrial methods for the production of polyols derived from renewable sources and the bio-based PUs prepared thereof are known from the patent literature; see, for example, **CA2541366** A (2006) and **CA2568765** A1 (2007, BAYER MATERIALSCIENCE AG); **WO2007020904** A1 (2007, MITSUI CHEMICALS POLYURETHANES); **WO2009095363** A1 (2009, BASF SE); **JPH05148352** A (1993, SHOWA HIGHPOLYMER, CO LTD); **JPH0413710** A (1992, REGURUSU KK); and **SU1016314** A1 (1983, INST FIZIOL IM I S BERITASHVIL).

PUs have a broad spectrum of types and properties (soft and flexible foams, coatings, elastomers, and fibers) and are used in a very wide range of applications. The market for bio-based PUs is small and premium applications are being targeted. As an example, Metzeler Schaum currently produces bio-based PU flexible foam from a sunflower oil and/or rapeseed oil polyol, the Rubex® Nawaro flexible foam for the furniture and auto industry [88]. Biodegradable PUs are used as “shock absorber” materials in shoes soles and heels and as a carpet backing using PU derived from soy. Biodegradable polyurethanes find applications also in regenerative medicine. Examples include the fabrication of porous scaffolds for use in soft tissue engineering and cartilage repair [89]. Other medical applications include bone graft substitutes and wound dressings.

TABLE 1.14 Commercially Available Polyols Derived from Natural Resources for the Production of Bio-Based Polyurethanes as Reviewed by Desroches et al. [90]

Bio-Based Polyols	Commercial Name	Manufacturer	Applications
Sorbitol	NEOSORBR®	ROQUETTE	Polyether PUs
Maltitol & sorbitol & isosorbide	POLYSORBR®	ROQUETTE	Polyether PUs
Polytrimethylene ether glycol	CERENOL™	DUPONT	PU elastomers and fibers
Epoxidized soybean oil	JEFFADD™ B650	HUNTSMAN	PU rigid foams, sprays, coatings, adhesives, mastices, elastomers
Epoxidized soybean oil	AGROL® AGROL® DIAMOND	BIOBASED TECHNOLOGIES	PUs
Epoxidized soybean oil	BIOH®	CARGILL	PU flexible foams
Epoxidized vegetable oils	SOVERMOL®	COGNIS, BASF	PU adhesives, binders, floor coatings, castings
Epoxidized vegetable oils (castor oil, linseed oil, soybean oil)	MERGINOL®	HOBUM OLEOCHEMICALS	PU foams, coatings, dispersions
Epoxidized vegetable oils (sunflower, rapeseed, soybean)	RADIAR®[1] RADIAR® 7291 RADIAR® 7292 RADIAR® 7293	OLEON (SOFIPROTEOL)	RADIAR® 7291 & 7292: flexible poly(ester urethane) foams; RADIAR® 7293: rigid poly(ether urethane) foams
Epoxidized vegetable oils (soybean)	BAYDUR PUL 2500	BAYER	PU flexible and rigid foams
Functionalized of vegetable oils (soybean)	Renuva™[2]	DOW CHEMICALS	PU flexible foams, coatings, adhesives, mastics, elastomers
Castor oil	Lupranol® BALANCE 50	BASF	poly(ether urethane) rigid foams, mattress
Soybean oil	SOYOL	URETHANE SOY SYSTEMS	PU foams, sealing, coatings
Fatty acid dimmers	PRIPOL™	CRODA	
Castor oil		MITSUI CHEMICALS	

[1] *Ex Novenol of NOVANCE.*
[2] *Production of this polyol has stopped.*

Merquinsa markets a range of bio-based poly(ester urethane)s and poly(ether urethane)s under the commercial name PEARLTHANE® ECO polyurethanes having a bio content between 20% and 90% including special extrusion polyether TPU grades and nonyellowing aliphatic TPU resins. The polyether TPUs are made of CERENOL™ (DuPont). CERENOL™ is a high-performance polyol (polyether diol) containing 50–100 wt% renewably sourced 1,3-propanediol derived from corn.

Another commercial product of a bio-based PU is DegraPol® (ab medica), which is a block poly(ester-urethane) consisting of a polyhydroxybutyrate-diol (hard segment) and a polycaprolactone-diol (soft segment) linked with trimethylhexamethylene diisocyanate (TMDI) units (7 wt%). Using various ratios of hard and soft segments it is possible to modulate the mechanical properties of the final product. DegraPol® shows a broad range of elastic modulus, making it a potential new material for the regeneration of many types of biological tissues.

1.11 POLYSACCHARIDES

Polysaccharides are high-molecular-weight (10^4–10^7) carbohydrate polymers composed of long chains of monosaccharide units bound together by glycosidic bonds. They possess a great structural diversity as a result of the diversity of the repeating units, type of glycosidic linkages involved, and the degree of branching. Common polysaccharides include cellulose (structural integrity in plants), starch (energy storage in plants), glycogen (energy storage in animals), and chitin (exoskeleton of insects). Many polysaccharides possess nonsugar components, such as organic acyl groups (e.g., acetate, succinate, piruvate) and inorganic groups (e.g., phosphate, sulfate) [91]. Polysaccharides often form tertiary structures through intra or intermolecular noncovalent linkages, which confer greater rigidity to the macromolecule and play an important role in determining the polymer's properties both in the solid state and in solution [92] (2011, **WO2011073874** A2, SETENTA E TRES MIL E CEM LDA).

Due to their physical and chemical properties, namely, their water retention ability, rheology, and/or film-forming capacity, polysaccharides are used in a wide variety of foods and industrial applications, including textiles, paints, pharmaceuticals and cosmetics, as emulsifying, stabilizing, or thickening agents [93]. Being materials obtained from living organisms, polysaccharides are usually nontoxic and biodegradable, which makes them biomaterials adequate for sustainable development (2010, **US2011159288** A1; 2011, **WO2011073874** A2, SETENTA E TRES MIL E CEM LDA).

The main applications of commercial polysaccharides, both natural (e.g., alginate, carrageenan, Guar gum, pectins, xanthan, gellan) and semisynthetic derivatives (e.g., methylcellulose, carboxymethylcellulose, hydroxypropylguar), are based on their ability to modify the physical properties of aqueous systems (hydrocolloids—compounds able to modify the physical properties of aqueous systems), being used mainly in the food industry, followed by the oil and pharmaceuticals industries. Some of these polysaccharides (e.g., alginate, pectins, pullullan, starch derivatives, cellulose derivatives) additionally possess the capacity to form biodegradable films, being used in the manufacturing of packages, vessels, and sheets, as well as in several agro-food, pharmaceuticals, and industrial applications (2010, **US2011159288** A1; 2011, **WO2011073874** A2, SETENTA E TRES MIL E CEM LDA).

Currently, the majority of the polysaccharides used in industry are obtained from plants (e.g., Guar gum, Arabic gum), algae (e.g., alginate, carrageenan), or crustacean (e.g., chitin), with microbial polysaccharides (e.g., xanthan, gellan, bacterial alginate) representing only a small fraction of the biopolymer's market. The last years have seen a growing interest in microbial polysaccharides due to their enhanced physical properties and the higher growth rates of the microorganisms; for instance, the growth rates of microorganisms is of the order of hours or a few days, while plants, algae, and animals have growth rates of the order of months or years (2010, **US2011159288** A1; 2011, **WO2011073874** A2, SETENTA E TRES MIL E CEM LDA).

1.11.1 Cellulose

Cellulose is a complex polysaccharide similar to starch from which it differs in the glycosidic bond between the groups (steric configuration). Compared to starch it is more resistant to hydrolysis because of the stronger hydrogen bonds.

Native cellulose cannot be thermoplastically processed due to the fact that cellulose has a decomposition temperature lower than its T_m. Modification of the native cellulose makes it possible to use in thermoplastic applications.

1.11.1.1 Cellulose Derivatives

The cellulosic derivatives are produced by chemical modification of cellulose. Commercially available thermoplastic cellulose derivatives are cellulose esters and ethers such as cellulose acetate (CA), cellulose acetate propionate (CAP), cellulose acetate butyrate (CAB), methyl cellulose, ethyl cellulose, hydroxypropyl cellulose, etc. Common properties of these cellulose derivatives are that they tend to have high stiffness, low ductility, good clarity, and a narrow thermal processing window. They also have moderate heat and impact resistance. Cellulose derivatives display considerable sensitivity to moisture, stemming from their propensity to strongly absorb water (hygroscopicity), which increases with the addition of plasticizers. The rigid, brittle, and hygroscopic nature of cellulose derivatives tends to limit their wider use in a variety of products and applications.

The biodegradability of cellulose esters varies substantially with the degree of substitution. As used herein the term *degree of substitution* or *DS* refers to the number of substituents per anhydroglucose unit where the maximum degree of substitution is 3. Cellulose or cellulose derivatives with a low degree of substitution, i.e., less than 1, are biodegradable at a relatively rapid rate. For example, cellulose acetate having a degree of substitution of about 1.5 will exhibit a relatively fast rate of biodegradation, while cellulose acetate having a degree of substitution as high as 2.5 can be degraded by certain microorganisms but the rate is slow (1992, **WO9209654** A2, EASTMAN KODAK CO). Examples of commercially available cellulose and its derivatives are shown in Table 1.15.

1.11.1.1.1 Cellulose Acetate

Cellulose acetate (CA) is the acetate ester of cellulose and is made by reacting cellulose with acetic acid. CA is not itself a thermoplastic since the decomposition temperature is below the melt temperature, but it is possible to induce melt-processible properties through the addition of a plasticizer. It is used for a variety of products that include, among other things, textiles (i.e., linings, blouses, dresses, wedding and party attire, home furnishings, draperies, upholstery, and slip covers), industrial uses (i.e., cigarette and other filters for tobacco products, ink reservoirs for fiber tip pens), high absorbency products (i.e., diapers and surgical products), photography film, and computer tape. As with many processes, the manufacturing process results in some waste product that is not utilized in the final, product, as well as considerable waste post consumer (2010, **US2010175691** A1, CELANESE ACETATE LLC).

TABLE 1.15 Commercially Available Cellulose and Its Derivatives

Biopolymer	Commercial Name	Manufacturer	Applications
CA	Tenite™ Acetate (7 grades)	Eastman (USA)	CA: ophthalmic sheet, tool handles;
CAB	Tenite™ Butyrate (3 grades)		CAB: automotive and furniture trims, displays and profiles, pen barrels, tool handles, toys and sporting goods;
CAP	Tenite™ Propionate (46 grades)		CAP: appliance parts, cosmetic and personal care containers, film and tubing for packaging, health care supplies, ophthalmic and optical care safety frames, toothbrush handles, sunglasses
CA	CA-320S NF/EP CA-320S CA-394-60S CA-398-10 CA-398-3 CA-398-30 CA-398-30L CA-398-6 CA-436-80S	Eastman (USA)	Osmotic drug delivery and taste-masking; coatings; molded and extruded articles; films, packaging, and paper and paperboard food contact applications; LCD displays, and photographic films
CAB	CAB-171-15 CAB-321-0.1 CAB-381-0.1 CAB-381-0.5 CAB-381-2 CAB-381-20 CAB-381-20B CAB-500-5 CAB-531-1	Eastman (USA)	Films, coatings, inks, nail care
CAP	CAP-482-0.5 CAP-482-20 CAP-504-0.2	Eastman (USA)	Printing inks and clear overprint varnishes, nail lacquer topcoats
CA (blends)	BIOGRADE® series: BIOGRADE® C 6509 CL BIOGRADE® C 6530 BIOGRADE® C 7500 C BIOGRADE® C 9550 BIOGRADE® C 9555	FKuR Kunststoff GmbH (DE)	BIOGRADE® C 6509 CL: cup, plate; BIOGRADE® C 6530: injection molded rigid parts; BIOGRADE® C 7500: ball pens, cosmetic pencils, bottle, keyboard; BIOGRADE® C 9550: ball pen, cutlery, closure
CAB	Cellidor® B 500-05 Cellidor® B 500-10 Cellidor® B 500-13 Cellidor® B 500-15 Cellidor® B 500-20 Cellidor® B 531-07 Cellidor® B 531-10 Cellidor® B 631-10 Cellidor® B 631-12	Albis Plastic (DE)	Optical goods, tools, writing materials, automotive construction
CAP	Cellidor® CP 2810-11 Cellidor® CP 300-10 Cellidor® CP 300-13 Cellidor® CP 300-15 Cellidor® CP 300-17 Cellidor® CP 300-20 Cellidor® CP 310-10	Albis Plastic (DE)	Optical goods, tools, writing materials, automotive construction
CA	Acetyloid®Acety®	Daicel Chemical Industry (JP)	Optical films for LCDs, cigarette filters, acetate fiber, and photographic film; Acetyloid®: plastic sheet for glass frames; Acety®: pellet for tools (screwdriver), oil tank, etc.

Continued

TABLE 1.15 Commercially Available Cellulose and Its Derivatives—cont'd

Biopolymer	Commercial Name	Manufacturer	Applications
CMC	CMC (23 grades)	Daicel Chemical Industry (JP)	Thickener, dispersion stabilizer
HEC	HEC (13 grades)	Daicel Chemical Industry (JP)	Dispersion stabilizer; general used and cosmetic applications
Cationic Cellulose	JELLNER (2 grades)	Daicel Chemical Industry (JP)	Hair-care conditioner
Microfibrillated cellulose)	CELISH (11 grades)	Daicel Chemical Industry (JP)	Binder of fibers and powders, paper strength enhancer in paper making, texture improver in foods, filtration agent for liquors, etc.
Ethylcellulose	Ethocel™	Dow Chemicals Co (USA)	Protective coatings, as binders, flavor fixative
Sawdust & binder	Fasal® BIO 322 Fasal® BIO 337 Fasal® BIO 465	IFA (AT)	Injection molding applications

CA, cellulose acetate; CAP, cellulose acetate butyrate; CAP, cellulose acetate propionate; CMC, sodium carboxymethyl cellulose); HEC, hydroxyethyl cellulose.

1.11.1.1.2 Cellulose Acetate Butyrate

Cellulose acetate butyrate (CAB) is made by treating fibrous cellulose with butyric acid, butyric anhydride, acetic acid, and acetic anhydride in the presence of sulfuric acid. Typically, it contains about 15% combined acetic and about 40% combined butyric acid.

1.11.1.1.3 Cellulose Acetate Propionate

Cellulose acetate propionate (CAP) is made by treating fibrous cellulose with propionic acid (propanoic acid), acetic acid, and anhydrides in the presence of sulfuric acid.

1.11.1.1.4 Cellulose Nitrate

Cellulose nitrate (CN) is made by treating fibrous cellulosic materials with a mixture of nitric and sulfuric acids. Celluloid was a major CN, plasticized with camphor, but it is of little use today.

1.11.2 Starch

Starch is a low cost, naturally occurring biopolymer. Since native starch generally has a granular structure, it needs to be destructurized (i.e., to destroy its crystallinity) before it can be melt processed. Commonly, destructurized starch is obtained by processing native starch in the melt by means of a plasticizer (e.g., glycerol) or a swelling agent (e.g., water), to a homogeneous mass, where the proportion of swelling or plasticizing agent can as a rule amount to 10–40 wt%, based on the overall weight of the mixture. Destructurized starch behaves as a thermoplastic polymer (TPS) and can be processed by conventional techniques. TPS is a homogeneous amorphous mass that at storage conditions crystallizes only insignificantly.

US4673438 A (1987, WARNER LAMBERT CO) describes such methods for the conversion of native starch to TPS and subsequent injection molding processing. Suitable naturally occurring starches can include corn starch, potato starch, sweet potato starch, wheat starch, sago palm starch, tapioca starch, rice starch, soybean starch, arrow root starch, bracken starch, lotus starch, cassava starch, waxy maize starch, high amylose corn starch, and commercial amylose powder. Blends of starch may also be used. Though all starches are useful herein, the most commonly practiced are native starches derived from agricultural sources, which offer the advantages of being abundant in supply, renewable, readily biodegradable, easily modified, and of low cost. Naturally occurring starches, particularly corn starch, wheat starch, and waxy maize starch, are the preferred starch polymers of choice due to their economy and availability.

Other examples of patents that disclose the manufacture of TPS include: **GB2205323** A (1988), **GB2206888** A (1989), **GB2208651** A (1989), **US5095054** A (1992), **US5427614** A (1995) of WARNER LAMBERT CO; **WO9202559** A1 (1992, CERESTAR HOLDING BV). For compositions and methods for manufacturing blends of TPS, see Chapter 3: Blending; Section: 3.3.2.5: Blending starch with biodegradable polymers, and Section: 3.3.1.5: Starch.

TPS is frequently used in short use applications such as packaging, containers, and cultivation articles. The main use of TPS alone is in soluble compostable foams such as loose fillers, and other expanded items as a replacement for polystyrene. Exemplary, commercially available starches are shown in Table 1.16.

The use of TPS as a commercial thermoplastic material has been limited for a number of reasons, including difficulty in processing, poor long-term mechanical properties,

TABLE 1.16 Commercially Available Starch-Based Products

Biopolymer	Commercial Name	Manufacturer	Applications
Corn starch	Mater-Bi®	Novamont (IT)[1]	Bags, mulch films disposable tableware, accessories, packaging, biofiller for the automotive sector
Corn starch	Plantic® HP Plantic® R1	Plantic (AU)	Packing foods and goods
Starch	BIOPLAST GF 106/02 BIOPLAST GS 2189 BIOPLAST WRAP 100 BIOPLAST TPS	Biotec (DE)	Food packaging, cosmetics packaging, bags, waste bags, foamed products, thermoformed trays, visit cards, etc.
Cereal grains and specific Limagrain maize varieties	Biolice®	Limagrain (FR)	Fast food cutlery, packaging, mulch films, bags (garbage, garden waste, and dog litter), clamshells, lining material for jute bags, canvas bags, and paper bags
Plants,cereals	VEGEMAT®	VEGEPLAST (FR)	Vineyard fasteners, coffee machine capsules, disposable cutlery, dog treats, parachute links, golf tees, candle wicks
Reclaimed potato starch	Solanyl® BP Solanyl® C1xxx grades (injection molding): C1001 C1201 C1203 Solanyl® C2xxx grades (thermoform grade) C2201 Solanyl® C8xxx grades (blown film): C8101 C8201	Rodenburg Biopolymers (NL)	Packaging, plant pots, disposable cutlery, cup holders, golf tees, toys, CD and DVD trays, plant stakes
Grafted starch[2]	Gaialene®	ROQUETTE (FR)	Packaging, bottles, foams, hangers, soles, thermoplastic specialties

[1]C. Bastioli and her team at Novamont S.p.A. in Novara, Italy, were winner(s) of the European Inventor Award of the year 2007 for inventing biodegradable polymers made from starch (category: SMEs/research).
[2]Nonbiodegradable copolymer; based on a 50/50 thermoplastic starch/fossil fuel-based polymer.

high sensitivity to fluctuations in ambient moisture, including poor dimensional stability, and the difficulty of forming homogeneous blends of TPS with more hydrophobic polymers that are less sensitive to fluctuations in moisture.

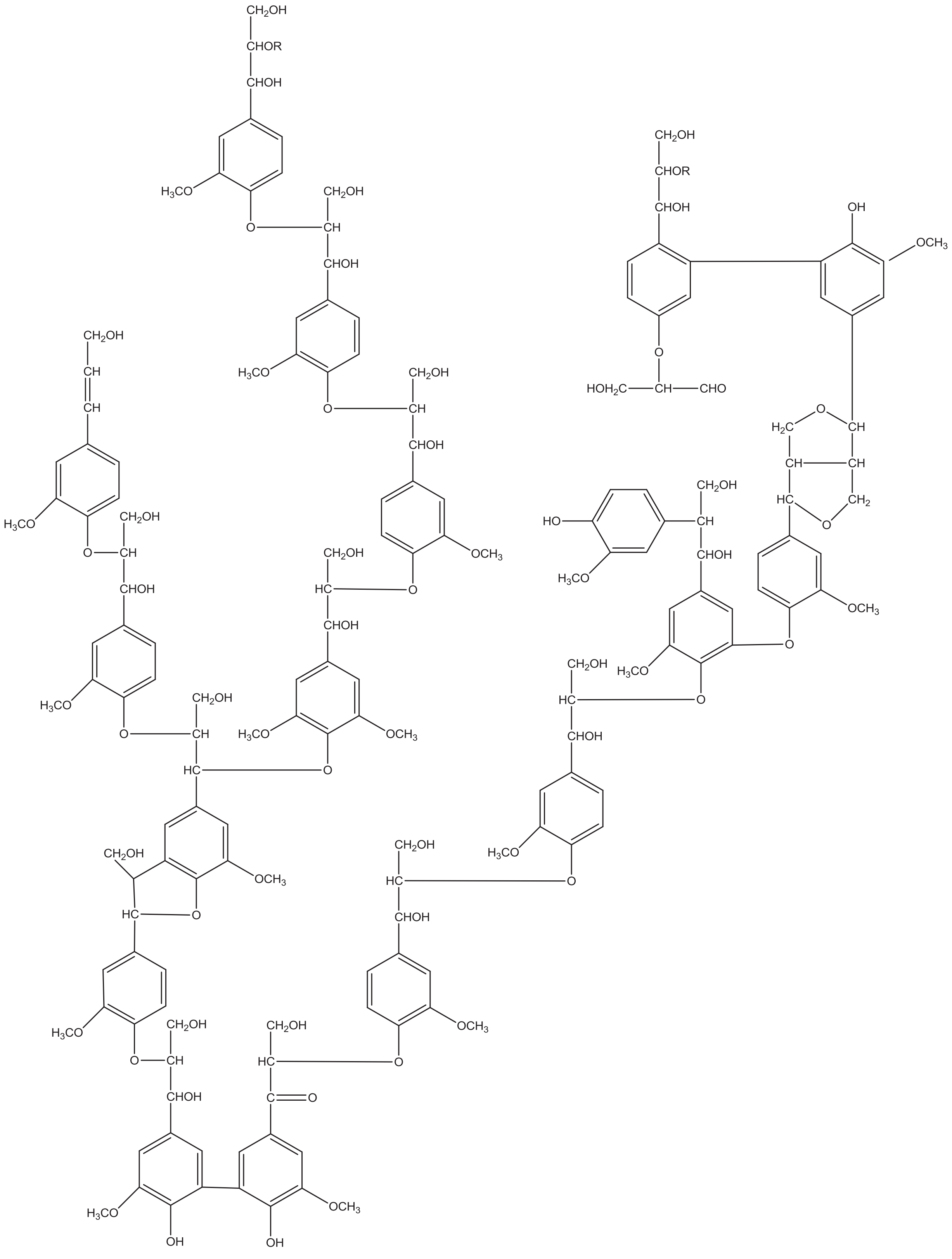
1.11.3 Chitin, Chitosan

Chitin and chitosan are highly basic polysaccharides. Chitin is the linear polymer of *N*-acetyl-D-glucosamine linked through a β-(1,4)-glycosidic bond and is called poly(β-[1,4]-*N*-acetyl-D-glucosamine) (or poly(*N*-acetyl-D-glucosamine)). Chitosan is the common name for poly (β-[1,4]-D-glucosamine) (also called poly(D-glucosamine)). Chitosan is chemically derived from chitin and is included in the cell walls of fungi and the exoskeletons of insects, and, most commonly, crustaceans. Chitin is inexpensively derived from widely available materials. It is available as an article of commerce from, for example, Primex Corporation (IS), Biopolymer Engineering, Inc. (USA), Biopolymer Technologies, Inc. (USA), and CarboMer, Inc. (USA).

Chitin is treated with strong alkalis to remove acetyl groups producing chitosan. Depending on the specific treatment of chitin, chitosan may vary in the degree of deacetylation. Chitosan is generally insoluble in water, but dissolves in dilute solutions of organic acids such as acetic, formic, tartaric, valeric, lactic, glycolic, and citric acids, and also dissolves in dilute mineral acids such as hydrochloric and sulfuric acids.

1.12 LIGNIN

Lignin is a complex polymer of phenylpropane units, which are crosslinked to each other by a variety of different chemical bonds (see Scheme 1.38). Lignin fills the spaces between the cell membranes of ligneous plants and turns them into



SCHEME 1.38 Possible structure of lignin. *Adapted from Ref. [94].*

wood, thereby producing a mixed body of pressure-resistant lignin and cellulose having good tensile strength. Depending on the type of wood, the phenyl groups of the lignin can be substituted by up to two methoxy groups and the propyl groups by up to two hydroxyl groups (2000, **WO0027923** A1, FRAUNHOFER GES FORSCHUNG; TECNARO GES ZUR IND ANWENDUNG). Besides cellulose, lignin is the second most common organic material on earth, about 20×10^9 tons of lignin being formed each year by photosynthesis. This ensures an almost infinite supply of lignin as a raw material without competing with food products. Approximately, 60×10^6 tons of lignin are produced annually as a by-product within the cellulose industry, mainly in the production of paper. Lignin may even be extracted from tree bark, sawdust or straw. Lignin is particularly recalcitrant to biodegradation, and also reduces the bioavailability of the other cell wall constituents.

Lignin has considerably improved material properties compared to other natural polymers, and is characterized by a relatively high strength, rigidity, impact strength, and high resistance with respect to ultraviolet light. Lignin is also a suitable material for heat and sound insulation.

One of the main sources of lignin is from spent pulping liquors, known as black liquor, where lignocellulosic materials, such as wood, straw, corn stalks, bagasse, and the like, are processed to separate the cellulose fibers or pulp from the lignin. Lignin includes both alkali lignin from the sulfate pulping process and lignin derived from other alkaline processes, such as the soda or modified soda processes, and sulfonated lignin, such as sulfite lignins from acid and neutral processes, or sulfonated alkali lignin. Alkali lignin is usually recovered from black liquor as water-insoluble products by acidification and precipitation procedures. Lignin obtained from the kraft, soda, or other alkaline processes is not recovered as a sulfonated product, but may easily be sulfonated, if desired, by reacting the product with a bisulfite or sulfite. The lignin sulfonate of commerce is usually sold as salts of sulfonic acid, such as calcium lignosulfonate. Alkali lignin from the cellulose industry is used as a binding agent for hardboard made from wood and cellulose, as a dispersing agent, and as a stabilizer in asphalt emulsions.

A further known natural starting material for obtaining corresponding natural substance polymers are some lignin derivatives. In **US3619222** A (1971, DARLING & CO) a modified protein base adhesive composition comprising a protein, a polyhydric compound, and a lignin extract (lignosulfonate) is disclosed. The compositions are useful as natural adhesives, glues (e.g., hot melts) displaying basically thermosetting and water-insoluble properties.

The lignin extract used is preferably a lignin sulfonate extract material that has been recovered from spent sulfite liquors produced by treatment of wood pulp and comprises in addition to lignin sulfonate, sugars and minor amounts of inorganic salts.

In **CH250077** A (1947, HOLZER TIBOR) a method for the production of molded articles is disclosed whereby sulfite waste liquor (a sulfonated lignin product from the lignin extraction) is treated with proteins, thus providing an elastomeric, tacky mass that is dried and hardened by means of suitable hardeners.

Although both documents, **US3619222** A (1971) and **CH250077** A (1947) disclose compositions based on natural starting materials, the starting materials themselves as well as the final products do not have the requisite thermoplastic properties and require suitable hardeners and other chemical compounds in order to obtain a material suitable for molding (2001, **WO0107166** A1, FRAUNHOFER GES FORSCHUNG).

DE19700902 A1, **DE19700903** A1, and **DE19700905** A1 (1998, HUETTERMANN A), **DE19700907** A1 (NESTE OY) and **DE19701015** A1 (1998, WIBMER GMBH U. CO. KG PAPIER-FORMTECHNIK) disclose intermediate products for the production of polymer products from lignin derivatives that are produced in the cellulose industry, wherein lignin derivatives are reacted with phenol oxidizing enzymes in the presence of oxidizing agents such as oxygen. These intermediate products are used as a coating agent for the production of waterproof papers and cartons, as a coating agent or binding agent for the production of particleboard, as a binding agent for starch for the production of waterproof starch derivatives, as an insulating material, and as a component of a composite material enriched with plant fibers.

DE4331747 A1 (1995, WUENNING P) discloses a natural granulated material that is produced from alkali lignin and proteins or protein derivatives, which can be decayed and composted, and which is produced through stereochemical modification through treatment with organic acids, in particular acetic acid. This material can be processed thermoplastically into structural parts.

WO9806785 A1 (1998, SILBIGER J) describes a similar composition, wherein lignin and a protein are heated and melted. This material is not suitable for most purposes since proteins are odorous and frequently hygroscopic, even when processed.

WO0027923 A1 (2000, FRAUNHOFER GES FORSCHUNG; TECNARO GES ZUR IND ANWENDUNG) discloses a biopolymer made from a polymer blend containing at least one lignin-based natural polymer, in particular based on alkali lignin produced during the extraction of cellulose, and at least one other synthetic and/or natural polymer that increases the impact resistance, with the exception of proteins. In a preferred embodiment, the lignin portion of the inventive plastic material is in the range of 2–90 wt%, in particular 5–65 wt%. The material is suitable as a substitute for wood or wooden materials due to its various properties, color, and consistency. Due to its good heat and sound insulating properties, the biopolymer is particularly suitable for the production of structural components such as profiles, e.g., for windows or doorframes, for door inner linings, etc. The material can also be used for producing housings for electric or electronic devices, e.g., TV and radio sets or the like.

DE19852034 C1 (2000, FRAUNHOFER GES FORSCHUNG; TECNARO GES ZUR IND ANWENDUNG) discloses a composition for the production of shaped bodies, containing up to 80% of lignin, up to 80% natural fibers, and up to 70% shellac. Materials that are reinforced with fibers to stabilize their shapes, e.g., cellulose fibers, require the addition of a natural processing aid. Shellac functions as a processing aid. Shellac is produced by the louse *Kerria lacca* to protect their eggs from external weather effects and can be melted at temperatures of around approximately 80 °C. The good film-forming properties of shellac contribute to favorable processing properties of the natural fiber mixture using extruders, injection molding machines, or presses.

DE10151386 A1 (2003, TECNARO GES ZUR IND ANWENDUNG) discloses a composition containing natural fibers, lignin, and/or lignin derivatives, and optionally small amounts of additives for forming thermoplastic reprocessing into profiled bodies and contains 1–20, preferably 8–12 wt% water on the mixture dry weight.

A commercially available product of lignin is Arboform® (TECNARO[2]), a biopolymer composed of three natural components: lignin, various cellulose fibers such as hemp and flax, and some natural additives. As a thermoplastic, it can be molded and is therefore also called liquid wood. The mixture of renewable resources is processed further through special procedures to form granules that can be used for various products manufactured by conventional plastic fabrication techniques.

1.13 VINYL POLYMERS

1.13.1 Polyolefins (Bio-Based)

WO2008067627 A2 (2008, BRASKEM SA) describes a method for the production of one or more olefins, namely propylene, and optionally ethylene and butylene, mainly from the residues of the processed renewable natural agricultural raw material (second-generation feedstock). The propylene is obtained from the gasification reaction of the lignocellulosic materials and of other organic products contained in the raw material residues, followed by the formation of methanol and its subsequent transformation into propylene, where this route may further generate ethylene and/or butylene as by-products. The propylene, ethylene, and butylene generated by the methods according to the present invention can be used for the obtainment of their known derivatives, preferably for the production of polypropylene and its copolymers and of polyethylene and its copolymers, resulting in polymers whose composition includes, when using only raw materials and residues from renewable natural sources, 100% carbon from renewable natural sources, as determined by the test method according to the ASTM D 6866-06 standard.

One other complementary alternative consists in the use of other raw materials of nonnatural (fossil) origin for the production of synthesis gas, for example, naphtha, natural gas, coal, recycled plastics, and combustion gas from thermoelectrical power generation plants, among others, provided that the end products (olefins and their known derivatives, as well as polymers such as polyethylene and its copolymers, polypropylene and its copolymers, and PVC include at least 50%, and preferably at least 80%, of carbon from a renewable natural source, as determined by the test method according to the ASTM D 6866-06 standard.

WO2011066634 A2 (2011, BRASKEM SA) describes a method for the production of olefins, e.g., ethylene used for preparing polyolefin such as polypropylene, comprising the production of carboxylic acids from the fermentation of at least one organic substrate from a renewable and natural raw material, followed by the subsequent anodic decarboxylation of the carboxylic acids thus obtained for forming the olefins. The carboxylic acids obtained by fermentation are propionic acid, butyric acid, valeric acid, or caproic, which generate ethylene, propylene, butylene, or pentene, respectively, through the anodic decarboxylation thereof. The organic substrates from renewable and natural raw materials are selected from starch, cellulose, hemicellulose, glycerol, sorbitol, lactose, lactates, and sugars. The fermentation process is performed in presence of bacteria such as those of the genera *Propionibacterium*, *Clostridium*, *Butyrivibrio*, and *Butyribacterium*; preferred bacteria are *Propionibacterium acidipropionici*, *Clostridium tyrobutyricum*, *Clostridium butyricum*, *Clostridium thermobutyricum*, *Clostridium ciditolerans*, *Clostridium acetobutylicumor*, or *Clostridium thermoamylolyticum*.

WO2009070858 A1 (2009, BRASKEM SA) describes an integrated process for the production of ethylene-butylene copolymers from at least one renewable natural raw material. The ethylene monomer is obtained by the ethanol dehydration reaction, in which ethanol is produced by the fermentation of sugars, and the 1-butylene co-monomer is obtained according to at least one of the following reactions: (1) dehydration reaction of 1-butanol directly produced by the fermentation of sugars; (2) dehydration reaction of 1-butanol obtained from ethanol via a chemical route, in which ethanol is produced by the

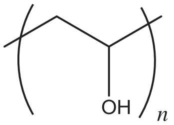
---

[2] The company TECNARO GmbH, a Fraunhofer spin off, was winner of the European inventor award 2010 (in the SMEs research category).

TABLE 1.17 Biopolyolefins

Biopolyolefins	Trade Name	Manufacturer	Applications
PE (LDPE, HDPE, LLDPE), PP	green PE green PP	BRASKEM SA	Personal care, cleaning, cosmetics, food and automotive industries
PE (based on Baskem's Green PE)	TERRALENE® series: TERRALENE® HD 3505 TERRALENE® LL 1101 (blend) TERRALENE® LL 1303 TERRALENE® WF 3516 (natural fiber reinforced green PE; low amount fibers) TERRALENE® WF 5525 (natural fiber reinforced green PE; medium amount of fibers) TERRALENE® WF 6534 (natural fiber reinforced green PE; low amount of fibers)	FKuR Kunststoff GmbH (DE)	TERRALENE® HD 3505: caps and closures, household articles, all kinds of boxes and containers; TERRALENE® LL 1101: blown film extrusion and lamination; TERRALENE® LL 1303: extrusion coating and lamination; TERRALENE® WF 3516, WF 5525 and WF 6534: injection molded rigid part

PE, polyethylene; LDPE, low density polyethylene; LLDPE, linear low density polyethylene; HDPE, high density polyethylene; PP, polypropylene.



SCHEME 1.39 Poly(vinyl alcohol) (PVOH).

fermentation of sugars; and/or (3) dimerization reaction of ethylene produced by the dehydration of ethanol obtained from the fermentation of sugars, followed by isomerization of the 2-butylene isomers then formed.

Bio-based polyethylenes (PE) have the same properties as PEs derived from fossil-based resources. Bio-based PEs are not biodegradable, and they are resistant to hydrolysis and oxidation as their fossil-based counterparts. Due to their thermoplastic properties bio-based PEs are suitable for physical recycling (also called mechanical recycling). Alternatively, they can be rendered oxo-degradable by use of prooxidant additives [95]. The commercially available biopolyolefins are shown in Table 1.17.

1.13.2 Poly(vinyl chloride) (Bio-Based PVC)

Ethylene derived from bioethanol can serve as raw material for the production not only of polyethylene but also of PVC. Solvay announced that it is going to invest \$135 million in a factory in Brazil for the production of 60,000 ton/year of bioethanol as basis for the production of bio-based PVC.

1.13.3 Poly(vinyl alcohol)

Poly(vinyl alcohol) (PVOH) is a water-soluble polymer prepared via the hydrolysis of poly(vinyl acetate) (see Scheme 1.39). PVOH is a water-soluble synthetic polymer that is used extensively in fibers, films, papers, and adhesives. PVOH is a thermoplastic material commonly used in laminates for food containers due to its excellent film-forming and oxygen-barrier properties. Commercially available PVOHs are shown in Table 1.18.

1.14 DIENE POLYMERS

1.14.1 *cis*-1,4-Polyisoprene

cis-1,4-polyisoprene is a hydrophobic and biodegradable polymer naturally occurring as latex in the laticiferous vessels or parenchymal (single) cells of rubber-producing plants such as *Hevea brasiliensis* [96]. Natural rubber contains 97 wt% *cis*-1,4-polyisoprene and about 3 wt% proteins. The protein moieties can be considered to be natural compatibilizers between the polyisoprene and other hydrophobic compounds such as starch. Natural rubber has been one of the first commercialized polymers, and its structure and properties, processing, and recycling have been studied extensively.

1.15 OTHER BIODEGRADABLE POLYMERS

1.15.1 Poly(ortho ester)s

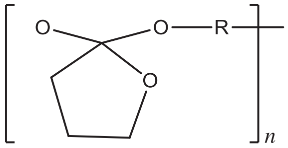
Poly(ortho ester)s (POE)s are hydrophobic biocompatible and bioerodible polymers potentially useful as a sustained drug delivery system. The development of POEs dates back to the early 1970s. POEs have evolved through four families, designated as POE I, POE II, POE III, and POE IV (see Scheme 1.40). Of these, only POE IV has been shown to have all the necessary attributes to allow commercialization [97].

The synthesis and characterization of the four distinct families of POEs have been described by Heller [98]. POE I is prepared by the transesterification of diethoxytetrahydrofuran with diols. POE II is prepared by the condensation of 3,9-bis (ethylidene 2,4,8,10-tetraoxaspiro [5,5] undecane) with diols to produce a linear polymer or with a triol to produce a crosslinked polymer. POE III is prepared by

TABLE 1.18 Poly(vinyl alcohol)

Biopolymer	Commercial Name	Manufacturer	Applications
High purity PVOH	GOHSENOL EG series: EG-05 EG-05P EG-40 EG-40P NH-17Q	Nippon Synthetic Chemical Industry Co. Ltd (JP)	Pharmaceuticals: binder, suspending agent, cataplasm; cosmetics: base resin for face pack, lotion, cream; electronics: fluorescent material binder, illuminant binder materials; ceramics: fine ceramic binder
Anionic PVOH	GOHSENAL series: T330H T-300 T-350	Nippon Synthetic Chemical Industry Co. Ltd (JP)	Printing stock, coat paper, NCR paper, release paper, emulsifying stabilizer, adhesive, film, drilling fluid control agents
Hydrophilic group-modified PVOH	ECOMATY series: WO-320R WO-320N	Nippon Synthetic Chemical Industry Co. Ltd (JP)	Ink jet printing
Modified PVOH with a sulfonic group (–SO_3X group) on its side chain	GOHSERAN series: L-3266 CKS-50 L-0302 L-0301	Nippon Synthetic Chemical Industry Co. Ltd (JP)	Emulsifier, dispersant, adhesive, coating agent, and binder
Low saponification hydrophilic PVOH	GOHSEFIMER series: LW-100 LW-200	Nippon Synthetic Chemical Industry Co Ltd (JP)	Hot melt resins, dispersing auxiliaries for suspension polymerization of vinyl chloride, adhesives, coating agents, binders and pressure-sensitive adhesives
PVOH	Mowiol®/Kuraray POVAL® Mowiflex TC® Exceval™ Kuraray POVAL® K Kuraray POVAL® L Kuraray POVAL® LM Kuraray POVAL® R	Kuraray (JP)	Adhesives, papers, building materials (additive for mortar, cement, oil well cementing, etc.), polymerization (emulsion/suspension), temporary binders for ceramics, gas barrier coating, films/foil, textiles sizing
PVOH	J-POVAL® Fully Hydrolyzed Type (10 grades) Medium Hydrolyzed Type (7 grades) Partially Hydrolyzed Type (17 grades)	JAPAN VAM & POVAL Co LTD (JP)	Textiles, paper processing, adhesives, dispersant, film formation, caking agents, construction
PVOH-*co*-plasticizer (polyalkyleneoxy acrylate)	VINEX®	Air Products & Chemicals	Blown and cast films, extrusion coating, fibers, tubing and profile, injection molding
PVOH, amorphous	Nichigo G-Polymer Powder type: AZF8035W OKS-6026 OKS-1011 OKS-8041 OKS-8049 OKS-1028 OKS-1027 OKS-1109 Pellet type: OKS-8049P OKS-8084P OKS-8042P	Nippon Gohsei (JP)	Powder type: used primarily for aqueous solution applications; pellet type: used primarily for melt-casting applications

PVOH, poly(vinyl alcohol).



SCHEME 1.40 Poly(ortho ester) (POE I).

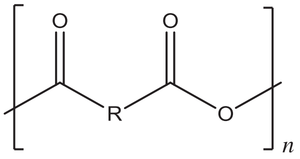
the condensation of a flexible triol with alkyl orthoacetate to produce ointment-like materials. POE IV is prepared by the condensation of a rigid triol with alkyl orthoacetate to produce solid materials. **US4079038** A (1978, ALZA CORP), **BE837935** A1 (1976, ALZA CORP), **US4131648** A (1978, ALZA CORP), and **US4180646** A (1979, ALZA CORP) disclose biodegradable or bioerodible POEs. These polymers are formed by a reaction between an orthoester (or orthocarbonate) such as 2,2-diethoxytetrahydrofuran and a diol such as 1,4-cyclohexanedimethanol. The reaction requires elevated temperature and reduced pressure and a relatively long reaction time. Drugs or other active agents are retained in the polymer matrix to be released as the polymer biodegrades due to hydrolysis of the labile linkages. **WO8103278** A1 (1981, STANFORD RES INST INT) discloses polymers prepared by reacting a polyol with a polyfunctional ketene acetal. These polymers represent a significant improvement over the aforementioned patents of ALZA CORP, since synthesis proceeds readily at room temperature and atmospheric pressure, and the resulting polymers have superior properties. Because of the backbone stability of POEs, excipients must be added in the matrix to promote degradation. These excipients, usually inorganic water-soluble salts, tend to swell in aqueous media and thus promote diffusional release.

1.15.2 Polyanhydrides

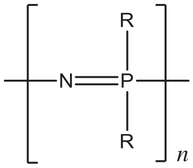
Polyanhydrides are biodegradable polymers characterized by anhydride bonds that connect repeat units of the polymer backbone chain (see Scheme 1.41). Synthesis of aromatic polyanhydrides was first reported in 1909. In the 1930s, Hill and Carothers prepared a series of aliphatic polyanhydrides intended as substitutes for polyester textile applications [99,100]. However, they were discarded because of their hydrolytic instability.

Traditionally, polyanhydrides have been prepared by melt condensation polymerization, by reacting dicarboxylic acid monomers with excess acetic anhydride at a high temperature, and under a vacuum to form the polymers. Catalysts may be used to achieve higher molecular weights and shorter reaction times. Generally, a one-step synthesis is used, which does not require purification.

Aliphatic homo-polyanhydrides have limited applications because of their high crystallinity and fast degradation. This is the case of poly(sebasic anhydride) [10]. To improve mechanical properties of polyanhydrides for specific medical applications, copolymers of anhydrides are used [101]. The degradation rate of polyanhydrides can be managed by adjusting the hydrophobic and hydrophilic components in the copolymer. Typical polyanhydrides include poly(carboxyphenoxy hexane-sebacic acid), poly(fumaric acid-sebacic acid), poly(imide-sebacic acid), and poly(imide-carboxyphenoxy hexane).



SCHEME 1.41 Polyanhydride.



SCHEME 1.42 Polyphosphazene (PPHOS); R can be either an alkoxy, or aryloxy, or amino group.

The main application of polyanhydrides is in the medical device and pharmaceutical industry. In vivo, polyanhydrides degrade into nontoxic diacid monomers that can be metabolized and eliminated from the body. Since their degradation products are safe, polyanhydrides are considered to be biocompatible. These polymers display superior physical and mechanical properties with respect to erodible carriers for controlled release drug delivery systems. The erosion rate of polyanhydrides can be changed several thousand fold only by changing the monomers or the composition of the copolymers (1998, **CA2202676** A1, UNIV MONTREAL). In contrast to POEs, polyanhydrides may be sufficiently labile in hydrolysis to produce heterogeneous erosion, without the addition of any excipient. Polyanhydrides and POEs offer a number of advantages over the more commonly used poly(lactide-*co*-glycolide) (PLGA) since they offer better control over polymer properties and erosional behavior. Synthesis methods, structures, and characterization of polyanhydrides have been reviewed by Kumar et al. [102]; see also Domb et al. [103], **EP0260415** A2 and **EP0266603** A1 (1988, MASSACHUSETTS INST TECHNOLOGY).

1.15.3 Polyphosphazenes

Polyphosphazenes (PPHOS)s are polymers with an inorganic backbone consisting of alternating phosphorus and nitrogen atoms, separated by alternating single and double bonds, and organic substituents (R) covalently bonded to the phosphorus atoms as side groups (see Scheme 1.42). Polymers with a wide range of properties can be synthesized from this polymer backbone by incorporating different side groups, by varying the side group in single-substituent

PPHOS, and/or by using two or more co-substituents. Individual PPHOS may be hydrophobic, amphiphilic, or hydrophilic; water stable or water erodible; crystalline or amorphous; bioinert or bioactive. The hydrophobicity of the PPHOS is increased by adding hydrophobic side groups such as aromatic groups to the backbone. Such polymers can be particularly useful as drug delivery carriers, plasma expanders, and biocompatible coatings for medical devices.

PPHOSs were first synthesized by the Allcock et al. [104]. Methods for the synthesis of various types of PPHOSs have been described by Allcock et al. [105–108]; Laurencin et al. [109,110]; Gunatillake and Adhikari [111]; **US4440921** A (1984), **US4495174** A (1985), and **US4880622** A (1989, RES CORP TECHNOLOGIES INC); **US4946938** A (1990, UNIV PITTSBURGH); **US6077916** A (2000, PENN STATE RES FOUND). The most widely used method for the synthesis of PPHO is the thermal ring-opening polymerization of hexachlorophosphazene [112].

PPHOs are desirable in many biomedical applications due to the biodegradability of the PPHO backbone. The main chain hydrolyses under physiological conditions to give, in addition to the corresponding side groups, low toxicity compounds including ammonia and phosphates. The most investigated application of PPHOs is their use as scaffolds for tissue engineering [112]. Even though PPHOSs have good physical properties, they have not been widely used due to their cost, and used only for limited purpose.

1.16 SOURCES OF BIOPOLYMERS

The source materials for biopolymers include both bio-based materials and fossil fuel-based raw materials. Biopolymers derived from bio-based materials (bio-based biopolymers) can be produced by biological systems (microorganisms, plants, and animals), or chemically synthesized from biological starting materials (e.g., sugar, starch, etc.). Biopolymers derived from fossil fuel–based raw materials include biodegradable polymers (e.g., PCL, PBS, etc.).

Nowadays, most bio-based biopolymers are derived from the so-called first-generation feedstock, which includes edible biomass such as sugar, starch, and plant oils, and nonedible sources such as natural rubber, one of the first used biopolymers. The fermentation of sugars derived from crops such as sugarcane and beets or the hydrolysis of starch derived from crops such as corn produces ethanol, which can be used as raw material for the production of a wide variety of biopolymers. Other products commercially produced by fermentation are, for example, lactic acid, *n*-butanol, acetone, and even polymers such as PHAs. There has been, however, concern that biopolymers obtained from edible materials are in direct competition with food and animal feed production. In particular, the production of biopolymers is claimed to have the same disadvantages/side effects associated with biofuels, i.e., raising food cost, deforestation for the creation of extra cultivation fields. This led the biopolymers industry to seek alternative feedstocks that will not compete with food markets in the future. Two categories of feedstock dominate research, namely nonedible biomass, the so-called second-generation feedstock, and alternative sources (see Table 1.19).

Second-generation feedstocks include food waste products and lignocellulose. Food waste products include nonedible, nonfood supplies such as waste cooking oil or fat and waste potato skins. Lignocellulose feedstocks include: (1) short rotation coppice such as willow, poplar,

TABLE 1.19 Feedstocks for the Production of Biopolymers

1st Generation (Edible and Non-edible Biomass)			2nd Generation (Non-edible Biomass)			Other Sources
Starch-rich plants	Sugar-rich plants	Oily-plants	Lignocellulose (short rotation coppice)	Lignocellulose by-products	Food by-products	Natural rubber
Corn	Sugarcane	Sunflower seeds	Willow	Forestry waste (e.g., wood chips)	Waste vegetable oil (e.g., cooking oil)	Micro-algae
Potato	Sugar beet	Soybean seeds	Poplar	Agricultural waste (e.g., straw, corn stover, bagasse)	Animal fat (lard tallow, waste grease)	Perennial grasses
Grain	Sweet sorghum		Miscanthus	Paper waste	Potato skins	Jatropha
Rice	Molasses	Rapeseed seeds	Switchgrass	Municipal waste	Spirulina dregs	Greenhouse gas (CO_2)
		Castor seeds				

or miscanthus, and (2) lignocellulose by-products such as forestry and agricultural residues such as sugarcane bagasse, sugarcane straw, corn straw, wheat straw, and rice straw, corn cobs, and wood kindling. The main components of these materials are cellulose, hemicellulose, and lignin. The hydrolysis of cellulose and hemicellulose by either acidic or enzymatic route produces various sugars, which are fermented in the presence of various microorganisms, the most important of them being the yeast *Saccharomyces cerevisiae* (2008, **WO2008067627** A2, BRASKEM SA). The conversion of lignocellulose by-products into a usable output is more difficult than other types of biomass; the main reason for this is that the protective shield of hemicellulose and lignin that surrounds cellulose has to be broken down, which is a highly energy intensive process [113]. Second-generation biomass does not provide a higher yield than sugarcane and is still linked to "food" crop market dynamic. In Brazil, second-generation technologies making optimal use of the biomass generated in sugar farming (conversion of the bagasse into ethanol instead of burning it) are seeing strong growth, despite the wide availability of sugarcane. To date, the industry is still in a nascent state, with most second-generation biorefinery plants (using cellulose material) only expected to be ready for large-scale commercial production in a few years [113]. Although the same feedstocks are used for the production of biofuels and biopolymers, there are, however, significant differences between the use of agricultural feedstocks for production of biofuels and biopolymers [2].

Galactic has already carried out research on second-generation biomass (lignocellulosic biomass), which consists of redeploying the residual nonedible parts of crops [114].

Another, not very widely used technology for reutilization of lignocellulosic materials is the gasification of lignocellulose and its transformation into synthesis gas (a mixture of CO and H_2). Using that process, practically all the carbon content of any form of organic matter can be transformed into carbon monoxide. The synthesis gas is used for the production of methanol, which, in turn, is used for the formation of olefins such as propylene. However, in spite of the innumerous developments achieved to date, there is still no commercial unit in operation for the production of synthesis gas from biomass or by reutilization of carbon dioxide, the main reason being the cost of the process as a whole, which is still high (2008, **WO2008067627** A2, BRASKEM SA).

Alternative sources include the use of third-generation biomass, which is based on microalgae for the production of biopolymers. This type of biomass, which is produced in an aquatic environment, has no need for fertile land and provides a high yield per hectare. Nevertheless, it does require the addition of nutrients and a CO_2 source as well as sunlight. Algae biopolymers were mainly evolved as by-products of algae biofuel production, where companies were exploring alternative sources of revenues along with those from biofuels. Companies active in the field of algae biopolymer research are Cereplast, Dow, and Petro Sun. Cereplast developed a new process, RezInnovation™, for the production of algae-based biopolymers [115]. Dow partnered with Algenol Biofuels to build a pilot plant, which will use algae to convert carbon dioxide emissions into ethanol. The obtained ethanol could replace fossil fuels in the production of ethylene, a feedstock for many polymers [116]. Petro Sun investigates the possibility of using the algae oil produced in its open-pond algae farm as feedstock for the production of biopolymers [117]. While algae-based biopolymers are in their infancy, once they are into commercialization they are likely to find applications in a wide range of industries. Soley Biotechnology Institute produces biopolymer from spirulina dregs. The company utilizes this dreg, which is left as byproduct when extracting useful products from Spirulina [118]. Representative patents on algae-based biopolymers are the following: **US4078331** A (1978) and **US4236349** A (1980, MOBIL OIL CORP) and **US2010272940** A1 (2010, KIMBERLY–CLARK WORLDWIDE, INC).

Biopolymers are also being produced from a greenhouse gas itself, namely CO_2. Novomer Inc. and SK Energy Co., Ltd. are commercializing polymers made from carbon dioxide, namely poly(propylene carbonate) (see Section 1.6.2).

PATENTS

Patent Number	Publication Date	Family Members	Priority Numbers	Inventors	Applicants	Title
AU3521984 A	19850523	US4620999 A 19861104; JP60122527 A 19850701; EP0142950 A2 19850529; EP0142950 A3 19870805; EP0142950 B1 19901010 AU576795 B2 19880908	GB19830030414 19831115	HOLMES P A	ICI PLC	Disposable bags.
BE837935 A1	19760514	ZA7600493 A 19770727; US4138344 A 19780606; US4093709 A 19780606; SE7600760 A 19760920; SE418189 B 19810511; NL7600881 A 19760730 NL174728 C 19840801; MX142986 A 19810203; JP51100194 A 19760903; IT1057070 B 19820310; IL48799 A 19790131; GB1502082 A 19780222; FR2299356 A1 19760827; ES444484 A1 19770916; DK32076 A 19930413; DK166360 B 19930413; DE2602994 A1 19760729; DE2602994 C2 19820826; CH635355 A5 19830331; CA1087345 A1 19801007; BR7600499 A 19760831; AU1041676 A 19770818; AT356903 B 19800610; AR213619 A1 19790228	US19750544808 19750128	CHOI NAM SOK; HELLER J	ALZA CORP	Drug delivery devices manufactured from poly(orthoesters) and poly(orthocarbonates).

CA2202676 A1	19981014	US5955068 A 19990921	CA19972202676 19970414	GOUIN S; ZHU X–X	UNIV MONTREAL	Biodegradable polanhydrides derived from dimers of bile acids, and use thereof as controlled drug release systems.
CA2541366 A	20061006	US2006229375 A1 20061012; SG161236 A1 20100527; SG126853 A1 20061129; RU2006110878 A 20071010; KR20060107330 A 20061013; JP2006291205 A 20061026; EP1712576 A1 20061018; CN102585200 A 20120718; CN1847279 A 20061018; CN1847279 B 20120118; BRPI0601137 A 20061205	US20050100221 20050406	HSIAO Y-L; SKORPENSKE R G; KAUSHIVA B D; MCDANIEL K G; PAZOS J F; HAGER ST L; HAIDER K W	BAYER MATERIALSCIENCE AG	Polyurethane foams made with alkoxylated vegetable oil hydroxylate.
CA2568765 A1	20070526	US2007123725 A1 20070531; SG132645 A1 20070628; MXPA06013551 A 20081009; KR20070055956 A 20070531; JP2007146163 A 20070614; ES2333038 T3 20100216; EP1790678 A1 20070530; EP1790678 B1 20091007; DE102005056432 A1 20070531; CN1974526 A 20070606; CN1974526 B 20120118; BRPI0605169 A 20070904; AT444983 T 20091015	DE200510056432 20051126	LORENZ K	BAYER MATERIALSCIENCE AG	Process for the production of polyols based on natural oils.
CH250077 A	19470815		CHT250077 19460924	HOLZER T	HOLZER T	Verfahren zur Herstellung von Formartikeln. “Method for producing molded bodies.”
CN101628972 A	20100120	CN101628972 B 20111005	CN20081132792 20080714	NING K; YUHONG L; JIANZHONG L	QINGDAO INST OF BIOMASS ENERGY	Method for preparing poly(ethylene succinate).
CN102002148 A	20110406	CN102002148 B 20120418	CN20101547712 20101117	JIAN D; ZHONGHUA B	ZHANGJIAGANG CHAINENG BIOLOG SCIENCE CO LTD	Method for preparing biodegradable poly(malic acid) material.

Continued

—Cont'd

Patent Number	Publication Date	Family Members	Priority Numbers	Inventors	Applicants	Title
CN1436803 A	20030820	CN1250603 C 20060412; JP2004263168 A 20040924; JP3929434 B2 20070613	CN2003105023 20030303	ZHAO XIAOJIANG; WANG XIANHONG; WANG FOSONG	CHANGCHUN APPLIED CHEMISTRY	Ternary catalyst for preparing aliphatic polycarbonate with high molecular weight.
DE10151386 A1	20030508	DE10151386 C2 20031016	DE20011051386 20011018		TECNARO GES ZUR IND ANWENDUNG	Zusammensetzung für die thermoplastische Verarbeitung zu Formkörpern und Verfahren zur Herstellung einer solchen Zusammensetzung. "Composition for the thermoplastic processing into molded bodies and method for producing such a composition."
DE19700902 A1	19980716		DE19971000902 19970114	HUETTERMANN A; RAUN-LUELLEMANN A; MAJCHERZCYK A; NOETZOLD S; KHARAZIPOUR A; HUETTERMANN J	HUETTERMANN A	Zwischenprodukt für die Herstellung von Polymerisaten aus Ligninderivaten. "Activated lignin intermediates for lignin polymers preparation" (no official title).
DE19700903 A1	19980716		DE19971000903 19970114	HUETTERMANN A; RAUN-LUELLEMANN A; MAJCHERZCYK A; NOETZOLD S; KHARAZIPOUR A; HUETTERMANN J	HUETTERMANN A	Zwischenprodukt für die Herstellung von Polymerisaten aus Ligninderivaten. "Activated lignin intermediates for lignin polymers preparation" (no official title).
DE19700905 A1	19980716		DE19971000905 19970114	HUETTERMANN A; GOES C; HOEPPNER M; MAJCHERCZYK A; BRAUN-LUELLEMANN A	HUETTERMANN A	Zwischenprodukt für die Herstellung von Polymerisaten aus Ligninderivaten. "Activated lignin intermediates for lignin polymers preparation" (no official title).

DE19700907 A1	19980716	WO9831825 A1 19980723; US6280855 B1 20010828; SK94299 A3 20000516; PL334520 A1 20000228; NZ336663 A 20010427; ID23445 A 20000420; HU0001972 A2 20001028; EP0960206 A1 19991201; CZ9902516 A3 19991117; CN1250482 A 20000412; CA2277279 A1 19980723; BR9806955 A 20000321; AU5664098 A 19980807	DE19971000907 19970114	VIIKARI L; HASE A; QVINTUS-lEINO P; NIKU-PAAVOLA M-L	NESTE OY	Zwischenprodukt für die Herstellung von Ligninpolymerisaten und dessen Verwendung zur Herstellung von Holzwerkstoffen. "Intermediate product for preparation of lignin polymers and use thereof for production of wood materials."
DE19701015 A1	19980716		DE19971001015 19970114	KHARAZIPOUR A; HUETTERMANN A; HUETTERMANN J	WIBMER GMBH U. CO. KG PAPIER-FORMTECHNIK	Zwischenprodukt für die Herstellung von Polymerisaten aus Ligninderivaten, sowie die Verwendung dieser Zwischenprodukte für die Herstellung von Beschichtungsmitteln für die Beschichtung von pflanzlichen Fasern für die Herstellung von Pflanztöpfen. "Intermediate products for the preparation of polymers based on lignin derivatives, and the use of these intermediate products for the coating of plant fibres for the preparation of plant pots."
DE19754418 A1	19990610	ZA9811205 A 19990609; WO9929768 A1 19990617; NO20002947 A 20000703; JP2001525473 A 20011211; EP1037943 A1 20000927; CN1281482 A 20010124; CA2313192 A1 19990617; AU1876399 A 19990628	DE1997154418 19971209	VOIGT MICHAEL; JESCHKE KURT; ECKERT ARMIN; MUELLER VOLKER	BAYER AG	Stabilisierte Formmassen biologisch abbaubarer materialien. "Stabilized molding compounds comprised of biologically degradable materials."
DE19852034C1	20000420	WO0027924 A1 20000518; US6706106 B1 20040316; JP2002529568 A 2002090; JP4843141 B2 20111221; ES2178491T T3 20021216; EP1129139 A1 20010905; EP1129139 B1 20020605; CA2350418 C 20090929; AU1552200 A 20000529; AT218601 T 20020615	DE19981052034 19981111	NAEGELE H; EYERER P; PFITZER J; EISENREICH N; INONE E; ECKL W	FRAUNHOFER GES FORSCHUNG; TECNARO GES ZUR IND ANWENDUNG	Zusammensetzung zur Herstellung von Formkörpern und Verfahren zur Herstellung von Formkörpern aus einer solchen Zusammensetzung. "Composition for producing molded bodies and method for producing molded bodies from such a composition."

Continued

—Cont'd

Patent Number	Publication Date	Family Members	Priority Numbers	Inventors	Applicants	Title
DE4327024 A1	19950216	US5644020 A 19970701; JP7102061 A 19950418; JP3493472 B2 B220040203; ES2154655 T3 20010416; EP0641817 A2 19950308; EP0641817 A3 19960807; EP0641817 B1 20001227	DE19934327024 19930812	TIMMERMANN R; DUJARDIN R; KOCH R	BAYER AG	Thermoplastisch verarbeitbare und biologisch abbaubare aliphatische Polyesteramide.
DE4331747 A1	19950323	WO9508594 A1 19950330; HUT75658 A 19970528; ES2115258 T3 19980616; EP0720634 A1 19960710; EP0720634 B1 19980218; AT163304 T 19980315; CZ9600822 A3 19960911; DK720634 T3 19981123	DE19934331747 19930920; WO1994EP03131 19940917	WUENNING P; WUENNING M	WUENNING P	Extrudiertes, faserverstärktes Naturstoff-Granulat zur thermoplastischen Weiterverarbeitung, sowie Verfahren zu seiner Herstellung. "Extrudable, fiber-reinforced natural substance granulate for thermoplastic processing, and process for its production."
EP0015123 A1	19800903	ES8103169 A1 19810516; EP0015123 B1 19821222; EP0036699 A1 19810930; EP0036699 B1 19830202; EP0036699 B2 19870902; DK73380 A 19800822; AU5560680 A 19800828; AU529981 B2 19830630	GB19790006076 19790221; GB19790006077 19790221; GB19790015858 19790508	HOLMES P A; WRIGHT L F; ALDERSON B; SENIOR P J	ICI PLC	A process for the extraction of poly-3-hydroxy-butyric acid from microbial cells.
EP0046335 A2	19820224	JP57174094 A 19821026; EP0046335 A3 19820310	GB19800026882 19800818	HOLMES P A; JONES E	ICI PLC	Extraction of poly(beta-hydroxybutyric acid).
EP0052459 A1	19820526	JP5015383 A 19930126; EP0052459 B1 19851204	GB19800036967 19801118; GB19810020991 1981070	HOLMES P A; WRIGHT L F; COLLINS STEPHEN HUGH	ICI PLC	Beta-hydroxybutyrate polymers.
EP0069497 A2	19830112	NZ201054 A 19851108; JPH06172501 A 19940621; EP0069497 A3 19830216; EP0069497 B1 19870415; JPH0747623 B2 19950524; AU8410882 A 19830113; AU560653 B2 19870416	EP19810305186 19811030; GB19810020991 19810707; GB19820013697 19820512	HOLMES PAUL ARTHUR; WRIGHT LEONARD FREDERICK; COLLINS STEPHEN HUGH	ICI PLC	Copolyesters and process for their production.

EP0260415 A2	19880323	US4757128 A 19880712; NL990036 I1 19991201; NL990036 I2 20010102; LU90462 A 20000103; JP63258924 A 19881026; GR3022577 T3 19970531 GR88300163 T1 19890131; ES2006417 T3 19970701; EP0260415 A3 19880518; EP0260415 B1 19961127; DE260415 T1 19890216; DE3751964 T2 19970605; CA1274339 A1 19900918; AT145657 T 19961215	US19860892809 19860801	DOMB AB; LANGER R	MASSACHUSETTS INST TECHNOLOGY	High molecular weight polyanhydride and preparation thereof.
EP0261572 A1	19880330	JP63101378 A 19880506; BR8704814 A 19880517	DE19863632103 19860920; DE19873708915 19870319	MUELLER M	BOEHRINGER INGELHEIM KG; BOEHRINGER INGELHEIM INT	Process for the production of lactide.
EP0266603 A1	19880511	US4789724 A 19881206; KR960006410 B1 19960515; JP63199227 A 19880817; DE266603 T1 19890216; DE3752381 T2 20051110; A1278141 C 19901218; AT285432 T 20050115	US19860920724 19861017	DOMB AB; LANGER R	MASSACHUSETTS INST TECHNOLOGY	Preparation of anhydride copolymers.
EP0349505 A2	19900103	WO9000067 A1 19900111; NO900878 A 19900514; NO302999 B1 19980518; JPH03500139 A 19910117; JP2842649 B2 19990106; IL90714 A 19940624; ES2121741 T3 19981216; EP0349505 B1 19980916; DE68928817 T2 19990408; DK46690 A 19900222; CA2314151 A1 19990701; CA1340634 C 19990706; AU3843889 A 19900123; AU636570 B 19930506; AT171076 T 19981015	SE19880002414 19880627	BOWALD S F; JOHANSSON E G	ASTRA MEDITEC AB	A novel surgical material.
EP0533144 A2	19930324	US5292860 A 19940308; JPH0593049 A 19930416; JP2777757 B2 19980723; EP0533144 A3 19940622; EP0533144 B1 19981216; DE69227878 T2 19990512	JP19910267255 19910917	SHIOTANI TAKENAGA; KOBAYASHI GENTA	KANEGAFUCHI CHEMICAL IND	Copolymer and its production.

Continued

—Cont'd

Patent Number	Publication Date	Family Members	Priority Numbers	Inventors	Applicants	Title
EP1106640 A2	20010613	US2001007899 A1 20010712; US6713595 B2 20040330; KR20010055721 A 20010704; JP2001187818 A 20010710; EP1106640 A3 20020116	KR19990056991 19991211	CHUNG H S; LEE J W; KIM D H; KIM D Y; LEE S W	IRE CHEMICAL LTD	Biodegradable copolyesters and their preparation.
EP1108737 A2	20010620	US2001004665 A1 20010621; US6399716 B2 20020604; KR20010057068 A 20010704; KR100366483 B1 20030114; JP2001187817 A 20010710; EP1108737 A3 20020116	KR19990058816 19991217	CHUNG H S; LEE J W; KIM D H; KIM D Y; LEE S W	IRE CHEMICAL LTD	Biodegradable copolyesters and their preparation.
EP1564235 A1	20050817	US2005182204 A1 20050818; EP1564235 B1 20070411	JP20040037556 20040216	OTOME S; IWAI K; SOHGAWA Y-H	NIPPON CATALYTIC CHEM IND	Biodegradable film.
EP327505 A2	19890809	ZA8900692 A 19891227; RU2026321 C1 9950109; PT89556 B 19940729; PT89556 A 19891004; PL277424 A1 19890904; PL159070 B1 19921130; PH25687 A 19910904; NZ227762 A 19900828; NO890361 A 19890804; NO307521 B1 200004017; MX172659 B 19940106; KR0139046 B1 19980501; JP7057827 B 19950621; JP2014228 A 19900118; IN174313 A1 19941105; IL89096 A 19920906; IE890281 L 19890803; HU206510 B 19921130;	GB19880002313 19880203	LAY G; REHM J; STEPTO ROBER F T; THOMA M	WARNER LAMBERT CO	Polymeric materials made from destructurized starch and at least one synthetic thermoplastic polymeric material.

		GR92300067 T1 19920831; GB2214918 A 19890913; FI890406 A 19890804; FI100977 B 19980331; ES2039315 T1 19931001; ES2039315 T3 19980116; ES2039315 T5 20020601; EP0327505 A3 19901010; EP0327505 B1 19970730; EP0327505 B2 20011114; DK36789 A 19890804; DK174534 B1 20030512; DE68928209 T2 19980903; DE68928209 T3 20020822; DE327505 T1 19920813; CN1036215 A 19891011; CN1034872 C 19970514; CA1334224 C 19950131; BR8900350 A 19890919; AU617411 B2 19911128; AU2887689 A 19890803; AT156166 T 19970815; AR247411 A1 19941229				
FR2782999 A1	20000310	WO0014154 A1 20000316; US7148272 B2 20061212; US2001031297 A1 20011018; FR2782999 B1 20020510; EP1112319 A1 20010704; EP1112319 B1 20030319; DE69906099 E 20030424; CA2342723 A1 20000316; AU5523499 A 20000327; AT234894 T 20030415	FR19980011269 19980909	REYNES P; MESSAGER A	ULICE SA	MéRiau biodégradable a base de polymère et de farine céréalière, son procédé de fabrication et ses utilisations.
FR2786098 A1	20000526	WO0030618 A1 20000602; US6630171 B1 20031007; JP2002530323 A 20020917; JP4927256 B2 20120509; ES2251236 T3 20060416; EP1131056 A1 20010912; EP1131056 B1 20051019; DE69927841 T2 20060713; AU1278000 A 20000603; AT306905 T 20051115	FR19980014863 19981120; WO1999FR02859 19991119	HUILLE S; NICOLAS F; BRISON N; SOULA G	FLAMEL TECH SA	Particles based on polyamino-acid(s) and methods for preparing same.

Continued

—Cont'd

Patent Number	Publication Date	Family Members	Priority Numbers	Inventors	Applicants	Title
GB1590261 A	19810528		GB19780003002 19780125	SHALABY W S; JAMIOLKOWSKI D D	ETHICON INC	Isomorphic copolyoxalates and sutures thereof.
GB2205323 A	19881207	US5382611 A 19950117; US5382611 X6 19950117; JPS63230701 A 19880927; IN167499 A1 19901110; GB2205323 B 19910130; FI880929 A 19880910; ES2053798 T3 19940801; DE3889751 T2 19941006; CN87105988 A 19881214; BR8800838 A 19881011; AU1275088 A 19880908; AU599761 B2 19900726; AT106409 T 19940615	GB19870005442 19870309	STEPTO ROBERT F T; TOMKA IVAN; DOBLER BEAT; PYRAH KEITH	WARNER LAMBERT CO	Destructurized starch and method for making same.
GB2206888 A	19890118	ZA8804695 A 19890426; YU126788 A 19890831; YU45506 B 19920528; US4900361 A 19900213; RU1799387 C 19930228; PT87881 A 19890630; PT87881 B 19950301; PL273393 A1 19890306; PL156365 B1 19920331; PH25985 A 19920113; NZ225245 A 19900327; NO882919 A 19890109; JPS6429404 A 19890131; JPH0641481 B2 19940601; IN172788 A1 19931127; IL86922 A 19911212; HUT49895 A 19891128; GR3006550 T3 19930630; GB2206888 B 19910206; FI883117 A 19890108; FI87225 B 19920831; FI87225 C 19921210; ES2053801 T3 19940801; EP0298920 A2 19890111; EP0298920 A3 19890315; EP0298920 B1 19921209; DK358488 A 19890108;	GB19870015941 19870707	SACHETTO JEAN PIERRE; STEPTO ROBERT F T; ZELLER HEINZ	WARNER LAMBERT CO	Destructurized starch essentially containing no bridged phosphate groups and process for making same.

		DE3876521 T2 19930422; CN1031380 A 19890301; CN1016346 B 19920422; CA1311237 C 19921208; BR8803120 A 19890124; AU1858288 A 19890112; AU605883 B2 19910124				
GB2208651 A	19890412	ZA8805889 A 19890426; US5405564 A 19950411; YU154488 A 19900228; YU45508 B 19920528; SU1612999 A3 19901207; PT88231 A 19890630; PT88231 B 19950301; PL274156 A1 19890502; PL156368 B1 19920331; PH27063 A 19930201; NZ225779 A 19900626; NO883547 A 19890220; NO303394 B1 19980706; MX169930 B 19930802; KR0130073 B1 19980407; JPH0197615 A 19890417; JPH066307 B2 19940126; IN175171 A1 19950513; IL87397 A 19920115; IE882440 L 19890218; IE61041 B1 19940907; HUT52130 A 19900628; GR3035425 T3 20010531; GB2208651 B 19910508; FI883720 A 19890219; FI93022 B 19941031; FI93022 C 19950210;	GB19870019485 19870818	STEPTO ROBERT F T; TOMKA IVAN; THOMA MARKUS	WARNER LAMBERT CO	Method of forming shaped articles made from pre-processed starch.

Continued

—Cont'd

Patent Number	Publication Date	Family Members	Priority Numbers	Inventors	Applicants	Title
		ES2051888 T3 19940701; ES2051888 T5 20010216; EP0304401 A2 19890222; EP0304401 A3 19900124; EP0304401 B1 19940302; EP0304401 B2 20001129; DK444388 A 19890219; DK171316 B1 19960902; DE3888046 T2 19940707; DE3888046 T3 20010322; CN1031314 A 19890301; CN1027726 C 19950301; CA1328711 C 19940426; BR8803404 A 19890228; AU2068188 A 19890223; AU602110 B2 19900927; AR244703 A1 19931130				
JP2001098065 A	20010410	JP3647689 B2 20050518	JP19990278020 19990930	KIDAI O; SHIRAHAMA R	MITSUBISHI CHEM CORP	Method for preparation of aliphatic polyester.
JP2003192884 A	20030709	JP3960797 B2 20070815	JP20010400253 20011228	NAKAZAWA KENJI; HIDA ETSUO; KONO TOSHINORI; KANAMORI KENJI; URAYAMA YUJI; OKUYAMA HISATSUGU	ASAHI DENKA KOGYO KK; TOYOTA MOTOR CORP	Polylactic acid-based polymer composition, molded article and method for producing the molded article.
JP2004175999 A	20040624	JP3680136 B2 20050810	JP20020346209 20021128	KOBAYASHI H; KAJIYAMA T; TAGUCHI T; TANAKA J	NAT INST FOR MATERIALS SCIENCE	Method for producing polymalic acid.
JP2005211041 A	20050811		JP20040025685 20040202	MUKOYAMA M	NIPPON CATALYTIC CHEM IND	Method for producing succinic acid.
JP2005264155 A	20050929		JP20040037556 20040216; JP20050038953 20050216	OTOME S; IWAI K; SAGAWA Y	NIPPON CATALYTIC CHEM IND	Biodegradable film.
JP2005320426 A	20051117	JP4621885 B2 20110126	JP20040139173 20040507	KOBAYASHI H; KAJIYAMA T; TAGUCHI T; TANAKA J	NAT INST FOR MATERIALS SCIENCE	Manufacturing process of polymalic acid copolymer.

JP2008115503 A	20080522		JP20060301186 20061107	TSUJI HIDETO; MIZUNO AKIRA; TAKASHIMA KAZUNORI; KATSURA SHINJI; NAKANO MICHIHIKO; HASHIMOTO MAKOTO	UNIV TOYOHASHI TECHNOLOG	Method for making stereocomplex polylactic acid material by application of electric field.
JP2011219736 A	20111104		JP20100065873 20100323; JP20110031495 20110217		TORAY IND INC	Polyalkylene terephthalate resin composition and fiber comprising same.
JP63251424 A	19881018	JP2507731 B2 19960619	JP19870085262 19870407	SASAKI S; SUMI T	UNITIKA LTD	Production of butylene adipate.
JP8003302 A	19960109	JP3342579 B2 20021111	JP19940162621 19940620	MUKAI K; KASAI M; IWAYA Y	UNITIKA LTD	Production of aliphatic polyester.
JP8301996 A	19961119		JP19950129216 19950427	YAGI T; YAMAMOTO M; MURAFUJI Y	KANEBO LTD	Method for polymerizing polyester.
JP9031174 A	19970204	JP3390571 B2 20030324	JP19950178758 19950714	MUKAI K; YAMADA Y; IWAYA Y	UNITIKA LTD	Polyethylene succinate of high molecular weight and production thereof.
JP9031176 A	19970204	JP3434622 B2 20030811	JP19950184271 19950720	TAKIYAMA E; FUJIMAKI T; HATANO Y; ISHIOKA R	SHOWA HIGHPOLYMER CO, LTD; SHOWA DENKO KK	Production of biodegradable aliphatic polyester.
JPH0413710 A	19920117	JPH0749459 B 19950531	JP19900116146 19900502	TORII H	REGURUSU KK	Polyurethane-based resin.
JPH05148352 A	19930615	JP3079716 B2 20000821	JP19910335579 19911126	DOI Y; TAKIYAMA E	SHOWA HIGHPOLYMER, CO LTD	Poduction of polylactide containing urethane bond.
JPS6136321 A	19860221	JPH0548258 B2 19930721	JP19840156565 19840727	IKADA YOSHITO; GEN JOKYU; HOSUROO JAMUSHIDEI	DAICEL CHEM; BIO MATERIAL UNIVERS KK	Novel polymer and its resin composition.

Continued

—Cont'd

Patent Number	Publication Date	Family Members	Priority Numbers	Inventors	Applicants	Title
SU1016314 A1	19830507		SU19792854648 19791217	ZAALISHVILI M M; KATSARAVA RAMAZ; KARTVELISHVILI T M	INST FIZIOL IM I S BERITASHVIL	"Process for producing polyester urethanes."
US1995970 A	19350326		US19390305474 19391121	TEETERS WILBER O	DU PONT	Modified glycolide resins.
US2002082363 A1	20020627	US6815529 B2 20041109; CN1306021 A 20010801; CN1116332 C 20030730	CN2000136189 20001227	ZHAO XIAOJIANG; WANG XIANHONG; WANG FOSONG	CHANGCHUN APPLIED CHEMISTRY	Catalyst for producing aliphatic polycarbonate and the preparation thereof.
US2002090687 A1	20020711		US20010754112 20010105	TRIPATHI GYANENDRA; MAHISHI LATA HANAMANTRAO; RAMACHANDER TURAGA VENKATA NAGA; RAWAL SHUBAN KISHEN	COUNCIL OF SCIENTIFIC & INDUSTRIAL RESEARCH; TRIPATHI GYANENDRA; MAHISHI LATA HANAMANTRAO; RAMACHANDER TURAGA VENKATA NAGA; RAWAL SHUBAN KISHEN	Process for the production of polyhydroxyoctanoate by *Streptomyces lividans*.
US2004023028 A1	20040205		US20030423209 20030425; US20020375453P 20020425	ASZEMSKI M J; CURRIER B L; LU L; ZHU X; JABBARI E	MAYO FOUNDATION	Blend, crosslinkable poly (propylene fumarate) for immobilization and controlled drug delivery.
US2005095679 A1	20050505		US20040974442 20041027; US20030515879P 20031030; US20040590727P 20040723	PRESCOTT A G; STOCK L R II	CRESCENT INNOVATIONS INC	Method for producing medical and commercial grade poly-gamma-glutamic acid of high molecular weight.

US2007117908 A1	20070524	CN1793198 A 20060628; CN100378138 C 20080402;	CN2005117300 20051121	ZHOU QINGHAI; ZHAO XIAOJIANG; WANG XIANHONG; WANG FOSONG; XIONG TAO; GAO FENGXIANG	CHANGCHUN APPLIED CHEMISTRY	Process for improving friability and cold-flow of carbon dioxide epoxy propylane copolymer.
US2010028512 A1	20100204		US20090577480 20091012; US20080210208 20080914; US20080040349P 20080328	KRIEGEL R M; HUANG X; SCHULTHEIS M W; BIPPERT D A; INSOLIA G E; KOLLS B; SUMMERVILLE S	COCA COLA CO	Bio-based polyethylene terephthalate packaging and method of making thereof.
US2010175691 A1	20100715	WO2010083356 A1 20100722; KR20110094345 A 20110823; MXPA11007535 A 20110831; EP2376538 A1 20111019; CN102239185 A 20111109	US20100686619 20100113; US20090144775P 20090115 US20100686619 20100113; US20090144775P 20090115	COMBS M T; WOODSON B R	CELANESE ACETATE LLC	Process for recycling cellulose acetate ester waste.
US2010272940 A1	20101028	WO2010125490 A2 20101104; WO2010125490 A3 20110414; MX2011011366 A 20111118; KR20120023624 A 20120313; EP2424937 A2 20120307; CN102414267 A 20120411; AU2010243295 A1 20111020	US20090430968 20090428	SHI BO; WANG J H	KIMBERLY–CLARK WORLDWIDE, INC	Algae-blended compositions for thermoplastic articles.
US2011065825 A1	20110317	US2012239135 A1 20120920; US8207240 B2 20120626; US8529617 B2 20130910	US20090559402 20090914	LAMBERT BYRON; WANG YUNBING; OBERHAUSER JAMES	ABBOTT CARDIOVASCULAR SYSTEMS INC	Method to minimize molecular weight drop of poly(L-Lactide) stent during processing.
US2011159288 A1	20110630		US20100968763 20101215; US20090286687P 20091215	CARVALHO FERNANDES DE MIRANDA REIS MARIA D ASCENSA; FREITAS OLIVEIRA RUI MANUEL; ANDRADE DE FREITAS MARIA FILOMENA; DELGADO ALVES VITOR MANUEL	SETENTA E TRES MIL E CEM LDA	Fucose-containing bacterial biopolymer.

Continued

—Cont'd

Patent Number	Publication Date	Family Members	Priority Numbers	Inventors	Applicants	Title
US2012214213 A1	20120823		US201113031350 20110221	CHEN G-Q; LI Z-J; GUO Y–Y; LU W-C; ZHOU Z–Z	TIANJIN GREEN-BIO MATERIAL CO LTD	Recombinant hosts and methods for manufacturing polyhydroxyalkanoate.
US2013085185 A1	20130404	WO2013049161 A1 20130404	US201213627545 20120926; US201161539695P 20110927	GUO KAI; MARTIN DAVID P	TEPHA INC	Controlled hydrolysis of poly-4-hydroxybutyrate and copolymers.
US2111762 A	19380322		US19360057851 19360106	CARLETON E	ELLIS FOSTER CO	Resinous compositions from oxalic acid and polyhydric alcohols and process of making same.
US2362511 A	19441114		US19310527854 19310404	LOWRANCE DOROUGH GEORGE	DU PONT	Polymeric lactide resin.
US3619222 A	19711109		US19700008019 19700202	WERLE E E; MITCHELL T	DARLING & CO	Modified protein composition and method of forming insoluble seals.
US4057537 A	19771108		US19750544788 19750128	SINCLAIR R	GULF OIL CORP	Copolymers of L-(–)-lactide and epsilon caprolactone.
US4078331 A	19780314		US19760680820 19760428	RAMUS J S	MOBIL OIL CORP	Process and culture composition for growth of alga and synthesis of biopolymer.
US4079038 A	19780314		US19760664127 19760305	CHOI NAM SOK; HELLER J	ALZA CORP	Poly(carbonates).
US4131648 A	19781226		US19750544805 19750128	CHOI NAM SOK; HELLER J	ALZA CORP	Structured orthoester and orthocarbonate drug delivery devices.
US4141087 A	19790227		US19770752374 19770119	SHALABY W S; JAMIOLKOWSKI D D	ETHICON INC	Isomorphic copolyoxalates and sutures thereof.
US4180646 A	19791225		US19780883123 19780303; US19750544808 19750128	CHOI NAM SOK; HELLER JORGE	ALZA CORP	Novel orthoester polymers and orthocarbonate polymers.
US4236349 A	19801202		US19780927698 19780724	RAMUS J S	MOBIL OIL CORP	Algae biopolymer production.
US4440921 A	19840403		US19820390350 19820621	ALLCOCK H R; NEENAN T X; KOSSA W C	RESEARCH CORP	Coupling of polyorganophosphazenes to carboxylic acid.
US4450150 A	19840522		FR19740034307 19741011; US19730361182 19730517	SIDMAN K R	LITTLE INC A	Biodegradable, implantable drug delivery depots, and method for preparing and using the same.

US4490326 A	19841225	US4490326 X6 19841225	US19820433177 19821006; US19810288274 19810730	BEROFF HOWARD; THOMPSON DARRELL R; MERICLE ROBERT W; TRAVIS JR WILLIAM C	ETHICON INC	Molding process for polydioxanone polymers.
US4495174 A	19850122		US19820390345 19820621	ALLCOCK H R; AUSTIN P E; NEENAN T X	RESEARCH CORP	Anesthetic polyorganophosphazenes.
US4673438 A	19870616		US19850796517 19851108; US19840579318 19840213	WITTWER F; TOMKA I	WARNER LAMBERT CO	Polymer composition for injection molding.
US4719246 A	19880112	JPS63241024 A 19881006; EP0272902 A2 19880629; EP0272902 A3 19881214; CA1292818 C 19911203	US19860944588 19861222	MURDOCH JOSEPH R; LOOMIS GARY L	DU PONT	Polylactide compositions.
US4880622 A	19891114		US19860865504 19860520	ALLCOCK H R; AUSTIN P E	RES CORP TECHNOLOGIES INC	Water-soluble phosphazene polymers having pharmacological applications.
US4946938 A	19900807		US19890388539 19890801	MAGILL J H; MERKER R L	UNIV PITTSBURGH	A process for the catalytic synthesis of polyphosphazenes.
US5095054 A	19920310		GB19880002313 19880203; US19890431715 19891102; US19890430764 19891102; US19890431672 19891102; US19890449313 19891208; US19890447741 19891208; US19890440955 19891122; US19890447979 19891208; US19890449095 19891208; US19890447747 19891208; US19890449314 19891208; US19890443791 19891122; US19890447730 19891208; US19890298603 19890118; US19890368486 19890619; US19890369978 19890622; US19890369983 19890622; US19890407643 19890718; US19890376057 19890706; US19890378120 19890711; US19890377981 19890711; US19890381620 19890718; US19890407644 19890718;	LAY GUSTAV; REHM JOHANNES; STEPTO ROBERT F T; THOMA MARKUS; SACHETTO JEAN-PIERRE; LENTZ DAVID J; SILBIGER JAKOB	WARNER LAMBERT CO	Polymer compositions containing destructurized starch.

Continued

—Cont'd

Patent Number	Publication Date	Family Members	Priority Numbers	Inventors	Applicants	Title
			US19890382870 19890720; US19890382869 19890720; US19890378536 19890711			
US5171308 A	19921215		US19920834794 19920213; US19900522134 19900511; US19910645849 19910125; US19910645995 19910125	GALLAGHER F G; HAMILTON C J; HANSEN S M; SHIN H; TIETZ R F	DU PONT	Polyesters and their use in compostable products such as disposable diapers.
US5315010 A	19940524	WO9500479 A1 19950105; US5391764 A 19950221; JPH08512066 A 19961217; EP0746543 A4 19960912; EP0746543 A1 19961211; EP0746543 B1 20020918; DE69431408 T2 20030116	US19940219667 19940329; US19930080562 19930621; US19910660355 19910222	KOSKAN L P; LOW K C; MEAH A R Y; ATENCIO A M	DONLAR CORP	Polyaspartic acid manufacture.
US5362777 A	19941108		CH19880004083 19881103; US19930115243 19930830; US19900536683 19900711; US19910785931 19911031	TOMKA I	TOMKA I	Thermoplastically processable starch and a method of making it.
US5427614 A	19950627	US5427614 X6 19950627	US19920836665 19920214; US19930133716 19931007	WITTWER FRITZ; TOMKA IVAN	WARNER LAMBERT CO	
US5439688 A	19950808		US19910790033 19911112; CH19890002829 19890728; CH19900003616 19901114; US19900555973 19900720	ORSOLINI P; HEIMGARTNER F	DEBIO RECH PHARMA SA	Process for preparing a pharmaceutical composition.
US5936045 A	19990810	NO973767 A 19971015; NO315203 B1 20030728; NO973766 A 19971015; NO315204 B1 20030728; JP2000504355 A 20000411; JP3452583 B2 20030929; FI973359 A 19970815; FI973358 A 19970815; ES2122792 T3 19981216; ES2122792 T5 20030216; DK0809666 T3 19990628; DK0809666 T4 20021202; AU4787096 A 19960904; AU4717996 A 19960904		WARZELHAN VOLKER; PIPPER GUNTER; SEELIGER URSULA; BAUER PETER; BEIMBORN DIETER BERNHARD; YAMAMOTO MOTONORI	BASF AG	Biodegradable polymers, the preparation thereof, and the use thereof for producing biodegradable moldings.

US6046248 A	20000404	US6046248 X6 20000404	DE19944440836 19941115; US19970975205 19971120; US19970836038 19970514	WARZELHAN VOLKER; BRAUN FRANK; KRONER MATTHIAS; SEELIGER URSULA; YAMAMOTO MOTONORI; BUESCHL RAINER	BASF AG	Biodegradable polymers, the preparation thereof and the use thereof for producing biodegradable moldings.
US6077916 A	20000620		US19980090374 19980604; US19970048523P 19970604	LAURENCIN C; ALLCOCK H; IBIM S; AMBROSIO A; KWON M	PENN STATE RES FOUND	Biodegradable mixtures of polyphoshazene and other polymers.
US6428767 B1	20020806	US2003082756 A1 20030501; US7169588 B2 20070130	US19990369796 19990806; US19970966794 19971110; US19950440293 19950512	BURCH R R; DORSCH R R; LAFFEND L A; NAGARAJAN V; NAKAMURA C	DU PONT; GENENCOR INT	Method for identifying the source of carbon in 1,3-propanediol.
WO0027923 A1	20000518	E19852081 C1 20000727; AU1774700 A 20000529; EP1129140 A1 20010905; EP1129140 B1 20020724; DE59902150 G 20020829; JP2002529567 A 20020910; ZA200103577 A 20020925; US6509397 B1 20030121; ES2183631 T3 20030316; JP3725428 B2 20051214	DE19981052081 19981111	NAEGELE H; PFITZER J; EISENREICH N; EYERER P; ELSNER P; ECKL W	FRAUNHOFER GES FORSCHUNG; TECNARO GES ZUR IND ANWENDUNG	Kunststoff-werkstoff aus einem polymer-blend. "Plastic material made from a polymer blend."
WO0043523 A2	20000727	WO0043523 A3 20011101; US2004172675 A1 20040902; US7504556 B2 20090317; US2010311131 A1 20101209; US8049065 B2 20111101; US2002040485 A1 20020404; US7455999 B2 20081125; JP2002534981 A 20021022; JP4986325 B2 20120725; ES2344000 T3 20100816; EP2088198 A2 20090812; EP2088198 A3 20130821; EP1208208 A2 20020529; EP1208208 B1 20090617; CA2360801 A1 20000727; CA2360801 C 20120605; AU2623100 A 20000807; AU778497 B2 20041209; AT434045 T 20090715	US19990235875 19990122	MADISON LARA; HUISMAN GJALT W; PEOPLES OLIVER P	METABOLIX INC	Transgenic systems for the manufacture of poly(3-hydroxy-butyrate-*co*-3-hydroxyhexanoate).

Continued

—Cont'd

Patent Number	Publication Date	Family Members	Priority Numbers	Inventors	Applicants	Title
WO0056376 A1	20000928	WO0056376 A9 20020711; US2002173558 A1 20021121; US6867247 B2 20050315; US2008095823 A1 20080424; US7553923 B2 20090630; US2008051490 A1 20080228; US2007135929 A1 20070614; US7268205 B2 20070911; US6548569 B1 20030415; US2002156150 A1 20021024; US6838493 B2 20050104; US2005107578 A1 20050519; US7179883 B2 20070220; PT1163019 E 20071206; JP2002539854 A 20021126; JP5031144 B2 20120919; ES2395057 T3 20130207; ES2295021 T3 20080416; EP2305324 A1 20110406; EP1867348 A2 20071219; EP1867348 A3 20080109; EP1867348 B1 20120516; EP1163019 A1 20011219; EP1163019 B1 20071024; DK1163019 T3 20080303; DE60036863 T2 20080731; CY1107044 T1 20120926; CA2368470 A1 20000928; CA2368470 C 20110517; AU4027700 A 20001009; AU778081 B2 20041111; AT376433 T 20071115	US19990126180P 19990325; US19990142238P 19990702	WILLIAMS SIMON F; MARTIN DAVID P; SKRALY FRANK A	METABOLIX INC	Medical devices and applications of polyhydroxyalkanoate polymers.

WO0062630 A1	20001026	WO0063268 A1 20001026; WO0063263 A1 20001026; US6306821 B1 20011023; US6884432 B2 20050426; JP2002542352 A 20021210; JP2002542339 A 20021210; JP2002542349 A 20021210; JP4644374 B2 20110302 EP1171006 A1 20020116; EP1194463 A1 20020410; EP1210379 A1 20020605; EP1194463 A4 20020925; EP1210379 A4 20020925; EP1171006 A4 20020925; EP1171006 B1 20060329; EP1210379 B1 20070321; EP1194463 B1 20091111; DE60026983 E 20060518; DE60034045 T2 20071122; CA2370357 A1 20070410; CA2369758 A1 20001026; CA2370330 A1 20001026; CA2370357 C 20001026; CA2369758 C 20070403; CA2370330 C 20090120; AU4644700 A 20001102; AU4351800 A 20001102; AU4349600 A 20001102; AU760358 B 20030515; AU770579 B2 20040226; AU775913 B2 20040819; AT321803 T 20060415 AT357468 T 20070415; AT448274 T 20091115	US19990129577P 19990416; US19990146991P 19990803; US19990167328P 19991124; US19990167388P 19991124	HE S; YASZEMSKI M J; MIKOS A G	UNIV WM MARSH RICE	Poly(propylene fumarate) cross linked with poly(ethylene glycol).
WO0107166 A1	20010201	SK962002 A3 20020604; PL354035 A1 20031215; HU0201525 A2 20020828; EP1200194 A1 20020502; DE19934259 A1 200102; CZ20020269 A3 20020717	DE1999134259 19990727	HOLLEY WOLFGANG; HUBER KONRAD; KATZSCHNER GREGOR; PFEIFFER THOMAS; SCHOENWEITZ CLAUDIA	FRAUNHOFER GES FORSCHUNG	Method for selectively separating predetermined materials in mixtures of materials.

Continued

—Cont'd

Patent Number	Publication Date	Family Members	Priority Numbers	Inventors	Applicants	Title
WO0111070 A2	20010215	WO0111070 A3 20010830; EP1222303 A2 20020717		BURCH R R; DORSCH R R; LAFFEND L A; NAGARAJAN V; NAKAMURA C	DU PONT	1,3-propanediol and polymer derivatives from a fermentable carbon source.
WO0112833 A2	20010222	WO0112833 A3 20010830; US2003157674 A1 20030821; US6514733 B1 20030204; US7067300 B2 20060627; PT1204755 E 20061130; KR20020059364 A 20020712; KR100785997 B1 20071214; JP2003507022 A 20030225; JP4716634 B2 20110706; EP1586647 A1 20051019; EP1204755 A2 20020515; EP1204755 B1 20060809; DE60029971 T2 20070516; CN1379818 A 20021113; CN101024843 A 20070829; CN1298852 C 20070207; CA2733616 A1 20010222; CA2380616 C 20110524; BR0013315 A 20020402	US19990149534P 19990818	EMPTAGE M; HAYNIE S; LAFFEND L A; PUCCI J; WHITED G	DU PONT	Process for the biological production of 1,3-propanediol with high titer.
WO0218477 A2	20020307	US6503538 B1 20030107; JP2004507600 A 20040311; JP5047446 B2 20121010; ES2275724 T3 20070616; EP1313794 A2 20030528; EP1313794 B1 20061129; DE60124929 T2 20070920; CA2419429 A1 20020307; CA2419429 C 20100727; AU8701501 A 20020313 AU2001287015 B2 20060601; AT346878 T 20061215	US20000651338 20000830	CHU CHIH-CHANG; KATSARAVA RAMAZ	CORNELL RES FOUNDATION INC	Elastomeric functional biodegradable copolyester amides and copolyester urethanes.
WO03057781 A	20030717	US2005001358 A1 20050106; EP1460107 A1 20040922; EP1460107 A4 20050126; EP1460107 B1 20090311; CN1522282 A 20040818; CN1246387 C 20060322; AU2002357605 A1 20030724; AU2002357605 B2 20051013; AU2002357605 B9 20060518	JP20010400252 20011228; JP20010400253 20011228	NAKAZAWA KENJI; TOBITA ETSUO; YUKINO TOSHINORI; URAYAMA HIROSHI; KANAMORI TAKESHI; OKUYAMA HISASHI	ASAHI DENKA KOGYO KK; TOYOTA MOTOR CORP	Polylactic acid-based resin compositions, molded articles and process for producing the same.

WO03097468 A1	20031127	US2005175801 A1 20050811; US2009030094 A1 20090129; US7799837 B2 20100921; KR20040104742 A 20041210; JP4476803 B2 20100609; EP1555209 A1 20050720; CN1652976 A 20050810; CN100436271 C 20081126 CA2486312 A1 20031127 AU2003242308 A1 20031202; AT469035 T 20100615	US20080232365 20080916; JP20020146095 20020521; US20040514048 20041110; WO2003JP06134 20030516	YAMANE K; KATO R; SATO H;	KUREHA CHEM IND CO LTD	Bottle excellent in recyclability and method for recycling the bottle.
WO2004041936 A1	20040521	US2006258833 A1 20061116; US7491754 B2 20090217; RU2005117628 A 20060120; PL376558 A1 20060109; JP4553733 B2 20100929; EP1566409 A1 20050824; EP1566409 A4 20060201; CN1711316 A 20051221; CN1308395 C 20070404; CA2503590 A1 20040521; BR0315787 A 20050913; AU2003277546 A1 20040607	JP20020325984 20021108	SENDA KENICHI; MIKI YASUHIRO	KANEKA CORP	Aqueous dispersion of biodegradable polyester and method for production thereof.
WO2004085533 A1	20041007	US2006264539 A1 20061123; JP2007524715 A 20070830; JP4277040 B2 20090610; EP1608700 A1 20051228; EP1608700 B1 20110629; DE10313939 A1 20041014; CN1809611 A 20060726; CN100439439 C 20081203	DE20031013939 20030327	MOSSEVELD H; WIERER K A; KOHLHAMMER K	WACKER POLYMER SYSTEMS GMBH	Verwendung von Polymerisaten zur Stärkemodifizierung. "Use of polymers for starch modification."
WO2007020904 A1	20070222	US2009127915 A 20090521; KR20080046655 A 20080527; KR100944893 B1 20100303; JP4932721 B2 20120516; EP1921098 A1 20080514; EP1921098 A4 20101027; EP1921098 B1 20120808; CN101238161 A 20080806; CN101238161 B 20110706	JP20050234527 20050812; WO2006JP315967 20060811	NOZAWA K; SASAKI M; OHKUBO K	MITSUI CHEMICALS POLYURETHANES	Composition for polyurethane foam, polyurethane foam obtained from the composition, and use thereof.

Continued

—Cont'd

Patent Number	Publication Date	Family Members	Priority Numbers	Inventors	Applicants	Title
WO2007033418 A1	20070329	US2009175921 A1 20090709; US7964696 B2 20110621; US2011287102 A1 20111124; JP2009508598 A 20090305; EP1945690 A1 20080723; EP1945690 A1 20080723; CN101296958 A 20081029; CN101296958 B 2012018	AU20050905192 20050920	GUNATILLAKE P A; MOORE T G; ADHIKARI R	POLYNOVO BIOMATERIALS PTY LTD; GUNATILLAKE P A	Chain extenders.
WO2008038648 A1	20080403	US2010086718 A1 20100408; US8048502 B2 20111101; KR20090054454 A 20090529; KR110018895 B1 20120319; EP2080787 A1 20090722; CN101541887 A 20090923; CN101541887 B 20120718	WO2007JP68633 20070926; JP20060260540 20060926	YOSHIKAWA S; YOSHIDA M; KOGURE M	TOYO SEIKAN KAISHA LTD	Readily degradable resin composition, and biodegradable container using the same.
WO2008067627 A2	20080612	WO2008067627 A3 20080724; US2010069691 A1 20100318; JP2010511634 A 20100415; EP2099735 A2 20090916; BRPI0605173 A 20080722; AU2007329122 A1 20080612	BR2006PI05173 20061205	MORSCHBACKER A L R D	BRASKEM SA	A method for the production of one or more olefins an olefin and a polymer.
WO2009070858 A1	20090611	US2011213104 A1 20110901; US8222354 B2 20120717; KR20100103783 A 20100928; JP2011506628 A 20110303; ES2372235T T3 20120117; EP2162475 A1 20100317; EP2162475 B1 20111012; AU2008331448 A1 20090611	BR2007PI04605 20071205	MORSCHBACKER A L R D	BRASKEM SA	Integrated process for the production of ethylene-butylene copolymer, an ethylene-butylene copolymer and the use of ethylene and 1-butylene, as comonomer, sourced from renewable natural raw materials.
WO2009095363 A1	20090806	US2010298460 A1 20101125; MX2010007943 A 20100810; KR20100126317 A 20101201; JP2011511105 A 20110407; EP2238195 A1 20101013; CN102089351 A 20110608	EP20080150748 20080129	MIJOLOVIC D; HAUNERT A; KUNST A; BAUER S; MIAO Q; ELING B	BASF SE	Method for the production of polyether polyols.
WO2009107425 A1	20090903	US2011027590 A1 20110203; JP2009202465 A 20090910; JP4972012 B2 20120711; EP2255951 A1 20101201; CN101945749 A 20110112	JP20080047985 20080228; WO2009JP50965 20090122	ABE SHUNSUKE	KUREHA CORP	Sequentially biaxially-oriented polyglycolic acid film, production process thereof and multi-layer film.

WO2009120457 A2	20091001	WO2009120457 A3 20091126; US2009246430 A1 20091001; US2011262669 A1 20111027; TW201002756 A 20100116; MXPA10009905 A 20100930; JP2011527348 A 20111027; EP2265659 A2 20101229; CN101970530 A 20110209; CA2718279 A1 20091001; AU2009229151 A1 20091001	US20080210208 20080914; US20080040349P 20080328	KRIEGEL R M; HUANG X; SCHULTHEIS M W	COCA COLA CO	Bio-based polyethylene terephthalate polymer and method of making the same.
WO2010022966 A2	20100304	WO2010022966 A8 20100506; WO2010022966 A3 20100624; US2012149920 A1 20120614; RU2011107123 A 20121010; MX2011001726 A 20110817; KR20110045097 A 20110503; EP2392570 A1 20111207; EP2321294 A2 20110518; CN102131796 A 20110720; CA2734102 A1 20100304	DE20081044947 20080829	HAGEN RAINER; VERWEIJ ADAM BASTIAAN; MUEHLBAUER UDO; KRICHELDORF HANS R; SCHULZE JOACHIM; TIETZ WOLFGANG; GOEHLER KLAUS-DIETER	UHDE INVENTA FISCHER GMBH; UHDE GMBH	Verfahren zur Herstellung eines Gemisches von Lactid-Derivaten. "Method for the production of a mixture of lactide derivatives."
WO2010123095 A1	20101028	WO2010123095 A1 20101028; JP2010254812 A 20101111; KR20120014243 A 20120216; CN102414247 A 20120411	JP20090106684 20090424	MATSUO T; KAMIKAWA M; OKA K; KONDO T; ITO H; SASE Y	HITACHI PLANT TECHNOLOGIES LTD	Method and device for synthesizing polyester.
WO2011002004 A1	20110106	US2012095169 A1 20120419; TW201114791 A 20110501; KR20120027425 A 20120321; EP2450388 A1 20120509; CN102459391 A 20120516	JP20090156063 20090630; JP20090254431 20091105	HIROKAZU; TOTANI YOSHIYUKI; TSUJI MASASHI; HASEGAWA AKIRA; HORI HIDESHI	MITSUI CHEMICALS INC	Polylactic acid resin, method for producing polylactic acid resin, polylactic acid resin composition, stereocomplex polylactic acid resin composition, and method for producing stereocomplex polylactic acid resin composition.
WO2011005664 A2	20110113	WO2011005664 A3 20110428; US7364875 B2 20080429; EP2451860 A2 20120516; CN102471473 A 20120523	WO2010US40829 20100701; US20090224134P 20090709; US20090223042P 20090705	SCOTT A	NOVOMER INC	Structurally precise poly(propylene carbonate) compositions.

Continued

—Cont'd

Patent Number	Publication Date	Family Members	Priority Numbers	Inventors	Applicants	Title
WO2011073874 A2	20110623	WO2011073874 A3 20110804; WO2011073874 A9 20110922; WO2011073874 A4 20111110; PT104888 A 20110615; MX2012006944 A 20121003; JP2013513397 A 20130422; EP2513325 A2 20121024; CN102971432 A 20130313; CA2782989 A1 20110623; AU2010331906 A1 20120621	PT20090104888 20091215	CARVALHO FERNANDES DE MIRANDA REIS MARIA D ASCENSA; FREITAS OLIVEIRA RUI MANUEL; ANDRADE DE FREITAS MARIA FILOMENA; DELGADO ALVES VITOR MANUEL	SETENTA E TRES MIL E CEM LDA	Fucose-containing bacterial polymer.
WO2012004402 A1	20120112		GB20100011542 20100708	STEVENS M M; MAY J R; GENTILINI C	IMP INNOVATIONS LTD	Process for preparation of polymer body.
WO2012141660 A1	20121018	US2014039096 A1 20140206; SK262011 A3 20121105; SG194040 A1 20131129; CN103459498 A 20131218; CA2833131 A1 20121018	SK20110000026 20110411	ALEXY PAVOL; CHODAK IVAN; BAKOS DUSAN; BUGAJ PETER; PAVLACKOVA MIROSLAVA; TOMANOVA KATARINA; BENOVIC FRANTISEK; PLAVEC RODERIK; MIHALIK MICHAL; BOTOSOVA MONIKA	USTAV POLYMEROV SAV	Biologically degradable polymeric composition with high deformability.
WO2013039266 A1	20130321		JP20110198712 20110912	KISHIDA HISANOR; HASEGAWA TAKASHI; NOMURA NOBUYOSHI; TAKAHASHI MAKOTO; SCHROEDER JOSEPH; NATAL MANUEL	HITACHI SHIPBUILDING ENG CO; TOHOKU ELECTRIC POWER CO; UNIV NAGOYA NAT UNIV CORP	Method to produce semi-crystalline polylactides.
WO2013087903 A1	20130620		EP20110194043 20111216	ZUPANCICH JOHN ANDREW	DSM IP ASSETS BV	Process for the manufacturing of a drug delivery system based on a polymer comprising a dispersed bioactive agent.

WO8103278 A1	19811126	ZA8103269 A 19820630; US4304767 A 19811208; SE8200068 A 19880808; SE455791 B 19880808; PT73035 A 1981061; PT73035 B 19841022; NZ197036 A 19840203; NL8120177 A 19820401; NL188166 C 19920416; JPS57500613 A 19820408; JPS60214745 A 19851028; JPS60221424 A 19851106; JPS2218719 A 19900831; JPH03732 A 19910107; JPH02218719 A 19900831; JPH039127 B2 19910207; JPH0355492 B2 19910823; JPH0216930 B2 19900418 IE811098 L 19811115; IE51287 B1 19861126; GR74902 A1 19840712; GB2086404 A 19820512; ES8207564 A1 19821216; EP0051667 A1 19820519; EP0051667 B1 19860305; DK16082 A 19820115; DE3148618 A1 19820715; CH657369 A5 19860829; CA1186438 A1 19850430; BE888829 A1 19810828; AU543991 B2 19850509; AT384615 B 19871210	US19800150052 19800515	HELLER J; HELWING R; PENHALE D	STANFORD RES INST INT	Polymers of di-(and higher functionality)ketene acetals and polyols.
WO9202559 A1	19920220	US5275774 A 19940104; JPH05501686 A 19930402; JP3280666 B2 20020513; ES2080958 T3 19960216; EP0495056 A1 19920722; EP0495056 B1 19951220; DK0495056 T3 19960129; DE69115673 T2 19960502; AT131831 T 19960115	GB19900017300 19900807	BAHR KARK-HEINZ; FITTON MICHAEL G; KOCH HELMUT	CERESTAR HOLDING BV	Starch treatment process.

Continued

—Cont'd

Patent Number	Publication Date	Family Members	Priority Numbers	Inventors	Applicants	Title
WO9209654 A2	19920611	WO9209654 A3 19921001; US5900322 A 19990504; US5900322 X6 19990504; US5559171 A 19960924; US5580911 A 19961203; US5599858 A 19970204; US5446079 A 19950829; US6342304 B1 20020129; SG47853 A1 19980417; NZ240799 A 19940126; MX9102312 A 19940131; KR100245905 B1 20000315; KR100220443 B1 19990915; JP2007138377 A 20070607; JP2006022472 A 20060126; JP2004084156 A 20040318; JP2003221464 A 20030805; JP2003128768 A 20030508; JP3530178 B2 20040524; JP2001354802 A 20011225; JP3393124 B2 20030407; JPH06504558 A 19940526; JP3362040 B2 20030107; IE914155 A1 19920603; HK1041708 A1 20041008; FI20000496 A 20000303; FI932450 A 19930528; ES2278424 T3 20070801 EP0559785 A1 199309 EP0559785 B1 19970312; DE69133554 T2 20071004; DE69132548 T2 20010628; DE69125170 T2 19970619; CN1183429 A 19980603; CN1183428 A 19980603; CN1183427 A 19980603; CN1183433 A 19980603;	US19900620225 19901130; US19910736262 19910723; US19910797512 19911121	BUCHANAN CHARLES M; GARDNER ROBERT M; WHITE ALAN W	EASTMAN CHEM CO	Aliphatic-aromatic copolyesters and cellulose ester/polymer blends.

		CN1072245 C 20011003; CN1183423 A 19980603; CN1076358 C 20011219; CN1183426 A 19980603; CN1062740 A 19920715; CN1324891 A 20011205; CN1131281 C 20031217; CA2095536 A1 19920531; CA2095536 C 19990216; BR9107138 A 19940405; AU9105091 A 19920625; AU664831 B2 19951207; AU4557496 A 19960606; AT349476 T 20070115; AT199383 T 20010315; AT150058 T 19970315				
WO9514740 A1	19950601	AU8133694 A 19950613	US19930160561 19931124	GALLAGHER F G; GRAY D S; HAMILTON C J; TIETZ R F; WALLENBERGER F T	DU PONT	Apertured structures of biodegradable polyesters.
WO9529710 A1	19951109	US5733951 A 19980331 AU2432295 A 19951129	US19940234551 19940428	MIKOS A G; YASZEMSKI M J; PAYNE R G	RICE UNIVERSITY	Poly(propylene fumarate).
WO9615174 A1	19960523	US6258924 B1 20010710; US6414108 B1 20020702; US6297347 B1 20011002; PT792310 E 20010928; PL320223 A1 19970915; NO972227 A 19970714; NO315121 B1 20030714; MX9703537 A 19970830; JPH11500468 A 19990112; JP3459258 B2 20031020; HUT77057 A 19980302; FI972060 A 19970514; FI117440 B 20061013; ES2156210 T3 20010616; EP0792310 A1 19970903; EP0792310 B1 20010411; DK0792310 T3 20010507; DE4440837 A1 19960523;	DE19944440837 19941115	WARZELHAN VOLKER; BRUCHMANN BERND; BOECKH DIETER; SEELIGER URSULA; YAMAMOTO MOTONORI; BAUER PETER	BASF AG	Biologisch abbaubare polymere, Verfahren zu deren Herstellung sowie deren Verwendung zur Herstellung bioabbaubarer Formkörper. “Biodegradable polymers, the production thereof and the use thereof for producing biodegradable moldings.”

Continued

—Cont'd

Patent Number	Publication Date	Family Members	Priority Numbers	Inventors	Applicants	Title
		CZ9701465 A3 19971015; CZ293001 B6 20040114; CN1170419 A 19980114; CN1075527 C 20011128; CA2205072 A1 19960523; CA2205072 C140C 20050111; AU2978195 A 19960606; AU691317 B2 19980514; AT200501 T 20010415				
WO9625446 A1	19960822	WO9625448 A1 19960822; US5889135 A 19990330; JPH11500157 A 19990106; ES2147918 T3 20001001; EP0809664 A1 19971203; EP0809666 A1 19971203; EP0809664 B1 20000517; EP0809666 B2 20020814; DK809664 T3 20000828; DE19505186 A1 19961031	DE19951005185 19950216	WARZELHAN V; PIPPER G; SEELIGER U; BAUER P; PAGGA U; YAMAMOTO M	BASF AG	Biodegradable polymers, process for producing them and their use in preparing biodegradable mouldings.
WO9806785 A1	19980219	US6284838 B1 20010904; ES2168652 T3 20020616; EP0918825 A1 19990602; DK918825 T3 20020325; CA2263290 A1 C13619980219; AT209669 T 20011215	CH19960001967 19960812; CH19960002687 19961031; CH19960003015 19961209; CH19970000013 19970106	SILBIGER J	SILBIGER J	Biodegradable composition.
WO9828357 A1	19980702	US6042820 A 20000328 US2005163745 A1 20050728; US6287604 B1 20010911; US6312732 B1 20011106; PT946624 E 20030829; NZ336718 A 20010126; JP2000509428 A 20000725; JP2003261661 A 20030919; JP2002138139 A 20020514; ES2196385 T3 20031216; EP0946624 A1 19991006; EP0946624 B1 20030402; DK946624 T3 20030714; DE69720516 T2 20040219; CA2275033 A1 19980702; CA2275033 C 20050802; BR9714065 A 20001024; AU5472198 A 19980717; AU729305 B2 20010201; AT236207 T 20030415	US19960770850 19961220	SOKOLL K K; CHONG P; KLEIN M H	CONNAUGHT LAB	Biodegradable copolymer containing alpha-hydroxy acid and alpha-amino acid units.

WO9851812 A2	19891119	WO9851812 A3 19990211; US2007280899 A1 20071206; US7906135 B2 20110315; US2011135707 A1 20110609; US8231889 B2 20120731 US6245537 B1 20010612; US2001009769 A1 20010726; US6623749 B2 20030923; US2004053381 A1 20040318; US7244442 B2 20070717; PT981381 E 20070430; ES2285770 T3 20071116; EP0981381 A2 20000301; EP0981381 B1 20070221; DK0981381 T3 20070604; DE69837141 T2 20071031; AU7486798 A 19981208; AT354600 T 20070315	US19970046211P 19970512; US19970054289P 19970731; US19970063501P 19971024; US19970065921P 19971117	WILLIAMS S F; MARTIN D P; GERNGROSS T; HOROWITZ D M	METABOLIX INC	Polyhydroxyalkanoates for in vivo applications.
WO9925756 A1	19990527	US2002061943 A1 20020523; US6958369 B2 20051025; EP0961805 A1 19991208; EP0961805 B1 20040414; DE19750846 C1 20000127; DK961805 T3 20040802; AT264355 T 20040415	DE19971050846 19971117	BERGER W; JEROMIN L; MIERAU UTA OPITZ G	BIOP BIOPOLYMER GMBH	Komponente zur Herstellung von Polymermischungen auf der Basis von Stärke und Verfahren zur Herstellung der Komponente. "Component for producing polymer mixtures on the basis of starch and a method for producing the same."
WO9929733 A1	19990617	US6482341 B1 20021119; PT1040127 E 20021031; NL1007735 C2 19990609; NL1009449 C6 19991221; HK1031887 A1 20021220; ES2175821 T3 20021116; EP1040127 A1 20001004; EP1040127 B1 20020605; DK1040127 T3 20020708; DE69805848 T2 20021107; CA2313516 A1 19990617; CA2313516 C 20080429; AU1446599 A 19990628; AT218585 T 20020615	NL19971007735 19971208; NL19981009449 19980619	JONGBOOM R O J; STUUT P I; RODENBURG J A	RODENBURG VEEVOEDERS B V	Biodegradable mouldings.

Continued

—Cont'd

Patent Number	Publication Date	Family Members	Priority Numbers	Inventors	Applicants	Title
WO9932536 A1	19990701	PT1042388 E 20070131; JP2001527101 A 20011225; ES2281147 T3 20070916; ES2394953 T3 20130207; ES2356350 T3 20110407; EP1042388 A1 20001011; EP2258742 A1 20101208; EP2196484 A1 20100616; EP2196484 B1 20120822; EP1659142 A1 20060524; EP1659142 B1 20100324; DK1042388 T3 20061211; DE69836439 T2 20070524; CA2314151 A1 19990701; AU1942999 A 19990712; AU751610 B2 20020822; AT345359 T 20061215; AT461957 T 20100415	US19970068455P 19971222	MARTIN DAVID P; SKRALY FRANK A; WILLIAMS SIMON F	METABOLIX INC	Polyhydroxyalkanoate compositions having controlled degradation rates.
WO9950345 A1	19991007	US6353086 B1 20020305; US6114495 A 20000905; JP2002509968 A 20020402; HK1036466 A1 20090206 EP1070097 A1 20010124; CN1299393 A 20010613; CN100379806 C 20080409; CA2325046 A1 19991007; CA2325046 C 20090310; BR9909283 A 20001226	US19980053836 19980401	KOLSTAD JEFFREY J; WITZKE DAVID ROY; HARTMANN MARK H; HALL ERIC STANLEY; NANGERONI JAMES FRANCIS	CARGILL, INC	Lactic acid residue containing polymer composition, product method for preparation and use.

REFERENCES

[1] Japan Bioplastics Association (JBPA). GreenPla®. (http://www.jbpaweb.net/english/english.htm).

[2] Niaounakis M. Biopolymers reuse, recycling, and disposal, chapter 10: economic evaluation and environmental impacts; section 10.3.2: source of feedstocks. 1st ed. Plastics Design Library (PDL); 2013. Access Online via Elsevier; p. 432.

[3] Ravenstijn J. Bioplastics in consumer electronics. Ind Biotechnol 2010;6:252–63.

[4] Public law 107–171—May 13. Farm Security and Rural Investment Act of 2002.

[5] United Sates Department of Agriculture (USDA). Biopreferred Program. USDA Biopreferred brand guide addendum-definitions and frequently asked questions. http://www.biopreferred.gov/FILES/Defintions_and_FAQs.pdf.

[6] Niaounakis M. Biopolymers reuse, recycling, and disposal, chapter 2: definition and assessment of (Bio)degradation; section 2.5: (Bio) degradation testing. 1st ed. Plastics Design Library (PDL); 2013. Access Online via Elsevier; p. 432.

[7] Niaounakis M. Biopolymers reuse, recycling, and disposal, chapter 9: regulatory aspects framework; section: 9.1: standards. 1st ed. Plastics Design Library (PDL); 2013. Access Online via Elsevier; p. 432.

[8] European bioplastics. Bioplastics. Fact Sheets: http://en.european-bioplastics.org/wp-content/uploads/2011/04/fs/Bioplastics_eng.pdf; October 2012.

[9] Raquez J-M, Deléglise M, Lacrampe MF, Krawczak P. Thermosetting (bio) materials derived from renewable resources: a critical review. Prog Polym Sci 2010;35:487–509.

[10] Vroman I, Tighzert L. Biodegradable polymers. Materials 2009;2:307–44.

[11] Mochizuki M, Hirami M. Structural effects on the biodegradation of aliphatic polyesters. Polym Adv Technol 1997;8:203–9.

[12] Dunsing R, Kricheldorf HR. Polylactones. Polym Bull 1985;14:491–5.

[13] Kricheldorf HR, Dunsing R. Polylactones, 8. Mechanism of the cationic polymerization of L,L-dilactide. Die Makromol Chem 1986;187:1611–25.

[14] Maharana T, Mohanty B, Negi Y. Melt–solid polycondensation of lactic acid and its biodegradability. Prog Polym Sci 2009;34:99–124.

[15] Auras R, Harte B, Selke S. An overview of polylactides as packaging materials. Macromol Biosci 2004;4:835–64.

[16] Ovitt TM, Coates GW. Stereoselective ring-opening polymerization of meso-lactide: synthesis of syndiotactic poly (lactic acid). J Am Chem Soc 1999;121:4072–3.

[17] Rutot D, Dubois P. Les (bio) polymeres biodegradables: l'enjeu de demain? Chim Nouv 2004:66–74.

[18] Radano CP, Baker GL, Smith M. Stereoselective polymerization of a racemic monomer with a racemic catalyst: direct preparation of the polylactic acid stereocomplex from racemic lactide. J Am Chem Soc 2000;122:1552–3.

[19] Tsuji H, Hyon SH, Ikada Y. Stereocomplex formation between enantiomeric poly (lactic acid)s. 3. Calorimetric studies on blend films cast from dilute solution. Macromolecules 1991;24:5651–6.

[20] Yui N, Dijkstra PJ, Feijen J. Stereo block copolymers of L-and D-lactides. Die Makromol Chem 1990;191:481–8.

[21] Liu T, Simmons TL, Bohnsack DA, Mackay ME, Smith MR, Baker GL. Synthesis of polymandelide: a degradable polylactide derivative with polystyrene-like properties. Macromolecules 2007;40:6040–7.

[22] Nair LS, Laurencin CT. Biodegradable polymers as biomaterials. Prog Polym Sci 2007;32:762–98.

[23] Loos K. Biocatalysis in polymer chemistry. Wiley-VCH; 2011.

[24] Steinbüchel A, Valentin HE. Diversity of bacterial polyhydroxyalkanoic acids. FEMS Microbiol Lett 1995;128:219–28.

[25] Witholt B, Kessler B. Perspectives of medium chain length poly (hydroxyalkanoates), a versatile set of bacterial bioplastics. Curr Opin Biotechnol 1999;10:279–85.

[26] Abe C, Taima Y, Nakamura Y, Doi Y. New bacterial copolyester of 3-hydroxyalkanoates and 3-hydroxy-ω-fluoroalkanoates produced by *Pseudomonas oleovorans*. Polym Commun 1990;31:404–6.

[27] Fritzsche K, Lenz RW, Fuller RC. An unusual bacterial polyester with a phenyl pendant group. Die Makromol Chem 2003;191:1957–65.

[28] Hocking P, Marchessault R. Biopolyesters. In: Griffin G, editor. Chemistry and technology of biodegradable polymers. London: Chapman and Hall; 1994. pp. 48–96.

[29] Müller H-M, Seebach D. Poly(hydroxyfettsäureester), eine fünfte Klasse von physiologisch bedeutsamen organischen Biopolymeren? Angew Chem 1993;105:483–509.

[30] Williams S, Peoples O. Biodegradable plastics from plants. CHEMTECH 1996;26:38–44.

[31] Delafield FP, Doudoroff M, Palleroni NJ, Lusty CJ, Contopoulos R. Decomposition of poly-β-hydroxybutyrate by pseudomonads. J Bacteriol 1965;90:1455–66.

[32] Steinbüchel A. Perspectives for biotechnological production and utilization of biopolymers: metabolic engineering of polyhydroxyalkanoate biosynthesis pathways as a successful example. Macromol Biosci 2001;1:1–24.

[33] Lemoigne M. Produits de déshydration et de polymérisation de l'acide β-oxybutyrique. Bull Soc Chim Biol 1926;8:770–82.

[34] De Koning G, Lemstra P. Crystallization phenomena in bacterial poly [(R)-3-hydroxybutyrate]: 2. Embrittlement and rejuvenation. Polymer 1993;34:4089–94.

[35] Korte F, Glet W. Hochdruckreaktionen. II. Die polymerisation von γ-Butyrolacton und δ-Valerolactam bei hohen drücken. J Polym Sci Part B Polym Lett 1966;4:685–9.

[36] Bailey WJ, Ni Z, Wu S-R. Synthesis of poly-ε-caprolactone via a free radical mechanism. Free radical ring-opening polymerization of 2-methylene-1,3-dioxepane. J Polym Sci Polym Chem Ed 1982;20:3021–30.

[37] Fei B, Chen C, Wu H, Peng S, Wang X, Dong L, et al. Modified poly(3-hydroxybutyrate-co-3-hydroxyvalerate) using hydrogen bonding monomers. Polymer 2004;45:6275–84.

[38] Rudnik E. Compostable polymer materials; 2010. Access Online via Elsevier.

[39] Pilla S. Handbook of bioplastics and biocomposites engineering applications. Wiley. com; 2011.

[40] Saito Y, Doi Y. Microbial synthesis and properties of poly (3-hydroxybutyrate-co-4-hydroxybutyrate) in *Comamonas acidovorans*. Int J Biol Macromol 1994;16:99–104.

[41] Koosha F, Muller R, Davis S. Polyhydroxybutyrate as a drug carrier. Crit Rev Ther Drug Carrier Syst 1989;6:117–30.

[42] Pouton CW, Akhtar S. Biosynthetic polyhydroxyalkanoates and their potential in drug delivery. Adv Drug Deliv Rev 1996;18:133–62.

[43] Shimamura E, Scandola M, Doi Y. Microbial synthesis and characterization of poly (3-hydroxybutyrate-co-3-hydroxypropionate). Macromolecules 1994;27:4429–35.

[44] Doi Y, Kitamura S, Abe H. Microbial synthesis and characterization of Poly(3-hydroxybutyrate-co-3-hydroxyhexanoate). Macromolecules 1995;28:4822–8.

[45] Huisman GW, de Leeuw O, Eggink G, Witholt B. Synthesis of poly-3-hydroxyalkanoates is a common feature of fluorescent pseudomonads. Appl Environ Microbiol 1989;55:1949–54.

[46] Caballero KP, Karel SF, Register RA. Biosynthesis and characterization of hydroxybutyrate-hydroxycaproate copolymers. Int J Biol Macromol 1995;17:86–92.

[47] Rai R, Yunos DM, Boccaccini AR, Knowles JC, Barker IA, Howdle SM, et al. Poly-3-hydroxyoctanoate P(3HO), a medium chain length polyhydroxyalkanoate homopolymer from Pseudomonas mendocina. Biomacromolecules 2011;12:2126–36.

[48] Matsumura S. Enzyme-catalyzed synthesis and chemical recycling of polyesters. Macromol Biosci 2002;2:105–26.

[49] Barakat I, Dubois P, Jerome R, Teyssie P. Living polymerization and selective end functionalization of iε-caprolactone using zinc alkoxides as initiators. Macromolecules 1991;24:6542–5.

[50] Wang Y, Kunioka M. Ring-opening polymerization of cyclic monomers with aluminum triflate. Macromol Symp 2005;224:193–206.

[51] Stjerndahl A, Wistrand AF, Albertsson A-C. Industrial utilization of tin-initiated resorbable polymers: synthesis on a large scale with a low amount of initiator residue. Biomacromolecules 2007;8:937–40.

[52] Jérôme C, Lecomte P. Recent advances in the synthesis of aliphatic polyesters by ring-opening polymerization. Adv Drug Deliv Rev 2008;60:1056–76.

[53] Storey RF, Sherman JW. Kinetics and mechanism of the stannous octoate-catalyzed bulk polymerization of ε-caprolactone. Macromolecules 2002;35:1504–12.

[54] Brode G, Koleske J. Lactone polymerization and polymer properties. J Macromol Sci Chem 1972;6:1109–44.

[55] Takiyama E, Fujimaki T. "BIONOLLE", biodegradable plastic through chemical synthesis. In: Doi Y, Fukuda K, editors. Studies in polymer science. Amsterdam: Elsevier; 1994. pp. 150–74.

[56] Maeda Y, Nakayama A, Iyoda J, Hayashi K, Yamamoto N. Synthesis and biodegradation of the copolymers of succinic anhydride with various oxiranes. Jpn J Polym Sci Technol 1993;50:723.

[57] Lu J, Qiu Z, Yang W. Fully biodegradable blends of poly (L-lactide) and poly (ethylene succinate): miscibility, crystallization, and mechanical properties. Polymer 2007;48:4196–204.

[58] Tokiwa Y, Calabia BP, Ugwu CU, Aiba S. Biodegradability of plastics. Int J Mol Sci 2009;10:3722–42.

[59] Guzman de D. SDK starts Bio-PBS sampling. Blog "ICIS Green Chemicals," http://www.icis.com/blogs/green-chemicals/2012/07/sdk-starts-bio-pbs-sampling.html; [12.07.2012].

[60] Ishioka D, Kitakuni E, Ichikawa Y. Biopolymers, polyesters III. Applications and commercial products. Aliphatic polyesters: 'Bionolle'. Weinheim: Wiley-VCH Verlag Gmbh; 2002. p. 275.

[61] Tokiwa Y, Suzuki T, Takeda K. Hydrolysis of polyesters by *Rhizopus arrhizus* lipase. Agric Biol Chem 1986;50:1323–5.

[62] Carothers WH, Arvin J, Dorough G. Studies on polymerization and ring formation. V. Glycol esters of oxalic acid. J Am Chem Soc 1930;52:3292–300.

[63] Jiang L, Liu B, Zhang J. Properties of poly (lactic acid)/poly (butylene adipate-co-terephthalate)/nanoparticle ternary composites. Ind Eng Chem Res 2009;48:7594–602.

[64] Coltelli M-B, Maggiore ID, Bertoldo M, Signori F, Bronco S, Ciardelli F. Poly(lactic acid) properties as a consequence of poly(butylene adipate-co-terephthalate) blending and acetyl tributyl citrate plasticization. J Appl Polym Sci 2008;110:1250–62.

[65] The Coca-Cola Company Press Releases. Press releases: the Coca-Cola company announces partnerships to develop commercial solutions for plastic bottles made entirely from plants. Atlanta December 15, 2011.

[66] Toray Industries Inc. Corporate communications section, Press releases. Toray succeeds in production of the World's first fully renewable, biobased polyethylene terephthalate (PET) fiber, http://www.toray.com/news/fiber/nr111115.html; [15.11.2011].

[67] Eerhart A, Faaij A, Patel M. Replacing fossil based PET with biobased PEF; process analysis, energy and GHG balance. Energy Environ Sci 2012;5:6407–22.

[68] Houck M, Huff R, Lowe P, Menold R. Poly (trimethylene terephthalate): A "New" type of polyester fibre. Forensic Science Communications; 2001: 3.

[69] Wu T, Li Y, Wu Q, Song L, Wu G. Thermal analysis of the melting process of poly (trimethylene terephthalate) using FTIR microspectroscopy. Eur Polym J 2005;41:2216–23.

[70] Schroeder H, Cella R. Polyesters, elastomeric. In: 2nd ed. Encyclopedia of polymer science and engineering, ;12. Wiley-Interscience; 1988. pp. 75–117.

[71] Quirk R, Alsamarraie M. Polyester thermoplastic elastomers. In: Handbook of elastomers: new developments and technology. Marcel Dekker, Inc.; 1988. pp. 341–73.

[72] Tijsma E, van Der Does L, Bantjes A, Vulić I. Mechanical properties and chemical stability of pivalolactone-based poly (ether ester) s. Polymer 1994;35:5483–90.

[73] Inoue S, Koinuma H, Tsuruta T. Copolymerization of carbon dioxide and epoxide with organometallic compounds. Die Makromol Chem 1969;130:210–20.

[74] Inoue S, Koinuma H, Tsuruta T. Copolymerization of carbon dioxide and epoxide. J Polym Sci Part B Polym Lett 1969;7:287–92.

[75] Wang J, Zheng L, Li C, Zhu W, Zhang D, Xiao Y, et al. Fully biodegradable blends of poly(butylene succinate) and poly(butylene carbonate): miscibility, thermal properties, crystallization behavior and mechanical properties. Polym Test 2012;31:39–45.

[76] Li X, Meng Y, Wang S, Rajulu AV, Tjong S. Completely biodegradable composites of poly (propylene carbonate) and short, lignocellulose fiber *Hildegardia populifolia*. J Polym Sci Part B Polym Phys 2004;42:666–75.

[77] Li X, Meng Y, Zhu Q, Xu Y, Tjong S. Melt processable and biodegradable aliphatic polycarbonate derived from carbon dioxide and propylene oxide. J Appl Polym Sci 2003;89:3301–8.

[78] Zhu K, Hendren R, Jensen K, Pitt C. Synthesis, properties, and biodegradation of poly (1, 3-trimethylene carbonate). Macromolecules 1991;24:1736–40.

[79] Pranamuda H, Chollakup R, Tokiwa Y. Degradation of polycarbonate by a polyester-degrading strain, *Amycolatopsis* sp. strain HT-6. Appl Environ Microbiol 1999;65:4220–2.

[80] Thielen M. Basics of polyamides. Bioplas Mag 2010;5:51–3.

[81] Oppermann-Sanio F, Steinbüchel A. Occurrence, functions and biosynthesis of polyamides in microorganisms and biotechnological production. Naturwissenschaften 2002;89:11–22.

[82] Bajaj I, Singhal R. Poly (glutamic acid)–an emerging biopolymer of commercial interest. Bioresour Technol 2011;102:5551–61.

[83] Hermand R. Biopolymers-making materials natures' way. New York: John Wiley; 1993.

[84] Kunioka M, Choi HJ. Properties of biodegradable hydrogels prepared by γ irradiation of microbial poly(ε-lysine) aqueous solutions. J Appl Polym Sci 1995;58:801–6.

[85] Ajinomoto and Toray to conduct joint research on biobased nylon, http://www.ajinomoto.com/about/press/g2012_02_13.html; [09.10.2012].

[86] Rodriguez-Galan A, Franco L, Puiggali J. Degradable poly (ester amide)s for biomedical applications. Polymers 2010;3:65–99.

[87] Vasile C, Zaikov G. Environmentally degradable materials based on multicomponent polymeric systems. CRC Press; 2009.

[88] Wolf O, Crank M, Patel M, Marscheider-Weidemann F, Schleich J, Hüsing B, et al. Techno-economic feasibility of large-scale production of bio-based polymers in Europe. European Communities; 2005.

[89] Guan J, Stankus JJ, Wagner WR. Development of composite porous scaffolds based on collagen and biodegradable poly (ester urethane) urea. Cell Transplant 2006;15:S17.

[90] Desroches M, Escouvois M, Auvergne R, Caillol S, Boutevin B. From vegetable oils to polyurethanes: synthetic routes to polyols and main industrial products. Polym Rev 2012;52:38–79.

[91] Sutherland IW. Microbial polysaccharides from Gram-negative bacteria. Int Dairy J 2001;11:663–74.

[92] Suresh Kumar A, Mody K, Jha B. Bacterial exopolysaccharides–a perception. J Basic Microbiol 2007;47:103–17.

[93] Moreno J, Vargas MA, Olivares H, Rivas J, Guerrero MG. Exopolysaccharide production by the cyanobacterium *Anabaena* sp. ATCC 33047 in batch and continuous culture. J Biotechnol 1998;60:175–82.

[94] Adler E. Lignin chemistry—past, present and future. Wood Sci Technol 1977;11:169–218.

[95] Niaounakis M. Biopolymers reuse, recycling, and disposal, chapter 2: define the terms; section 2.3: biopolymers versus oxodegradable polymers. 1st ed. Plastics Design Library (PDL); 2013. Access Online via Elsevier; p. 432.

[96] Roberts AD. Natural rubber science and technology. Oxford: Oxford University Press; 1988.

[97] Heller J, Barr J, Ng SY, Abdellauoi KS, Gurny R. Poly (ortho esters): synthesis, characterization, properties and uses. Adv Drug Deliv Rev 2002;54:1015–39.

[98] Heller J. Poly (ortho esters). In: Langer R, Peppas N, editors. Biopolymers I. Springer Berlin/Heidelberg; 1993. pp. 41–92.

[99] Hill JW, Carothers WH. Studies of polymerization and ring formation. XIV. A linear superpolyanhydride and a cyclic dimeric anhydride from sebacic acid. J Am Chem Soc 1932;54:1569–79.

[100] Hill JW. Studies on polymerization and ring formation. VI. Adipic anhydride. J Am Chem Soc 1930;52:4110–4.

[101] Ibim SEM, Uhrich KE, Attawia M, Shastri VR, El-Amin SF, Bronson R, et al. Preliminary in vivo report on the osteocompatibility of poly (anhydride-*co*-imides) evaluated in a tibial model. J Biomed Mater Res 1998;43:374–9.

[102] Kumar N, Langer RS, Domb AJ. Polyanhydrides: an overview. Adv Drug Deliv Rev 2002;54:889–910.

[103] Domb AJ, Ron E, Langer R. Poly (anhydrides). 2. One-step polymerization using phosgene or diphosgene as coupling agents. Macromolecules 1988;21:1925–9.

[104] Allcock HR, Kugel RL. Synthesis of high polymeric alkoxy-and aryloxyphosphonitriles. J Am Chem Soc 1965;87:4216–7.

[105] Allcock HR. Polyphosphazenes: new polymers with inorganic backbone atoms. Science 1976;193:1214–9.

[106] Allcock HR. Poly (organophosphazenes)—unusual new high polymers. Angew Chem Int Ed Engl 1977;16:147–56.

[107] Allcock HR. Polyphosphazenes. J Inorg Organomet Polym 1992;2:197–211.

[108] Allcock HR. Inorganic—organic polymers. Adv Mater 1994;6:106–15.

[109] Laurencin CT, Koh HJ, Neenan TX, Allcock HR, Langer R. Controlled release using a new bioerodible polyphosphazene matrix system. J Biomed Mater Res 1987;21:1231–46.

[110] Laurencin CT, Norman ME, Elgendy HM, El-Amin SF, Allcock HR, Pucher SR, et al. Use of polyphosphazenes for skeletal tissue regeneration. J Biomed Mater Res 1993;27:963–73.

[111] Gunatillake PA, Adhikari R. Biodegradable synthetic polymers for tissue engineering. Eur Cells Mater J 2003;5:1–16.

[112] Teasdale I, Brüggemann O. Polyphosphazenes: multifunctional, biodegradable vehicles for drug and gene delivery. Polymers 2013;5:161–87.

[113] King D, Inderwildi OR, Wiliams A. The future of industrial biorefineries. Cologny/Geneva: World Economic Forum; 2010. p. 39, ill.

[114] Bourg V, Chivrac F, Berthé V. Bioplastic innovation, http://bioplastic-innovation.com/; [09.10.2012].

[115] Cereplast, http://www.cereplast.com/innovation; [09.10.2012].

[116] Dow. In: Winder D, http://www.dow.com/news/corporate/2009/20090629a.htm; [09.10.2012].

[117] Kram J. PetroSun commences algae-farm operations. Biodiesel Mag April 15, 2008. [in the May 2008 issue].

[118] Soley Institute, http://algaeinstitute.com; [09.10.2012].JP2005320426 A

Chapter 2

Properties

The properties of a polymer can be divided into three broad classes: (1) intrinsic properties, which refer to the polymer itself; (2) processing properties, which refer to the behavior of the polymer during forming; and (3) product properties, which refer to the properties of the polymer as an entity [1]. These three categories of properties are interrelated; for example, an increase in melting temperature (T_m), which is an intrinsic property, is accompanied by an increase in heat resistance, which is a product property.

2.1 INTRINSIC PROPERTIES

Intrinsic properties are properties that are inherent to the polymer itself and are dependent mainly on its chemical composition and/or structure[1]. Intrinsic properties can be classified further into molecular and bulk properties. Intrinsic molecular properties depend mainly on the chemical nature of the constituting monomer units, while intrinsic bulk properties depend mainly on the polymer structure.

2.1.1 Density

One of the intrinsic physical properties that can differ from polymer to polymer is the density. The density of polymers typically ranges from less than 1.0 g/cm^3 to over 1.7 g/cm^3. Table 2.1 lists the ranges of densities of several biodegradable polymers versus common nonbiodegradable polymers. These density ranges are indicative as they are dependent on several factors, such as thermal history, stretching, purity of the components, etc. For instance, poly(glycolic acid) (PGA) in an unoriented, crystallized form has a density of at least 1.50 g/cm^3; a PGA of low crystallinity has a density lower than 1.50 g/cm^3.

As can be seen for this table, most biodegradable polymers have higher densities than conventional polymers derived from fossil fuel resources. Poly(lactic acid) (PLA), which is the most widely used biodegradable polymer, has an average density of about 1.250 g/cm^3, which is much higher than polyolefins (0.880–0.970 g/cm^3). The higher density values of biodegradable polymers imply higher energy consumption (e.g., transportation costs), a factor that shall be taken into consideration when evaluating the environmental impact of biodegradable polymers.

2.1.2 Transition Temperatures and Crystallinity

Crystallinity is not a genuine intrinsic property of the material as it depends on several parameters including thermal history, orientation of chains, etc. However, for reasons of economy, crystallinity is placed under the heading of intrinsic properties. The crystallinity of a polymer affects several other properties such as melt viscosity, modulus, tensile strength, transparency, heat resistance, etc.

2.1.2.1 Poly(lactic acid)

Commonly used PLA has a $T_m = 155\,°C$ and a crystallinity of about 16%, and is characterized by slow crystallization rate, long shaping cycle, low melt viscosity, and low thermal stability. Commercially available PLA at present is mostly poly(L-lactic acid) (PLLA) containing less than 8% D-lactic acid. A PLLA with an D-lactic acid content more than 8% is amorphous, i.e., it has no T_m. The crystallinity of PLA generally increases with increasing optical purity. PLLA with an optical purity of 97% has a glass transition temperature (T_g) of 53–63 °C, a melting temperature of 173–178 °C, and a crystallinity of around 37%. The T_m of PLLA can be increased 40–50 °C, and its heat deflection temperature can be increased from approximately 60 °C to up to 190 °C by physically blending the polymer with poly(D-lactic acid) (PDLA). PDLA and PLLA form a highly regular stereocomplex with increased crystallinity. A stereocomplex[2] PLA (scPLA), which is obtained by mixing together equal amounts of PLLA and PDLA, has a higher melting point ($T_m > 200\,°C$) and crystallinity than those of PLLA and PDLA. The temperature stability is maximized when a 50/50 blend is used, but even at lower concentrations of 3–10% of PDLA, there is still a substantial improvement. In the latter case, PDLA acts as a nucleating agent, thereby increasing the crystallization rate.

---

[1] Actually, all intrinsic properties relate to a material with a distinct processing history; for more, see van Krevelen [1].

[2] Stereocomplex means a crystal structure that poly(L-lactic acid) (PLLA) and poly(D-lactic acid) (PDLA) form alternating helices. The stereocomplex is formed by interaction between PLLA and PDLA, which is stronger than interaction between L-lactic acid units or interaction between D-lactic acid units.

Biopolymers: Processing and Products. http://dx.doi.org/10.1016/B978-0-323-26698-7.00002-7

TABLE 2.1 Densities[1] of the Main Biodegradable Polymers versus Common Nonbiodegradable Polymers

Polymer	Density (g/cm^3)
P3HB	1.177–1.260
PHBHV	1.250
PLA	1.210–1.250
PLLA	1.250–1.290
PDLA	1.250–1.270
scPLA	1.210–1.342
PGA	1.500–1.690
PCL	1.060–1.130
PBS	1.260
PBSA	1.230
PBAT	1.210
VLDPE	0.880–0.915
LLDPE	0.915–0.925
HDPE	0.941–0.970
UHMWPE	0.930–0.935
MDPE	0.926–0.940
LDPE	0.910–0.0.940
PP	<1.0 (e.g., 0.905)
GPPS	1.000
HIPS	1.040–1.070
ABS	1.040–1.120
Nylon 6 or 66	1.130–1.140
PC/ABS	1.120–1.150
PET	>1.2
PBT	>1.3
PVC	>1.3
POM	>1.4

ABS, acrylonitrile-butadiene-styrene; GPPS, general purpose polystyrene; HDPE, high density polyethylene; HIPS, high impact polystyrene; LDPE, low density polyethylene; LLDPE, linear low density polyethylene; MDPE, medium density polyethylene; Nylon 6, polycaprolactam; Nylon 66, poly(hexamethylene adipamide); P3HB, poly(3-hydroxybutyrate); PBSA, poly(butylene succinate-*co*-adipate); PBAT, poly(butylene adipate-*co*-terephthalate); PBT, poly(butylene terephthalate); PC, polycarbonate; PDLA, poly(D-lactic acid); PE, polyethylene; PET, poly(ethylene terephthalate); PGA, poly(glycolic acid); PHBHV, poly(3-hydroxy butyrate-*co*-3-valerate); PLA, poly(lactic acid); PLLA, poly(L-lactic acid); POM, polyoxymethylene (polyacetal); PP, polypropylene; PVC, poly(vinyl chloride); scPLA, stereocomplex PLA; UHMWPE, ultra-high-molecular-weight polyethylene; VLDPE, very low density polyethylene.

[1] *Reported values are mostly based on international standards such as ASTM D792.*

2.1.2.2 *Poly(glycolic acid)*

PGA is highly crystalline (45–55%), with a T_m (220–225 °C) and a T_g of 35–40 °C.

2.1.2.3 *Polyhydroxyalkanoates*

A variety of polyhydroxyalkanoates (PHAs) have been produced, having a wide range of physical properties, depending on the hydroxyacid monomer composition used [2]. The range of physical properties include T_m between about 40 °C and 180 °C, T_g between about −55° and 5 °C, degree of crystallinity between 0% and 80%, and elongation at break between about 5% and 500%. The rate of crystallization can be controlled. As the molecular weight is reduced, the T_g remains relatively constant, however, the T_m is reduced.

PHAs composed of short-chain-length monomers (containing 3–5 carbon atoms) are semicrystalline, aliphatic polyesters. PHAs composed of medium-chain-length monomers (containing 6–14 carbon atoms) are elastomers and have low crystallinity.

Representative examples of short-chain PHAs are poly(3-hydroxybutyrate) (P3HB), poly(4-hydroxybutyrate) (P4HB), and poly(3-hydroxybutyrate-*co*-valerate) (PHBHV). P3HB is highly crystalline having a T_g of 4 °C and a T_m of 180 °C. PHBHV has somewhat lower crystallinity and lower T_m. In PHBHV no significant change is observed in crystallinity though its properties depend on the composition of 3-hydroxyvalerate (3HV), and there is no significant change in elasticity even if the composition of 3HV is increased. That is, it does not happen that elongation is well over 100%. This is because 3HB and 3HV have structural difference in only one methylene group in the side chain. P4HB has a T_g of −51 °C and a T_m of 60 °C [3].

Medium-chain-length PHAs have $T_g s$ between −25 °C and 65 °C and $T_m s$ in the range of 42–65 °C. Representative examples of medium-chain-length PHAs are poly(3-hydroxybutyrate-*co*-3-hydroxyhexanoate) (PHBHHx) and poly(3-hydroxybutyrate-*co*-3-hydroxyoctanoate) (PHB0) [4]. The crystallinity of PHBHHx decreases rapidly and significant change of properties is observed when the composition of 3HH is increased. This is because 3HB and 3HH have structural difference in two methylene groups in the side chain—cf. PHBHV. Comparison of properties of PHBHV and PHBHHx is shown in Tables 2.2 and 2.3.

2.1.2.4 *Poly(ε-caprolactone)*

Poly(ε-caprolactone) (PCL) is a semicrystalline thermoplastic aliphatic polyester having a relatively low melting temperature (60 °C) and T_g (−60 °C).

The transition temperatures (T_g, T_m) of the main biopolymers are summarized in Table 2.4.

2.1.3 Solubility

The solubility of a biopolymer is determined by its morphology (polarity, presence or absence of crystallinity, etc.) and composition. Generally, biopolymers with high crystallinity are more difficult to dissolve than those with low crystallinity. Furthermore, the thermal history of the biopolymer may also affect solubility.

Amorphous PLA is soluble in most organic solvents such as chlorinated hydrocarbons, benzene, tetrahydrofuran (THF), and dioxane. Crystalline PLA is soluble in chlorinated hydrocarbons and benzene at elevated temperatures. The scPLA is hardly soluble in most kinds of solvents. Furthermore, PLA is nearly insoluble in supercritical carbon dioxide ($scCO_2$); in particular, PLA is not completely soluble in pure supercritical carbon dioxide, even at a high pressure of 80 MPa or above and a high temperature of 190 °C or above [6].

TABLE 2.2 Properties of Poly(3-hydroxybutyrate-*co*-3-valerate) (PHBHV) (2002, EP1266984 A1, KANEKA CORP)

Properties of PHBHV (Biopol®)			
	Composition of 3HV[1] (% by mole)		
Characteristics	**0**	**10**	**20**
Crystallization degree (%)	60 ± 5	55 ± 5	52 ± 5
Melting temperature (°C)	180	140	130
Tensile strength (MPa)	40	25	20
Elongation at break (%)	8	20	50

[1] *3HV, 3-hydroxyvalerate.*

PGA, because of its high degree of crystallization (45–55%), is not soluble in most organic solvents; the exceptions are highly fluorinated organics such as hexafluoroisopropanol.

The solubility of PHA homopolymers is in general very low. These aliphatic polyesters are totally insoluble in water and in most organic solvents, which appear to be poor solvents, with the exception of some halogenated solvents such as chloroform (trichlormethane), methylene chloride (dichloromethane), and ethylene dichloride (1,2-dichloroethane). Cyclic carbonic acid esters such as ethylene carbonate or propylene carbonate were also proposed as solvents for P3HB (1997, **BE850332** A1, AGROFERM A G). However, these solvents are very corrosive in the hot state in which they have to be used and attack taps and joints of apparatuses. Halogenated hydrocarbons are on the whole toxic and represent a hazard for any who have to work with them; they also pollute the environment.

The solubility of PHA copolymers depends on the type and relative amounts of the constituent monomers, allowing the choice of a wide range of solvents. Copolymers of 3-hydroxybutyric acid and other hydroxyacid comonomers have significantly different solubility characteristics from those of P3HB; for example, acetone is not a good solvent for P3HB but is very useful for dissolving copolymers of 3-hydroxybutyric acid and 3-hydroxyacids containing 6–12 carbon atoms [7,8].

A list of solvents for a range of biodegradable polyesters is shown in Table 2.5.

2.1.4 Mechanical Properties

2.1.4.1 *Poly(lactic acid)*

The mechanical properties of PLA depend on its optical purity and molecular weight. A higher molecular weight raises tensile strength and elastic modulus, and lowers the elongation at break. Commonly used PLA (D-lactic acid

TABLE 2.3 Properties of (Poly-3-hydroxybutyrate-*co*-3-hydroxyhexanoate) (PHBHHx) (2002, EP1266984 A1, KANEKA CORP)

Properties of PHBHHx					
	Composition of 3HH[1] (% by mole)				
Characteristics	**0**	**10**	**14**	**17**	**31**
Crystallization degree (%)	60 ± 5	44 ± 5	40 ± 5	38 ± 5	24 ± 5
Melting temperature (°C)	180	129	123	119	73
Tensile strength (MPa)	43	21	23	20	6
Elongation at break (%)	5	400	760	<800	<800

[1] *3HH, 3-hydroxyhexanoate.*

TABLE 2.4 Transition Temperatures (T_g, T_m) of the Main Biopolymers

Biopolymer	T_g (°C)	T_m (°C)	Commercial Products	Manufacturer
PLA			Ingeo™:	NatureWorks
	55.0–60.0	–	10361D	
	55.0–60.0	–	8052D	
	55.0–60.0	145–160	7001D	
	55.0–60.0	155–170	7032D	
	55.0–60.0	145–160	6350D	
	55.0–60.0	125–135	6302D	
	55.0–60.0	165–170	6251D	
	55.0–60.0	165–170	6204D	
	55.0–60.0	165–170	6201D	
	55.0–60.0	165–170	6202D	
	55.0–60.0	155–170	032D	
	55.0–60.0	145–160	4043D	
	55.0–60.0	145–160	4044D	
	55.0–60.0	NA	4060D	
	55.0–60.0	155–170	3001D	
	55.0–60.0	145–160	3052D	
	55.0–60.0	180	3100HP	
	55.0–60.0	155–170	3251D	
	55.0–60.0	180	3260HP	
	55.0–60.0	145–160	2003D	
	55.0–60.0	180	2500HP	
			Terramac®:	Unitika Ltd.
	57	170	TE-8300	
	57	170	TE-8210	
	57	170	TE-7300	
	57	170	TE-7307	
	57	170	TE-7000	
	57	170	TE-1070	
	57	170	TE-1030	
	57	170	TE-2000	
	57	170	TP-4000	
	57	170	TP-4-3-	
			HV-6250H	
PLLA	55–63 (T_c 100–120)	173–178		
PDLA	55	Amorphous		
scPLA	60	220–230		
sbPLA	55	185–195		
PGA	35–40	220–225	Kuredux®	Kureha Corp
P3HB			Biocycle®:	PHB Industrial Brasil S.A.
	135[1]	175	1000	
	135[1]	168	189C-1	
	137	168	189D-1	
	135	168	18BC-1	
P4HB	−51	60		[3,5]
PHBHV	0	170	Biopol®	Metabolix
PCL	−60	60	Tone®	Union Carbide
PBAT	−33	105–115	Ecoflex® S BX 7000	BASF AG
	−33	112	Eastar® bio 14766	Eastman Chemical Company

TABLE 2.4 Transition Temperatures (T_g, T_m) of the Main Biopolymers—cont'd

Biopolymer	T_g (°C)	T_m (°C)	Commercial Products	Manufacturer
PBS	−30/−32	114–116	Bionolle 1001	Showa High Polymer Ltd
PBSA	−35/−45	93–96	Bionolle® 3001	Showa High Polymer Ltd
PES	−4	102	Bionolle® 6000	Showa High Polymer Ltd
Poly(ester amide)	Estimated ≥ 10 Estimated ≥ 10	125 175	BAK® 1095 BAK®2195	Bayer AG
PEC	15–25/10–28			PAC Polymers Inc.
PBC	−38	Amorphous		
PPC	35–44	120–140		Novomer Inc
Starch modified	70–85			

P3HB, poly(3-hydroxybutyrate); P4HB, poly(4-hydroxybutyrate); PBAT, poly(butylene adipate); PBS, poly(butylene succinate); PBSA, poly(butylene succinate-*co*-adipate); PBST, poly(butylene succinate-*co*-terephthalate); PDLLA, atactic poly(D, L-lactic acid); PES, poly(ethylene succinate); PHBHV, poly (3-hydroxybutyrate-*co*-3-hydroxyvalerate); PLA, poly(lactic acid); PLLA, poly(L-lactic acid); PPC, poly(propylene carbonate); poly(ester amide), copolymer prepared from adipic acid, 1,4-butanediol, and 6-aminocaproic acid; sbPLA, stereoblock PLA; scPLA, stereocomplex PLA.

[1] *Vicat softening temperature (ASTM D 1525).*

content of about 5%) is a brittle material having little elongation at break (about 6% up to 11%), Young's modulus of 900–1300 MPa and tensile strength of 61–73 MPa [9].

scPLA has better mechanical properties than those of PLLA and PDLA.

PLA has similar mechanical properties to PET, but has a significantly lower maximum continuous use temperature.

2.1.4.2 Polyhydroxyalkanoates

PHA polymers composed of short-chain-length monomers (containing 3–5 carbon atoms), such as P3HB and PHBHV, have little elongation, are brittle, and tear easily under mechanical constraint. PHBHV is less brittle and tougher than P3HB. With increasing monomer chain length, the material gets more flexible. Poly(3-hydroxyoctanoate) (PHO), for example, is an elastomer. PHAs with longer side chains have characteristics similar to waxes.

The elongation at break of P3HB and PHBHV is in the range of 4–42%, whereas the same property for P4HB is about 1000% [10]. Similarly, the values of Young's modulus and tensile strength for P3HB and PHBHV are 3.5–0.5 GPa and 40–16 MPa, respectively (for increasing HV content to 25 mol%), compared to 149 MPa and 104 MPa, respectively for P4HB [10].

The physical and mechanical properties—with the exception of elongation at break—of P3HB are remarkably similar to those of polypropylene (PP), even though the two polymers have quite different chemical structures (see Table 2.6).

P4HB is ductile and does not exhibit brittle fracture characteristics, while its tensile strength is comparable to that of polyethylene. The mechanical properties of P4HB also compare well to poly(trimethylene carbonate). Table 2.7 compares the mechanical properties of P4HB with those of PGA and PCL.

PHBHHx has similar mechanical properties to those of linear low density polyethylene (LLDPE) [4]. Comparison of properties of PHBHV and PHBHHx is shown in Tables 2.2 and 2.3.

2.1.5 Gas Barrier Properties

Important physical properties of films are permeability to oxygen and permeability to moisture vapor. Conventional films fall into three main classes in terms of permeability. First, films such as poly(vinylidene chloride) have low permeability to oxygen and to moisture vapor. Second, films such as polyethylene and PP have low permeability to moisture vapor but high permeability to oxygen. Third, films such as nylon and plasticized PVC and polyacrylonitrile have low permeability to oxygen but rather high permeability to water vapor, and, in particular, the oxygen permeability increases as the humidity increases.

A biodegradable polymer expected to replace the conventional gas barrier polymers, such as ethylene-vinyl alcohol copolymer (EVOH) and polyamide, is PGA, which has a gas barrier property that is at least several times compared with nylon MXD6 and less liable to cause a lowering in barrier property at a high humidity than EVOH. PGA is excellent in gas barrier properties, such as oxygen gas barrier property, carbon dioxide gas

TABLE 2.5 List of Solvents Suitable for a Range of Aliphatic Polyesters

Biopolymer	Solvent	Patent
PLA	Ester-based solvents: methyl acetate, ethyl acetate, propyl acetate, butyl acetate; ketone solvents: methyl ethyl ketone (MEK), methyl isobutyl ketone (MIBK), cyclohexanone; aromatic solvents: toluene, xylene	**JP2009185108** A (2009, TOYO BOSEKI)
PLLA/PDLA (1/1)	Methylene chloride (dichloromethane), chloroform (trichlormethane), ethylidene dichloride (1,1-dichloroethane), dioxane, 1,1,1,2-tetrachloroethane, pentane, petroleum ether, hexane, heptane, diethyl ether, triethylamine, t-butyl methyl ether, cyclohexane, acetone, methyl isobutyl ketone, MEK, diethyl ketone, *o*-xylene, *m*-xylene, *p*-xylene, toluene, dimethoxyethane, benzene, 1-chlorobutane, tetrahydrofuran (THF), hexamethylphosphoramide (HMPA), 2-ethoxyethyl ether, N,N-dimethylacetamide, dimethylformamide (DMF), pyridine, benzonitrile, 1-methyl-2-pyrrolidinone, acetic anhydride, dimethyl sulfoxide (DMSO), chlorobenzene, carbon disulfide, 1,2-dichlorobenzene, nitromethane, 1,1,2-trichlorotrifluoroethane, carbon tetrachloride	**US2013030129** A1 (2013, HYUNDAI MOTOR CO LTD; UNIV KOREA IND UNIV COOP FOUND)
PGA	Hexafluoroacetone sequihydrate, hexafluoroisopropyl alcohol	**US3737440** A (1973); **US3902497** A (1975, AMERICAN CYANAMID CO)
P3HB	Partially halogenated hydrocarbons: ethylene dichloride (1,2-dichloroethane), chloroform, methylene chloride (dichloromethane)	**EP0015123** A1 (1980, ICI PLC)
P3HB	Chloroform	**US3275610** A (1966, MOBIL OIL CORP)
P3HB	Halogenated hydrocarbons: methylene chloride, chloroform, trichloroethylene	**EP0479043** A1 (1992, DANUBIA PETROCHEM POLYMERE)
P3HB	Halogenated hydrocarbons: 1,2-dichloroethane, 1,1,2-trichloroethane, 1,1,2,2-tetrachloroethane, 1,2,3-trichloropropane	**FR2446859** A1 (1980, SOLVAY)
P3HB	1,2-dichloroethane/methanol (1/5–1/30)	**DD239609** A1 (1986, AKAD WISSENSCHAFTEN DDR)
P3HB	Pyridine	**US3036959** A (1962, GRACE W R & CO)
P3HB	Methylene chloride/ethanol (1/1–20/1)	**US3044942** A (1962, GRACE W R & CO)
P3HB	Cyclic carbonic acid esters: ethylene carbonate or propylene carbonate	**BE850332** A1 (1977, AGROFERM A G)
P3HB	Methyl lactate, ethyl lactate	**WO9708931** A2 (1997, BUNA SOW LEUNA OLEFINVERB GMBH)
P3HB	Acetic anhydride	**DD239609** A1 (1986, AKAD WISSENSCHAFTEN DDR)
PHBHV, P3HB4HB, P3HB-OH	Esters: butyl acetate, isobutyl acetate, ethyl lactate, isoamyl acetate, benzyl acetate, 2-methoxy ethyl acetate, tetrahydrofurfuryl acetate, methyl propionate, propyl propionate, butyl propionate, pentyl propionate, butyl butyrate, isobutyl isobutyrate, ethyl butyrate, methyl valerate, ethyl valerate, benzyl benzoate, methyl benzoate, dimethyl succinate, dimethyl glutarate, dimethyl adipate, ethylene glycol diacetate; alcohols: isobutyl alcohol, 1-butanol, 2-methyl-1-butanol, 3-methyl-1 butanol, 1-pentanol, 3-pentanol, amyl alcohol, allyl alcohol, 1-hexanol, heptanol, octanol, cyclohexanol, 2-ethylhexanol, tetrahydrofurfuryl alcohol, furfuryl alcohol, benzyl alcohol; diols: 1,2-propanediol, ethylene glycol diethyl ether; ketones: acetophenone, furaldehyde, methyl isobutyl ketone, MEK, g-butyrolactone, methyl n-amyl ketone, 5-methyl-2-hexanone; acids: acetic acid, acrylic acid, acetic anhydride; amides: dimethyl acetamide, DMF; amines: 1,2-diaminopropane; cyclic carbonic acid esters: propylene carbonate aromatics: α-methylstyrene, toluene, ethyl benzene, 1,2,3-trimethylbenzene, 1,2,4-trimethylbenzene, 1,3-dimethoxybenzene, isopropylbenzene (cumene), benzaldehyde, 1,3-dioxane, 1,4-dioxane, 1-nitropropane, toluene-2,4-diisocyanate ethylene glycol diacetate, DMSO	**WO9846782** A1 (1998, MONSANTO CO)

TABLE 2.5 List of Solvents Suitable for a Range of Aliphatic Polyesters—cont'd

Biopolymer	Solvent	Patent
PCL	Chloroform, 4-dioxane, DMF, N-methyl-2-pyrrolidone (NMP), DMSO	**JP2004161931** A (2004, KANAZAWA INST OF TECHNOLOGY); **US2005253292** A1 (005, UNIV CHUNG YAN CHRISTIAN)
PBAT	THF, methylene chloride, chloroform (hexafluoroisopropanoic acid, HFIP)	**WO2007074042** A2 (2007, BASF SE)
PBSA	Methylene chloride, chloroform	**JP2004161931** A (2004, KANAZAWA INST OF TECHNOLOGY)

P3HB, poly(3-hydroxybutyrate); P3HB-OH, hydroxyl-terminated P3HB; P3HB4HB, poly(3-hydroxybutyrate-*co*-4-hydroxybutyrate); PHBHV, poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate); PBAT, poly(butylene adipate-*co*-terephthalate); PBSA, poly(butylene succinate-*co*-adipate); PCL, poly(ε-caprolactone); PLA, poly(lactic acid); PLLA, poly(L-lactic acid); PDLA, poly(D-lactic acid).

barrier property, and water vapor barrier property. More specifically, a PGA film of thickness of 25 µm has an oxygen permeability and carbon dioxide permeability (as measured at a temperature of 23 °C and 80% relative humidity, measured in accordance with JIS K 7126) of generally less than 100 cc/m^2.day.atm and less than 300 cc/m^{2}day.atm, respectively; and a water vapor permeability (as measured at a temperature of 40 °C and 90% relative humidity, measured in accordance with JIS Z 0208) of generally less than 100 g/m^2.day (1997, **EP0805175** A1; 1997, **EP0805176** A1 1997, KUREHA CHEMICAL IND CO LTD).

The high gas barrier property of PGA is attributable to tight molecular alignment owing to a high density of about 1.5 g/cm^3. The density of PGA can be increased further by tightening of molecular alignment due to stretching and crystallization, which effectively function to increase the gas barrier property by themselves (2005, **WO2005072944** A1, KUREHA CORP).

PLA-molded articles have very poor barrier properties against a gas such as oxygen or carbon dioxide and steam. Specifically, the oxygen permeability of a PLA film is about five times lower than those of aromatic polyester films that have been conventionally used, at 23 °C under a relative humidity of 80%, and a steam-barrier property thereof is about 10 times lower at 40 °C under a relative humidity of 90%. Therefore, PLA is not suitable for making films for wrapping food or containers for cosmetics and bottles for beverages, and the number of possible applications is limited (2010, **WO2010038537** A1, KUREHA CORP).

PLA has a relatively high gas permeability. An oriented PLLA film of thickness 100 µm has an oxygen permeability of 200 cm^3/m^2 × bar and a water vapor permeability at 23 °C and 0–85% relative humidity of about 30 g/m^2 × day (1994, **WO9424198** A1, BASF AG). The barrier properties of the PLA-molded article can be improved by laminating it with a resin having a good barrier property such as an EVOH or polyamide. Such barrier materials, however, have poor biodegradability and increase the burden on the environment. Therefore, a multilayer film in which PGA, which is biodegradable, is used as a barrier material has hitherto been proposed (2006, **JP2006130847** A, TOHCELLO CO LTD). The multilayer film is formed by co-extruding the PGA and the PLA to obtain a multilayer sheet, and biaxially stretching the sheet under predetermined conditions (2010, **WO2010038537** A1, KUREHA CORP).

TABLE 2.6 Comparison of Properties of Poly (3-hydroxybutyrate) and Polypropylene (2007, WO2007095708 A1; WO2007095709 A1; WO2007095710 A1; WO2007095711; WO2007095712 A1, PHB IND SA)

Properties	P3HB	PP
Degree of crystallinity (%)	80	70
Average molar mass (g/mol)	4×10^5	2×10^5
Melting temperature (°C)	175	176
Glass transition temperature (°C)	−5	−10
Density (g/cm^3)	1.2	0.905
Modulus of flexibility (GPa)	1.4–3.5	1.7
Tensile strength (MPa)	15–40	38
Elongation at break (%)	4–10	400
UV resistance	Good	Poor
Solvent resistance	Poor	Good

P3HB, poly(3-hydroxybutyrate); PP, polypropylene.

TABLE 2.7 Comparison of Mechanical Properties of Poly(4-hydroxybutyrate) (P4HB), Poly(glycolic acid) (PGA) and Poly(ε-caprolactone) (PCL)

Property	Compression Molded P4HB Film	Oriented P4HB Fiber	PGA	PCL
Tensile strength (MPa)	50	580–800	60–100	20–40
Tensile modulus (MPA)	70	670	6500	200–400
Elongation at break (%)	~1000	~25–90	2–20	80–1000
Hardness shore D	53	ND	NR	NR

Complied by Williams S. [5].

Shogren [11] measured the water vapor transmission rates of several biodegradable polyesters at 25 °C and found to range from 13 to 2900 g/m^2/day and increase in the order:

$$\text{PHBHV} < \text{PLA (cryst.)} < \text{PLA (amorph.)} < \text{PLC} < \text{P3HB} < \text{PEAM} < \text{CAP} < \text{CA},$$

wherein:

CA: cellulose acetate (Eastman Chemical)
CAP: cellulose acetate propionate (Eastman Chemical)
P3HB: poly(3-hydroxybutyrate) (Showa Highpolymer C.)
PCL: poly(ε-caprolactone)—Tone P767P (Union Carbide)
PEAM: poly(ester amide)—BAK 2095 (Bayer, Inc.)
PHBHV: poly(3-hydroxybutyrate-*co*-3-valerate) (Zeneca Bioproducts)

2.1.6 Transparency

Amorphous PLA articles have excellent transparency. These processed items do not contain large crystals of size equal to or larger than the wavelength of light beams that can cause light scattering. Transparency is the most characteristic feature of PLA, not shown in any other biodegradable polymer. However, these transparent articles are usually inferior in heat resistance due to the amorphous state. For example, amorphous PLA containers are excellent in transparency but poor in heat resistance, and thus cannot be used for hot water or a microwave oven. As a result, the uses of these transparent items have been restricted.

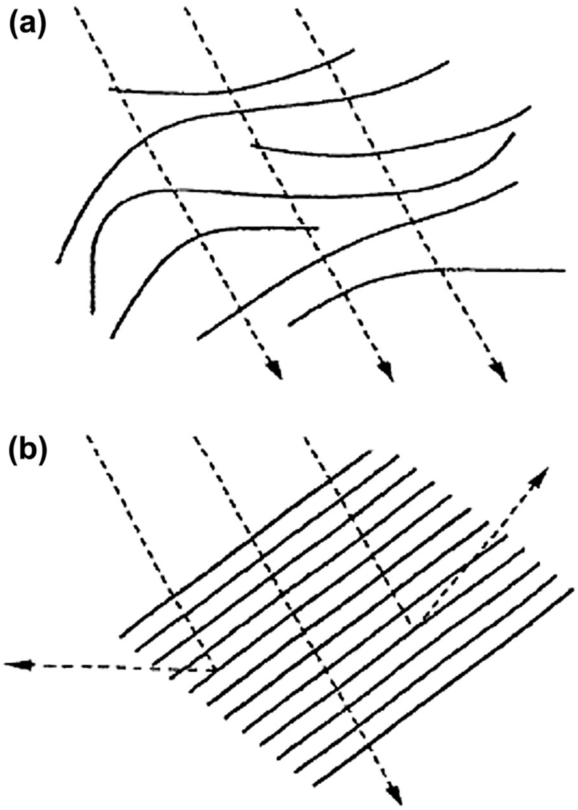


FIGURE 2.1 Schematic view illustrating: (a) a noncrystalline state of poly(lactic acid) (PLA) chains, which gives a transparent state; (b) a crystalline state of PLA chains, which gives an opaque state due to whitening (2005, **US2005242466** A, SUMITOMO ELEC FINE POLYMER INC).

The reason why PLA can take on transparency is that light is transmitted without inhibition by crystals as shown in Figure 2.1(a) in a noncrystalline state where the chains PLA are randomly present without crystallization. When PLA material is heated to a temperature equal to or higher than its T_g, noncrystalline chains of PLA begin to move and noncrystalline parts gradually change into crystals. As shown in (b), when a degree of crystallinity becomes high, light is reflected and the transparency is lost (2005, **US2005242466** A, SUMITOMO ELEC FINE POLYMER INC).

Since PLA has a T_g of about 60 °C that is a relatively low temperature, when a surrounding temperature of a molded article formed from PLA exceeds 60 °C, transparency thereof cannot be maintained and the article becomes opaque. Air temperature or water temperature in nature does not easily reach 60 °C, but it is a temperature reachable at the inside or window materials of an automobile whose windows are closed in the warmest summer weather, for example. When a transparent material gradually loses transparency by elevation of temperature due to light absorption, use conditions and applications thereof may be limited.

Other crystalline aliphatic polyesters such as poly(butylene succinate) (PBS) usually crystallize and become opaque immediately after forming due to presence of crystals that have a size equal to or larger than the wavelength of light.

The transparency and heat resistance of an aliphatic polyester molded product can be improved simultaneously by reducing the size of crystallites as small as possible and raising the crystallinity as little as possible. The growth of the crystals can be controlled by addition of a transparent nucleating agent such as aliphatic carboxylic acid amide, aliphatic carboxylic acid salt, aliphatic alcohol, or aliphatic carboxylic acid ester having a T_m of 40–300 °C. The transparent nucleating agent is said, concerning the crystal, to have inhibiting action of excess growth in “size,” increasing action in “numbers” and accelerating action in “crystallization” velocity (1997, **EP0780428** A1; **JPH09278991** A MITSUI CHEMICALS INC). When the transparent nucleating agent, such as aliphatic amide, is added to PLA, an increase in crystallization rate of PLA can be observed compared with the case of an additive-free PLA. However, the effect of the addition is not sufficient; therefore, in order to obtain a molded article having a sufficient crystallinity, a heat treatment after molding is required. Further, because the crystallinity of PLA is low, the crystal solidification in a mold at the time of, for example, injection molding, tends to be insufficient. As a result, there are some defects such that the molded article is deformed at the time of mold releasing (2007, **WO2007094477** A1, NEC CORP; UNITIKA LTD).

The mechanism for developing transparency by the transparent nucleating agent in the crystalline polymer–formed items can be explained as follows:

When a polymer molding is crystallized without addition of a transparent nucleating agent, a small number of crystal nuclei provide a basis of crystal growth. Thus, a relatively small number of crystals are generated and each crystal grows to a large size. As a result, the crystals having a size equal to or larger than the wavelength of visible light are formed, scatter visible light, and inhibit straight propagation thereof. Consequently, formed items of crystalline polymer become opaque.

When a polymer-formed item is crystallized in the presence of the transparent nucleating agent, the transparent nucleating agent becomes a basis of crystal growth and provides an overwhelmingly large number of crystals as compared with the case in the absence of the transparent nucleating agent. As a result, the crystals thus formed have a considerably small size as compared with the wavelength of visible light, visible light propagates straight without scattering, and the formed items of crystalline polymer comprising the transparent nucleating agent become transparent (1997, **EP0780428** A1, MITSUI CHEMICALS INC).

2.1.7 Electromagnetic Properties

The study of the electrical and dielectric properties of biopolymers, in particular, the absorption of electromagnetic waves of different frequency bands, is of great scientific and practical interest. Biopolymers are used in a variety of biological and medical applications including diagnostic applications such as MRI and CT (e.g., biopolymer-based CT and MRI bioimaging probes). Their composites find potential applications as dielectric materials (e.g., for capacitors) or conductive materials. The dielectric properties of PLA, PCL, starch esters, and their (nano)composites have been studied by a number of researchers in the frequency ranges of 10^{-1}–10^{6} Hz [12–15], 0.5–10 GHz [16], and 85–118 GHz [17,18].

2.2 PROCESSING PROPERTIES

The processing properties include properties such as viscosity, melt flow index, melt strength, etc. Although these properties give indications about the behavior of the material during forming (e.g., in extrusion), a practitioner needs more detailed information such as the processing conditions of each particular material at the various stages of production. The processing properties of a polymer determine the ease and economy of manufacturing a plastic article and determine to a great extent its properties.

Usually, biopolymers such as PLAs and PHAs are difficult to process via extrusion because of their sensitivity to moisture and high temperatures.

2.2.1 Poly(lactic acid)

PLA is a crystalline polymer that has low melt viscosity required for the shaping of articles, inadequate temperature stability, slow crystallization rate, and long molding cycle.

PLA has a T_m that can range from 165 °C to 185 °C, and is processed at temperatures of 185–190 °C. At these temperatures unzipping and chain scission reactions leading to loss of molecular weight, as well as thermal degradation, are known to occur. A reduction in molecular weight during processing is a problem for PLA because of its effect on melt viscosity. Furthermore, processing PLA at high temperatures and for a prolonged period tends to favor the formation of lactide in the molten polymer. The formation of lactide can reduce melt viscosity and melt elasticity. In addition, the lactide may flash out of the polymer during processing, causing fumes and fouling equipment. Consequently, PLA has a very narrow processing window. A preferred method for increasing melt elasticity, while maintaining low viscosity, is by broadening the molecular weight distribution of the material. Bridging and branching are ways for increasing chain entanglement, and thereby broaden the molecular weight distribution.

A widely used method for improving PLA processability is based on T_m depression by the random incorporation of small amounts of lactide enantiomers of opposite configuration into the polymer (i.e., adding a small amount of D-lactide to the L-lactide to obtain PDLA). However, the T_m depression is accompanied by a significant decrease in crystallinity and crystallization rate, and deterioration of the heat resistance [18].

The melt elasticity can be improved by broadening the molecular weight distribution of PLA. Bridging and branching (i.e., by peroxide modification) are preferred methods, which increase chain entanglement and broaden the molecular weight distribution (1999, **WO9950345** A1, CARGILL INC).

PLA has a low crystallization rate, and its crystallization thereof does not proceed sufficiently when molded in a short period of time, and the molded product has inferior properties such as heat resistance and elastic modulus. In particular, when PLA is processed by injection molding in which orientation is not carried out, there are problems that the molded product is liable to have a low degree of crystallinity and deform at a temperature over T_g of about 60 °C (see Section 2.3.2).

PLA has the tendency to stick to the metal of the mold during processing because of its slow crystallization rate, thereby affecting the appearance of the article. Mold release agents, which are typically added to prevent the sticking of biopolymers to metal surfaces during processing, add also to surface contamination once the part is removed from the mold.

Various methods have been proposed for alleviating such problems. For example, a method in which moldability is imparted by adding higher fatty acid bisamides to PLA so that blocking is prevented is disclosed in **JPH06299054** A (1994, MITSUI TOATSU CHEMICALS). A method in which mold release properties and molding workability are imparted by adding fatty acid amides to a thermoplastic polymer composition consisting chiefly of a PLA is disclosed in **JPH0827363** A (1996, MITSUI TOATSU CHEMICALS); and a method in which the degradation rate is controlled by adding aliphatic carboxy acid amides or the like to a polymer consisting mainly of a PLA is disclosed in **JPH08183898** A (2003, SHIMADZU CORP; KANEBO LTD).

2.2.2 Poly(glycolic acid)

PGA has a high crystallization temperature T_{c2} (detected in the course of its cooling from a molten state by means of a differential scanning colorimeter, DSC) and a relatively small temperature difference ($T_m - T_{c2}$) between T_m and the crystallization temperature T_{c2} thereof. A polymer small in this temperature difference tends to crystallize upon cooling of a sheet or fiber extruded from such a polymer from its molten state and is difficult to provide a transparent formed product. Therefore, the forming processing of the PGA has involved a problem that forming conditions such as forming temperature and stretching temperature are limited to narrow ranges (2009, **WO2009107425** A1, KUREHA CORP).

The crystalline PGA has a small temperature difference ($T_{c1} - T_g$) between a crystallization temperature T_{c1} (detected in the course of heating of its amorphous substance by means of DSC) and the T_g thereof. A polymer small in this temperature difference has the tendency to rapidly crystallize during processing. The high crystallization rate of PGA is liable to cause problems in shapability or product appearance, such as failure in stable stretching, thickness irregularity in the shaped product, or opacification (whitening) of the shaped product, etc. due to crystallization of PGA in the case of shaping in combination with another thermoplastic polymer. The crystalline PGA can provide an amorphous PGA sheet by, for example, melt processing it into the form of a sheet and quenching the resultant sheet (2008, **WO2008004490**; 2009, **WO2009107425** A1, KUREHA CORP).

Further, PGA has insufficient melt stability and has a tendency to easily generate gasses upon its melt processing. More specifically, in the conventional PGA, a temperature at which the weight loss upon heating reaches 3% is about 300 °C. In addition, it has been found that many additives such as a catalyst deactivator, a nucleating agent, a plasticizer, and an antioxidant deteriorate the melt stability of PGA. When the melt stability of PGA is insufficient, forming or molding conditions such as forming or molding temperature are limited to narrow ranges, and the quality of the resulting formed or molded product is easy to be deteriorated (2003, **WO2003037956** A1, KUREHA CHEMICAL IND CO LT).

2.2.3 Polyhydroxyalkanoates

PHAs such as P3HB and PHBHV have the disadvantage of being highly thermosensitive. As such, the processability of PHAs is quite problematic, since their high melting temperatures require processing temperatures (about 180 °C) that contribute to their extensive thermal degradation in the melt. Since the melting temperature is above the decomposition temperature of PHA, the PHA will undergo thermolysis that causes the molecular weight of PHA to decrease at the elevated temperature [19–21].

By controlling the processing conditions it is possible to minimize the thermal degradation of PHA during processing into pellets. Factors that can affect such degradation include the temperature at which extrusion is performed, the time of exposure to such temperatures, screw speed, shear heating, and screw and die design. Another technique to improve the thermostability of PHAs includes the use of lactones and lactams to crosslink the polymer or reacting the PHA with acetic anhydride and capping terminal hydroxyl groups of the PHA. However, these attempts chemically modify the PHAs. **WO9905207** A1 (1999, MONSANTO CO) gives an overview of thermostability of PHAs and discloses the use of phosphorous-containing compounds, oxides, hydroxides, or carboxylic acid salts of metals from Groups I to V of the Periodic Table as thermal stabilizers for PHA.

PHAs also have slow crystallization rates and tend to stick to metal. It has been difficult to prepare films from PHAs due to their frequently unacceptable processing and mechanical characteristics, for example, poor melt strength, rapid aging, and brittleness (1999, **WO9905207** A1, MONSANTO CO).

2.2.4 Poly(ε-caprolactone)

Due to its low T_g (−60 °C) and T_m (60 °C), PCL is difficult to be processed by conventional techniques for thermoplastic materials, such as film blowing and blow molding. Films produced thereby are tacky, as extruded, and noisy to the touch, and have low melt strength over 130 °C. Furthermore, due to the low crystallization rate of PCL, the crystallization process proceeds for a long time after production of the product, causing variation in the crystallinity and bringing undesirable changes to the properties (1992, **WO9219680** A1, NOVAMONT SPA).

2.3 PRODUCT PROPERTIES

The product properties are in principle determined by combinations of intrinsic and processing properties [1].

2.3.1 Mechanical Behavior

As mentioned earlier (Section 2.1.4) PHAs such as P3HB and PHBHV have the disadvantages of being brittle and having little elongation. Consequently, a coating film formed by applying an aqueous dispersion containing such resins also has little elongation and is brittle when applied to sheet film or paper, and there is also the problem of cracks, which occur by folding.

Table 2.8 compares the mechanical properties of PLA and PBS with those of polystyrene (PS) and acrylonitrile-butadiene-styrene (ABS), which are general-use polymers. From this table, it is seen that PLA is hard and fragile, and that PBS is soft. Furthermore, it can be seen that PLA is poor in heat durability and that PBS has higher heat durability than ABS, as a result of comparison of the thermal characteristics (2006, **WO2006054493** A1, PANASONIC CORP).

PBS has mechanical properties similar to that of LLDPE.

TABLE 2.8 Comparison of Mechanical Properties of PS, ABS, PLA, and PBS (2006, WO2006054493 A1, PANASONIC CORP)

Property	PS	ABS	PLA	PBS
Bending modulus (MPa)	2250	2100	4500	1950
Bending strength (MPa)	47	70	132	55
Izod impact strength (J/m)	80	200	46	ND
Heat deformation temperature (°C)	80	96–100	66	97

ABS, acrylonitrile-butadiene-styrene; PBS, poly(butylene succinate); PLA, poly(lactic acid); PS, polystyrene.

2.3.1.1 Friction and Wearing Resistance

The wearing resistance of a polymer depends on the coefficient of friction, stiffness, resilience, and degree of brittleness.

PLA fibers have a high surface friction coefficient and low wearing resistance. For instance, wearing resistance in accordance to JIS L 0849 is generally required to be of grade 3 or better, but that of conventional PLA fibers is as low as grade 1. The low wearing resistance of PLA is a major problem when it is used as material for clothing and industrial uses. If conventional PLA fibers are used in applications such as outerwear, uniforms, and sportswear, the quality degrades through fluffing, whitening, shine, and so on in the shoulders, elbows, knees, hips, or the like, which are often submitted to wearing in daily life, or color migration to innerwear, and other such problems. Furthermore, PLA fiber can also suffer flattening and removal of piles and holes in extreme cases when applied to producing automobile interior finishing materials such as upholstery, carpets, and other components that tend to be strongly abraded. As a result, the development of PLA fiber products for applications requiring wearing resistance such as apparel, interior goods, car interiors, and the like has not progressed very far (2004, **WO2004020708** A1; 2010, **WO2010074015** A1, TORAY INDUSTRIES).

The high surface friction coefficient of PLA fibers has also caused problems in the yarn making, yarn treatment, cloth cutting, and sawing processes. In the melting and spinning process, fluffing or yarn being easily cut occur because of the large friction quotient between the yarn and the guide or the like, when the yarn travels at the high speeds of 1000–7000 m/min. In addition, in the drawing process the yarn twines around the roller and easily breaks. Yarn break and fluffing often occur due to friction between the yarns and the twisted body, or between yarns, during the yarn treatment process, particularly the temporary standing process, largely decreasing the ability to smoothly pass through processing steps and the quality of the product (2004, **WO2004020708** A1, TORAY INDUSTRIES).

In general, in the industrial fabric cutting process, a plurality of clothing items are superposed and then cut, and here in the case of cloth using conventional PLA fibers, they tend to fuse with each other because of the large shearing heat generated between the cutter and the fiber.

In the sawing process, at normal sawing speed, fibers fuse, thus deteriorating the quality of the product, through the generation of friction heat between the machine needles and the fibers; or polymer deposits on the machine needles necessitate frequent replacement of machine needles, therefore, lowering processing speed, and subsequently productivity. It is considered that the high friction coefficient of PLA fibers causing these problems depends on the polymer matrix, and that these problems are inevitable with PLA fibers.

As a means of improving the wearing resistance of PLA, processes for depressing hydrolysis, for instance, have been disclosed (**JP2000136435** A, UNITIKA LTD; 2001, **JP2001261797** A, TORAY INDUSTRIES). In **JP2000136435** A (2000, UNITIKA LTD) the hydrolysis is depressed during fiber production processes by minimizing the moisture content in PLA. **JP2001261797** A (TORAY INDUSTRIES) proposes to add a monocarbodiimide compound in producing hydrolysis resistant fiber. It has been found, however, that the fibers in either case maintain the tendency to fibrillation inherent in PLA and have not been improved in terms of initial wearing resistance as compared with conventional products, though they suffer less abrasion over time as PLA is less brittle (2010, **WO2010074015** A1, TORAY INDUSTRIES).

In the manufacturing process of films, sheets, and the like, a lubricant is sometimes added to the polymer in order to improve the antiblocking characteristic of chips or fused polymers or to facilitate the release of the mold from the die or roller. However, in the field of fibers, the addition of a lubricant has been avoided, because fiber macula, dying macula, or other product quality deteriorations easily occur from blending unevenness, heat decomposition, bleed out, or the like of the lubricant.

JP2004204406 (2004) A, **JP2004204407** (2004), and **JP2004091968** A (2004) of TORAY INDUSTRIES disclose a PLA staple fiber having good slipperiness and provide various kinds of fiber structures such as spun yarn produced by using the PLA fiber. The PLA staple fiber contains a fatty acid bisamide and/or an alkyl-substituted fatty acid monoamide in an amount of 0.1–5 wt% based on the total fiber. The PLA staple fiber can be used as a binder fiber as it is, and a fiber structure such as spun yarn, nonwoven fabric, and wadding can be produced by using the PLA staple fiber.

2.3.1.2 Impact Resistance

PLA suffers from one major drawback, which is its lack of impact strength and poor cutting resistance compared to other polymers, and especially PET. This is particularly problematic for sheets where cracks will appear upon cutting or for thermoformed articles, which need to be stamped into the desired shape through a die cutting process. This may lead to breakage of thermoformed PLA trays upon conveying or of PLA bottles when exposed to mechanical stress such as shock or even to broken-off pieces being locked up in produced articles, such as food-packaging trays (2009, **EP2065435** A1, SUKANO MAN & SERVICES AG). A means for overcoming this drawback is the addition of impact modifiers (see also Chapter 5: Compounding; Section 5.5.2.2: Impact Modifiers).

2.3.2 Heat Resistance

An article made of PLA is usually amorphous, due to its slow crystallization rate, and has an inferior heat resistance. In particular, a thermoformed article made of PLA is dimensionally stable (i.e., heat resistant) at temperatures up to about 60 °C. As a result an amorphous PLA container is not suitable for use at an elevated temperature; for example, a food container made of PLA, such as cups for hot beverages, cannot be used for hot food and drink or in a microwave oven (2007, **US2007259195**, FAR EASTERN TEXTILE LTD).

For the purpose of imparting heat resistance to the molded articles made of PLA, a large number of methods for increasing the crystallinity content and accelerating the crystallization rate have been reported.

Crystallinity can be increased either by increasing the mold temperature close to the crystallization temperature of PLA and prolonging the cooling time or by heat treating (annealing) the amorphous formed item after processing (2003, **WO03016015** A1, CARGILL DOW LLC; 2008, **US2008258357** A1, NATUREWORKS LLC). **JP2001354223** A (2001, TOYO SEIKAN KAISHA LTD) discloses a method for imparting heat resistance and dimension stability to at least a part of a container that comprises a layer made of PLA by applying heat crystallization. The heat crystallization is effected by heating under ultrasonic irradiation the mouth and neck portions of the container, which is a blow-molded article, having a crystalline nucleus or by heating the mouth and neck portions under the condition of partially forming the crystalline nucleus at a preform stage (see also Chapter 8: Surface Treatment; Section 8.2.3: Heat Treatment). The heat treatment accelerates rapid growth of crystals, such as spherulites, which have a size equal to or larger than the wavelength of light beams and result in light scattering, or crystals that grow up to a size larger than the wavelength of visible light, and the processed items thus obtained become opaque. Furthermore, this method reduces productivity as the molding cycle is prolonged (2005, **WO2005097894** A1, NISSAN CHEMICAL IND LTD).

The crystallization rate of PLA can be accelerated by increasing either the rate of crystal growth or the steady state concentration of nuclei in the polymer matrix. In general, an increase in nucleation density can be readily accomplished by compounding PLA with nucleating agents that are either physical (inactive) or chemical (active) in nature. The nucleating agents accelerate crystal growth by becoming the primary crystal nuclei of crystalline polymer and lower the crystal size by improving the crystallization rate at the same time. **JPH08193165** A (1991, MITSUI TOATSU CHEMICALS) discloses a method for producing a molded article by injection molding, blow molding, or compression molding PLA to which talc, silica, or calcium lactate is added as a crystal nucleating agent. However, this method has the disadvantage that the crystallization of the polymer is insufficient without a heat treatment and the productivity is low with a lower crystallization rate of the polymer (2003, **WO3074593** A1, UNITIKA LTD). **WO03074593** A1 (2003, UNITIKA LTD) has proposed a production method in which a crystal nucleating agent such as talc is added to PLA to prepare a sheet having a fast crystallization rate, and molding is conducted with a heated mold in a short time by using the sheet thus obtained. Inorganic nucleating agents used in the prior art include calcium carbonate, talc, silicon dioxide, or kaolinite. These inorganic nucleating agents can reduce the transparency of the article made therefrom. Additionally, when another flexible biodegradable polymer is blended for the purpose of improving the impact resistance, the time of a molding cycle is required to be increased by a factor of a few, and hence no practical workability is attained. Another method involves the addition to PLA of a so-called transparent nucleating agent such as an aliphatic carboxylic acid amide, an aliphatic carboxylic acid salt, an aliphatic alcohol, or an aliphatic carboxylic acid ester (1997, **EP0780428** A1; **JPH09278991** A, MITSUI CHEMICALS INC). The sheet obtained is high in transparency before molding, but is decreased in transparency by crystallization and additionally requires a long heat treatment time for crystallization (2007, **WO2007142106**, UNITIKA LTD). The crystallization rate of PLA can also be significantly increased by adding a low molecular compound having an amide group and a layered clay mineral organized with an organic onium salt to PLA (2003, **JP2003226801** A, TOYOTA CENTRAL RES & DEV).

Another way to improve the heat resistance of PLA involves the blending with another polymer. **EP0446852** A2 (1991, BOEHRINGER INGELHEIM KG) proposes a method in which PGA and its derivative are added as a crystal nucleus agent to PLLA to increase the crystallization speed for reduction of an injection molding cycle time and to improve the mechanical characteristics of the resulting molded article. However, **JPH08193165** A (1991, MITSUI TOATSU CHEMICALS) reported that an attempt was made to produce a molded article by injection molding by the method of **EP0446852** A2 (1991) but failed at a mold temperature of not lower than T_g.

JPH11106628 A (1994, SHIMADZU CORP) discloses a method in which wax is employed as a crystal nucleus agent and a crystallization promoter, and a molded article is heat treated at a crystallization temperature or kept in a mold set at the crystallization temperature for a predetermined period. However, the wax employed as the crystal nucleating agent is generally less compatible with PLA, thereby to be bled out. Therefore, only a small amount of the wax is added, which is insufficient for formation of crystal nuclei (2003, **WO03074593** A1, UNITIKA LTD).

A further method of crystallization is through stretching orientation. A method has been proposed in which a certain stretching is conducted before molding (2001, **JP2001162676** A, MITSUBISHI PLASTICS IND). However, the sheet of **JP2001162676** A (2001) is more difficult to mold than the unstretched sheet, in particular, difficult to subject to deep-draw molding; additionally, the residual strain of the molded article obtained from the sheet is large, and hence the molded article is disadvantageously deformed at a temperature $T \geq T_g$ (2007, **WO2007142106**, UNITIKA LTD).

There is also a method in which the above-described transparent nucleating agent and the above-described stretching orientation are used in combination (2004, **JP2004345150** A, KANEBO LTD; KANEBO SYNTHETIC FIBERS LTD). The disclosed method is claimed to improve the crystallization rate on the basis of the combination of the use of a crystal nucleating agent and the application of the stretching orientation in molding so as to maintain the transparency after crystallization. However, in general, the extent of stretching is significantly varied from portion to portion of the molded article, and hence it is difficult, particularly at low stretching, to increase the heat resistance of the whole molded article (2007, **WO2007142106**, UNITIKA LTD).

A recent method for improving the heat resistance of PLA involves the formation of stereocomplexes. A stereocomplex PLA (scPLA), which is obtained by mixing together PLLA and PDLA, has a T_m higher (>200 °C) than that of ordinary PLA. The stereocomplex affects the crystallization behavior of the PLA and contributes to the promotion of the crystallization, and hence improvement of the heat resistance can be attained (2006, **WO2006088241** A1, TEIJIN LTD; MUSASHINO KAGAKU KENKYUSHO; MUTUAL CORP; YOSHIHARU KIMURA; 2008,

WO2008155980 A1, YOSHINO KOGYOSHO CO LTD). In principle, the heat resistance of a PLA article can be increased quite significantly if these stereocomplex crystallites are present in sufficient quantities. However, no methods have been developed for the production of scPLA articles on a large scale because of the high T_m and the slow rate at which the stereocomplex crystals form. PDLA and PLLA, the constituent polymers of scPLA, tend to degrade rapidly at temperatures needed to melt the stereocomplex crystallites.

2.3.3 Water Resistance

Most polyesters are resistant to water. P3HB, PHBHV, and PCL are very resistant to water. This resistance is probably due to their high hydrophobicity and crystallinity, which preclude water uptake [22]. PLA is hydrophobic, and its T_g deteriorates rapidly in moist conditions.

PGA is a hydrolyzable aliphatic polyester, and a PGA film is usually combined (e.g., laminated) with another thermoplastic polymer rather than being used by itself to improve the properties thereof including moisture resistance (2009, **WO2009107425** A1, KUREHA CORP).

Another hydrolyzable aliphatic polyester is poly(β-malic acid) [23].

Common water-soluble biodegradable polymers include starch, cellulose, and their derivatives. Representative examples include carboxymethyl cellulose, hydroxyethyl cellulose, xanthan, pullulan, poly(amino acid)s, poly(aspartic acid), and poly(glutamic acid). Poly(vinyl alcohol) is a water-soluble synthetic biodegradable polymer [23].

2.3.4 Antistatic Properties

Most biopolymers are liable to be electrified by friction, wherein dust and dirt adhere to them, thereby spoiling the appearance thereof. An aliphatic polyester that is hydrophobic is easily charged, and the half-life of the built-up charge is long. Accordingly, a fibrous-formed article obtained by processing an aliphatic polyester into a fiber is likely to be electrostatically charged, and, thus is not easy to use. An aliphatic polyester film has the disadvantage of high electrical insulation and tends also to be easily electrostatically charged. As a result, an operator can receive an electric shock at the winding or slitting the film, while spark discharge can sometimes lead to an ignition accident. Furthermore, running of the film can become unstable at the printing or other fabrication step, and sticking can remarkably lower workability (1997, **EP0802219** A2, MITSUI CHEMICALS INC).

For this reason, it is necessary to provide the molding with antistatic performance. A well-known method for imparting a biopolymer with antistatic properties involves the use of antistatic agents (see Chapter 5: Compounding and Additives; Section 5.5.2.11: Antistatic Additives).

2.3.5 Flammability/Flame Retardancy

PLA is flammable (see Table 2.9), and when it is used in applications requiring high-degree of flame retardancy such as applications to housings of electrical household appliances and office automation appliances and automobile components, countermeasures for flame retardation are required. As a general method for flame retardation, flame retardants are added to the polymer.

Flame retardancy refers to the property of not continuing combustion or not generating afterglow after removing an ignition source. A flame retardant is a component that when added to a polymer contributes to improvement of flame retardancy of the polymer (see Chapter 5: Compounding and Additives; Section 5.5.2.3: Flame Retardants).

In general, it is difficult to impart flame retardancy to biopolymers. While great efforts have been devoted to research, no biopolymer compositions have been developed having a satisfactory flame retardant effect. A large number of additives have been used to try to impart flame retardancy to PLA; e.g., aluminum hydroxide powder or magnesium hydroxide powder (1996, **JPH08252823** A, FUJITSU LTD); surface-treated metal hydroxide (2004, **WO2004022650** A1; 2005, **JP2005139441** A, MITSUBISHI PLASTICS INC); phosphazene compounds (2007, **JP2007308660** A, MITSUBISHI PLASTICS IND; 2011, **EP2363434** A1, FUJI XEROX CO LTD), etc.

2.3.6 Aesthetic Properties

Aesthetic properties refer to properties that determine the reactions (perceptions) of the senses: the eye (color, luster, covering power, appearance), and the tactile sense, viz., the

TABLE 2.9 Comparison of PLA and PET Properties (2007, **WO2007095712** A1, PHB IND SA)

Properties	PLA	PET
Flammability	Burn 2 min after removal from the flame	Burn 6 min after removal from the flame
Resilience	64% of recuperation with 10% of deformation	51% of recuperation with 10% of deformation
Coating	Good	Poor
Gloss	Very high up to low	Medium up to low
Wrinkling resistance	Excellent	Good
Density (g/cm^3)	1.25	1.34

tactile corpuscles of the skin (handle). The aesthetic properties are a subcategory of product properties, and as such are determined by the intrinsic properties of the material and by the "added" properties, that is to say on those obtained during processing [1].

2.3.6.1 Decoration

The decoration of biopolymers is feasible provided the adhesion requirements of the decorating process—coating, painting, metallization, laser marking, printing—are met. However, the decoration of biopolymer articles is hindered by several problems [24].

The surface characteristics of various biopolymers, and in particular aliphatic polyesters such as PLA and PHA, have relatively high surface tensions that are near 50 mN/m (37 mN/m dispersive component and 13 mN/m polar component). This is a great attribute from a surface wet-out standpoint of most decorating liquids such as inks and paints, but this is rarely the surface condition exposed after the molding process.

Furthermore, some of the additives used to improve the processing and performance properties of a biopolymer article can cause surface contamination. Traditional plasticizers for PLA or PHAs are prone to migrate ("bleed" or "bloom") to the surface of the article, jeopardizing the operations of surface finishing, including printing on the product.

Surface contamination can have a negative impact on molecular attraction, causing liquids to fail to wet the surface. The surface energy of biopolymer articles must significantly exceed the surface tension of liquids by a recommended level of 10 mN/m to prevent paint or ink picking/liftoff and delaminations. Reliable and repeatable measurements of wettability and adhesion are critical to successfully painting, printing, coating, and laminating three-dimensional biopolymers materials [24].

As mentioned earlier (Section 2.1.7) most biopolymers are liable to be electrified by friction, etc. wherein dust and foreign substances are adhered to the surface of an article formed from such a biopolymer, thereby spoiling its appearance. A way to overcome this problem is to render the article antistatic.

2.3.6.2 Gloss

Gloss is a measure of how shiny or reflective a material is at a specific angle based on refractive index.

PLA has good gloss and clarity (see Section 2.1.6) for aesthetic appeal. It has a lower optical haze (in accordance with ASTM-D1003-95) and more adequate transparency than the other biodegradable polymers, and a gloss of 130% or more (in accordance with ASTM-D2457-70: at 45 deg) (2005, **WO2005052056** A1, ASAHI KASEI LIFE & LIVING CORP). PLA's optical properties resemble those of clear polystyrene, and has better gloss than PET (see Table 2.9).

It has been established that a high gloss finish, which may be desirable for many types of applications, will likely result in a high coefficient of friction.

2.3.6.3 Color

Without undue experimentation, one can use color-matching techniques to identify a particular location in spherical color space. For example, a skilled person can use the teachings of **WO2004095319** A1 (2004, POLYONE CORP) to digitally map color space using specific polymer carriers and colorants as raw material ingredients. Alternatively, one can make small samples called plaques for visual review.

2.3.6.4 Surface Effects

Frequently, the preparation of a colored biopolymer article does not involve merely color but also special effect features, such as metallics, pearls, granite, translucent, fluorescents, iridescents, marbles, etc.

WO2011040905 A1 (2012, POLYONE CORP) discloses a biodegradable polyester article that is made to appear lustrously metallic or pearlescent by the addition of polymethylpentene (PMP) and nonmetallic, nonpearlescent colorant, and optionally other functional additives. The colorant can be pigment(s), dye(s), or combination thereof. A stretch blow molded polymer article, such as a bottle, using the PMP in an aliphatic polyester, can simulate the appearance of a metallic surface or a pearlescent luster even though nonmetallic and nonpearlescent colorants are used. Among the various aliphatic polyesters proposed are PLA, and PHAs such as P3HB or PHBHV.

With metallics and pearls already simulated by use of a PMP color concentrate in the aliphatic polyester, these other special effects can be added to create even more eye-catching effects for the biopolymer article in use or on sale. Nonlimiting examples of such additives are commercially available from PolyOne Corporation (USA) (www.polyone.com) and marketed under the following brands: OnColor FX colorants, PolyOne colorants, etc.

2.3.6.5 Color Stability

Color stability generally refers to the resistance of a polymer to yellowing.

Lactic acid–based polymers are prone to developing a yellow/brown color upon prolonged exposure to heat. This is undesirable for many applications where a clear color is desirable (1999, **WO9950345** A1, CARGILL INC).

PGA obtainable by the ring-opening polymerization of glycolide at elevated temperatures (205–235 °C) for long periods of time (1969, **US3468853** A, AMERICAN CYANAMID CO) is sensitive to coloration upon polymerization.

A colored PGA gives a product of diminished commercial value. In addition, it is difficult to color PGA to the desired tone using coloring agents. It has been reported that considerably colored articles offer hygienic problems in the fields of food packaging material and medical appliances (2003, **WO03006525** A1, KUREHA CHEMICAL IND CO LTD). By carrying out the ring-opening polymerization at a temperature of 185–190 °C, which is lower than the T_m (about 220 °C) of PGA, it is theoretically possible to obtain less-colored polymers (1965, **BE654236** A, AMERICAN CYANAMID CO). However, lower polymerization temperatures render the resulting polymer likely to crystallize and solidify during polymerization reactions, whereby the polymerization reactions tend to become inhomogeneous. The resulting PGA is so poor in melt stability that when extrusion molded into various articles such as sheets, films, and fibers, it is difficult to carry out extrusion molding in a stable fashion because of large melt viscosity changes (2003, **WO03006525** A1, KUREHA CHEMICAL IND CO LTD).

US2668162 A (1954, DU PONT) discloses a PGA production process wherein glycolide mixed with a polymerization catalyst is subjected to ring-opening polymerization at 150–200 °C to produce a low-molecular-weight polymer, and the polymer is then heated to 220–245 °C to increase its melt viscosity. With this process, however, it is difficult to prevent coloration of the resulting PGA because a time-consuming heating step is needed and rapid heating tends to lead to heating variations (2003, **WO03006525** A1, KUREHA CHEMICAL IND CO LTD).

WO03006525 A1 (2003, KUREHA CHEMICAL IND CO LTD) discloses a PGA that is less colored and improved in melt stability.

WO03006525 A1 (2003, KUREHA CHEMICAL IND CO LTD) discloses a PGA obtained by ring-opening polymerization of glycolide, which has:

1. a weight-average molecular weight (M_w) in the range of 10,000–1,000,000
2. a narrow molecular weight distribution in the range of 1.0–2.5 as represented by a weight-average molecular weight-to-number-average molecular weight ratio (M_w/M_n)
3. a yellowness index of up to 40 as measured using a sheet obtained by press molding and crystallization of said PGA.

A narrow molecular weight distribution of PGA implies that the material is subjected to substantially uniform biodegradation because of a reduced amount of the low-molecular-weight part susceptible to biodegradation. By regulating the molecular weight distribution to a narrow range and adjusting the M_w of PGA, it is possible to control the biodegradation rate at will.

On the other hand, when the polymerization reaction is carried out at high polymerization temperatures for a long period of time for the adjustment of the molecular weight distribution of PGA, the resulting polymer is sensitive to coloration. At lower polymerization temperatures, however, the molecular weight distribution tends to become wide. With this in mind, after the ring-opening polymerization for PGA was carried out at 120–250 °C for 3 min to 50 h, an additional polymerization was performed at a temperature 10–50 °C lower than the polymerization temperature for 1–50 h. As a result, a PGA having a sharply controlled molecular weight distribution can be obtained while its coloration is considerably reduced. For this process, it is preferable that the first polymerization for PGA should be carried out at a relatively high temperature for a relatively short time.

Furthermore, it has been observed that a biodegradable aliphatic-aromatic copolyester product obtained in the reaction was discolored, often ranging from pink to red in color. This presents a problem in that the aesthetic appearance of a nonwhite polymer product is an obstacle to employing the polymer in end uses where the discoloration is apparent and cannot be readily overcome or masked with pigments, whitening agents, or fillers(2013, **US2013018142**, POLYONE CORP).

Biopolymer articles that are exposed to natural sunlight are subject to ultraviolet rays that can affect the color of the article. Therefore, for certain applications, it is customary to add ultraviolet light (UV) stabilizers in the polymer either by direct mixing or by means of a color concentrate used to color the polymer (see Chapter 5: Compounding and Additives; Section 5.4.2.5: Light and UV Stabilizers).

2.3.7 Environmental Behavior

Biodegradation is a functional decay of material, e.g., loss of strength, substance, transparency, etc. where it is known to be identifiable with exposure of the material to a living environment, which may itself be very complex, and the property loss may be attributable to physical or chemical actions as first steps in an elaborate chain of processes.

Biodegradable polymers decompose under environmental influences in an appropriate and demonstrable time scale. This degradation usually takes place by hydrolysis and/or oxidation, but predominantly by the action of microorganisms such as bacteria, yeasts, fungi, and algae.

The environmental effects of biopolymers have been discussed analytically by the author in his previous book: Biopolymers: Recycling, Reuse and Disposal, Elsevier, 2013 [25].

2.3.7.1 Types and Mechanisms of (Bio) degradation

Changes in polymer properties due to physical, chemical, or biological reactions resulting in bond scissions and subsequent chemical transformations are categorized as polymer degradation. The various types of degradation may be classified either by the inducing mechanisms or by the nature of the agents causing degradation. The main degradation mechanisms are:

1. depolymerization
2. random scission
3. elimination

The main agents, who initiate degradation and the corresponding types of degradation are:

1. heat (thermal degradation)
2. heat plus oxygen (thermo-oxidative degradation)
3. visible light, UV (photodegradation)
4. high energy radiation (e.g., X-rays, γ-rays)
5. mechanical stress (mechanochemical degradation)
6. chemical attack (e.g., solvolysis/hydrolysis, ozonolysis, catalytic degradation)
7. biological organisms (biodegradation aerobic, anaerobic)

2.3.7.1.1 Thermal Degradation

Thermal degradation of thermoplastic polymers occurs during processing at temperature $T \geq T_m$, when the polymer is transformed from solid to melt. The thermal degradation of PLA is attributed mainly to random main chain scission and unzipping depolymerization reactions. The random degradation reaction involves hydrolysis by trace amounts of water, oxidative degradation, *cis*-elimination, and inter- and intramolecular transesterification reactions [26]. Above 200 °C, PLA can degrade through inter- and intramolecular ester exchange, *cis*-elimination, radical and concerted nonradical reactions, resulting in the formation of CO, CO_2, acetaldehyde and methylketene [27]. There are suggestions that the thermal degradation of PLA is a nonradical, "backbiting[3]" ester interchange reaction involving the –OH chain ends [28,29]. Depending on the point in the backbone at which the reaction occurs (see Scheme 2.1), the product can be a lactide molecule (reaction a_1), an oligomeric ring (reaction a_2), or acetaldehyde plus carbon monoxide (reaction b). At temperatures in excess of 270 °C, homolysis of PLA occurs [30]. The formation of acetaldehyde is expected to increase with increasing process temperature due to the increased rate of the degradation reactions [31].

Almost all the active chain end groups, residual catalysts, residual monomers, and other impurities enhance the thermal degradation of PLA. As a consequence of these reactions, when PLA is melt processed during the manufacture of industrial products at high temperatures, undesired molecular weight reduction and weight loss occur [32].

The thermal instability of PHAs during melt processing has triggered the interest in the thermal degradation of PHAs, and especially P3HB.

The thermal degradation behavior of PHB has been discussed in many reports, in which a random chain scission by β-elimination has been considered as the dominant mechanism based on the presence of crotonic acid and oligomers with a crotonate end group at almost all chain ends of the pyrolysis products [33–36]. Kawalec et al. [37] proposed an E1cB mechanism proceeding via α-deprotonation by a carboxylate anion to produce the same products. There were suggestions that other reactions out of the random scission occur during the PHB thermal characterization. Ariffin et al. [38] detected the presence of crotonic anhydride and its oligomers as minor products from condensation reactions between carboxyl groups. The anhydride production must be one reaction out of the conforming process to the random degradation statistics and contribute to the complexity of PHB pyrolysis. Based on the above results, Ariffin et al. [38] proposed that an anhydride formation process, i.e., dehydration as a minor reaction should be included in the thermal degradation pathways of PHB, in which the random β-elimination is predominant. Expected thermal degradation pathways of PHB are illustrated in Scheme 2.2. The anhydride formation is one of mechanisms out of processes conforming to the random scission statistics. The β-elimination leads to oligomeric acids and finally crotonic acid with monotonous decrease in the molecular weight, while the dehydration may get in the way of the decrease. Moreover, the production of anhydrides may influence the reactions caused by carboxyl groups, such as the E1cB mechanism [37] and inter-/intratransesterifications, contributing to the complexity of PHB pyrolysis.

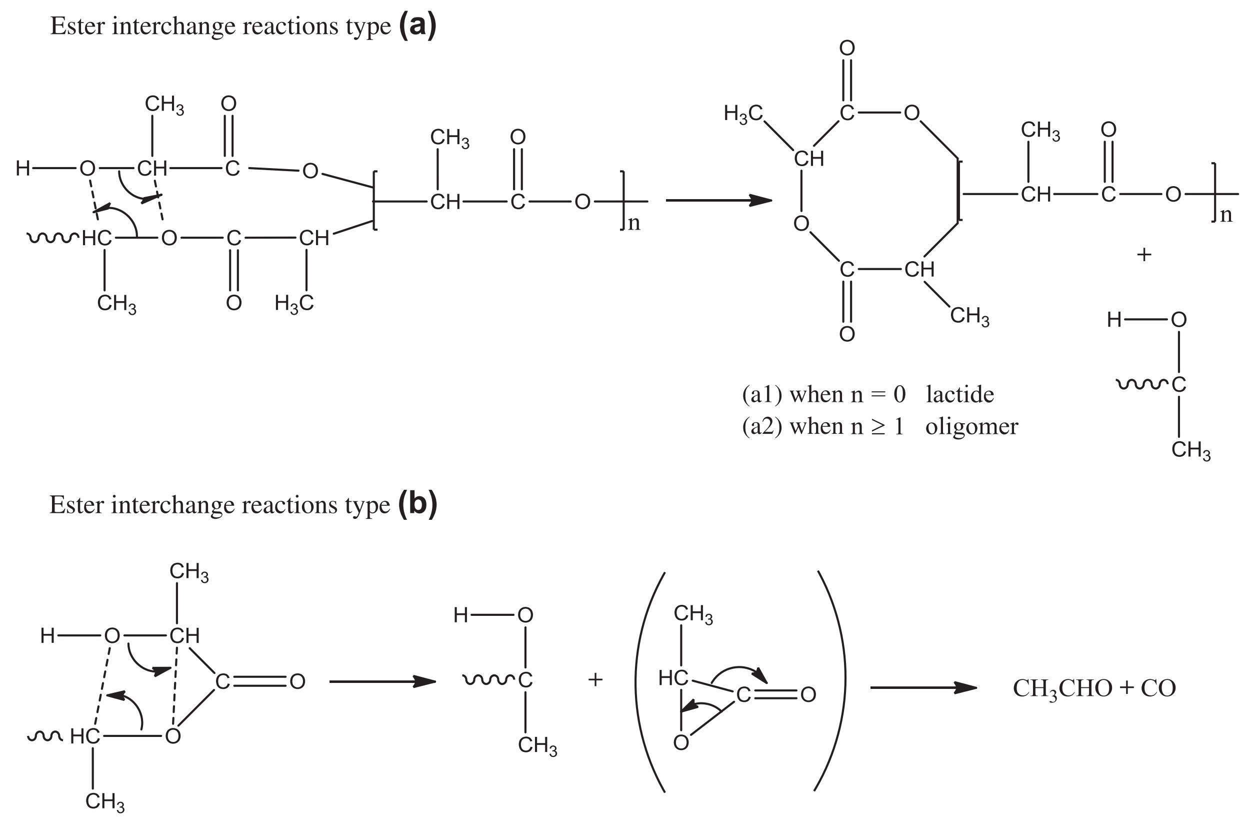
2.3.7.1.2 Photodegradation

Photodegradation of polymers is induced by the action of light and is attributed to photochemical reactions arising from the absorption of UV radiation by carbonyl groups present on the polymer backbone. The photodegradation mechanisms are mainly expressed by the Norrisch reactions that transform the polymers by photoionization (Norrisch I) and chain scission (Norrisch II). Photodegradation can conduce to Norrisch reactions and/or crosslinking reactions, or oxidative processes [39]. The photodegradation mechanism of PLA and PCL has been suggested to proceed via the Norrisch-type photocleavage, especially the Norrisch II-type reaction, which explains the chain scission (decrease of molecular weight), formation of C═C double bonds and hydroperoxide O–H at newly formed chain terminals [40–43] as is shown in Scheme 2.3.

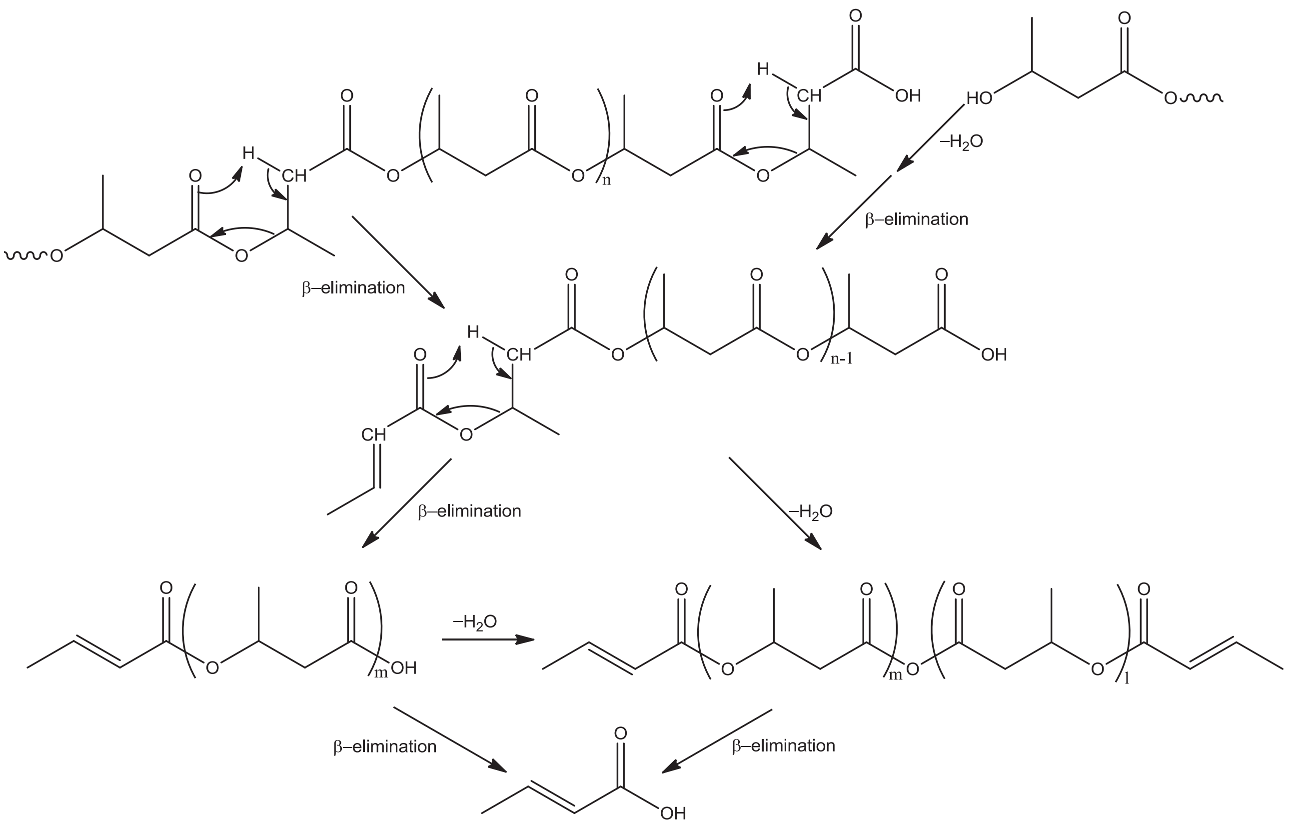
Sakai et al. proposed other photodegradation mechanisms in which the UV degradation of PLA comprised a dissociation reaction at the RCOO–R′ bond followed by the dehydrogenation of α-hydrogen on an asymmetric carbon [45]. Taking into account the reported mechanism, Yasuda et al. proposed a possible photodegradation mechanism shown in Scheme 2.4 [46]. In this mechanism, the Norrisch II type reaction was ignored because of the nondetection of acrylic acid.

---

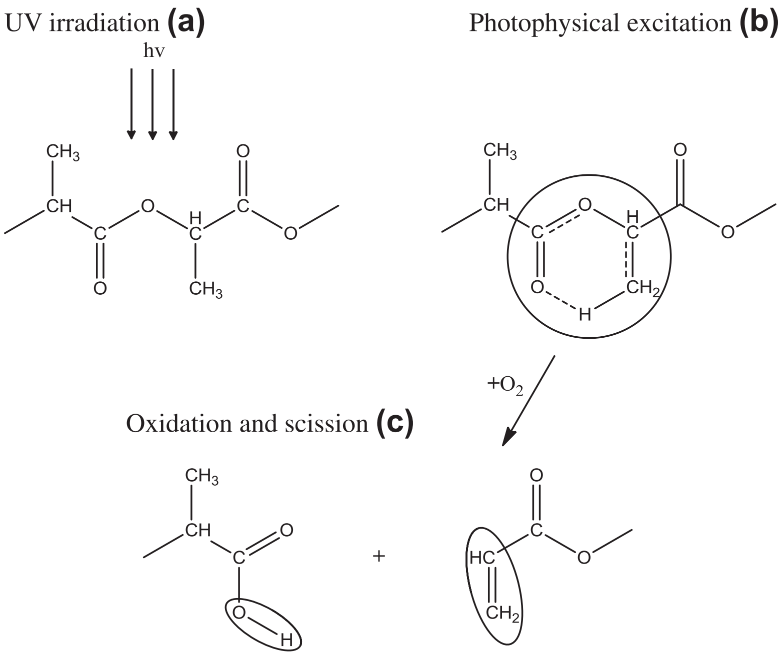
[3] Backbiting refers to the formation of cyclic compounds through intramolecular reactions between the carboxylic end group of the chain and the ester bond of the chain.



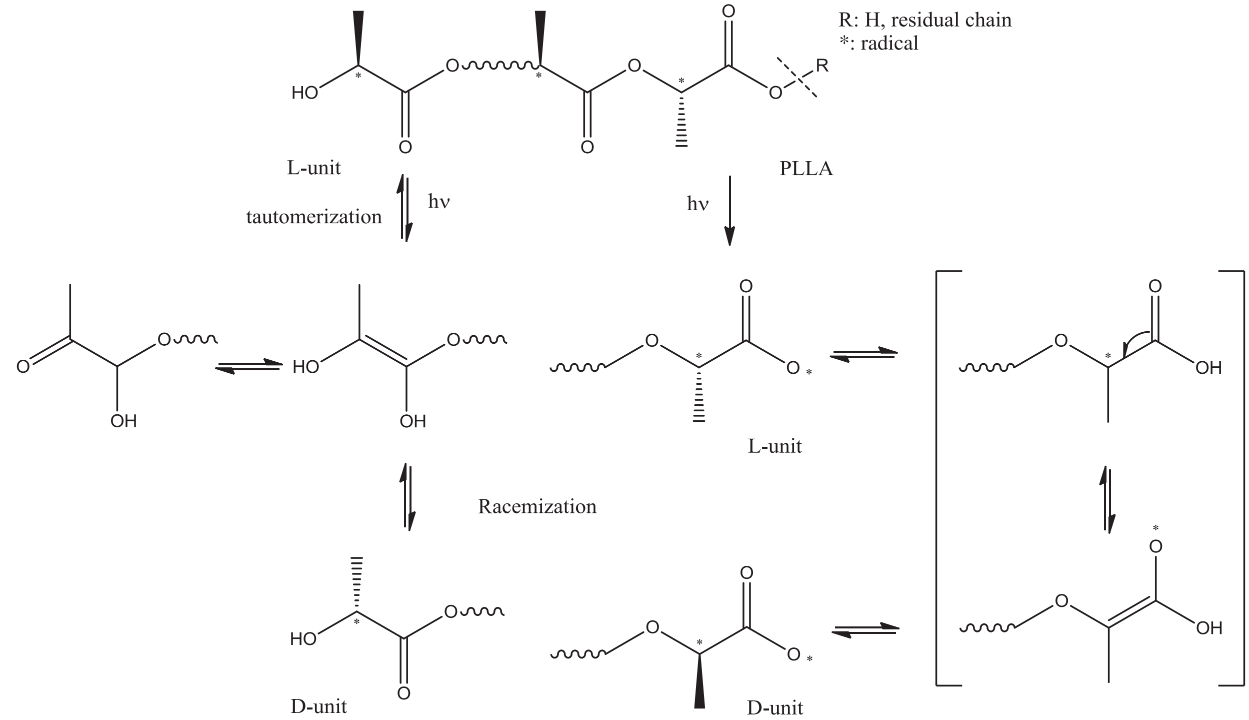
SCHEME 2.1 Thermal degradation of PLA according to McNeill and Leiper [29].



SCHEME 2.2 Thermal degradation pathways of PHB according to Ariffin et al. [38]; l, m, and n mean repetition numbers of 3-hydroxybutyrate unit and the numbers of l and m are less than the number of n.



SCHEME 2.3 Norrisch II photodegradation mechanism of PLA according to Belbachir et al. [44].



SCHEME 2.4 Possible photodegradation mechanisms of poly(L-lactide) (PLLA) under UV according to Yasuda et al. [46].

Instead, it was assumed that an RCOO–R′ bond is cleaved to produce carbonyl and alkyl radicals, which abstract a tertiary proton on chiral carbon, resulting in a racemization equilibrium at the carbonyl chain end unit. At another chain end, the hydroxyl group must be predominant because of hydrolysis accelerated by the irradiation. The hydroxyl chain end unit is highly mobile and therefore reactive, like L-lactic acid, resulting in the shifting into a racemization equilibrium under irradiation. The racemization equilibrium converts the original L-lactate units into D,L-lactate units at both chain ends, thus, the D-unit formation ratio becomes statistically close to the chain scission ratio [46].

Crosslinking and chain scission reactions were found to be the main degradation mechanisms of poly(butylene adipate-*co*-terephthalate) (PBAT) or Ecoflex® (BASF AG) biodegradable mulch films when exposed to solar radiation [47,48].

2.3.7.1.3 Mechanical Degradation

Biopolymer articles can undergo several mechanical degradations during processing, storage and use. Mechanical degradation can take place due to shear forces, tension, and/or compression [49,50]. Agitation, grinding, or extrusion are the main causes of mechanical degradation during processing. The basic phenomenon involved when subjecting the polymer to very powerful shearing forces is the breakage of the molecule. Mechanical degradation reduces the average molecular weight of the polymer.

Although mechanical factors are not predominant during biodegradation, they can activate or accelerate it. In field conditions, mechanical stresses act in synergy with the other environmental parameters such as temperature, UV, humidity, etc. [39].

2.3.7.1.4 Hydrolysis

The most prevailing type of degradation of biodegradable polymers is mainly hydrolysis of ester linkages or other labile bonds or hydrolytically unstable backbone. In general, the hydrolytic degradation is thought to proceed through a series of somewhat overlapping steps including:

- initial hydrolysis yielding polymers with reduced molecular weight (i.e., conversion of polymers to oligomers);
- continued loss of molecular weight (i.e., formation of smaller oligomers) and gradual loss of plasticizers incorporated into the material;
- initial loss of physical properties (e.g., pliability);
- loss of further properties resulting in an opaque and hazy material;
- major loss of physical properties, such as tensile strength and form stability (correlated with a reduction in molecular weight of the polymer down to a $M_n < 50{,}000\,\text{Da}$);
- weight loss and volume loss, until the material is essentially degraded to monomers or small oligomers.

The hydrolysis of PLA is a good example to demonstrate the mechanism of abiotic hydrolysis. As illustrated in Scheme 2.5, the cleavage of the ester bonds by absorption of water produces a successive reduction in molecular weight.

The hydrolysis of semicrystalline biodegradable biopolymers occurs initially in the amorphous phase and forms low-molecular-weight, water-soluble fragments. This reduction in molecular weight in the amorphous phase does not result in reduction of the mechanical properties as the crystalline regions provide the required strength to the structure. Then, hydrolysis of crystalline phase occurs, which results in loss of molecular weight and mechanical properties.

There are two main ways by which biopolymers can be hydrolyzed, passively by chemical hydrolysis or actively by enzymatic reaction. The latter method is most important for naturally occurring polymers such as polysaccharides and PHAs. PLA and PGA degrade by simple hydrolysis of the ester bond not requiring the presence of enzymes to catalyze hydrolysis.

2.3.7.1.5 Biodegradation

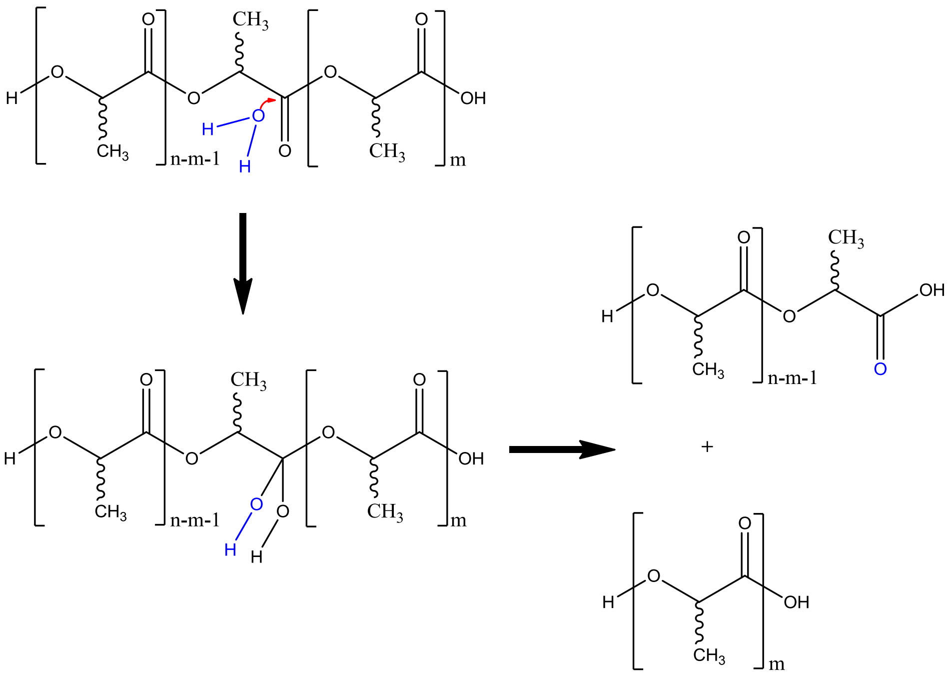
Biodegradation reactions are typically enzyme catalyzed and generally occur in aqueous media. Bio-based polymers containing hydrolyzable linkages, such as aliphatic polyester, protein, cellulose, and starch, are generally susceptible to biodegradation by the hydrolytic enzymes of microorganisms. The hydrophilic/hydrophobic character of polymers greatly affects their biodegradability, with more polar polymers being more readily biodegradable as a general rule. Other important polymer characteristics that affect biodegradability include crystallinity and chain flexibility.

Biodegradation starts when microorganisms begin growing on the surface of the biopolymer and secrete enzymes that break down the biopolymer into oligo- or monomeric units such as hydroxy acids. In the case of aliphatic polyesters, the hydroxy acids are then taken up by the microorganisms and used as carbon sources for growth. In an aerobic environment the biopolymers are degraded to carbon dioxide and water, whereas in an anaerobic environment the degradation products are carbon dioxide and methane (biogas) [53] [54].

As can be seen in Scheme 2.6, a minor part of the organic compound of the biopolymer is converted to biomass. The biomass yield is in the range 10–40 wt%, depending on the biopolymer. The intermediates/residues comprise nondegraded carbon compounds and/or in-between degradation products [54]. The whole biodegradation process can vary from days to months to years, and it depends on the type of polymer. Over a long period of time, eventually cell biomass and other intermediates will be mineralized to CO_2.

Biodegradation is a composite effect of different mechanisms that proceed simultaneously or consecutively on the polymer. Exemplary mechanisms of biodegradation include disintegration, dispersion, dissolution, erosion, hydrolysis, and enzymatic degradation. Most of the microbial reactions are sequential so that the end product of metabolism of a given substrate by one organism becomes the substrate for another organism (**WO9928366** A1, 1999, UNIV NEBRASKA).

Biodegradation processes can affect polymers in a number of ways. Microbial processes that can affect polymers include mechanical damage caused by growing cells, direct enzymatic effects leading to breakdown of the polymer structure, and secondary biochemical effects caused by excretion of substances other than enzymes that may directly affect the polymer or change environmental conditions, such as pH or redox conditions.



SCHEME 2.5 Hydrolysis of PLA [51,52].

Aerobic biodegradation

Biopolymer $+ O_2 \longrightarrow CO_2 + H_2O$ + biomass (microbes) + intermediates/residues

Anaerobic biodegradation

Biopolymer $\longrightarrow CH_4 + CO_2$ + biomass (microbes) + intermediates/residues

SCHEME 2.6 Schematic representation of aerobic and anaerobic biodegradation reactions [54].

P3HB and PCL are primarily attacked by enzymes at the surface. PLA is initially degraded by a nonenzymatic catalyzed hydrolysis mechanism, which is temperature dependent. Enzymes are large molecules and are unable to diffuse through the crystalline regions of PLA. As a result, little enzymatic degradation occurs at the beginning of the degradation process. Enzymatic involvement can produce pores and fragmentation, making more polymer regions accessible to the enzymes. Hydrolysis is also the principal mechanism by which enzymes degrade cellulose-based polymers. The first step in depolymerization occurs outside of microbial cells through the action of extraordinary enzymes. After cleavage, the resulting small oligomers can be transported into cells for final mineralization [55].

The biodegradability of PLA is lower than that of other commonly known biodegradable polymers such as P3HB, PCL, or PBS. For example, the quantities of biodegradable polymer-degrading bacteria in these polymers can be represented by the following sequence: P3HB ≥ PCL > PBS > PLA (2004, **EP1375592** A1, NAT INST OF ADVANCED IND SCIEN). PLA breaks down only slowly in the soil and, if composted, decomposes only at high temperatures.

In an aliphatic-aromatic polyester, the amount of aromatic acid in the chain is typically lower than 49%, since the percentage of biodegradation of the polyesters decreases significantly above said threshold. It is reported in the literature [56] that aliphatic-aromatic copolyesters such as PBAT with a molar fraction of terephthalate of 42 mol%, biodegrade completely to form compost in 12 weeks, whereas products with 51 mol% of molar fraction of terephthalate show a percentage of biodegradation of less than 40%. This different behavior was attributed to the formation of a higher number of butylene terephthalate sequences with a length greater than or equal to 3, which are less easily biodegradable.

Cellulose and cellulose derivatives with a low degree of substitution (DS), i.e., DS < 1, are biodegradable. Cellulose is degraded in the environment by both anaerobic and aerobic microorganisms. Typical biodegradation products include cell biomass, methane (anaerobic only), carbon dioxide, water, and other fermentation products. Cellulose acetate is resistant to attack by microorganisms. Removal of the acetylate groups (deacetylation) by chemical hydrolysis and cetylesterases allows the degradation of the cellulose backbone [57].

PATENTS

Patent Number	Publication Date	Family Members	Priority Numbers	Inventors	Applicants	Title
BE654236 A	19650409	US3297033 A 19670110; GB1043518 A 19660921	US19630320543 19631031	EMIL SCHMITT EDWARD; ALBERT POLISTINA ROCCO	AMERICAN CYANAMID CO	File de suture chirurgicaux. "Surgical sutures."
BE850332 A1	19770713	US4101533 A 19780718 SE7700296 A 19770715; NL7700308 A 19770718; JPS5287169 A 19770720; IT1082451 B 19850521; GB1568719 A 19800604; FR2338291 A1 19770812; DE2701278 A1 19770721; CH618455 A5 19800731; CA1091600 A1 19801216; AU2124177 A 19780720; AU512448 B2 19801009	CH19760000403 19760114	LAFFERTY ROBERT M; HEINZLE ELMAR	AGROFERM A G	Utilisation d'esters carboniques cycliques comme solvant pour l'acide poly-(β-hydroxy-butyrique). "Cyclic carbonic acid esters as solvents for poly-(β-hydroxybutyric acid)."
DD239609 A1	19861001		DD19850278981 19850726	SCHMIDT JOACHIM; SCHMIECHEN HELMUTH; REHM HELGA; TRENNERT MARIKA	AKAD WISSEN-SCHAFTEN DDR	Verfahren zur Gewinnung von Poly-β-hydroxybuttersäure aus getrockneten Bakterienbiomassen. "Process for the production of poly-β-hydroxybutyric acid from dried bacterial biomass."
EP0015123 A1	19800903	ES8103169 A1 19810516; EP0015123 A1 19800903; EP0015123 B1 19821222; EP0036699 A1 19810930; EP0036699 B1 19830202; EP0036699 B2 19870902; DK73380 A 19800822; AU5560680 A 19800828; AU529981 B2 19830630	GB19790006076 19790221; GB19790006077 19790221; GB19790015858 19790508	HOLMES PAUL ARTHUR; WRIGHT LEONARD FREDERICK; ALDERSON BARRY; SENIOR PETER JAMES	ICI PLC	A process for the extraction of poly-3-hydroxy-butyric acid from microbial cells.
EP0304293 A2	19890222	US4876331 A 19891024; EP0304293 A3 19900207; EP0304293 B1 19930317; DE3879320 T2 19930624	JP19880049015 19880302; JP19880178448 19880718; JP19870204537 19870818; JP19870204538 19870818; JP19870316446 19871215	DOI YOSHIHARU	MITSUBISHI CHEM IND	Copolyester and process for producing the same.
EP0440165 A2	19910807	JPH03224492 A 19911003; EP0440165 A3 19911023	JP19900018502 19900129	NISHIMURA ATSUO; IMANAKA MAMORU; NIITSU HIROMI; NISHIOKA MASAAKI; GOTOH KATSUHIKO	SHOWA DENKO KK	Biodegradable or bio compatible copolymer and process for producing same.

EP0446852 A2	19910918	JPH04220456 A 19920811; EP0446852 A3 19920819; DE4007882 A1 19910919; DE4007882 C2 19940310	DE19904007882 19900313	ENTENMANN GUENTHER; BIELZER RAFFAEL; OFFERGELD HEINZ	BOEHRINGER INGELHEIM KG	Verwendung von Polyglycolsäure und ihrer Derivate als Nukleierungsmittel. “Use of polyglycolic acid and its derivatives as nucleating agent.”
EP0466050 A1	19920115	US5138029 A 19920811; JPH0465425 A 19920302	JP19900179170 19900706	MASAAKI NISHIOKA; HIDEMITSU TAKINISHI; SHIRO FUKUYAMA; ATSUO NISHIMURA; HIROMI NIITSU	SHOWA DENKO KK	Biodegradable or biocompatible copolymer and process for producing same.
EP0479043 A1	19920408	US5213976 A 19930525; JPH04264125 A 19920918; GR3018034 T3 19960229	AT19900002018 19901005	BLAUHUT WILFRIED; GIERLINGER WOLFGANG; STREMPFL FRIEDRICH	DANUBIA PETROCHEM POLYMERE	Verfahren zur Gewinnung eines durch einen Mikroorganismus intrazellulär aufgebauten Polyhydroxyalkanoates aus dem Zellmaterial und Polyhydroxyalkanoatflocken. “Process for the production of a polyhydroxyalkanoate from the cell material of a microorganism and polyhydroxyalkanoate flocks.”
EP0533144 A2	19930324	US5292860 A 19940308; JPH0593049 A 19930416; JP2777757 B2 19980723; EP0533144 A3 19940622; EP0533144 A2 19930324	JP19910267255 19910917	SHIOTANI TAKESHI; KOBAYASHI GENTA	KANEGAFUCHI CHEMICAL IND	Copolymer and method for production thereof.
EP0780428 A1	19970625	US2002002252 A1 20020103; US6417294 B1 20020709; EP0780428 B1 20060419; DE69636049 T2 20061130		OBUCHI SHOJI; KAWAGUCHI TATSUYA; NAKATA TOMOYUKI; WATANABE TAKAYUKI; KITAHARA YASUHIRO; SUZUKI KAZUHIKO; AJIOKA MASANOBU	MITSUI CHEMICALS INC	Films and molded articles formed from aliphatic polyester compositions containing nucleating agents.
EP0802219 A2	19971022	EP0802219 A3 19980513; EP0802219 B1 20011024; US6139948 A 20001031; US5914188 A 19990622; DE69707547 T2 20020627	JP19960096616 19960418; JP19960105125 19960425	KOBAYASHI NAOKI; IKADO SHUHEI; KAWANO AKIRA; KUROKI TAKAYUKI; WANIBE HIROTAKA	MITSUI CHEMICALS INC	Coated aliphatic polyester film.
EP0805175 A1	19971105	US5853639 A 19981229; KR100233184 B1 19991201; JPH1060136 A 19980303; JP3731838 B2 20060105; EP0805175 B1 20040922; DE69730771 T2 20050929	JP19960134217 19960430; JP19970105160 19970408	KAWAKAMI YUKICHIKA; SATO NOBUO; HOSHINO MITSURU; KOUYAMA TOSHITAKA; SHIIKI ZENYA	KUREHA CHEM IND CO LTD	Oriented polyglycolic acid film and production process thereof.

Continued

—Cont'd

Patent Number	Publication Date	Family Members	Priority Numbers	Inventors	Applicants	Title
EP0805176 A1	19971105	US5908917 A 19990601; KR100244057 B1 20000201; JPH1060137 A 19980303; JP4073052 B2 20080409; EP0805176 B1 20040929; DE69730897 T2 20051006	JP19960134218 19960430; JP19970105161 19970408	KAWAKAMI YUKICHIKA; SATO NOBUO; HOSHINO MITSURU; KOUYAMA TOSHITAKA; SHIIKI ZENYA	KUREHA CHEMICAL IND CO LTD	Polyglycolic acid sheet and production process thereof.
EP1266984 A1	20021218	US2003088052 A1 20030508; US6645622 B2 20031111; JP2002371431 A 20021226; JP4562316 B2 20101013; EP1266984 B1 20070912; DE60222326 T2 0080605	JP20010175239 20010611	YAMANE HIDEKI	KANEKA CORP	Process for preparing biodegradable fibers.
EP1375592 A1	20040102	US2004034128 A1 20040219; US6987138 B2 20060117; JP2004018681 A 20040122; JP3742842 B2 20060208; EP1375592 B1 20060222; DE60303642 T2 20060921	JP20020175661 20020617	OKIWA YUTAKA; RAKU TAKAO	NAT INST OF ADVANCED IND SCIEN	Biodegradable polylactide resin composition.
EP2065435 A1	20090603	US2009162683 A1 20090625; JP2009144152 A 20090702	EP20070405339 20071129; EP20080405294 20081128	GUILLAUME DOUARD	SUKANO MAN & SERVICES AG	Biodegradable polyester compositions.
EP2363434 A1	20110907	US2011218278 A1 20110908; US8148453 B2 20120403; JP2011178932 A 20110915; CN102190874 A 20110921	JP20100045840 20100302	MASAYA IKUNO; MASAYUKI OKOSHI; KENJI YAO; MASAHIRO MORIYAMA	FUJI XEROX CO LTD	Resin composition and molded product.
FR2446859 A1	19800814	US4310684 A 19820112; JPS5599195 A 19800728; JPS6254475 B2 19871116; FR2446859 B1 19810130 EP0014490 A1 19800820; EP0014490 B1 19821013	FR19790001862 19790122	VANLAUTEM NOEL; GILAIN JACQUES	SOLVAY	Process for the separation of poly-beta-hydroxybutyrates from a biomass.
JP2000136435 A	20000516	JP4335987 B2 20090930	JP19980313136 19981104	MATSUOKA FUMIO	UNITIKA LTD	Wear resistant polylactic acid-based fiber and its production.
JP2001162676 A	20010619	JP3866465 B2 20070110	JP19990348909 19991208	YOSHIGA NORIO	MITSUBISHI PLASTICS IND	Polylactic acid molding and its molding method.
JP2001261797 A	20010926	JP3440915 B2 20030825	JP20000070098 20000314	MATSUMOTO HIROSHIGE; MASUDA TOYOHIKO; MAEDA YUHEI	TORAY INDUSTRIES	Aliphatic polyester resin and molded product.

JP2003226801 A	20030815	JP3945264 B2 20070718	JP20020027171 20020204	OKAMOTO HIROTAKA; NAKANO MITSURU; USUKI ARIMITSU; TAKEUCHI HISATO	TOYOTA CENTRAL RES & DEV	Polylactic acid composite material and molded product.
JP2004091968 A	20040325	JP4114443 B2 20080709	JP20020254201 20020830	KIMURA TOSHIAKI; NONAKA SHUICHI; OCHI TAKASHI	TORAY INDUSTRIES	Polylactic acid fiber with high wear resistance and method for producing the same.
JP2004161931 A	20040610	JP4297680 B2 20090715	JP20020330998 20021114	OGAWA TOSHIO; OSAWA SATOSHI	KANAZAWA INST OF TECHNOLOGY	Biodegradable resin emulsion adhesive.
JP2004204406 A	20040722		JP20020377242 20021226	KIMURA TOSHIAKI; MAEDA YUHEI; MOCHIZUKI KATSUHIKO	TORAY INDUSTRIES	Polylactic acid staple fiber and fiber structure composed thereof.
JP2004204407 A	20040722	JP4075611 B2 20080416	JP20020377243 20021226	KIMURA TOSHIAKI; OCHI TAKASHI; MAEDA YUHEI	TORAY INDUSTRIES	Crimped polylactic acid yarn for carpet.
JP2004244457 A	20040902	JP4348960 B2 20091021	JP20030033592 20030212	ITO TAKURO	TOYO SEIKAN KAISHA LTD	Polyester resin composition, stretched molded article and method for producing stretched molded article.
JP2004345150 A	20041209	JP4145193 B2 20080903	JP20030143048 20030521	ITO YUMI	KANEBO LTD; KANEBO SYNTHETIC FIBERS LTD	Method for manufacturing heat-set molded product.
JP2005139441 A	20050602		JP20040300971 20041015; JP20030355568 20031015	TANAKA KAZUYA; KATO YUKIO; TAKAGI JUN	MITSUBISHI PLASTICS IND	Injection molded product.
JP2006130847 A	20060525	JP4530809 B2 20100825	JP20040324270 20041108	SAWAI TORU	TOHCELLO CO LTD	Biaxially stretched polyester multilayered film and its manufacturing method.
JP2007308660 A	20071129	JP5339670 B2 20131113	JP20060141728 20060522	TANAKA KAZUYA; KATO YUKIO	MITSUBISHI PLASTICS IND	Resin composition and injection molding.
JP2009185108 A	20090820		JP20080023520 20080204	MIYAMOTO TAKASHI	TOYO BOSEKI	Solution of a polylactic acid based resin.
JPH06299054 A	19941025	JP3308335 B2 20020729	JP19930086490 19930413	SUZUKI KAZUHIKO; WATANABE TAKAYUKI; KITAHARA YASUHIRO; AJIOKA MASANOBU	MITSUI TOATSU CHEMICALS	Molding method of lactic acid polymer.
JPH08183898 A	19960716	JP3419575 B2 20030623	JP19940327439 19941228	MATSUI MASAO; FUJII YASUHIRO; KOSEKI HIDEKAZU; KONDO YOSHIKAZU; HIRAI YOSHIAKI	SHIMADZU CORP; KANEBO LTD	Polylactic acid composition and its molded product.

Continued

—Cont'd

Patent Number	Publication Date	Family Members	Priority Numbers	Inventors	Applicants	Title
JPH08193165 A	19960730	JP3359764B B2 20021224	JP19940313009 19941216; JP19930327858 19931224; JP19940280810 19941115	SUZUKI KAZUHIKO; NAKADA TOMOYUKI; WATANABE TAKAYUKI; KITAHARA YASUHIRO; AJIOKA MASANOBU	MITSUI TOATSU CHEMICALS	Heat resistant lactic acid polymer molding.
JPH08252823 A	19961001		JP19950058649 19950317	HATAYA TAKAFUMI	FUJITSU LTD	Manufacture of nonflammable biodegradable plastic.
JPH0827363 A	19960130	JP3852958 B2 20061206	JP19940160314 19940712	SUZUKI KAZUHIKO; NAKADA TOMOYUKI; WATANABE TAKAYUKI; KITAHARA YASUHIRO; AJIOKA MASANOBU	MITSUI TOATSU CHEMICALS	Lactic acid polymer composition.
JPH09278991 A	19971028	JP3411168 B2 20030526	JP19960341905 19961220; JP19950333533 19951221; JP19960025602 19960213	OBUCHI SEIJI; KAWAGUCHI TATSUYA; NAKADA TOMOYUKI; WATANABE TAKAYUKI; KITAHARA YASUHIRO; SUZUKI KAZUHIKO; AJIOKA MASANOBU	MITSUI TOATSU CHEMICALS	Production of aliphatic polyester molded product and molded product produced thereby.
JPH11106628 A	19990420	JP3747592 B2 20060222	JP19970272376 19971006	KANAMORI KENJI; KOSEKI HIDEKAZU	SHIMADZU CORP	Polylactic acid-based composition or molded product and its production.
US2005242466 A	20051103	KR20060047208 A 20060518; JP2005306943 A 20051104; JP4238174 B2 20090311; DE102005018086 A1 20051208; CN1690105 A 20051102	JP20040123461 20040419	KANAZAWA SHINICHI; KAWANO KIYOSHI; YOSHII FUMIO; YAGI TOSHIAKI; NAGASAWA NAOTSUGU	SUMITOMO ELEC FINE POLYMER INC	Process for producing transparent material made of polylactic acid and transparent material made of polylactic acid.
US2005253292 A1	20051117	US7452491 B2 20081118	US20040844786 20040513	LAI JUIN Y; HO MING-HUA; KUO PEI Y; HSIEH HSYUE-JEN; HSIEN TZU-YAN; WANG DA M	UNIV CHUNG YAN CHRISTIAN	Method for forming scaffolds.
US2007259195 A1	20071108		TW20060116224 20060508	CHOU MING-TSE; CHANG LI-LING; WU ROY	FAR EASTERN TEXTILE LTD	Polylactic acid composition, transparent heat resistant biodegrad-able molded article made of the same, and method for making the article.
US2008258357 A1	20081023	US7670545 B2 20100302	US20080163466 20080627; US20020223451 20020819	BOPP RICHARD C; WHELAN JASON	NATURE-WORKS LLC	Method for producing semicrystalline polylactic acid articles.

US2013018142 A1	20130117	WO2013012705 A1 20130124	US201113183807 20110715	ALIDEDEOGLU HUSNU ALP; KANNAN GANESH	SABIC INNOVATIVE PLASTICS IP	Method for color stabilization of poly(butylene-*co*-adipate terephthalate).
US2013030129 A1	20130131	KR20130014717 A 20130212 DE102011086224 A1 20130131 CN102898667 A 20130130		HONG CHAE HWAN; HAN DO SUCK; NAM BYEONG UK	HYUNDAI MOTOR CO LTD; UNIV KOREA IND UNIV COOP FOUND	Manufacturing method of poly lactic acid stereocomplex using solvent casting method.
US2668162 A	19540202		US19520277726 19520320	LOWE CHARLES E	DU PONT	Preparation of high molecular weight polyhydroxyacetic ester.
US3036959 A	19620529		US19600058154 19600926	NOEL BAPTIST JAMES	GRACE W R & CO	Process for preparing poly-beta-hydroxybutyric acid.
US3044942 A	19620717		US19600058614 19600927	NOEL BAPTIST JAMES	GRACE W R & CO	Process for preparing poly-beta-hydroxybutyric acid.
US3275610 A	19660927		US19640354231 19640324	COTY VERNON F	MOBIL OIL CORP	Microbial synthesis of polymers.
US3468853 A	19690923	AMERICAN CYANAMID CO	US19660557607 19660615	SCHMITT EDWARD EMIL; POLISTINA ROCCO ALBERT	AMERICAN CYANAMID CO	Process of polymerizing a glycolide
US3737440 A	19730605		US19710171320 19710812	SCHMITT E; BAILEY W	AMERICAN CYANAMID CO	Polyglycolic acid solutions.
US3902497 A	19750902	JPS51116079 A 19761013; IT1050278 B 19810310; FR2265412 A1 19751024; FR2265412 B1 19781006; GB1490425 A 19771102; DE2513159 A1 19751009; CA1045548 A1 19790102; BR7531268 A 19751223; AU7822275 A 19760819; AR205109 A1 19760405	US19740454353 19740325	CASEY DONALD JAMES	AMERICAN CYANAMID CO	Body absorbable sponge and method of making.

Continued

—Cont'd

Patent Number	Publication Date	Family Members	Priority Numbers	Inventors	Applicants	Title
WO03006525 A1	20030123	US7067611 B2 20060627; TWI238834 B 20050901; JP2004534135 A 20041111; JP4231781 B2 20090304; ES2301658 T3 20080701; EP1404738 A1 20040407; EP1404738 B1 20080305; DE60225445 T2 20090326; CN1525986 A 20040901; CN100413906 C 20080827; AT388182 T 20080315	JP20010208801 20010710; JP20010208804 20010710	YAMANE KAZUYUKI; KAWAKAMI YUKICHIKA	KUREHA CHEMICAL IND CO LTD	Polyhydroxycarboxylic acid and its production process.
WO03016015 A1	20030227	US2003038405 A1 20030227; US2008259054 A1 20081023; US8392851 B2 20130305; US2008259054 A1 20081023; US8392851 B2 20130305; JP2004538178 A 20041224; JP4307254 B2 20090805; EP1463619 A1 20041006; EP1463619 A4 20041103; EP1463619 B1 20080116; DE60224729 T2 20090122	US20010313685P 20010820	BOPP RICHARD C; WHELAN JASON	CARGILL DOW LLC	Method for producing semicrystalline polylactic acid articles.
WO03074593 A1	20030912	US2005165142 A1 20050728; US7854880 B2 20101221; KR20040097146 A 20041117; KR100942443 B1 20100217; KR20040097146 A 20041117; JP2003253009 A 20030910; HK1078601 A1 20071109; EP1484356 A1 20041208; EP1484356 A4 20100609; EP1484356 B1 20111228; CN1639235 A 20050713; CN1325543C C 20070711; AU2003213398 A1 20030916	JP20020059603 20020306	NISHIMURA HIROSHI; HIOKI MASANOBU	UNITIKA LTD	A polylactic acid molding and a process for producing the same.
WO2003037956 A1	20030508	WO03037956 A9 20040521; US2003125431 A1 20030703; US6951956 B2 20051004; US2003125508 A1 20030703; JP2009030068 A 20090212; JP4704456 B2 20110615; JP4256779 B2 20090422;	US20020132578 20020425; JP20020007839 20020116; JP20010335443 20011031	YAMANE KAZUYUKI MIURA HIROMITSU; ONO TOSHIHIKO; NAKAJIMA JUNJI; ITOH DAISUKE	KUREHA CHEMICAL IND CO LTD	Crystalline polyglycolic acid, polyglycolic acid composition and processes for production of both.

		EP1449864 A1 20040825; EP1449864 A4 20050420; EP1449864 B1 20091202; EP1914258 A1 20080423; EP1914258 B1 20101124; CN1827686 A 20060906; CN1827686 B 20100512; CN1608093 A 20050420; CN1280333 C 20061018; CA2710098 A1 20030508; CA2710098 C 20121023; CA2464635 A1 20030508; CA2464635 C 20110322; AU2002343784 B2 20080131; AU2002343784 C1 20080911; AT489415 T 20101215; AT450556 T 20091215				
WO2004020708 A1	20040311	US2011165370 A1 20110707; US8101688 B2 20120124; US2005203258 A1 20050915; TWI321600 B 20100311; KR20050058484 A 20050616; EP1548161 A1 20050629; EP1548161 A4 20080820; EP1548161 B1 20100825; CN1678777 A 20051005; CN100429338 C 20081029	JP20020254201 20020830; JP20020377241 20021226	KIMURA TOSHIAKI; NONAKA SHUICHI; OCHI TAKASHI; SAKAI TAKAAKI; MOCHIZUKI KATSUHIKO; MAEDA YUHEI	TORAY INDUSTRIES	Polylactic acid fiber, yarn package, and textile product.
WO2004022650 A	20040318	US2006100313 A1 20060511; US7439283 B2 20081021; TWI331164 B 20101001; KR20050057167 A 20050616 KR100954924 B1 20100427; JP2008308693 A 20081225; JP4708457 B2 20110622 JP4194558 B2 20081210; EP1544250 A1 20050622; EP1544250 A4 20051123; EP1544250 B1 20090624; CN1681884 A 20051012; CN100447199 C 20081231; AU2003264393 A1 20040329	JP20020261673 20020906	TANAKA KAZUYA TAKAGI JUN	MITSUBISHI PLASTICS INC	Flame retardant resin composition and flame-retardant injection-molding.
WO2004095319 A2	20041104	WO2004095319 A3 20050602; US2007139667 A1 20070621; EP1627332 A2 20060222; CN1777795 A 20060524	US20030464719P 20030423	RUSSELL SCOTT O; BATES SUSAN H	POLYONE CORP	Digitally mapped formulaic color space and method of making and using same.

Continued

—Cont'd

Patent Number	Publication Date	Family Members	Priority Numbers	Inventors	Applicants	Title
WO2005052056 A1	20050609	US2007160782 A1 20070712; US7879440 B2 20110201; EP1816164 A1 20070808; EP1816164 A4 20080102; EP1816164 A8 20071128; CN1906248 A 20070131; CN1906248 B 20100616	JP20030394285 20031125; JP20040076982 20040317; JP20040076981 20040317; JP20040076797 20040317; JP20040115212 20040409	YATSUZUKA MICHIHIRO; SUKIGARA MASAYUKI; ITADA MITSUYOSHI	ASAHI KASEI LIFE & LIVING CORP	Matte film.
WO2005072944 A1	20050811	US2011101573 A1 20110505; US2007172611 A1 20070726; JP4767690 B2 20110907; EP1710075 A4 20100609; CN1914030 A 20070214; CN100528544 C 20090819	JP20040024258 20040130	SATO TAKASHI; ITOH DAISUKE; TOBITA HISANORI; SUZUKI SATORU	KUREHA CORP	Biaxially stretched polyester multilayered film and its manufacturing method.
WO2005097894 A1	20051020	US2007299170 A1 20071227; US2007299170 X6 20071227; US7531585 B2 20090512; TWI382056 B 20130111; KR20070009584 A 20070118; KR101152973 B1 20120611; JP4973848 B2 20120711; ES2379361 T3 20120425; EP1736510 A1 20061227; EP1736510 A4 20080521: EP1736510 B1 20111221; CN1938378 A 20070328; CN100384937 C 20080430; AT538176 T 20120115	JP20040097361 20040330	OZAWA MASAAKI; KAWAMURA YASUO; KASAI MIKIO	NISSAN CHEMICAL IND LTD	Polylactic acid resin composition.
WO2006088241 A1	20060824	US2008161505 A1 20080703; KR20070105990 A 20071031; EP1849833 A1 20071031; EP1849833 A4 20100811; CN101124280 A 20080213; CA2598470 A1 20060824	JP20050080382 20050220	KIMURA YOSHIHARU	TEIJIN LTD; MUSASHINO KAGAKU KENKYUSHO; MUTUAL CORP	Process for producing polylactic acid.
WO2007074042 A2	20070705	WO2007074042 A3 20071206; US2008274885 A1 20081106; RU2008129640 A 20100127; RU2413412 C2 20110310; ES2336491T T3 20100413 EP1965636 A2 20080910; EP1965636 B1 20091202; CA2631449 A1 20070705; CA2631449 C 20130903; BRPI0620442 A2 20120222; AT450146 T 20091215	EP20050028144 20051222	MARTIN INGRID; AUWETER HELMUT; ISRAELS RAFEL; DOMBO PETER; JAKOB JURGEN; CASANELLO DIEGO LOPEZ; BOHN HERIBERT	BASF SE	Biodegradable seed dressing formulations.

WO2007094477 A1	20070823	US2009069463 A 20090312; US8586658 B2 20131119; CN103232694 A 20130807; CN101384662 A2 20090311	JP20060035892 20060214	SERIZAWA SHIN; YANAGISAWA TSUNENORI; INOUE KAZUHIKO; IJI MASATOSHI; KABASHIMA YOHEI; UEDA KAZUE; KAMIKAWA HIROO; FUKAWA NORIO	NEC CORP; UNITIKA LTD	Polylactic acid resin composition and molded item.
WO2007095708 A1	20070830	US2009082491 A1 20090326; JP2009527593 A 20090730; DOP2007000038 A 20070830; CA2641922 A1 20070830; BRPI0600681 A 20071120; AU2007218992 A1 20070830	BR2006PI00681 20060224	NASCIMENTO JEFTER FERNANDES; PACHEKOSKI WAGNER MAURICIO; AGNELLI JOSE AUGUSTO MARCONDES	PHB IND SA	Environmentally degradable polymeric blend and process for obtaining an environmentally degradable polymeric blend.
WO2007095709 A1	20070830	US2009018235 A1 20090115; JP2009527594 A 20090730; DOP2007000034 A 20070915; CA2641924 A1 20070830; BRPI0600683 A 20071120; AU2007218993 A1 20070830	BR2006PI00683 20060224; WO2007BR00045 20070223	NASCIMENTO JEFTER FERNANDES; PACHEKOSKI WAGNER MAURICIO; AGNELLI JOSE AUGUSTO MARCONDES	PHB IND SA	Environmentally degradable polymeric composition and process for obtaining an environmentally degradable polymeric composition.
WO2007095710 A1	20070830	US2009043000 A1 20090212; MX2008010889 A 20080904 KR20080103052 A 20081126; JP2009527595 A 20090730; EP1987075 A1 20081105; DOP2007000033 A 20070915; CN101389677 A 20090318; CA2641925 A1 20070830; BRPI0600782 A 20071120; AU2007218994 A1 20070830	BR2006PI00782 20060224	NASCIMENTO JEFTER FERNANDES; PACHEKOSKI WAGNER MAURICIO; VICINO JOSE RICARDO DE LELLO	PHB IND SA; KEHL IND E COM LTDA	Composition for preparing a degradable polyol polyester, process for obtaining a polyol polyester, an elastomer, foams, paints and adhesives, and a degradable polyol polyester foam.
WO2007095711 A1	20070830	US2009030112 A1 20090129; JP2009527596 A 20090730; DOP2007000032 A 20070915; CA2641926 A1 20070830; BRPI0600783 A 20071120; AU2007218995 A1 20070830	BR2006PI00783 20060224	NASCIMENTO JEFTER FERNANDES; PACHEKOSKI WAGNER MAURICIO; ARENA DAWSON BUIM; COELHO ANA CRISTINA	PHB IND SA; LOGOS QUIMICA LTDA	Biodegradable polymeric composition and method for producing a biodegradable polymeric composition.
WO2007095712 A1	20070830	US2009023836 A1 20090122; JP2009527597 A 20090730; DOP2007000036 A 20070915; CA2641927 A1 20070830; BRPI0600787 A 20071120; AU2007218996 A1 20070830	BR2006PI00787 20060224	NASCIMENTO JEFTER FERNANDES; PACHEKOSKI WAGNER MAURICIO; AGNELLI JOSE AUGUSTO MARCONDES	PHB IND SA	Environmentally degradable polymeric composition and method for obtaining an environmentally degradable polymeric composition.

Continued

—Cont'd

Patent Number	Publication Date	Family Members	Priority Numbers	Inventors	Applicants	Title
WO2007142106 A1	20071213	US2009186990 A1 20090723; JP5274251 B2 20130828; TW200811240 A 20080301; KR20090023336 A 20090304 EP2025713 A1 20090218; CN101443410 A 20090527; CN101443410B B 20120606	JP20060154788 20060602	INUI YUKIKO; HASHIMOTO MASANORI; YOSHIDA MASAHIRO	UNITIKA LTD	Polylactic acid based heat-resistant sheet.
WO2008004490 A1	20080110	US2009275692 A1 20091105; US8003721 B2 20110823; JP5291461B B2 20130918; CN101484528 A 20090715; CN101484528 B 20111207; ES2445337 T3 20140303	JP20060188004 20060707	SUZUKI YOSHINORI; YAMANE KAZUYUKI; SATO HIROYUKI; WATANABE TAKAHIRO	KUREHA CORP	Aliphatic polyester composition and method for producing the same.
WO2008155980 A1	20081224	US2010105835 A1 20100429; KR20100018605 A 20100217; KR101158487 B1 20120621; JP2009001622 A 20090108; EP2169005 A1 20100331; EP2169005 A4 20100811; CN101778902 A 20100714; CN101778902 B 20121128; CA2692189 A1 20081224; CA2692189 C 20140325; AU2008264647 A1 20081224; AU2008264647 B2 20110120	JP20070161810 20070619	KITORA SHUICHI; SUZUKI MASATO	YOSHINO KOGYOSHO CO LTD	Molded article having heat resistance and impact resistance.
WO2009107425 A1	20090903	US2011027590 A1 20110203; JP2009202465 A 2009-09-10; JP4972012 B2 2012-07-11; CN101945749 A 20110112	JP20080047985 20080228	ABE SHUNSUKE	KUREHA CORP; ABE SHUNSUKE	Successively biaxially stretched polyglycolic acid film, process for producing the successively biaxially stretched polyglycolic acid film, and multilayered film.
WO2010038537 A1	20100408	US2011190456 A1 20110804; JP2010084001 A 20100415; EP2336244 A1 20110622; CN102171289 A 20110831	JP20080254229 20080930	ITOH DAISUKE; TOHMIYA NAOKO	KUREHA CORP	Polyglycol acid resin composition and molded body thereof.
WO2010074015 A1	20100701	US2011262683 A1 20111027; TW201031700 A 20100901; KR20110098970 A 20110902; JP2010150721 A 20100708; CN102325931 A 20120118	JP20080332097 20081226	MOCHIZUKI KATSUHIKO; KATO YASUUMAZAWA; SADANORI; ONOUE YOSUKE	TORAY INDUSTRIES	Polymer alloy fiber and fiber structure.

WO2011040905 A1	20110407	US2012165422 A1 20120628; CN102575076 A 20120711; CA2775703 A1 20110407	WO2009US58812 20090929	VERNON GARY; ROSENDALE DAVID	POLYONE CORP	Polyester articles having simulated metallic or pearlescent appearance.
WO9209654 A2	19920611	WO9209654 A3 19921001; US5900322 A 19990504; US5900322 X6 19990504; US5559171 A 19960924; US5580911 A 19961203; US5599858 A 19970204; US5446079 A 19950829; US6342304 B1 20020129; SG47853 A1 19980417; NZ240799 A 19940126; MX9102312 A 19940131; KR100245905 B1 20000315; KR100220443 B1 19990915; JP2007138377 A 20070607; JP2006022472 A 20060126; JP2004084156 A 20040318; JP2003221464 A 20030805; JP2003128768 A 20030508; JP3530178 B2 20040524; JP2001354802 A 20011225; JP3393124 B2 20030407; JPH06504558 A 19940526; JP3362040 B2 20030107; IE914155 A1 19920603; HK1041708 A1 20041008; FI20000496 A 20000303; FI932450 A 19930528; ES2278424 T3 20070801 EP0559785 A1 199309 EP0559785 B1 19970312; DE69133554 T2 20071004; DE69132548 T2 20010628; DE69125170 T2 19970619; CN1183429 A 19980603; CN1183428 A 19980603; CN1183427 A 19980603; CN1183433 A 19980603; CN1072245 C 20011003; CN1183423 A 19980603; CN1076358 C 20011219; CN1183426 A 19980603; CN1062740 A 19920715; CN1324891 A 20011205; CN1131281 C 20031217; CA2095536 A1 19920531;	US19900620225 19901130; US19910736262 19910723; US19910797512 19911121	BUCHANAN CHARLES M; GARDNER ROBERT M; WHITE ALAN W	EASTMAN CHEM CO	Aliphatic-aromatic copolyesters and cellulose ester/polymer blends.

Continued

—Cont'd

Patent Number	Publication Date	Family Members	Priority Numbers	Inventors	Applicants	Title
		CA2095536 C 19990216; BR9107138 A 19940405; AU9105091 A 19920625; AU664831 B2 19951207; AU4557496 A 19960606; AT349476 T 20070115; AT199383 T 20010315; AT150058 T 19970315				
WO9219680 A1	19921112	SK390192 A3 19941207; SK279993 B6 19990611; RU2095379 C1 19971110; PL297375 A1 19930628; PL174799 B1 19980930; NO925049 A 19921230; LV12151 A 19981020; LV12151 B 19981220; KR960008112 B1 19960620; JPH06502676 A 19940324; JP2527523 B2 19960828; HUT63644 A 19930928; HU216971 B 19991028; GR3024078 T3 19971031; FI925978 A 19921231; FI115138 B 20050315; ES2103943 T3 19971001; EP0539541 A1 19930505; EP0539541 B1 19970709; DK0539541 T3 19970915; DE539541 T1 19970130; DE69220754 T2 19971204; CZ9203901 A3 19931013; CZ285748 B6 19991013; CA2084994 A1 19921104; CA2084994 C 20010904; BR9205258 A 19930727; AU1650992 A 19921221; AU658180 B2 19950406; AT155161 T 19970715	EP19910112942 1991080; IT1991TO00327 19910503; IT1992TO00199 19920310; IT1992TO00282 19920327	BASTIOLI CATIA; BELLOTTI VITTORIO; DEL TREDICI GIANFRANCO; LOMBI ROBERTO; MONTINO ALESSANDRO; PONTI ROBERTO	NOVAMONT SPA	Biodegradable polymeric compositions based on starch and thermoplastic polymers.
WO9424198 A1	19941027	DE4313136 A1 19941027	DE19934313136 19930422	STERZEL HANS-JOSEF	BASF AG	Mit Metallen oder Siliziumoxiden beschichtetes Polylactid als Verpackungsmaterial. "Polylactide coated with metal or silicon oxide for use as packaging material."

WO9520614 A1	19950803	US5602227 A 19970211; US5498692 A 19960312; USRE36548 E 20000201; TW383316 B 20000301; SK97096 A3 19970409; SG49114 A1 19980518; RU2137784 C1 19990920; PL315691 A1 19961125; PL178568 B1 20000531; NZ276325 A 19980728; NO963104 A 19960927; JPH09508423 A 19970826; ID23491 A 19950907; HUT75180 A 19970428; HU218160 B 20000628; FI962997 A 19960726; ES2188648 T3 20030701; EP0739368 A1 19961030; EP0739368 B1 20030226; DE69432189 T2 20031204; CZ9602192 A3 19961211; CN1142839 A 19970212; CN1097603 C 20030101; CA2181791 A1 19950803; CA2181791 C 20010424; BR9408512 A 19970304; AU9820098 A 19990304; AU1056895 A 19950815	US19940306349 19940915; US19940187969 19940128	NODA ISAO	PROCTER & GAMBLE	Biodegradable copolymers.
WO9520615 A1	19950803	ZA9500657 A 19950929; US5502116 A 19960326; US5536564 A 19960716; TW385320 B 20000321; SK96996 A3 19970604; SG47812 A1 19980417; RU2144047 C1 20000110; PL315682 A1 19961125; PL181098 B1 20010531; NZ279627 A 19980626; MX9603065 A 19970628; JPH09508424 A 19970826; ID23288 A 19950810; FI962996 A 19960726; ES2251716 T3 20060501; EP0741753 A1 19961113; EP0741753 B1 20051228; DE69534715 T2 20060831; CZ9602211 A3 19970115;	US19940189029 19940128	NODA ISAO	PROCTER & GAMBLE	Biodegradable copolymers and plastic articles comprising biodegradable copolymers of 3-hydroxyhexanoate.

Continued

—Cont'd

Patent Number	Publication Date	Family Members	Priority Numbers	Inventors	Applicants	Title
		CN1139936 A 19970108; CN1071341 C 20010919; CA2181795 A1 19950803; CA2181795 C 20010424; BR9506664 A 19970916; AU1680995 A 19950815; AU703156 B2 19990318; AT314410 T 20060115				
WO9708931 A2	19970313	WO9708931 A3 19970424; EP0848759 A2 19980624; EP0848759 B1 20011031; DE19623778 A1 19971218	DE1995133459 19950909; DE1996123778 19960614	METZNER KLAUS; SELA MARION; SCHAFFER JUERGEN	BUNA SOW LEUNA OLEFINVERB GMBH	Extraktionsmittel für Polyhydroxyalkansäuren. "Agents for extracting polyhydroxyalkane acids."
WO9846782 A1	19981022	US6043063 A 20000328 EP0975788 A1 20000202 AU6971598 A 19981111	US19970043017P 19970415	KURDIKAR DEVDATT L; STRAUSER FRED E; SOLODAR A JOHN; PASTER MARK D; ASRAR JAWED	MONSANTO CO	Methods of PHA extraction and recovery using non-halogenated solvents.
WO9905207 A1	19990204	US2002061944 A1 20020523; US6620869 B2 20030916; US2004039092A1 20040226; US2004039092 X6 20040206; US7208535 B2 20070424; EP0996670 A1 20000503; EP0996670 B1 20060531; DE69834726 T2 20070606; AU8587998 A 19990216; AT328035 T 20060615	US19970053720P 19970725	ASRAR JAWED; PIERRE JEAN R	MONSANTO CO	PHA compositions and methods for their use in the production of pha films.
WO9928366 A1	19990610	US6121033 A 20000919; US6191176 B1 20010220; US5990266 A 19991123; AU1709099 A 19990616	US19970067514P 19971204; US19980204338 19981202	TADROS RAEF M; TIMM DELMAR C	UNIV NEBRASKA	Degradable polyesters.
WO9950345 A1	19991007	US6114495 A 20000905; US6353086 B1 20020305; JP2002509968 A 20020402; HK1036466 A1 20090206; EP1070097 A1 20010124; CN1299393 A 20010613; CN100379806 C 20080409; CA2325046 A1 19991007; CA2325046 C 20090310; BR9909283 A 20090505; BR9909283 B1 20090505	US20000621927 20000724; US19980053836 19980401	KOLSTAD JEFFREY J; WITZKE DAVID ROY; HARTMANN MARK H; HALL ERIC STANLEY; NANGERONI JAMES	CARGILL INC	Lactic acid residue containing polymer composition and product having improved stability, and method for preparation and use thereof.

REFERENCES

[1] Van Krevelen D. Properties of polymers: their correlation with chemical structure; their numerical estimation and prediction, from additive groups contributions. 3rd ed. New York: Elsevier; 1990.

[2] Steinbüchel A, Valentin HE. Diversity of bacterial polyhydroxyalkanoic acids. FEMS Microbiol Lett 1995;128:219–28.

[3] Martin DP, Williams SF. Medical applications of poly-4-hydroxybutyrate: a strong flexible absorbable biomaterial. Biochem Eng J 2003;16:97–105.

[4] Rai R, Keshavarz T, Roether JA, Boccaccini AR, Roy I. Medium chain length polyhydroxyalkanoates, promising new biomedical materials for the future. Mater Sci Eng R Rep 2011;72:29–47.

[5] Williams Simon F, Rizk S, Martin David P. Poly-4-hydroxybutyrate (P4HB): a new generation of resorbable medical devices for tissue repair and regeneration. Biomed Tech/Biomed Eng 2013:439.

[6] Lee JM, Lee B-C, Hwang S-J. Phase behavior of poly(L-lactide) in supercritical mixtures of carbon dioxide and chlorodifluoromethane. J Chem Eng Data 2000;45:1162–6.

[7] Abe H, Doi Y, Fukushima T, Eya H. Biosynthesis from gluconate of a random copolyester consisting of 3-hydroxybutyrate and medium-chain-length 3-hydroxyalkanoates by *Pseudomonas* sp. 61-3. Int J Biol Macromol 1994;16:115–9.

[8] Kato M, Bao H, Kang C-K, Fukui T, Doi Y. Production of a novel copolyester of 3-hydroxybutyric acid and medium-chain-length 3-hydroxyalkanoic acids by *Pseudomonas* sp. 61-3 from sugars. Appl Microbiol Biotechnol 1996;45:363–70.

[9] Garlotta DA. Literature review of poly(lactic acid). J Polym Environ 2001;9:63–84.

[10] Saito Y, Doi Y. Microbial synthesis and properties of poly (3-hydroxybutyrate-co-4-hydroxybutyrate) in *Comamonas acidovorans*. Int J Biol Macromol 1994;16:99–104.

[11] Shogren R. Water vapor permeability of biodegradable polymers. J Environ Polym Degr 1997;5:91–5.

[12] Pluta M, Jeszka JK, Boiteux G. Polylactide/montmorillonite nanocomposites: structure, dielectric, viscoelastic and thermal properties. Eur Polym J 2007;43:2819–35.

[13] Nakagawa T, Nakiri T, Hosoya R, Tajitsu Y. Electrical properties of biodegradable polylactic acid film. Industry Applications. IEEE Trans 2004;40:1020–4.

[14] Hirai N, Maeno Y, Tamura H, Kaneko D, Tanaka T, Ohki Y, et al. Dielectric properties of biodegradable polylactic acid and starch ester. Solid Dielectrics, 2004 ICSD. In: Proceedings of the 2004 IEEE international conference on 2004, vol. 1. 2004. pp. 87–9.

[15] Shinyama K, Fujita S. Study on the electrical properties of a biodegradable plastic. Properties and Applications of Dielectric Materials. In: Proceedings of the 7th international conference on 2003, vol. 2. 2003. pp. 707–10.

[16] Zawawi NA, Ismail A, Khalina A, Mahdi MA. Investigation on the microwave properties of kenaf and Rice-Husk fiber reinforced pla composite utilizing one-port coaxial transmission line reflection method. Key Eng Mater 2011;471:868–73.

[17] Meriakri VV, Kalenov D, Parkhomenko MP, Zhou S, Fedoseev NA. Dielectric properties of biocompatible and biodegradable polycaprolone and polylactide and their nanocomposites in the millimeter wave band. Am J Mater Sci 2012;2:171–5.

[18] Kalenov DS, Meriakri VV, Parkhomenko MP, Zhou S. Dielectric properties of biocompatible and biodegradable polycaprolone and polylactide and their nanocomposites in the millimeter wave band. AIP Conf Proc 2012;1459:77–9.

[19] Grassie N, Murray EJ, Holmes PA. The thermal degradation of poly(-(d)-β-hydroxybutyric acid): part 2—changes in molecular weight. Polym Degrad Stab 1984;6:95–103.

[20] Grassie N, Murray EJ, Holmes PA. The thermal degradation of poly(-(d)-β-hydroxybutyric acid): part 1—identification and quantitative analysis of products. Polym Degrad Stab 1984;6:47–61.

[21] Grassie N, Murray EJ, Holmes PA. The thermal degradation of poly(-(d)-β-hydroxybutyric acid): part 3—the reaction mechanism. Polym Degrad Stab 1984;6:127–34.

[22] Vert M, Li S, Garreau H, Mauduit J, Boustta M, Schwach G, et al. Complexity of the hydrolytic degradation of aliphatic polyesters. Angew Makromol Chem 1997;247:239–53.

[23] Gross RA, Kalra B. Biodegradable polymers for the environment. Science 2002;297:803–7.

[24] Rory AW, Enercon Industries Corporation. Green plastics: can they be decorated? Plast Decor Mag 2011:34–41.

[25] Niaounakis M. Biopolymers reuse, recycling, and disposal. 1st ed. 2013. Access Online via Elsevier.

[26] Södergard A, Stolt M. Properties of lactic acid based polymers and their correlation with composition. Prog Polym Sci 2002; 27:1123–63.

[27] Kopinke FD, Remmler M, Mackenzie K, Möder M, Wachsen O. Thermal decomposition of biodegradable polyesters—II. Poly(lactic acid). Polym Degrad Stab 1996;53:329–42.

[28] McNeill I, Leiper H. Degradation studies of some polyesters and polycarbonates—1. Polylactide: general features of the degradation under programmed heating conditions. Polym Degrad Stab 1985;11:267–85.

[29] McNeill IC, Leiper HA. Degradation studies of some polyesters and polycarbonates—2. Polylactide: degradation under isothermal conditions, thermal degradation mechanism and photolysis of the polymer. Polym Degrad Stab 1985;11:309–26.

[30] Tsuji H, Fukui I, Daimon H, Fujie K. Poly(L-lactide) XI. Lactide formation by thermal depolymerisation of poly(L-lactide) in a closed system. Polym Degrad Stab 2003;81:501–9.

[31] Lim LT, Auras R, Rubino M. Processing technologies for poly(lactic acid). Prog Polym Sci 2008;33:820–52.

[32] Nishida H. Thermal degradation. In: Auras RA, Lim LT, Selke SEM, Tsuji H, editors. Poly(lactic acid): synthesis, structures, properties, processing, and applications. Wiley; 2010. p. 401.

[33] Morikawa H, Marchessault RH. Pyrolysis of bacterial polyalkanoates. Can J Chem 1981;59:2306–13.

[34] Ballistreri A, Garozzo D, Giuffrida M, Impallomeni G, Montaudo G. Analytical degradation: an approach to the structural analysis of microbial polyesters by different methods. J Anal Appl Pyrolysis 1989;16:239–53.

[35] Kopinke FD, Remmler M, Mackenzie K. Thermal decomposition of biodegradable polyesters—I: poly (β-hydroxybutyric acid). Polym Degrad Stab 1996;52:25–38.

[36] Gonzalez A, Irusta L, Fernandez-Berridi MJ, Iriarte M, Iruin JJ. Application of pyrolysis/gas chromatography/Fourier transform infrared spectroscopy and TGA techniques in the study of thermal degradation of poly (3-hydroxybutyrate). Polym Degrad Stab 2005;87:347–54.

[37] Kawalec M, Adamus G, Kurcok P, Kowalczuk M, Foltran I, Focarete ML, et al. Carboxylate-induced degradation of poly (3-hydroxybutyrate)s. Biomacromolecules 2007;8:1053–8.

[38] Ariffin H, Nishida H, Shirai Y, Hassan MA. Anhydride production as an additional mechanism of poly (3-hydroxybutyrate) pyrolysis. J Appl Polym Sci 2009;111:323–8.

[39] Lucas N, Bienaime C, Belloy C, Queneudec M, Silvestre F, Nava-Saucedo JE. Polymer biodegradation: mechanisms and estimation techniques–a review. Chemosphere 2008;73:429–42.

[40] Tsuji H, Echizen Y, Nishimura Y. Photodegradation of biodegradable polyesters: a comprehensive study on poly(l-lactide) and poly(ε-caprolactone). Polym Degrad Stab 2006;91:1128–37.

[41] Ikada E, Takeuchi Y, Ashida M. Possibility of poly(lactic acid) as a photodegradable polymer. Kobunshi Ronbunshu 1992;49:527–33.

[42] Ikada E. Role of the molecular structure in the photodecomposition of polymers. J Photopolym Sci Technol 1993;6:115–22.

[43] Ikada E. Photo-and bio-degradable polyesters. Photodegradation behaviors of aliphatic polyesters. J Photopolym Sci Technol 1997;10:265–70.

[44] Belbachir S, Zaïri F, Ayoub G, Maschke U, Naït-Abdelaziz M, Gloaguen JM, et al. Modelling of photodegradation effect on elastic–viscoplastic behaviour of amorphous polylactic acid films. J Mech Phys Solids 2010;58:241–55.

[45] Sakai W, Kinoshita M, Nagata M, Tsutsumi N. ESR studies of photosensitized degradation of poly (L−lactic acid) via photoionization of dopant. J Polym Sci A Polym Chem 2001;39:706–14.

[46] Yasuda N, Wang Y, Tsukegi T, Shirai Y, Nishida H. Quantitative evaluation of photodegradation and racemization of poly(l-lactic acid) under UV-C irradiation. Polym Degrad Stab 2010;95:1238–43.

[47] Kijchavengkul T, Auras R, Rubino M, Ngouajio M, Fernandez RT. Assessment of aliphatic–aromatic copolyester biodegradable mulch films. Part II: laboratory simulated conditions. Chemosphere 2008;71:1607–16.

[48] Kijchavengkul T, Auras R, Rubino M, Ngouajio M, Fernandez RT. Assessment of aliphatic–aromatic copolyester biodegradable mulch films. Part I: field study. Chemosphere 2008;71:942–53.

[49] Briassoulis D. Mechanical behaviour of biodegradable agricultural films under real field conditions. Polym Degrad Stab 2006;91:1256–72.

[50] Briassoulis D. Analysis of the mechanical and degradation performances of optimised agricultural biodegradable films. Polym Degrad Stab 2007;92:1115–32.

[51] Lunt J. Large-scale production, properties and commercial applications of polylactic acid polymers. Polym Degrad Stab 1998;59:145–52.

[52] Hu H-T, Shin T-C, Lee S-Y, Chen C-C, Yang J-C. Influence of hydrolytic degradation on the surface properties of poly-5d/95l-lactide resorbable bone plates. Polym Degrad Stab 2011;96:1522–9.

[53] Williams S, Peoples O. Biodegradable plastics from plants. Chemtech 1996;26:38–44.

[54] Wilde de B. Chapter 5: international norms on biodegradability and certification procedures. In: Bastioli C, editor. Handbook of biodegradable polymers. Smithers Rapra Technology; 2005.

[55] Itävaara M, Siika-aho M, Viikari L. Enzymatic degradation of cellulose-based materials. J Environ Polym Degrad 1999;7:67–73.

[56] Witt U, Yamamoto M, Seeliger U, Müller R-J, Warzelhan V. Biodegradable polymeric Materials—not the origin but the chemical structure determines biodegradability. Angew Chem Int Ed 1999;38:1438–42.

[57] Puls J, Wilson S, Hölter D. Degradation of cellulose acetate-based materials: a review. J Polym Environ 2011;19:152–65.

Chapter 3

Blending

3.1 BLENDS IN GENERAL

Polymer blends or alloys[1] are physical or mechanical mixtures of two or more polymers, wherein between macromolecular chains of different polymers either only secondary intermolecular interactions exist or the chains of different polymers are only partially co-crosslinked. The polymer blends are mainly formed from conventional polymers and are widely utilized for the purposes of improving the disadvantages of the individual polymers. In case the polymers to be blended are incompatible, the polymer mixture: (1) separates into the respective phases due to differences in viscosity, molecular weight, and molecular structure; (2) displays a coarsely dispersed structure; (3) in most cases raises the Barus effect (or extrudate swelling) at melt/kneading causing a difficulty of pelletizing the melted strand; (4) an uneven mixing is exposed on the surface of the obtained injection molded article; and (5) a pearl gloss, a surface exfoliation, or a flow mark is often brought about in appearance of the molded article (2006, **WO2006030951** A1, TORAY INDUSTRIES).

Biopolymers are seen as promising, sustainable alternatives to conventional petrochemical products. Until now, however, their widespread use was hampered by sometimes unsatisfactory material properties of these polymers, while the processability of nearly all pure biodegradable biopolymers is not comparable with those of conventional thermoplastics. Blending of a biopolymer with another polymer, not necessarily a biodegradable one, is an effective way to modify its properties. The blending of biodegradable biopolymers reduces the overall cost of the material and modifies the desired properties and degradation rates. Compared to copolymerization method, blending may be a much easier and faster way to achieve the desired properties [1].

In order to obtain a benefit in the processing or performance properties, the base polymer and additive polymer should exhibit some compatibility or miscibility.[2] Miscibility of the blends is one of the most important factors affecting the final polymer properties. Some of the advantages of producing miscible blends are single-phase morphology and reproducibility of the mechanical properties.

Typical experimental techniques for determining polymer blend miscibility involve the measurement of the optical clarity of a film made from the blend, measurement of the appropriate mechanical properties, and measurement of the glass transition temperature (T_g) by dynamic mechanical analysis (DMA) or differential scanning calorimetry (DSC). If a blend is miscible, films made from the blend will generally be optically clear. Likewise, mechanical properties of a blend, such as tensile strength or tangent modulus, are often intermediate between those of the blend components. Furthermore, a miscible amorphous blend will show a single T_g intermediate between that of the component homopolymers, while an immiscible or partially miscible blend will show multiple T_g's. In the case of a completely immiscible blend, the T_g's will be those of the homopolymers. For partially miscible blends, the T_g's will be intermediate values corresponding to partially miscible phases rich in one of the components. The variation in binary blend T_g can be modeled by the Fox–Flory equation:

$$T_{g12} = T_{g1}\,(W_1) + T_{g2}\,(W_2)$$

where T_{g12} is the T_g of the blend, T_{g1} and T_{g2} are the T_g's of homopolymers, and W_1 and W_2 are the weight percent (wt%) of each component in the blend. Since the Fox equation does not take into account specific interaction between the blend components, the Gordon–Taylor equation:

$$T_{g12} = T_{g1} + \left(kW_2\,(T_{g2} - T_{g12})\,/W_2\right)$$

where k is a constant, is often preferred in blend analysis. For a homogenous, well-mixed system, a plot of T_{g12} versus $W_2\,(T_{g2} - T_{g12})/W_1$ will yield a straight line the slope of which is equal to k and the ordinate intercept will be equal to T_{g1}. The constant k is often taken as a measure of secondary interactions between the blend components. When k is equal to 1, the Gordon–Taylor equation reduces to a simple

---

[1] The terms blends and alloys are often used in literature interchangeably possibly because of the convenience of semantics equating the two concepts. While the term "blend" is a general term for a mixture of two or more polymers, the term "alloy" is generally used to describe a specific type of blend, namely a "compatibilized blend" that offers a unique combination or enhancement of properties ((1) Narayan R. Compatibilization of Lignocellulosics with Plastics. In: Rowell RM, Schultz TP, Narayan R, editors. Emerging Technologies for Materials and Chemicals from Biomass. Washington, DC: American Chemical Society; 1992. pp. 57–75; (2) 1995, **WO9504108** A1, EVERCORN INC). However, the use of the term "polymer alloy" for a polymer blend is discouraged, as the former term includes multiphase copolymers but excludes incompatible polymer blends.

[2] Although the terms "miscibility" and "compatibility" are used quite often interchangeably in the prior art their meaning is not the same; for example a compatible polymer blend is an immiscible polymer blend that exhibits macroscopically uniform physical properties—see also the Glossary.

Biopolymers: Processing and Products. http://dx.doi.org/10.1016/B978-0-323-26698-7.00003-9

weight average of the component T_g's (1992, **WO9209654** A2, EASTMAN CHEM CO).

The miscibility of a polymer blend may be evaluated also from the cold crystallization (T_c), and melting (T_m) temperatures of the blend. The most popular method is based on the T_g of the polymer blend.

Blending a (bio)polymer having a relatively high T_g with a (bio)polymer having a relatively low T_g results often in polymer blends that, in many cases, exhibit the desired characteristics of each polymer by itself, in some cases exhibiting even better properties, while diminishing or minimizing the negative aspects of the individual (bio) polymers.

Those biopolymers that have a $T_g > 10\,°C$, preferably >20 °C or even >30 °C, are characterized as being generally "stiff"; while those biopolymers that have a $T_g < 0\,°C$, preferably <–20 °C or even <–30 °C are characterized as being generally "flexible." In addition, "stiff" polymers are generally more crystalline, while "flexible" polymers are generally less crystalline and more amorphous. A stiffer polymer, however, will usually be more brittle. Even though the distinction between "stiff" and "flexible" biopolymers may be somewhat arbitrary, such classifications are useful when determining which polymers to blend together in order to obtain a polymer blend having the desired performance criteria.

Therefore, the addition of a flexible (tough) (bio)polymer to a brittle (bio)polymer matrix improves the impact resistance, while certain decrease in strength and modulus is accepted. In particular, blending of brittle biopolymers with flexible polymers is believed to achieve optimized properties and performances (2002, **WO0216468** A1, KHASHOGGI E IND; 2003, **US2003166748** A1, and **US2003166779** A1, BIOTEC BIOLOG NATURVERPACK.

Blending is aimed to broaden the applications of biopolymers for products of either higher added value (e.g., applications of biopolymer in medicine), or high volume (e.g., applications of biopolymers in food packaging). Proposals for the preparation of biopolymer blends are known from a large number of patents and scientific articles [2]. Although the use of blends to form biodegradable materials is known to provide certain film physical properties, the use of polymer blends necessarily complicates the processes used to produce films, coatings, and laminates. The great problem in the case of biopolymer blends lies, as a rule, in that those mixtures that are biodegradable have only limited possibilities for use in the area of engineering plastics, thereby explaining the relatively modest success to date. On the other hand, polymer blends having improved properties are either not biodegradable or degradable with increased effort, or else are too expensive. In particular, formation of miscible blends especially with nonbiodegradable polymers can slow down or even inhibit the degradation of the biodegradable components [1].

3.2 BLENDING BIOPOLYMERS WITH OTHER BIOPOLYMERS

In the field of biodegradable materials, the two most critical issues in developing a functional biopolymer blend are: (1) miscibility or compatibility of the biopolymer blend components, and (2) complete biodegradability of the components.

The miscibilities of biopolymers with other biopolymers as reported in literature are presented in Table 3.1.

3.2.1 Blending Different Aliphatic (co)polyesters

Blends of aliphatic polyesters with other aliphatic or aliphatic–aromatic (co)polyesters have been the subject of a very large number of patents. Table 3.2 presents a list of the patents outlined in the Section 3.2.1.

3.2.1.1 Blends of Poly(Lactic Acid)

Poly(lactic acid) (PLA) is one of the most popular and commercially available aliphatic polyesters. However, the inherent brittleness, low melt viscosity, and low heat deflection temperature (HDT) of PLA have restricted its applications. In order to overcome these drawbacks, it is common practice to modify PLA by copolymerization (see Chapter 7: Chemical Treatment, Section 7.1: Chemical Modification), or physical blending.

3.2.1.1.1 Blending Optical Isomers of PLA

The blending of a poly(L-lactic acid) (PLLA) and a poly-D-lactic acid (PDLA) in a one-to-one ratio in the presence of suitable stereoselective catalysts can lead to the formation of a stereocomplex PLA (scPLA), which has a T_m (220–230 °C) approximately 50 °C higher than that of the homochiral polymers PLLA and PDLA (170–180 °C) [44]. In addition, it is known that certain mechanical properties, solvent resistance, and gas barrier property are improved by stereocomplex formation. Methods of producing scPLA are described in Chapter 1: Introduction, Section 1.2.1.1.1: Poly(lactic acid).

However, the thermomechanical properties of the materials obtained by blending the optical isomers of PLA are unsatisfactory in heat resistance and impact resistance, especially for use in automobile parts (2012, **US2012245292** A1, HYUNDAI MOTOR CO LTD). Presently, the industrial production of scPLA faces the following challenges (2010, **WO2010134454** A1, TOYO BOSEKI):

TABLE 3.1 Miscibilities of Biopolymers with Other Biopolymers

Biopolymer 1	Biopolymer 2	Other Component(s)	Miscibility	Literature Article
PLA	P3HB (2–20 wt%)		Immiscible	[3]
PLA (75, 50, 25 wt%)	P3HB (25, 50, 75 wt%)		Immiscible	[4]
PLA	P3HB (commercial grade) P3HB-UHMW		Immiscible (in the whole range)	[5]
PLLA (low M_w)	P3HB		Miscible (in the whole range)	[6]
PLA	P3HB ($M_w = 9400$) (≤50 wt%); P3HB ($M_w = 140,000$)		Miscible Immiscible	[7]
PLA	P3HB (low M_w) (≤50 wt%)		Miscible	[8]
PLA	PHBHV (HV = 40 mol%)		Immiscible	[9]
PLA (75 wt%)	P3HB (25 wt%)	Polyester plasticizer (Lapol® 108) (5, 7 wt%)	Miscible	[10]
PLA	P3HB	PVAc	Miscible	[11]
PLA (25, 50, 75%)	PHBHV (75, 50, 25%)		Immiscible	[12]
PLA (80, 60, 40, 20%)	PHBHV (20, 40, 60, 80%)		Immiscible	[13]
PLA	PHBHV		Immiscible (in the whole range)	[14]
PLA	PHBHV		Immiscible (in the whole range)	[15]
PLA	PHBHV (>30 wt%)		Immiscible	[16]
PLA	PHBHV		Immiscible	[17]
PLA	PHBHx		Immiscible	[18]
PLA (80, 20 wt%)	PHBHx (20, 80 wt%)		Immiscible	[19]
PLA	PCL		Immiscible	[20]
PLA	PBS		Immiscible	[21,22]
PLLA	PBES		Miscible partially	[23]
PLA	PBAT		Immiscible	[24]
PLLA	CS (30 wt%), HACS (30, 40 wt%)		Immiscible	[25]
PLLA	PIP		Immiscible	[26]
PLA	PPC		Miscible partially	[27]
P3HB	P3HB4HB (<50 wt%) P3HB4HB (>50 wt%)		Miscible Immiscible	[28]
P3HB (70 wt%)	Starch (30 wt%)		Miscible	[29]
P3HB	PCL		Immiscible	[30]
P3HB	PBA		Immiscible	[30]
P3HB (20–80 wt%)	PBS (20 wt%) PBS (>20 wt%)		Miscible partially Immiscible	[31]

Continued

TABLE 3.1 Miscibilities of Biopolymers with Other Biopolymers—cont'd

Biopolymer 1	Biopolymer 2	Other Component(s)	Miscibility	Literature Article
P3HB (10, 20, 30 wt%)	PPC (90, 80, 70 wt%)		Miscible	[32]
P3HB	CAB		Miscible	[33,34]
PHBHV (80, 50, 20 wt%)	PCL (20, 50, 80 wt%)		Immiscible	[35]
PHBHV	PPC		Immiscible	[36]
PHBHV (80, 70, 70, 50 wt%)	Starch (20, 30, 40, 50 wt%)		Immiscible	[37]
PCL	Starch		Immiscible	[38]
PCL	a-P3HB	PCL-*b*-PEG	Miscible	[39]
PCL	CAB		Immiscible	[40]
PBS	PES		Miscible partially	[41]
PBS	PBC		Immiscible	[42]
PBS	CDA		Miscible	[43]

a-PHB, atactic poly(3-hydroxybutyrate); CDA, cellulose diacetate; CS, corn starch; HACS, high-amylose corn starch; PBA, poly(butylene adipate); PBAT, poly(butylene adipate-*co*-terephthalate); PBC, poly(butylene carbonate); PBS, poly(butylene succinate); PBES, poly(butylene succinate-*b*-ethylene succinate); PCL-*b*-PEG, block copolymers of poly(ethylene glycol) (PEG) with poly(ε-caprolactone); PES, poly(ethylene succinate); P3HB, poly(3-hydroxybutyrate); P3HB4HB, poly(3-hydroxybutyrate-*co*-4-hydroxybutyrate); P3HB-UHMW, ultra-high-molecular-weight poly(3-hydroxybutyrate); PHBHx, poly(3-hydroxybutyrate-*co*-3-hydroxyhexanoate); PHBHV, poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate); PIP, poly(*cis*-1,4-isoprene); PDLA, poly(D-lactic acid), poly(D-lactide); PLA, poly(lactic acid), polylactide; PLLA, poly(L-lactic acid), poly(L-lactide); PPC, poly(propylene carbonate); PVAc, poly(vinyl acetate).

TABLE 3.2 Blends of Aliphatic (Co)Polyesters with Other Aliphatic (Co)Polyesters

Biopolymer 1	Biopolymer 2	Other Components 3	Patent
PLA (85-60 pbw)	Lactic acid-polyester (15-40 pbw)		**WO0170846** A1 (2001, DAINIPPON INK & CHEMICALS)
PLA (100 wt%)	PBS (10-50 wt%)	Biodegradable plasticizer (e.g. acetyltributylcitric acid, triacetin, dibutyl sebacate, triethyleneglycol diacetate) (5-25 wt%)	**WO9945067** A1 (1999, MITSUI CHEMICALS INC)
PLA (10-90 wt%)	Aliph. polyester (e.g. PBS, PBA, PBSA, PES, PEA, PESA) and/or aliphatic-aromatic polyester	Opt. compatibilizer	**US5883199** A (1999, UNIV MASSACHUSETTS)
PLA or PBS	PEOx (1-30 wt%)		**WO2008038648** A1 (2008, TOYO SEIKAN KAISHA LTD)
PLA-*b*-PAA (e.g. PBS)	PCL, PBS		**JPH08245866** A (1996, SHIMADZU CORP)
PLA (60-50 w.t%)	PCL (40-50 wt%)		**DE4300420** A1 (1994, BASF AG)
PLA	PCL (Placcel® H7, Daicel Chem), PBS (Bionolle® 1010, Showa High Polymer K.K), PBSA (Bionolle® 3010, Showa High Polymer K.K)		**JPH09111107** A (1997, MITSUBISHI PLASTICS IND)

TABLE 3.2 Blends of Aliphatic (Co)Polyesters with Other Aliphatic (Co)Polyesters—cont'd

Biopolymer 1	Biopolymer 2	Other Components 3	Patent
PLA (≥80 wt%)	PBS (≤10 wt%) and PCL (≤10 wt%)		**GB2488811** A (2012, CLEANING AND PAPER DISPOSABLES PLC)
PGA	Low mol. wt PLA (1-50 wt)		**WO2008004490** A1 (2008, KUREHA CORP)
PHA (60-85 wt%)	PLA (15-40 wt%)		**CN101775199** A (2010, SHENZHEN ECOMANN BIOTECHNOLOGY)
PHA (5-95 wt%)	PLA (95-5 wt %)	Plasticizer (2-67 pbw); reactive additive (0.05-5 wt%)	**WO2012141660** A1 (2012, USTAV POLYMEROV SAV)
P3HB	PCL	Copolymerization catalyst	**CA2029747** A1 (1991, AGENCY IND SCIENCE TECHN; JSP CORP)
P3HB	PCL	Additive (filler, nucleant, thermal stabilizer, processing aid)	**WO2007095708** A (2007, PHB IND SA)
P3HB	PCL	Poly(ε-caprolactone-*b*-ethylene glycol) as a compatibilizing agent	**JP2002069279** A (2002, DAICEL CHEM)
PHA (P3HB, P3HV, PHBHV)	P3HB, P3HV, PHBHV, PCL, PLA, PBS	Inorg. oxygen-contg. compound as a transesterification catalyst	**WO9411440** A2 (1994, ZENECA LTD)
PHBHx (80-20 wt%)	PBSA (20-80 wt%); e.g. Bionolle® 3001 (Showa Highpolymer Co, Ltd.)		**US2003204028** A1 (2003, PROCTER & GAMBLE)
Aliphatic polyester carbonate (99-50 pbw)	P3HB (1-50 pbw)		**JPH0827362** A (2003, MITSUBISHI GAS CHEM CO INC)

P3HB, poly(3-hydroxybutyrate); P3HV, poly(3-hydroxyvalerate); PAA, poly(alkylene alkanoate); PAPI, poly(methylene polyphenyl isocyanate); PBS, poly(butylene succinate); PBA, poly(butylene adipate); PBSA, poly(butylene succinate-*co*- adipate); PCL, poly(ε-caprolactone); PES, poly(ethylene succinate); PEA, poly(ethylene adipate); PEOx, poly(ethylene oxalate); PESA, poly(ethylene succinate-*co*- adipate); PGA, poly(glycolic acid) or polyglycolide; PHA, polyhydroxyalkanoate; PHBHx, poly(3-hydroxybutyrate-*co*-3-hydroxyhexanoate); PHBHV, poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate); PLA, poly(lactic acid) or polylactide.

1. Although it is advantageous to use a high-molecular-weight PLA in order to attain a practical strength, it is difficult to form scPLA efficiently during the course of crystallization from the combination of PLLA and PDLA, each having a high molecular weight of not less than 100,000 [45], and a large number of homocrystals of PLLA and PDLA, and a small number of stereocomplex crystals are formed by merely blending; and the formed material has an insufficient heat resistance.
2. Although it has been known that the efficiency of stereocomplex formation is improved by kneading in a molten state, degradation of the polymer caused by heat and drop of the T_m of scPLA due to transesterification between PLLA and PDLA also occur.

The above problems have been addressed by a number of patents in an effort to develop a scPLA having both a high molecular weight and a high stereocomplex crystal content.

JP2007100104 A (2007, TORAY INDUSTRIES) discloses a method of converting PLLA and PDLA into a block copolymer, which forms a scPLA with a high T_m (200 °C). The block copolymer has the segment lengths satisfying the condition: $Y < X/2$, where X is the weight average molecular weight (M_w) of the PLA block copolymer and Y is the M_w of one segment unit.

JP2003096285 A (2003, TORAY INDUSTRIES) discloses a method for improving the efficiency of stereocomplex formation by reducing the molecular weight of one PLA. The scPLA is obtained by melting and mixing PLLA and PDLA, wherein a relationship between the M_w of PLLA and M_w of PDLA satisfies the condition: $M_w(\text{PLLA}) - M_w(\text{PDLA}) \geq 50{,}000$.

JP2008291268 A (2008, TORAY INDUSTRIES) discloses a method for easily obtaining a PLA block copolymer that forms a scPLA having a high molecular weight and a high T_m. The PLA block copolymer preparation method comprises the following steps: (1) preparing each of PLLA and PDLA and each having a M_w of 9000–65,000; (2) mixing PLLA and PDLA obtained at step (1); and (3) solid state polymerizing the mixture of PLLA and PDLA obtained at step (2) at a temperature, T, in the range $120\,°C \leq T < T_m$.

JP2007191625 A (2007, TEIJIN LTD; MUSASHINO KAGAKU KENKYUSHO; MUTUAL CORP; KIMURA YOSHIHARU) discloses a method for producing a PLA composition containing scPLA or a PLA block copolymer from a mixture of PLLA and PDLA by copolymerizing another component to one PLA in order to improve the compatibility with the other PLA.

JP2008063356 A (2008, TEIJIN LTD) discloses a method for producing a PLA composition containing scPLA comprising the steps of: (1) making a mixture of PLLA and PDLA in a weight ratio of PLLA/PDLA of 10/90–90/10; and (2) heat treating them in a temperature range from a melting temperature derived from the homocrystal of PLA or above to a temperature lower than a melting temperature derived from the stereocomplex crystal.

All these methods aim at improving the PLA itself, and they are not using a general-purpose PLA. Moreover, there have not been proposed any solutions for the previously described problem of transesterification reactions between PLLA and PDLA in promoting stereocomplex formation or in melt molding resulting in lowering of T_m (2010, **WO2010134454**, A1, TOYO BOSEKI).

JP2007191548 A (2007, TEIJIN CHEMICALS; TEIJIN LTD) discloses a method of heat treating a mixture of PLLA and PDLA at a high temperature of 260–300 °C. However, the method has the disadvantages of consuming much energy and lowering the molecular weight by thermal decomposition of the PLAs, while the mechanical properties may be deteriorated or coloring may be induced (2010, **WO2011002004**, MITSUI CHEMICALS INC).

EP2112199 A1 (2009, PURAC BIOCHEM BV) discloses a PLA blend comprising PDLA and PLLA bonded to an anionic clay mineral and the other of PDLA and PLLA not bonded to the anionic clay.

3.2.1.1.2 Blending PLA with Other Aliphatic (co)polyesters

Blends of PLA with various flexible biodegradable polyesters such as poly(butylene succinate) (PBS), poly(ε-caprolactone) (PCL), poly(3-hydroxybutyrate) (P3HB), poly(hydroxybutyrate-*co*-3-hydroxyvalerate) (PHBHV), poly(butylene adipate-*co*-terephthalate) (PBAT), etc. have been reported in the literature (see Table 3.1). However, these materials prepared by simple blending still suffer from poor impact resistance due to the phase separation and poor interfacial adhesion between the two immiscible components.

In order to improve the impact resistance of PLA while maintaining its biodegradability, **WO0170846** A1 (2001, DAINIPPON INK & CHEMICALS) has disclosed the addition of a lactic acid polyester (15–40 pbw) to PLA (85–60 pbw) as an impact resistance modifier. The lactic acid polyester can be produced by any of the following methods:

1. reacting lactide and polyester component in the presence of a polymerization catalyst;
2. polycondensing lactic acid to obtain PLA, and then dehydrating and polycondensing PLA in the presence of polyester component; and
3. obtaining polylactic acid–polyester block copolymer by melting and kneading PLA (e.g., Lacty®, Shimadzu Co) and polyester component in the presence of a transesterification catalyst.

The polyester component itself is obtained by esterification of dicarboxylic acid and diol. Particularly preferred dicarboxylic acids are dimeric acids having 20–45 carbon atoms (e.g., Empol® 1061 or 1062, Cognis Japan, Ltd.), since a polyester composition having superior transparency and superior impact resistance can be obtained in the case of adding the lactic acid polyester derived from a polyester component that uses this compound to PLA.

Although **WO0170846** A1 provides a PLA composition of improved impact resistance, this method requires polymerization starting from the initial lactide to synthesize an impact-resistant copolyester of PLA, and needs further blending and extrusion so as to improve the impact resistance of PLA. Therefore, besides involving a process that is too complex to have high industrial applicability, this technical means will also significantly compromise the transparency of PLA and limits its commercial applications (2010, **US2010167048**, FAR EASTERN NEW CENTURY CORPORATION).

DE4300420 A1 (1994, BASF AG) discloses a PLA-based blend by blending PLA (50–40 wt%) with an aliphatic polyester, such as PCL (50–40 wt%) in the melt, granulating, cooling, drying, crystallizing by raising the temperature, and annealing the crystallized granules for 2–50 h at 5–20 °C below the T_m of PLA, to give a block copolymer. The block copolymer has increased flexibility and is suitable for film production.

JPH08245866 A (1996, SHIMADZU CORP) discloses a method of blending a PLA-based copolymer with a flexible aliphatic polyester (≤50 wt%) such as PCL or PBS. The PLA-based copolymer is prepared by block copolymerizing an aliphatic polyester such as poly(alkylene alkanoate) (PAA) comprising an aliphatic dicarboxylic acid and linear diol with PLA. The aliphatic polyester used for the copolymer is the same or nearly the same with the flexible aliphatic polyester acting as a plasticizer. Due to the chemical affinity between the PLA-based copolymer and the flexible aliphatic polyester, the surface staining of the composition due to plasticizer exudation and the loss of clarity and gloss of molded items obtained from the composition can be prevented.

JPH09111107 A (1997, MITSUBISHI PLASTICS IND) discloses a biodegradable polymer film prepared from a polymer blend comprising PLA and a flexible aliphatic polyester having a $T_g \leq 0\,°C$. Preferred aliphatic polyesters are PCL, PBS, or poly(butylene succinate adipate (PBSA); corresponding commercial products are Placcel® H7 (Daicel Chem), Bionolle® 1010 (Showa High Polymer K.K) and Bionolle® 3010 (Showa High Polymer K.K). The film is claimed to have good impact strength, dimensional stability, and chemical stability under heat and humidity conditions.

However, in order to provide sufficient flexibility (an elastic modulus of 1000 MPa or less) for PLA, the last two techniques require the addition of a large amount of the flexible aliphatic polyester, for example, ≥60 wt% PBS. As a result, the above characteristics of PLA are impaired.

WO9945067 A1 (1999, MITSUI CHEMICALS INC) discloses blends of PLA (100 wt%) and PBS (10–50 wt%), with the addition of a biodegradable plasticizer (5–25 wt%). The disclosed blends are claimed to provide significant improvement in tear resistance and in the balance of mechanical properties in film manufactured from such blends. However, the described films are not transparent and have fairly low tear strengths, of the order of 120 g (measured according to JIS P8116). In addition, the presence of a plasticizer limits use of the film in contact with food products and it ages rather quickly, for use as an agricultural mulch film (2002, **WO02059199** A1, NOVAMONT SPA) (see also Chapter 5: Compounding; Section 5.5.2.1: Plasticizers).

US5883199 A (1999, UNIV MASSACHUSETTS) discloses blends of PLA (10–90 wt%) and aliphatic or aliphatic–aromatic polyester (90–10 wt%) with the polyester imparting ductility to PLA by forming either a continuous or co-continuous phase. Suitable aliphatic polyesters include PBS, poly(butylene adipate) (PBA), PBSA, poly(ethylene succinate) (PES), poly(ethylene adipate) (PEA) and poly(ethylene succinate adipate) (PESA). A preferred aliphatic polyester is PBS, and a suitable commercial product can be selected from the Bionolle® series (Bionolle® 1000, 2000, 3000, 6000, and 7000). Optionally, a compatibilizer may be added to the blends. PLA and the aliphatic polyester are immiscible, but synergistically compatible in the blends, i.e., the properties of the blends are greater than that of the mixtures of PLA and aliphatic polyester determined by the additive rule of mixture. Compared to PLA alone, the blend has improved tensile and mechanical properties such as stiffness, toughness, and elongation at break, as well as excellent biodegradability and aging properties. The tear resistance of the described blends is, however, very poor (2002, **WO02059199** A1, NOVAMONT SPA).

WO2008038648 A1 (2008, TOYO SEIKAN KAISHA LTD) discloses a biodegradable polymer blend comprising: an aliphatic polyester (A) and an aliphatic polyester (B) (1–30 wt%), which is biodegradable at a higher degradation rate than that of the aliphatic polyester (A) and which has a melt viscosity of 50 Pa s or less (measured at shear rate of 1 rad/s at 190 °C) or a solution viscosity (η_{inh}) of 0.25 dl/g or less (measured at a concentration of 0.4 g/dl at 30 °C in a solvent of *m*-chlorophenol and 1,2,4-trichlorobenzene mixed at a weight ratio of 4:1). Preferably, the aliphatic polyester (A) includes PLA or PBS and the aliphatic polyester (B) includes poly(ethylene oxalate) (PEOx).

GB2488811 A (2012, CLEANING AND PAPER DISPOSABLES PLC) discloses a method of producing a biodegradable polymer blend comprising: providing PLA (≥75 wt%); blending between 0.5 wt% and 15 wt% of a first polyester having an average molecular weight of not more than 40,000 and a melt flow index (MFI) >7 g/10 min (measured with 2.16 kg at 80 °C) with the PLA; blending 0.5–15 wt% of a second polyester having an average molecular weight greater than that of the first polyester and an MFI less than the first polyester with PLA and the first polyester. The preferred embodiment consists of ≥80 wt% of PLA, ≤10 wt% of PBS and ≤10 wt% of PCL.

3.2.1.2 Blends of Poly(Glycolic Acid)

WO2008004490 A1 (2008, KUREHA CORP) discloses a method of improving the properties of poly(glycolic acid) (PGA) including lowering of its crystallization rate, by blending a low-molecular-weight PLA with PGA. A significant decrease in the crystallization rate can even be obtained with a PLA amount of 1 wt%. Thus, a blend with a weight ratio of PGA/PLA = 99/1 exhibited a crystallization temperature during heating[3] $T_{c1} = 96\,°C$ and a crystallization temperature during cooling[4] $T_{c2} = 137\,°C$, that is, a higher T_{c1} and a lower T_{c2} than PGA ($T_{cp1} = 93\,°C$ and $T_{c2} = 146\,°C$), whereby a slower crystallization rate was confirmed (see Chapter 2: Properties; Section 2.1.1.2: Crystallinity and Morphology). This means that the crystallization speed is lowered to about 2/3–1/10 of that of PGA alone, leading to a remarkably increased formability as represented by remarkable suppression of whitening during forming even in the case of forming of the composition alone, and further easy accomplishment of composite forming with a wide range of thermoplastic polymers having a diversity of thermal properties also in the case of composite forming (e.g., lamination) with another thermoplastic polymer. Also in the range of PGA/PLA in excess of 95/5 and up to 50/50, a further improvement in formability and an improvement in moisture resistance can be attained.

---

[3] Exothermic peak detected in a DSC thermogram during the course of heating at a heating rate of 10 °C/min.

[4] Exothermic peak detected in a DSC thermogram during the course of cooling at a cooling rate of 10 °C/min.

3.2.1.3 Blends of Polyhydroxyalkanoates

Polyhydroxyalkanoates (PHAs) are known for their high biodegradation rate in most environmental conditions (aerobic and anaerobic), owing to their intrinsic enzymatic nature. This makes them desirable components in blends with other biodegradable polyesters, as they contribute to promote the blends' biodegradability and expand the means by which they may be disposed of. As a result, the blends exhibit outstanding mechanical integrity and strength during use, including under wet conditions, yet they easily break down in most encountered environments, over a fairly short amount of time (2003, **US2003204028** A1, PROCTER & GAMBLE).

WO2004076582 A1 (2004, METABOLIX) discloses a method of preparing a PHA blend comprising blending a first PHA with a second PHA, wherein: the first PHA is a copolymer consisting of a comonomer 1-A and a comonomer 1-B; the second PHA is a copolymer consisting of a comonomer 2-A and a comonomer 2-B; the first PHA copolymer and the second PHA copolymer are the same copolymer, in which the ratio of comonomer 1-A:comonomer 1-B in the first PHA is different from the ratio of comonomer 2-A:comonomer 2-B in the second PHA; comonomer 1-A and comonomer 2-A are both 3-hydroxybutyrate; the first PHA and the second PHA are miscible; and the first PHA has a first T_{g1} and the second PHA has a second T_{g2}, wherein the difference $T_{g1} - T_{g2} \geq 5\,°\text{C}$.

A number of studies on P3HB/PLA and PHBHV/PLA blends have been reported [3–16,46,47]. According to them, P3HB and PHBHV are immiscible with PLA at all concentrations; especially, PLA is immiscible with P3HB, when both components have high molecular weights. Further, it was found that mechanical properties of the blends are intermediate between those of the individual pure components [22]. Moreover, most of these blends cannot be simply mixed with a third polymer since almost always a steep decrease in the mechanical properties values is observed.

PHA/PLA blends have also formed the object of numerous patents.

CN101775199 A (2010, SHENZHEN ECOMANN BIOTECHNOLOGY) discloses a PHA/PLA blend comprising PHA (60–85 wt%) and PLA (15–40 wt%). The PHA/PLA blend is claimed to have better toughness and high rigidity, and, thereby, can be widely applied to injection molding products, such as cosmetic bottles, preservation boxes, and display shells and plates for construction engineering and the like, and has higher economic value.

WO2012141660 A1 (2012, USTAV POLYMEROV SAV) discloses a biodegradable polymer composition containing PHA (5–95 wt%) and PLA (95–5 wt%) with addition of 2–67 parts of plasticizer or mixture of plasticizers per 100 parts of the polymeric blend. The invention covers also composition containing 0.05–5 wt% of a reactive additive. Plasticizers are selected from esters of citric acid, esters of glycerol, esters of phosphoric acid, esters of sebacic acid, and other liquid organic low molecular polyesters. The reactive additive is selected from acrylic polymers, epoxidized acrylic polymers, diisocyanates and their derivatives, epoxidized oils, oligomeric copolymers of various monomers with glycidyl methacrylate, and other species.

Blends of PHAs with synthetic biodegradable polyesters have also been reported in literature [30,31,39,48–50]. By blending PHAs with fossil fuel–based biodegradable polyesters such as PCL and PBS, materials with improved properties and processing can be obtained. Of particular interest are blends with faster crystallization rates, increased rates at which the thermoplastic loses tackiness, as well as the increased mechanical strength of the resin during processing and increased strength of the finished thermoplastic product.

Blends of P3HB and PBS showed some limited miscibility at low concentrations (P3HB/PBS = 20/80) and immiscibility at all other concentrations (40/60, 60/40, 80/20) [31].

Blends of PHBHV and PCL were found to be immiscible at all concentrations (20/80, 50/40 wt%) [35]. Blends of P3HB and PCL were also immiscible at all concentrations, but they formed mechanically compatible films containing phase-separated partially crystalline domains. Their mechanical properties varied considerably with composition [48]. Blending, however, did not readily resolve the issue of mechanical fragility and lack of flexibility of such high crystallinity PHAs, while maintaining the biodegradable nature of these materials.

In conclusion, incompatibility between PHAs and fossil fuel–based biodegradable polyesters remains a major problem. Furthermore, the addition of a nonrenewable biodegradable polyester such as PCL in large quantity reduces the weight fraction of the renewable P3HB in the overall blend composition.

P3HB has been blended as well with natural rubber to improve its toughness [51]. But these blends have dropped drastically elastic modulus and tensile strength.

Several patents have also made claims with regard to a blending approach for improving the mechanical properties of PHAs by disclosing blends with synthetic biodegradable polyesters, but with only limited success.

CA2029747 A1 (1991, AGENCY IND SCIENCE TECHN; JSP CORP) discloses a biodegradable polymer composition and a molded product formed thereof comprising P3HB and PCL. The molded product may be produced by melt mixing a blend of P3HB and PCL with a copolymerization catalyst to copolymerize a portion of the PCL with a portion of P3HB, thereby to obtain a P3HB/PCL copolymer-containing melt, which is subsequently shaped into a desired form.

WO9411440 A2 (1994, ZENECA LTD) discloses a polymer composition comprising a first PHA component and a second different aliphatic polyester component and an inorganic oxygen containing compound. The inorganic oxygen-containing compound may be acting as a transesterification catalyst. It is an oxy compound of a metal from group IIA, IIIA, or IVA of the periodic table or a metalloid having a valency of at least 3 from a B group of the periodic table. The first polyester component is selected from P3HB, poly(3-hydroxyvalerate) (P3HV), or PHBHV. The second polymer component is selected from P3HB, P3HV, PHBHV, PCL, PLA, or PBS.

The blends disclosed in the aforementioned patent applications, **CA2029747** A1 and **WO9411440** A2, fall short in exhibiting the ductility and toughness desired in a large variety of applications, as evidenced by the mechanical properties disclosed in their examples (2003, **US2003204028** A1, PROCTER & GAMBLE).

JP2002069279 A (2002, DAICEL CHEM) discloses a compatible polyester blend comprising P3HB, PCL, and poly(ε-caprolactone-*b*-ethylene glycol) as a compatibilizing agent. The blend has improved flexibility such as elongation at break and tensile strength, in comparison to an incompatible blend consisting of P3HB and PCL, which are immiscible with each other.

US2003204028 A1 (2003, PROCTER & GAMBLE) discloses a biodegradable polyester blend containing 80–20 wt% of a PHA copolymer comprising at least two randomly repeating units, and 20–80 wt% of a PAA. Examples of blends include poly(3-hydroxybutyrate-*co*-3-hydroxyhexanoate) (PHBHx) with PBSA (e.g., Bionolle® 3001, a PBSA containing a fraction of urethane linkages, of Showa Highpolymer Co, Ltd.). The PHA and PAA blend is claimed to have remarkable mechanical strength and toughness, high biodegradation rate, ease of processability, and potentially low cost. The latter point is supported by the fact that both PHA and PAA, such as PBS for instance, are largely based upon C4-chemistry and can in principle be derived from commodity renewable resources, via bacterial synthesis or fermentation followed by polycondensation reactions.

JPH0827362 A (2003, MITSUBISHI GAS CHEM CO INC) discloses a biodegradable polymer blend comprising: (1) an aliphatic polyester carbonate (99–50 pbw) obtained by condensing an aliphatic dibasic acid, preferably succinic acid, with an aliphatic dihydroxy compound, preferably 1,4-butanediol, and a diaryl carbonate (e.g., diphenyl carbonate), and (2) P3HB (1–50 pbw). The biodegradable blend is claimed to have excellent mechanical strength, flowability, and injection moldability.

WO2007095708 A (2007, PHB IND SA) discloses biodegradable polymer blend, comprising P3HB or copolymers thereof and PCL and, optionally, at least one additive defined by a filler, nucleant, thermal stabilizer, and processing aid. The blend resulting from the mixture of the biodegradable polymers, P3HB and PCL, and at least one additive, can be utilized in the manufacture of injected food packages, injected packages for cosmetics, tubes, technical pieces, and several injected products.

3.2.2 Blending Aliphatic–Aromatic Copolyesters with Aliphatic (co)polyesters

Biodegradable polyester blends composed of (1) aliphatic–aromatic copolyesters and (2) aliphatic (co)polyesters selected from the group consisting of PLA, PCL, and PHA are known (1997, **WO9615173** A1, BASF AG; 1999, **US5883199** A, UNIV MASSACHUSETTS). Ideally, these blends combine the desirable properties of the individual components, for example, the generally good processing and mechanical properties of the aliphatic–aromatic copolyesters with the usually relatively low cost availability and environmentally nonhazardous preparation and disposal of the aliphatic (co)polyesters.

However, it is often difficult in practice to achieve the desired combination of properties. PLA and PHAs require complicated predrying before mixing in order to prevent degradation of the polymers. The mixtures have inadequate bubble stability in particular for film applications. This applies particularly to mixtures with more than 20 wt% of PLA or PHAs and less than 80 wt% of aliphatic–aromatic copolyester. Furthermore, thick films in particular manufactured from the mixtures of the prior art have inadequate puncture resistance. This arises especially in the case of thick films, which mainly comprise PLA or PHA.

PLA and PBAT are immiscible (see Table 3.1) but have complementary properties. PLA is high in tensile strength and elastic modulus (63 MPa and 3.4 GPa, respectively) but brittle (elongation at break 3.8%), while PBAT is flexible and tough, therefore, blending PLA with PBAT becomes a natural choice to improve PLA properties without compromising its biodegradability [24]; while PLA can be toughened by flexible PBAT, this happens at the cost of a certain degree of strength and modulus loss [52].

WO02059199 A1 (2002) and **EP1227129** A1 (2002) of NOVAMONT SPA disclose a blend of three biodegradable polyesters including an aromatic–aliphatic polyester (A) with a T_m of 50–170 °C, an aliphatic polyester (B) with a $M_w > 40{,}000$ and a T_m of 40–170 °C and PLA (C) containing at least 75% of L-lactic and/or D-lactic acid with a $M_w > 30{,}000$. The concentration of A varies, with respect to (A + B) in the range of 40–70 wt%, and the concentration of C with respect to (A + B + C) is 5–30 wt%. Preferably, (A) is PBAT (Ecoflex® 0700) and (B) is poly(butylene sebacate) (PBSE) or PCL.

US2005137332 A1 (2005, EASTMAN CHEMICAL COMPANY) discloses a polymer blend comprising 70–80 wt% of at least one flexible biodegradable polymer (A) having a $T_g < 0$ °C and 30–20 wt% of at least one rigid biodegradable polymer (B) having a $T_g > 10$ °C; wherein said polymer blend has a notched Izod impact strength of at least 7.5 ft-lbs/in. or 400.5 J/m (measured according to ASTM D256). Exemplary flexible biodegradable polymers (A) are PCL, certain aliphatic–aromatic copolyesters, PHBHV, PBS, PES, PBSA. Exemplary rigid biodegradable polymer (B) are PLA, copolyester plus lactic acid (CPLA), and PGA. The technique can be divided into four main systems: (1) A/B = (aliphatic–aromatic copolyester)/(PLA or CPLA); (2) A/B = PCL/P3HB; (3) A/B = PHBHV/PGA; and (4) A/B = (PBS or PES or PBSA)/PLA. Although in this technique the blending of biodegradable polymers such as aliphatic–aromatic copolyester with PLA can improve the impact resistance of PLA while maintaining the original biodegradability, it has the disadvantage of compromising the transparency (2010, **US2010167048**, FAR EASTERN NEW CENTURY CORPORATION).

WO2006074815 A1 (2006, BASF AG) discloses a biodegradable polyester mixture comprising: (1) at least one aliphatic–aromatic copolyester (5–80 wt%); (2) at least one biodegradable (co-)polyester, selected from the group comprising PLA, PCL, PHAs, and PAAs (20–95 wt%); (3) 0.1–15 wt% (a) of an epoxide-containing copolymer made from styrol, acrylate ester, and/or methacrylate ester, (b) of a bisphenol-A-epoxide or an epoxide-containing natural oil, fatty acid ester, or fatty acid amide; (4) additive (0–15 wt%); and (5) inorganic or organic fillers (0–50 wt%). The disclosed polyester mixture differs from that of the previous patent **WO9615173** A1 in particular via the branching agent (component 3).

CN102504506 A (2012, UNIV SHANGHAI JIAOTONG) discloses a method for improving the blending of PLA with PBAT by adding a compatibilizer. The compatibilizer is added after melting the PLA/PBAT and mixed at 140–220 °C for 5–60 min to obtain the modified blend. The amount of compatibilizer is 0.001–90 wt% of the PLA/PBAT blend. The compatibilizer contains an isocyanate group of the formula R-$(NCO)_n$ in the molecular chain, wherein R is organic group and $n > 2$. A preferred compatibilizer is polymethylene polyphenyl isocyanate (PAPI). The disclosed method has the advantage of lowering surface tension, reducing dispersed phase size, and improving two-phase compatibility.

WO2009137058 A1 (2009, METABOLIX INC) discloses blends of PHAs and biodegradable aliphatic–aromatic polyesters, methods of making such compositions, and articles and pellets formed from such blends. The biodegradable aliphatic–aromatic polyester is selected from PBAT, poly(tetramethylene adipate-*co*-terephthalate) (PTeMAT), poly(ethylene adipate terephthalate) (PEAT), poly(butylene succinate terephthalate) (PBST), or poly(ethylene succinate terephthalate) (PEST); preferably, PBAT is used. Examples of commercially available aromatic/aliphatic polyesters are PBAT and PTeMAT, sold correspondingly as Ecoflex® (BASF) and Origo-Bi® (Novamont; ex EASTAR BIO®, formerly Eastman Chemical).

Blends of PBAT with PHAs such as P3HB are used for producing food packages and, particularly, for packaging food to be frozen. PBAT improves the performance of these products, since it retains the freshness, taste, and aroma in hamburger boxes, snack trays, disposable coffee cups, packages for meat or fruit, and fast-food packages. PBAT is water resistant, tear resistant, flexible, allows printing thereon, and can be thermo welded.

Some exemplary blends of aliphatic polyesters with aliphatic–aromatic copolyesters are presented in Table 3.3.

3.2.3 Blending Aliphatic Polycarbonates with Aliphatic Polyesters

A typical aliphatic polycarbonate is poly(propylene carbonate) (PPC). PPC has attracted much attention because of its environmental friendly nature such as utilizing the greenhouse gas waste and biodegradability (see Chapter 1: Introduction; Section 1.6.2 Poly(propylene carbonate)). However, PPC exhibits poor mechanical properties and thermal stability. To improve the plasticity of PPC and its processability, some blending systems containing PPCs have been studied.

TABLE 3.3 Blends of Aliphatic (co)polyesters with Aliphatic–Aromatic Copolyesters

Aliphatic (co)polyester	Aliphatic–Aromatic Copolyester	Other Components 3	Patent
PLA (5–30 wt%)	PBAT (e.g., Ecoflex® 0700) (20–60 wt%) and PBSE (30–48 wt%) or PCL (40 wt%)		**WO02059199** A1 (2002, NOVAMONT SPA); **EP1227129** A1 (2002, NOVAMONT SPA)
PLA	PBAT (e.g., Ecoflex® FBX7011)	Compatibilizer (0.001–90 wt%) (e.g., PAPI)	**CN102504506** A (2012, UNIV SHANGHAI JIAOTONG)
PHA (5–95 wt%, pref. 10–40 wt%)	PBAT (Ecoflex®) or (PTeMAT (Origo-Bi®, ex Eastar Bio®)		**WO2009137058** A1 (2009, METABOLIX INC)

PBAT, poly(butylene adipate terephthalate); PBSE, poly(butylene sebacate); PCL, poly(ε-caprolactone); PLA, poly(lactic acid), polylactide; PAPI, polymethylene polyphenyl isocyanate; PTeMAT, poly(tetramethylene adipate-*co*-terephthalate).

Yang et al. reported that in P3HB/PPC blends P3HB showed complete miscibility with PPC for the P3HB/PPC weight ratios of 30/70, 20/80, and 10/90. The brittleness of P3HB was reduced apparently by blending with abundant PPC [32]. Li et al. reported that a PHBHV/PPC (30/70 weight ratio) melt blend incurs a certain extent of transesterification reaction, and the crystallinity and linear growth rate of spherulites of PHBHV could decrease by the addition of PPC [53]. Tao et al. reported that PPC/PHBHV blends were immiscible, but the addition of PHBHV could improve the thermal stability of PPC. Ma et al. reported a PLA/PPC blend system in which PLA and PPC were partially miscible but compatible to some extent owing to similar chemical nature of the blend components [27].

US2007117908 A1 (2007, CHANGCHUN APPLIED CHEMISTRY) discloses a method for preparing a blend of PPC, comprising the steps of: uniformly mixing 50–98 pbw of a PPC, 2–50 pbw of a PBS or PBSA, 1 pbw of a maleic anhydride, and 0.5–3.0 pbw of SiO_2 in a high speed blender; vacuum drying the mixture; and mixing the vacuum-dried mixture in a Banbury mixer. The disclosed blend is claimed to reduce the brittleness and cold flowability of PPC.

3.2.4 Blending Cellulose Derivatives with Biodegradable Polymers

Cellulose esters are characterized by high stiffness, low ductility, good clarity, and narrow thermal processing window. They also have moderate heat and impact resistance. However, the general rigid and brittle nature of cellulose esters resulted in limited applications (2012, **US2012015142** A1, KIMBERLY CLARK CO).

In order to improve the performance of cellulose esters, blending cellulose derivatives with other polymers has been explored. The prior art blends of cellulose ester with biodegradable polymers are prepared by solution blending. Solution-prepared films typically have different morphology and properties from the films of the same composition produced by melt processing. This is because melt processing cannot achieve the molecular level mixing that can be achieved in a solution blending process. However, the solution blending method is not preferred due to the use and recovery of solvents as well the corresponding environmental impact (2011, **US2011152818** A1, KIMBERLY CLARK CO).

The short carbon chain cellulose alkanoate derivatives such as cellulose acetate and cellulose propionate have high T_ms, making them unsuitable for blending with PHA; for example, most of these cellulose esters have T_ms of over 230–240 °C or higher, while P3HB has T_m of 177 °C and a thermal decomposition temperature of about 200 °C. Therefore, most cellulose esters, even some cellulose acetate butyrate (CAB) compositions having high T_m, cannot be melt blended with P3HB due to decomposition of the PHA (2011, **US2011152818** A1, KIMBERLY CLARK CO).

US2011152818 A1 (2001, KIMBERLY CLARK CO) discloses a melt processed thermoplastic polymer film made from a blend of 5–95 wt% of a thermoplastic cellulose having a T_m of 100–200 °C, and 5–95 wt% of PHAs with an average molecular weight of at least 20,000 g. Commercially available thermoplastic cellulose derivatives are cellulose esters and ethers such as cellulose acetate (CA), cellulose acetate propionate (CAP), cellulose butyrate, and cellulose acetate butyrate (CAB), methyl cellulose, ethyl cellulose, hydroxypropyl cellulose, etc. PHA is selected from P3HB, PHBHV, poly(3-hydroxybutyrate-*co*-4-hydroxybutyrate) (P3HB4HB), PHBHx, and poly (3-hydroxybutyrate-*co*-3-hydroxyoctanoate) (PHBO).

WO9209654 A2 (1992, EASTMAN KODAK CO) discloses binary blends of either cellulose esters and aliphatic–aromatic copolyesters, or cellulose esters and aliphatic polyesters, as well as ternary blends of cellulose esters, aliphatic polyesters, and/or aliphatic–aromatic copolyesters and a nonbiodegradable polymer as well as fibers, molded objects, and films prepared therefrom. The binary blends comprise 5–98 wt% of a cellulose ester having a DS of 1.7–2.75 and 2–95 wt% of an aliphatic polyester.

The ternary blend comprises 4–97 wt% of a cellulose ester having a DS of 1.7–40, 2–95 wt% of an aliphatic polyester and/or aliphatic–aromatic copolyester, and 1–94 wt% of a nonbiodegradable polymer such as PVAc or ethylene-vinyl acetate copolymer.

The cellulose ester is selected from cellulose acetate (CA), cellulose propionate (CP), cellulose butyrate (CB), cellulose acetate propionate (CAP), cellulose acetate butyrate (CAB), or cellulose propionate butyrate. The aliphatic polyester is selected from P3HB, PHBHV, poly(hexamethylene glutarate), poly(hexamethylene adipate), poly(ethylene succinate) (PES), poly(butylene glutarate), poly(butylene adipate) (PBA), poly(butylene succinate) (PBS), poly(ethylene glutarate), poly(ethylene adipate) (PEA), poly(diethylene glutarate), poly(diethylene adipate), poly(diethylene succinate), or poly(hexamethylene succinate). The aliphatic–aromatic copolyester is selected from poly(tetramethylene glutarate-*co*-terephthalate), poly(ethylene succinate-*co*-terephthalate) (PEST), poly(ethylene adipate-*co*-terephthalate), poly (tetramethylene adipate-*co*-terephthalate) (PTeMAT), or poly(hexamethylene adipate-*co*-terephthalate).

JP2003082160 A (2003, TORAY INDUSTRIES) discloses a method of improving the moldability of cellulose esters by blending PLA (10–50 wt%) having a M_w of 1000–20,000, as a plasticizer, with cellulose esters (30–90 wt%). The cellulose esters are chosen from cellulose acetate (CA), cellulose acetate propionate (CAP), CAB, and/or cellulose acetate phthalate. It is preferable that the degree of substitution of hydroxyl group in the cellulose (average number of hydroxyl group substituted with cellulose ester), DS is 0.5–2.9 with respect to glucose unit. Furthermore, in view of compatibility or ability to be mixed with PLA, it is preferable that the degree of substitution is 1.5–2.9, more preferable 2.0–2.8. When the substitution degree is low (DS < 1), the cellulose ester is prone to biodegradation.

WO2004087812 A1 (2004, TORAY INDUSTRIES) discloses a PLA-based composition for forming, e.g., biaxially stretched film and molded articles therefrom, by blending PLA having a $M_w > 50{,}000$, and cellulose ester. The PLA and cellulose ester are solvated and/or have a phase structure with 0.01 μm or smaller in the PLA-based composition. The cellulose ester is selected from CA, cellulose diacetate, cellulose triacetate, CAP, CAB, and cellulose acetate phthalate.

Example: PLA (95 wt%) of $M_w = 160{,}000$ and CAP (5 wt%) having an acetate degree of substitution DS = 0.1, were mixed and supplied to twin screw extruder set at 225 °C. The raw material had light transmittance of 83% in visible light wavelength of 400 nm and $T_g = 75$ °C. The raw material was extruded to form a pellet. The pellet was molded to form a biaxially stretched film. The film had crystallinity degree of 67%, haze of 21%, tensile strength of 70 MPa, and elasticity of 10%.

US2012015142 A1 (2012, KIMBERLY CLARK CO) discloses a tertiary blend of a poly(alkylene carbonate) (1–95 wt%), a thermoplastic cellulose derivative (95–1 wt%), and a PHA compatibilizer (1–20 wt%).

3.2.5 Blending Starch with Biodegradable Polymers

The multitude of biopolymer blends proposed in the prior art are to a great extent constructed on the basis of starch or use starch as a minority component. Starch is a particularly suitable biopolymer because it is derived from renewable resources, is readily available, and has a favorable price (see Chapter 1: Introduction; Section 1.11.2: Starch). Because native starch is hardly suitable as a technically usable polymer, it is preferred to use the so-called thermoplastic starch (TPS) formed by melt mixing starch with a plasticizer such as glycerol or water) or destructurized starch.

EP0542155 A2 (1993, TOMKA IVAN) discloses a method in which TPS (20–50 vol.%) and a cellulose ester (30–60 vol.%) are thoroughly blended with a softener or a phasing agent (5–25 vol.%) at a temperature of approximately 160–200 °C, and the blend, which is at least almost homogenous, is then extruded or processed by injection molding. The cellulose ester may be cellulose acetate, cellulose propionate, cellulose butyrate, or a mixture thereof. An exemplary phasing agent is epoxidized soybean oil and an exemplary softener is acetyl triethyl citrate, respectively. The addition of the cellulose ester results in a biopolymer blend with enhanced resistance to moisture having mechanical properties that are markedly superior to those of pure TPS. However, this method yields a material with limited tensile strength (2001, **EP1097967** A2, NIPPON CATALYTIC CHEM IND).

Techniques have also been proposed for the blending of starch, a chemically modified starch, and/or TPS with an aliphatic polyester in order to improve cost, formability, and biodegradability of products. **WO9219680** A1 (1992, NOVAMONT SPA); **EP0444880** A2 (1993, AGENCY IND SCIENCE TECHN, CHUO KAGAKU KK); **EP0535994** A1 (1993, AGENCY IND SCIENCE TECHN, RES INST INNOVATIVE TECH EARTH, CHUO KAGAKU KK); **JPH05331315** A (1993, AGENCY IND SCIENCE TECHN, CHIKYU KANKYO SANGYO GIJUTSU); and **JPH08188671** A (1996, AGENCY IND SCIENCE TECHN; CHIKYU KANKYO SANGYO GIJUTSU) disclose biopolymer blends consisting essentially of starch and an aliphatic polyester having a T_m of 45–130 °C, for example, PCL, where the starch is preferably destructurized with water. The blends are produced by kneading a starchy substance selected from nongelatinized granular starch and gelatinized starch and the aliphatic polyester at a temperature higher than the T_m of the aliphatic polyester in the presence of water in an amount of 1–45 wt% based on the weight of the starchy substance.

However, this process can induce the hydrolysis of the aliphatic polyester by the water, weakening it. Moreover, this process is, in general, insufficient to make compatible the aliphatic polyester and the starch. In addition, aliphatic polyesters have only moderate material properties, for example, with regard to T_m, tensile strength, etc., which is why even corresponding blends using TPS have only moderate properties, thereby placing in question the possibility for use in the field of engineering plastics. Furthermore, starch is quite hydrophilic relative to thermoplastic polymers with which melt is blended. Melt mixing of starch with other thermoplastic polymers therefore typically results in the formation of multiphase morphology having a high interfacial tension that can negatively impact the physical and mechanical properties of the resulting polymer composition. Compatibilizers are often used to reduce the degree of phase separation that can occur when a biodegradable polyester is melt blended with starch [54].

Furthermore, such polymer compositions also tend to suffer from poor processing behavior, particularly in their conversion into products such as film or sheet. For example, conventional polyester/starch polymer compositions typically exhibit poor processing behavior during blown film production. In particular, the polymer compositions may be prone to bubble instability, excessive film blocking, shear sensitivity of the polymer melt, thermal degradation of the polymer melt, evolution of volatiles, poor melt strength, tackiness of the polymer melt, and a narrow processing window. Such processing problems generally increase scrap rates and reduce output. Attempts have been made to address such processing problems. For example, slower and gentler processing techniques can be adopted, and specialized processing equipment has been developed. However, such measures either reduce throughput and/or add cost to the manufacturing process (2010, **WO2010051589** A1, TRISTANO PTY LTD).

WO2010051589 A1 (2010, TRISTANO PTY LTD) addresses or ameliorates one or more of the aforementioned disadvantages or shortcomings associated with existing compositions and/or their method of manufacture by disclosing a biodegradable polymer composition comprising the following components (1)–(6) and/or product(s) formed from a reaction between the components: (1) one or more biodegradable polyesters (20–80 wt%); (2) polysaccharide (2–60 wt%); (3) polymer having pendant carboxylic acid groups (0.3–25 wt%); (4) transesterification catalyst (0.005–0.475 wt%); (5) polyepoxide (0.1–1 wt%); and (6) fatty acid sodium salt (0.01–0.5 wt%). In some embodiments, the polysaccharide (2) is in the form of TPS. In that case, the biodegradable polymer composition will also comprise one or more plasticizers in an amount of up to about 2.5 wt%. The biodegradable polyesters are selected from PCL, PLA, P3HB, PES, PBAT, PHBHV, PBS, PBA, CAB, CAP, and combinations thereof. Suitable types of polymer having pendant carboxylic acid groups include ethylene acrylic acid copolymer, ethylene acrylic acid–vinyl alcohol copolymer, poly(acrylic acid), poly(methacrylic acid), ethylene-methacrylic acid copolymers, poly(acrylamide-acrylic acid), and combinations thereof.

Examples:

Example 1: Preparation of masterbatch

35 kg of acetic ester starch (DS = 0.5) having a water content of less than 1 wt%, 8.5 kg PBAT, 14 kg of glycerol, 6 kg of sorbitol, 1.2 kg of distilled monoglyceride (GMS), 6 kg of ethylene-acrylic acid (EAA) (9% acid, melt flow index = 20), 3 kg ethylene vinyl acetate (EVA), 0.2 kg sodium stearate, and 0.12 kg sodium hydroxide dissolved in a minimum amount of water were melt mixed in a ZSK-65 Twin Screw Extruder (L/D = 48). Prior to melt mixing these components, the solid materials were dry blended first in a high speed mixer and the liquid materials then added to provide for a uniform distribution of all components. The temperature profile of the extruder was set at 100 °C/130 °C/160 °C/150 °C/140 °C. The rotation speed of the screw was set at 300 rpm. A vacuum of −0.06 to −0.08 bar was applied during extrusion. The polymer melt was extruded as a strand, air cooled, and cut into pellets. The masterbatch was found to have an MFI >4 g/10 min at 190 °C with 2.16 kg, and a water content of <0.2 wt%.

Example 2: Preparation of a biodegradable polymer composition.

A composition consisting of 30 wt% of the masterbatch prepared in Example 1, 52.7 wt% PBAT, 7 wt% PCL, 3 wt% PLA, 2 wt% GMS, 0.3 wt% polyepoxide (Joncryl® ADR-4368) and 5 wt% talc was first dry blended and then melt mixed using a ZSK-65 Twin Screw Extruder with a rotational speed of 200 rpm. The temperature profile of the extruder was set at 80 °C/130 °C/170 °C/170 °C/160 °C/130 °C. A vacuum of −0.04 to −0.05 bar was applied during extrusion. The resulting extrudate was water cooled and cut into pellets and was found to have an MFI of 7 g/10 min, at 190 °C with 2.16 kg. The polymer composition prepared in accordance with Example 2 was blown into 20-μm-thick film on a standard LDPE blown film line.

WO9504108 A1 (1995, EVERCORN INC) discloses a biodegradable moldable composition comprising a compatible blend of a hydrophobic, water-repellent starch ester and a biodegradable polyester, and optionally a biodegradable and miscible plasticizer and/or a compatible filler. The starch ester (e.g., propionate- or acetate/propionate-modified starch) has a degree of substitution of about 1.0–2.5 DS, and preferably an amylose content greater than 50%, and most preferably greater than 70%. The biodegradable polyester is selected from PCL, PLA, PGA, P3HB, or PHBHV. The products of the disclosed composition possess water repellant properties while still retaining their biodegradability. The water resistance of the starch esters is improved by blending with high-molecular-weight biodegradable polyesters, especially with semicrystalline polyesters such as PCL or PHBHV, and similar biodegradable polyesters. This is further achieved by engineering the appropriate degree of substitution and molecular weight of the starch ester component, by blend composition, choice of (co)polyester composition, and plasticizer composition.

WO9631561 A1 (1996, BIOTEC BIOLOG NATURVERPACK) discloses a polymer composition that is at least partially biodegradable comprising: TPS formed from starch and a plasticizer such as glycerol or sorbitol and a polymer selected from aliphatic–aromatic polyester copolymers, aromatic polyesters, polyesteramides, and polyesterurethanes. The composition is formed by melting and mixing TPS and the polymer under conditions that reduce or maintain the water content of the composition at less than about 1 wt% while in a melted state. However, this method faces some limitations in that mixing an active hydrogen-containing compound, such as sorbitol or glycerol, with a biodegradable polyester at high temperature deteriorates the properties of the polymer. Furthermore, the method does not compatibilize sufficiently the biodegradable polymer and TPS (2001, **EP1097967** A2, NIPPON CATALYTIC CHEM IND).

JPH07330954 A (1994, SHOWA HIGHPOLYMER) discloses a composition comprising an aliphatic polyester (100 pbw) having a number-average molecular weight, $M_n \geq 15{,}000$ and $T_m \geq 70\,°C$, and starch (1–300 pbw). The aliphatic polyester is a PAA-type polyester obtained by adding 0.1–30 pbw poly(ethylene glycol) (a) having a $M_n \geq 300$ to 100 pbw mixture of a polyhydric alcohol (b) excluding the ingredient (a) and a polybasic acid (or anhydride) (c) to polycondense the ingredients (a), (b), and (c). The introduction of the polyethylene glycol in the formation of the aliphatic polyester aims to increase the compatibility with the starch. The polyhydric alcohol component (b) is preferably selected from ethylene glycol, 1,4-butanediol, and cyclohexanedimethanol. The polybasic acid is preferably succinic acid or adipic acid, considering the compatibility with the starch and properties of aliphatic polyester obtained. The disclosed composition is claimed to have excellent water resistance and be capable of being freely regulated in biodegradability and molded into a desired shape while retaining material properties sufficient for practical use. However, the introduction of the polyethylene glycol in the formation of the aliphatic polyester is not an easy process. Moreover, this process disturbs crystalline structure, and, therefore, it decelerates the rate of crystallization in the stage of molding (2001, **EP1097967** A2, NIPPON CATALYTIC CHEM IND).

JPH10152602 A (1998, SEKISUI CHEMICAL CO LTD) discloses a biodegradable polymer composition obtained by mixing an aliphatic polyester (a) having a melt viscosity of 1000–15,000 P at 200 °C with starch (b) and a polyethylene glycol (c) having a M_n of 100–20,000 in such amounts that the ratio of component (a) to component (b) is 95/5–60/40 by weight, and 1–200 pbw component (b) is present per 100 pbw total of components (a) and (c). It is preferred that the aliphatic polyester is one having a linear structure, because it can give a biodegradable polymer composition having a higher rate of biodegradation. With a view to the inhibition of hydrolysis during melt kneading, the starch is desirably one in the form of a powder having a mean particle diameter of 50 μm or below and predried at 150 °C for about 5 h to a water content of ≤1 wt%. The biodegradable polymer composition is claimed to have a good moldability and can give a product exhibiting an excellent elongation at break and mechanical properties without any complicated step such as stretching and having a good biodegradability. However, the use of polyethylene glycol, which is highly hydrophilic, could render the resultant mixture sticky, due to the absorption/adsorption of moisture; the biodegradable polymer can lose mechanical properties with the passing of time due to water absorption by the polyethylene glycol, or even polyethylene glycol to be so hydrophilic that the compatibility with the biodegradable polymer becomes very low (2001, **EP1097967** A2, NIPPON CATALYTIC CHEM IND).

JPH06313063 A (1994, TSUTSUNAKA PLASTIC KOGYO) discloses a composition that is produced by mixing (a) 100 pbw of a starchy substance such as starch and modified starch with (b) 5–40 pbw of an aliphatic polyester having a molecular weight of 30,000–70,000 (e.g., P3HB) and (c) 1–5 pbw of a low-molecular aliphatic polyester having a molecular weight of 300–3000 (e.g., PCL). The composition is claimed to have excellent elongation property, moldability, impact resistance, mechanical strength, and water resistance, and be useful for the molding of articles such as food packaging containers.

JPH10158485 A (1998, DAICEL CHEM) discloses a biodegradable polymer composition that is produced by mixing a high-molecular-weight aliphatic polyester (a) with a low-molecular-weight PCL (b) as a flow improver and starch (c) in a specified weight ratio. The flow modifier (b) prepared by grafting a caprolactone monomer onto a low-molecular-weight PCL or PVA (M_n of 500–20,000) is kneaded with a natural or modified starch (c), and the mixture is mixed with the high-molecular-weight aliphatic polyester (a) (M_n of 50,000–200,000) (e.g., P3HB). The resulting mixture is mixed with a plasticizer, resin additives, a filler, etc., and the entire mixture is melt kneaded with, e.g., a kneader to obtain a composition comprising 85–10 wt% component (a), 5–20 wt% component (b), and 10–70 wt% component (c). The composition is claimed to have excellent biodegradability and mechanical properties.

However, there is no evidence in either patent **JPH06313063** A or **JPH10158485** A that the synthesis of two types of aliphatic polyesters of high and low molecular weight with the intention to increase compatibility with the starch is an easy process. Moreover, the described methods alone are applicable to specific aliphatic polyesters, therefore, they are conditioned in their use (2001, **EP1097967** A2, NIPPON CATALYTIC CHEM IND).

EP1097967 A2 (2001, NIPPON CATALYTIC CHEM IND) discloses a method comprising the step of mixing a biodegradable polymer with a starch additive and an anionic surfactant. The anionic surfactant is a sulfonic-acid-group-containing anionic surfactant. Specific examples of the biodegradable polymer include: high-molecular aliphatic polyesters and/or biodegradable polymers containing aromatic dicarboxylic acids as essential structural units. However, the proposed method is insufficient to make compatible the mixture of biodegradable polymer and starch, especially if the biodegradable polymer has high molecular weight. Furthermore, the presence of a starch in significantly high amounts abolishes or reduces transparency, which limits their use.

WO2008037749 A2 (2008) and **WO2008037744** A2 (2008) of NOVAMONT SPA disclose biodegradable multiphase compositions comprising a continuous phase composed of a matrix of at least one tough hydrophobic polymer (58–90 wt%) incompatible with the starch and a nanoparticulate-dispersed starch phase (10–42 wt% with average dimension of less than 0.25 μm). The hydrophobic matrix is made of tough polyesters from diacid-diol, such as the aliphatic aromatic polyesters (e.g., Ecoflex®, BASF AG).

FR2782999 A1 (2000, ULICE SA) discloses a biodegradable material based on a dispersive blend, e.g., a homogeneous mixture of a biodegradable polymer and cereal flour. The biodegradable polymer is selected from the group consisting of BIOPOL®, BAK®, ECO-PLA®, BIOMAX®, MATER-BI®, and ECOFLEX®.

FR2918383 A1 (2009, CT VALORISATION IND AGRO RESSO) discloses a biodegradable polymer composition comprising a biodegradable polymer such as PLA, wheat flour, and a functionalized PLA as a compatibilizing agent. The functionalized PLA is obtained in reactive extrusion by grafting a maleic anhydride monomer on the polymer chain by the decomposition of a peroxide. The functionalized PLA compatibilizer improves the cohesion energy between polymer phase and flour (see also Chapter 7: Chemical Treatment (in bulk); Section 7.1: Chemical Modification).

Table 3.4 presents a list of the patents outlined in the section.

3.2.6 Blending Lignin with Biodegradable Polymers

Blends of lignin with biodegradable polymers, with or without fiber reinforcement, are a promising option for the manufacture of low cost biodegradable materials. Films containing up to 30 wt% of commercial pine kraft lignin mixed with wheat starch were found to improve the mechanical properties of starch films, with the low-molecular-weight fraction of the pine kraft lignin acting mainly as a starch plasticizer [55,56]. Lignin, wood flour–based PCL composites have also been reported [57]. Maleic anhydride grafted PCL was used as a

TABLE 3.4 Blends of Starch with Other Biodegradable Polymers

Component 1	Component 2	Component 3	Patent
Starch (TPS)	PCL (1–45 wt%)	Nonionic surfactant	**WO9219680** A1 (1992, NOVAMONT SPA); **JPH05331315** A (1993) and **JPH08188671** A (1996, AGENCY IND SCIENCE TECHN); CHIKYU KANKYO SANGYO GIJUTS; **EP0444880** A2 (1993, AGENCY IND SCIENCE TECHN, CHUO KAGAKU KK); **EP0535994** A1 (1993, AGENCY IND SCIENCE TECHN, RES INST INNOVATIVE TECH EARTH, CHUO KAGAKU KK)
Starch (TPS) (20–50 vol.%)	Cellulose ester (e.g., CA, CAP, CAB) (30–60 vol.%)	Phasing agent (e.g., epoxidized soybean oil) or softener (e.g., acetyl triethyl citrate) (5–25 vol.%)	**EP0542155** (1993, TOMKA IVAN)
Propionate-, acetate/propionate-modified starch	PLA, PGA, P3HB, PHBHV		**WO9504108** A1 (1995, EVERCORN INC)
Starch (TPS)	Polyester (aromatic polyesters, aliph.-aromatic polyester copolymers, polyester amides, polyester urethanes)	Plasticizer (glycerol, sorbitol, sugar alcohols, hydroxy acids, PVOH)	**WO9631561** A1 (1996, BIOTEC BIOLOG NATURVERPACK)
Starch	Aliph. or aliph.-aromatic polyester	Sulfonic-acid group-contg. Anionic surfactant	**EP1097967** A2 (2001, NIPPON CATALYTIC CHEM IND)
Starch	PAA-type polyester		**JPH07330954** A (1994, SHOWA HIGHPOLYMER)
Starch	Aliph. polyester	Polyethylene glycol	**JPH10152602** A (1998, SEKISUI CHEMICAL CO LTD)

Continued

TABLE 3.4 Blends of Starch with Other Biodegradable Polymers—cont'd

Component 1	Component 2	Component 3	Patent
Starch (100 pbw)	P3HB (M_n 30,000–70,000) (5–40 pbw) and PCL (300–3000) (1–5 pbw)		**JPH06313063** A (1994, TSUTSUNAKA PLASTIC KOGYO)
Starch (10–70 wt%)	P3HB ($M_n = 50{,}000$–200,000) (85–10 wt%) and caprolactone-grafted PCL or PVA ($M_n = 500$–20,000) (5–20 wt%)		**JPH10158485** A (1998, DAICEL CHEM)
Starch (TPS)	PCL, PLA, P3HB, PES, PBAT, PHBHV, PBS, PBA, CAB, CAP	Polymer having pendant carboxylic acid groups (e.g., ethylene (meth)acrylic acid copolymer); transesterification catalyst; polyepoxide; fatty acid sodium salt; opt. plasticizer	**WO2010051589** A1 (2010, TRISTANO PTY LTD)
Starch	PBAT		**WO2008037749** A2 (2008) and **WO2008037744** A2 (2008 NOVAMONT SPA)
Wheat flour	PLA	Maleic anhydride-grafted PLA	**FR2918383** A1 (2009, CT VALORISATION IND AGRO RESSO)
Cereal flour	PHBHV (BIOPOL®[1]), poly(ester-amide) BAK®,[2] MATER-BI®, PBAT (ECOFLEX®)		**FR2782999** A1 (2000, ULICE SA)

CA, cellulose acetate; CAB, cellulose acetate butyrate; CAP, cellulose acetate propionate; P3HB, poly(3-hydroxybutyrate); PAA, poly(alkylene alkanoate); PBA, poly(butylene adipate); PBAT, poly(butylene adipate-*co*-terephthalate); PBS, poly(butylene succinate); PCL, poly(ε-caprolactone); PGA, poly(glycolic acid), polyglycolide; PHBHV, poly(hydroxybutyrate-*co*-3-hydroxyvalerate); PLA, poly(lactic acid), polylactide; PVOH, poly(vinyl alcohol); TPS, thermoplastic starch.

[1] *Monsanto's rights to BIOPOL® were sold to Metabolix (US) in 2001.*

[2] *Bayer stopped the production of BAK® in 2001.*

compatibilizer for improving tensile properties [58]. Lignin acted also as a new type of nucleating agent in improving the thermal properties of lignin-P3HB composites [59]. Lignin is also used as adhesion promoter in cotton fiber–reinforced PLA composites [60]. A lignin/PLLA blend has been reported to retain its thermomechanical properties when the content of lignin is less than about 20%. The lignin would accelerate the thermal degradation of PLLA when the content of lignin was more than 20 wt% [61].

WO2010139056 A1 (2010, UNIV GUELPH) discloses a biodegradable biopolymer composite comprising lignin, grass fibers, and PBS. The grass fiber is switchgrass, Miscanthus, hemp, jute, and/or kenaf. The PBS is provided preferably as a blend of PBS and PHBHV. The biocomposite comprises less than 65% lignin. The thermomechanical properties of the material can be controlled by increasing or reducing the lignin content.

3.2.7 Blending Natural Rubber with Biodegradable Polymers

JPH10274494 A (1998, SHOWA RUBBER; TOKYO ELECTRIC POWER CO) discloses a rubber composition obtained by uniformly and homogeneously mixing 100 pbw of natural rubber with 2–70 pbw of biodegradable polymer selected from PLA, poly(alkylene alkanoate)s (PAAs) and starch having faster biodegradation rate than that of the natural rubber. The rubber composition is used for the manufacture of a sponge ball for cleaning the heat exchanger of a power plant. Accordingly, the decomposition is accelerated as compared with a cleaning sponge not mixed with the biodegradable polymer.

JP2000319446 A (2000, NISHIKAWA RUBBER CO LTD) discloses a biodegradable rubber composition capable of being produced with a rubber kneader by compounding a natural rubber with a biodegradable polymer and a filler. The natural rubber is exemplified by ribbed smoked sheet (RSS), white crepe, pale crepe, or estate brown crepe, and among them, RSS is preferable in respect to its economical profitability. The biodegradable polymer is an aliphatic polyester, preferably PLA. The filler used is preferably one that exerts little influence on the environment after decomposition, such as carbon black, silicon dioxide, titanium oxide, aluminum hydroxide, bentonite, diatomaceous earth, starch, wood flour, or chitin. The mixing ratio is 5–500 pbw of PLA, preferably 5–300 pbw of PLA, per 100 pbw of natural rubber. The biodegradable rubber composition is claimed to have enhanced shape retention, extrudability, and expansion moldability.

JP2003183488 A (2003, TECHNO POLYMER CO LTD) discloses a PLA composition comprising crystalline PLA (e.g., 75–93 wt%), and a rubber component (25–7 wt%) selected from natural rubber and *cis*-1,4-polyisoprene. A preferred type of natural rubber is RSS. The PLA-based composition has a good balance between stiffness and impact resistance. Despite the improvement in properties, the incompatibility between two polymer phases is a major drawback [26].

JP2004143315 A (2008, TOYOTA MOTOR CORP) discloses a biopolymer blend comprising a continuous phase of PLA and a dispersion phase of natural rubber, evenly and finely dispersed in the continuous phase. The dispersed phase preferably has an average diameter ≤100 μm. The powder of PLA preferably has an average particle diameter ≤400 μm. An inorganic filler is preferably added to the polymer blend material. The blend is obtained by charging and heating one or more kinds of material selected from the group consisting of the natural rubber and a synthetic rubber in a kneader to plasticize the materials, adding a powder of PLA to the plasticized materials and kneading the resultant mixture at a temperature lower than the T_m of PLA. The rubber/PLA blend has improved impact strength.

Example: Latex SMR CV60 (natural rubber) (15 g) was kneaded for 3 min and plasticized. Lacty® 9030 (Shimadzu) powder components (PLA powder) (30 g) was kneaded with plasticized natural rubber for 5 min. The obtained kneaded material was removed, cooled to room temperature, and ground to a diameter of 3 mm. The mixture was extrusion molded to obtain a compact of polymer blend material having bending elastic modules of 33.2 J/m and impact strength of 1.64 GPa (measured according to JIS K-6911).

WO2008090590 A1 (2008, SEED COMPANY LTD) discloses an elastomer composition containing crosslinked natural rubber particles that are dispersed like islands in a matrix of a biopolymer. The elastomer composition is used as a base material of an eraser. The biopolymer is selected from PLA, poly(butylene succinate) (PBS), polyamide 11 (PA11), P3HB, cellulose acetate (CA), esterified starch, chitosan-cellulose-starch and starch-modified polyvinyl alcohol. Both components of the elastomer composition are derived from renewable resources and are recyclable.

WO2010010696 A1 (2010, SEED COMPANY LTD) is a modification of the previous patent application, and discloses an abradant-containing eraser based on a similar elastomer composition. The abradant-containing eraser is produced by melting and kneading the abradant-containing elastomer composition, and PVC, preferably originating from an eraser made of PVC, more preferably from wastes of the eraser generated at the time of molding, and molding the kneaded mixture.

3.3 BLENDING BIOPOLYMERS WITH SYNTHETIC NONBIODEGRADABLE POLYMERS

There have been attempts to improve the end-use properties of biodegradable polymers using a large number of nonbiodegradable fossil fuel–based polymers. Several of these blends are immiscible having sharp interfaces, coarse phase morphologies, and poor mechanical properties (see Table 3.5). As all of these fossil fuel–based polymers introduced as blend components are nonbiodegradable, the blend compositions are at best biodisintegrable and not fully biodegradable.

P3HB blends with random ethylene-propylene rubber (EPR) and ethylene-vinyl acetate (EVAc) copolymers were found to be immiscible, presenting distinct and unaltered T_m and T_g [72,73]. P3HB and poly(vinyl acetate) (PVAc) blends were found to be miscible, with T_m and T_g values intermediate between those of P3HB and PVAc. PVAc reduced the crystallinity and crystallization rate of P3HB, which constituted the most marked phenomenon at higher concentrations of PVAc [73,86]. P3HB blends with poly(ethylene oxide) (PEO) were found to be miscible, but observed a decrease in the values of T_m and T_g of P3HB proportional to the amount of PEO in the blend [74,87,88]. The T_g and depression of the T_m provide miscibility criteria for P3HB/PEO blends [75]. A thorough review of the blends of P3HB or PHBHV with synthetic nonbiodegradable polymers is provided by Ha and Cho [89].

Blends of starch and synthetic nonbiodegradable thermoplastic polymers, are well known in the prior art [90]. Starch is quite hydrophilic relative to nonbiodegradable thermoplastic polymers that are typically melt mixed with it. Melt mixing of starch with these thermoplastic polymers therefore typically results in the formation of multiphase morphology having a high interfacial tension, which can negatively impact on the physical and mechanical properties of the resulting polymer composition. Phase compatibilizers have been employed to reduce the degree of phase separation that can occur when a nonbiodegradable polymer is melt mixed with starch.

3.3.1 Biopolymer in Majority

3.3.1.1 Poly(Lactic Acid)

Many patents have been disclosed in an attempt to improve the flexibility, impact resistance, heat resistance, and foamability of biopolymers by blending these materials with other synthetic nonbiodegradable polymers; for example, PLA has been blended with a variety of fossil fuel–based nonbiodegradable polymers selected from the polymer group of poly(ethylene terephthalate) (PET), polystyrene, polyethylene, polypropylene, poly(vinyl chloride) (PVC), PVAc, poly(alkyl acrylate), aromatic polycarbonate (PC)

TABLE 3.5 Miscibilities of Biopolymers with Synthetic Nonbiodegradable Biopolymers

Biopolymer	Synthetic Polymer	Miscibility	Literature
PLA	PVAc (5–30 wt%)	Miscible	[30]
PLA	PVPh	Miscible partially	[62]
PLA	PEO (<50 wt%)	Miscible	[63]
PLA	POM	Miscible partially	[64]
PLA	PC	Immiscible	[65]
PLA	ABS	Immiscible	[66]
PLA	PP	Immiscible	[67,68]
PLLA	LLDPE	Immiscible	[69]
PDLA	PMA	Miscible	[70]
PDLA	PMMA	Miscible	[70]
PDLA	PVP	Immiscible	[71]
PLLA	PVP	Immiscible	[71]
P3HB	EPR	Immiscible	[72,73]
P3HB	PEO	Miscible	[74–76]
P3HB	PMMA	Immiscible	[76]
P3HB (≤20 wt%); P3HB (>20 wt%)	PMMA	Partially miscible [77] Immiscible [76]	[76,77]
P3HB (20 wt%)	PCHMA	Immiscible	[77]
P3HB	PVAc	Miscible	[30,73]
P3HB	PVC	Miscible	[30]
P3HB	PVDF	Miscible	[78]
P3HB	PVPh	Miscible	[79]
PHBHV (HV = 8 mol%) PHBHV (HV = 18 mol%)	PVC	Immiscible Miscible	[80]
PHBHV (80, 50, 30 wt%)	PS (20, 50, 80 wt%)	Immiscible	[35]
PHBHV (80, 50, 30 wt%)	SAN (20, 50, 80 wt%)	Miscible	[35]
PCL	PVC	Miscible	[40,81]
Starch	EAA, urea and polyols	Partially miscible	[82]
Starch	LLDPE and octenyl succinate	Immiscible	[83]
TPS	LDPE and MAPE	Miscible	[84]
TPS	PE and MAH and dicumyl peroxide	Partially miscible	[85]

CAB, cellulose acetate butyrate; ABS, acrylonitrile-butadiene-styrene copolymer; EAA, ethylene-acrylic-acid copolymer; EPR, ethylene-propylene rubber; EVAc, ethylene-vinyl acetate copolymer; LDPE, low density polyethylene; LLDPE, linear low density polyethylene; MAH, maleic anhydride; MAPE, maleic anhydride-*g*-polyethylene; P3HB, poly(3-hydroxybutyrate); PC, aromatic polycarbonate; PCHMA, poly(cyclohexyl methacrylate); PCL, poly(ε-caprolactone); PE, polyethylene; PEO, poly(ethylene oxide); PHBHV, poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate); PDLA, poly(D-lactic acid), poly(D-lactide); PLA, poly(lactic acid), polylactide; PLLA, poly(L-lactic acid), poly(L-lactide); PMA, poly(methyl acrylate); PMMA, poly(methyl methacrylate); POM, polyoxymethylene; PP, polypropylene; PS, polystyrene; PVAc, poly(vinyl acetate); PVC, poly(vinyl chloride); PVDF, poly(vinylidene fluoride); PVP, poly(vinyl pyrrolidone); PVPh, poly(*p*-vinylphenol); SAN, styrene-acrylonitrile copolymer; TPS, thermoplastic starch.

and their copolymers (1990, **WO9001521** A1; **AU4223889** A BATTELLE MEMORIAL INSTITUTE). However, if PLA is simply mixed with a synthetic nonbiodegradable polymer such as polyethylene and polypropylene, a uniform polymer composition will not be obtained because these polymer components may not be compatible with each other. Thus, its impact resistance will be low and its appearance will be poor, making it impossible to provide a polymer composition with physical properties good enough for normal services.

As a solution to problems arising from such poor compatibility, **JPH09316310** A (1997, KANEBO LTD) discloses a resin composition comprising PLA and a modified polyolefin in a weight ratio of 99.5/0.5–40/60. The modified polyolefin has one of the following structures (1) and (2): (1) an epoxidized olefin copolymer made from (a) an α-olefin, (b) a monomer having an ethylenic bond and a glycidyl group, and (c) a (meth)acrylic ester or styrene; and (2) a copolymer obtained by grafting an unsaturated carboxylic acid or a derivative thereof onto a copolymer of ethylene with another α-olefin. The PLA composition has good strength and impact resistance and can be decomposed by microorganisms at a regulated rate, by incorporating the modified polyolefin into PLA in a specific weight ratio. However, according to **WO2006103969** A1 (2006, TORAY INDUSTRIES), a sufficient shock resistance and flexibility will not be achieved if the content of PLA is large. On the contrary, as the content of the modified polyolefin increases, the difference between the number of carboxyl terminal groups in PLA and that of the glycidyl groups in the modified polyolefin will become too large, allowing unreacted glycidyl groups to remain and possibly allowing the properties of the resin composition to change during the molding process. Furthermore, modified polyolefin is high in price, and therefore it will be difficult to provide a low price polymer composition if modified polyolefin has to be used in large amounts.

JPH10251498 A (1998, KANEBO LTD) discloses a PLA-based composition prepared by mixing PLA with a syndiotactic polypropylene (s-PP) to obtain a molded product thereof. The PLA is either PLLA, PDLA, poly(D-lactic-*co*-L-lactic acid) (PDLLA), and a copolymer of lactic acid with at most 50 wt% of another component or a mixture of the homo- or copolymer with another polymer. The s-PP is obtained by polymerizing propylene in the presence of a metallocene catalyst, and imparts lowered crystallinity, lowered T_m, a change in flexibility, and frictional coefficient, etc. to PLA. PLA is compatible with s-PP. When the composition comprises 99–85 wt% of PLA and 1–15 wt% of s-PP, it can show improved performance and considerable transparency. Furthermore, the composition is claimed to be advantageous in cost and improved in hardness, brittleness, impact resistance, and melt flow.

JP2005232228 A (2005, TOSOH CORP) discloses in one of its embodiments a PLA/LLDPE blend in a ratio 1/99–1/99, preferably 95/5–30/70, and most preferably 90/10–50/50.

WO2013108817 A (2013, NAT INST OF ADVANCED IND SCIEN) discloses a biobased polymer blend comprising 10–90 wt% of biobased high density polyethylene (HDPE) and 90–10 wt% of PLA to achieve a total of 100 wt%, and additionally 1–20 wt% of a compatibilizing agent. The production method for the biobased polymer blend is carried out in a cylinder by applying a shear flow field and a stretching field and melt kneading the biobased polyethylene, PLA, and the compatibilizing agent.

KR20110064122 A (2010, SAMYANG CORP) discloses a method for manufacturing a PLA-based composition comprising the following steps of: (1) forming PLA by performing ring opening polymerization after providing lactide and lactic acid oligomers (molecular weight of 3000–6000) to a melt kneading device; (2) melt kneading PLA and a thermoplastic nonbiodegradable polymer in a melt kneading device. The thermoplastic polymer is preferably an aromatic polycarbonate (TRIREX® 3030P, Samyang); acrylonitrile-butadiene-styrene (ABS) copolymer and poly(alkylene terephthalate) may also be used. The content of thermoplastic polymer is 0.1–50 wt%. The PLA prepared in step (2) has improved compatibility with the nonbiodegradable polymer.

KR20100079986 A (2010, SAMYANG CORP), which is a modification of the previous patent application, discloses a polymer composition comprising 100 pbw of polymer blend including PLA (20–80 wt%), aromatic polycarbonate (2–72 wt%), and ABS copolymer (2–72 wt%); 1–15 pbw of PET, 2–15 pbw of core–shell structured methyl methacrylate-butadiene-styrene (MBS) copolymer, and 0.2–3 pbw of a carbodiimide-based compound; preferably a recycled PET is used.

KR20110108736 A (2011, SAMYANG CORP), which is also a modification of the previous patent application, discloses a polymer composition comprising PLA (16–82 wt%), recycled PET (15–60 wt%), MBS (2–15 wt%), epoxy group containing acrylic ester gum (0.3–3.0 wt%), nucleating agent (0.3–3.0 wt%), and an antihydrolysis agent (0.3–3.0 wt%).

A further method adds an acrylic acid ester resin having a relatively low T_g to PLA [70]. Similarly, **JP2003286401** A (2003, TORAY INDUSTRIES) discloses a PLA-based composition comprising PLA and a second polymer mainly comprising an unsaturated alkyl carboxylate–based unit that has a $T_g \leq 10°C$, such as poly(methyl acrylate), poly(methyl methacrylate), poly(butyl acrylate), and the like. The second polymer has a $M_w \leq 30{,}000$ g/mol. **JP2004010842** A (2004, IDEMITSU PETROCHEMICAL CO) discloses a PLA-based composition comprising PLA and an acrylic acid ester-based oligomer.

FR2902434 A1 (2007, ARKEMA FRANCE) discloses a PLA-based composition exhibiting improved impact resistance comprising PLA (60–97 wt%) and a mixture of compounds A and B (3–40 wt%) in which: A is a copolymer of ethylene and of an unsaturated monomer bearing at least one epoxide or carboxylic acid or carboxylic acid anhydride function, and optionally of alkyl (meth)acrylate; B is a copolymer of ethylene and of alkyl (meth)acrylate; said mixture having a weight ratio A/A + B) of between 0.10 and 0.49. Preferably, A is an ethylene-alkyl (meth)acrylate-maleic anhydride terpolymer or an ethylene-alkyl (meth) acrylate-glycidyl methacrylate terpolymer; and B is a copolymer of ethylene and of alkyl (meth)acrylate.

Example: A typical composition comprised: PLA (80 wt%), ethylene-methylacrylate-glycidyl methacrylate (EMA–GMA) terpolymer (2 wt%), and ethylene-butyl acrylate (EBA) (18 wt%).

US2012245292 A1 (2012, HYUNDAI MOTOR CO LTD) discloses a method for preparing a PLA-based composition comprising melting and mixing PLLA (60–80 wt%), PDLA (15–30 wt%), and poly(ethylene-alkyl acrylate-glycidyl methacrylate) (5–10 wt%) at 190–195 °C, and injecting the composition into a casting mold, whose surface temperature is 100–110 °C. The disclosed method is claimed to reduce manufacturing cost and remarkably improves the mechanical properties of PLA. The disclosed blend is claimed to have superior heat resistance, tensile strength, and impact strength, especially one having significantly improved properties as compared to the currently known blend of optical isomers of PLA, and can be used for automobile interior and exterior parts.

WO9622330 A2 (1996, CARGILL INC) discloses a method to improve the toughness of PLA by adding an epoxidized rubber modifier (10–40 wt%) capable of reacting with PLA to reduce phase separation and thus increase the impact resistance of PLA. However, this technology can significantly reduce the biodegradability and transparency of PLA and also has a limited improving effect on impact resistance (2010, **US2010167048**, FAR EASTERN NEW CENTURY CORPORATION).

JPH07109413 A (1995, MITSUI TOATSU CHEMICALS) discloses a polymer composition comprising: (1) an aromatic polycarbonate and (2) a lactic acid–based polymer consisting of PLA and/or a copolymer of lactic acid (derivative) with other hydroxycarboxylic acid. The polymer composition is claimed to have iridescence, high flowability, and a well-balanced combination of thermal and mechanical properties. The amounts of the components (1) and (2) are preferably 10–90 wt% and 90–10 wt%, respectively, from the standpoint of enhancing iridescence, and are preferably 50–90 wt% and 50–10 wt%, respectively, from the standpoint of thermal and mechanical properties. However, there have been problems that applications of the obtained product are limited due to its pearl gloss and that its productivity is inferior due to the Barus effect at melt/kneading (2006, **WO2006030951** A1, TORAY INDUSTRIES).

EP0896013 A1 (1999, SHIMADZU CORP) discloses the use of a crosslinked aromatic carbonate (PC) as a modifier to improve the impact resistance of PLA. The PLA/PC weight ratio is 40/50–99/1, preferably 60/40–95/5. If the weight ratio of PLA is less than 60, the characteristics of PLA, that is, good mechanical strength and transparency, are not apparent. On the other hand, if the blend ratio of said crosslinked polycarbonate (PC) is less than 5, its improving effect on the brittleness of PLA is weak. However, it has been reported that the claimed composition is inferior in compatibility, serious in the Barus effect, and has a problem of pearl gloss (2006, **WO2006030951** A1, TORAY INDUSTRIES).

JP2000017038 A (2000, KANEBO LTD; RES INST INNOVATIVE TECH EARTH; KANEBO SYNTHETIC FIBERS LTD) discloses an expandable PLA-based composition comprising: (1) PDLLA having a molar ratio of L-form to D-form of 95/5–60/40 or 40/60–5/95; (2) at least one amorphous polymer selected from the group consisting of an aromatic polycarbonate, a polystyrene, and a copolymerized PET having a $T_g > 60\,°C$ at a weight ratio of (1)/(2) of 99/1–80/20, and 0.5–5 wt%, based on PDLLA (1), of a polyisocyanate compound having an isocyanate group of ≥2 eq/mol. According to **WO2008123367**[5] A1 (2008, SEKISUI PLASTICS CO., LTD), the PDLLA constitution has a molar ratio of the optical isomer component of the L-form or the D-form, whichever is less, of 5 mol% or more, and the PDLLA is low in crystallinity or amorphous and is poor in heat resistance. Therefore, a molded article obtained from this resin composition has insufficient heat resistance, i.e., about 50 °C at most, which has caused problems in practical use.

JP2010143947 A (2010, NAGOYA CITY) discloses a PLA-based composition obtained by melting/mixing a PLA, an aromatic polycarbonate (PC), and a multifunctional isocyanate compound. The weight ratio PLA/PC is 90/10–10/90, and 0.1–5.0 pbw of the multifunctional isocyanate compound is mixed based on 100 pbw of PLA and PC.

WO2006030951 A1 (2006, TORAY INDUSTRIES) discloses a polymer composition comprising: (1) PLA (75–10 wt%), (2) an aromatic polycarbonate (25–90 wt%) and (3) a polymer compound to which a glycidyl compound or an acid anhydride is grafted or copolymerized (1–50 pbw with respect to 100 pbw of the total of component (1) and component (2). As the polymer compound to which the glycidyl compound or the acid anhydride is grafted or copolymerized, an acrylic resin or styrene resin is preferably mentioned.

US2010056700 A1 (2010, CHEIL IND INC) discloses a polymer composition comprising a blend consisting of PLA (25–80 wt%), an aromatic polycarbonate (20–75 wt%), and a compatibilizer capable of forming a stereocomplex with the PLA. When the PLA of the blend primarily consists of PLLA, the compatibilizer can include PDLA. When the PLA of the blend consists of PDLA, the compatibilizer can include PLLA.

The preparation of blends of PLA and polyurethane is also known per se. **WO2005040282** A1 (2005, KYOWA HAKKO CHEMICAL CO LTD) discloses such a blend, which contains, in addition to PLA, a poly (ethyl vinyl

---

[5] See Chapter 9: Foaming and foamed products; section 9.5: Expandable particles.

ether)-based polyurethane as a softening agent (see also Chapter 5: Compounding; Section 5.5.2.1 Plasticizers).

WO2011157691 A1 (2011, BASF SE) discloses a method for the production of blends from thermoplastic polyurethanes (TPU) and PLA by: (1) reacting at least one thermoplastic polyurethane with at least one diisocyanate or a diisocyanate prepolymer, which comprises at least two isocyanate groups, or a mixture thereof, in the melt, reducing the molecular weight of the thermoplastic polyurethane and forming a thermoplastic polyurethane having an excess of isocyanate end groups; (2) introducing at least one PLA in the melt of the product from step (1) and reacting the product from step (1) with the PLA at a temperature of less than 190 °C; and (3) cooling the blend thus obtained, wherein no polyols are added in steps (1)–(3). The amount of PLA in step (2) is in the range of 50–97 wt%. A schematic diagram of a preferred mixing method in a twin-screw extruder is shown in Figure 3.1.

3.3.1.2 Polyhydroxyalkanoates

Articles made by melt processing compositions containing a major proportion of a P3HB are often relatively highly crystalline, although where PHBHV is employed, the crystallinity may be somewhat reduced. This high crystallinity often renders brittle articles fabricated from this polymer. It is therefore often desired, when using P3HB as molding material, to improve the toughness of P3HB polymer by incorporation of an impact modifier.

EP0052460 A1 (1982, ICI PLC) discloses, in some of its embodiments, polymer blends of P3HB or PHBHV with chlorinated polyethylene (CPE), chlorosulfonated polyethylene (CSPE), ethylene-vinyl acetate copolymer (EVA) or ABS copolymer. CPE or CSPE can exhibit a toughening effect on P3HB and so act as impact modifiers. The toughening effect is attributed to the chlorine atoms of the rubbery polymers, which possibly enable hydrogen bonding to occur with the carbonyl groups of the P3HB polymer, resulting in at least partial miscibility between the polymers. To be effective as an impact modifier, the additive polymer should have a $T_g < 10\,°C$. Preferably, the amount of impact modifier is 10–50 wt%, based on the combined weight of impact modifier and P3HB. The other impact modifiers used, such as EVA and ABS, appear not to be effective as impact modifiers for P3HB polymers.

The polymer blend can be prepared by blending the nonbiodegradable polymer with a solution of P3HB in a volatile solvent and then removing said solvent by volatilization. An alternative method of making a polymer blend comprises forming a slurry of the nonbiodegradable polymer, P3HB, and a volatile liquid, and then removing said liquid by volatilization.

JP2005232232 A (2005, TOSOH CORP) discloses a blend consisting of P3HB and/or PLA and halogenated elastomer, such as CSPE, in a ratio 1/99–1/99, preferably 95/5–30/70, and most preferably 90/10–50/50.

JP2005232228 A (2005, TOSOH CORP) in one of its embodiments discloses a P3HB/LLDPE blend in a ratio 1/99–1/99, preferably 95/5–30/70, and most preferably 90/10–50/50.

Example: P3HB (BIOCYCLE® 1000) (100 pbw) was predried at 80 °C for 4 h. CSPE (TOSO-CSM® TS-430, TOSOH, CO.) (40 pbw) having a chlorine content of 35 wt%, maleic acid anhydride modified polyethylene

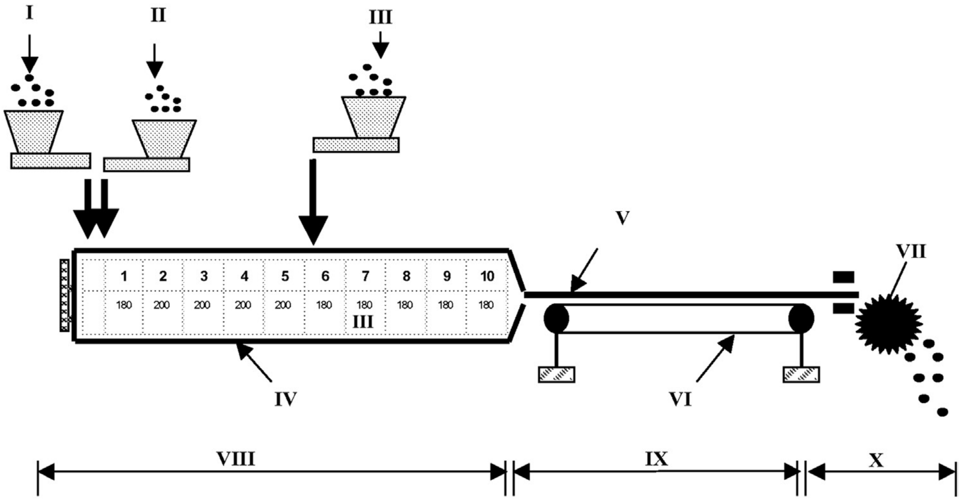


FIGURE 3.1 Schematic diagram of a preferred mixing process in a twin screw extruder (2011, **WO2011157691** A1, BASF SE). I, Thermoplastic polyurethane (TPU); II, Additives; III, Ground poly(lactic acid) (PLA); IV, Twin screw extruder (type Coperion ZSK 25 Werner & Pfleiderer, L/D = 42); V, TPU + PLA; VI, Air cooler; VII, Granulator; VIII, Compounding region; IX, Cooling region; X, Granulation region.

(MAPE) (2 pbw) having maleic acid anhydride modification amount of 3 wt%, epoxidized soybean oil (Adeka sizer O-130P) (1 wt%), talc (LSM 300) (100 pbw), and hindered-type phenol thermostabilizer (Irganox® 1010) (0.5 pbw), were added. The resulting mixture was melt extruded with phosphorus type stabilizer (Irgafos® 168) (0.5 pbw), at resin temperature of 181 °C and rotation speed of 60 rpm. The extruded strand was solidified and pelletized. The obtained resin composition had crystallization temperature of 136 °C, $T_m = 177\,°C$, $M_w = 370{,}000$, Izod impact strength of 164 J/m and solidification time of 15 s.

CN102181137 A (2011, SHANDONG ECOMANN TECHNOLOGY CO LTD) discloses a polymer blend comprising PHA (30–80, preferably 30–50 wt%), PLA (10–60, preferably 20–40 wt%), polyoxymethylene (POM, polyacetal) (1–30, preferably 1–10 wt%), filler (0–50, preferably 0.5–30), and additive (0–5, preferably 0.5–3.5 wt%). The disclosed blend is claimed to have good compatibility and impact resistance, and can be used in a wide range of products. However, the addition of POM is considered to have a limited improving effect on the brittleness and impact resistance of PLA and can significantly reduce its biodegradability (2010, **US2010167048**, FAR EASTERN NEW CENTURY CORPORATION).

WO2013077210 A1 (2013, HITACHI CHEMICAL CO LTD) discloses a method of preparing a polypropylene/PLA composition, which comprises a step wherein the polypropylene (component A) and PLA (component B) are melted and kneaded in the presence of a peroxide (component C) and a carboxylic acid anhydride (component D1) and/or a thermoplastic compound (component D2) having a specific functional group.

3.3.1.3 Aliphatic Polycarbonates

US4912149 A (1990, AIR PROD & CHEM) discloses blends of PPC with PVAc in various proportions ranging from 10 to 90 wt% of each polymer. A PPC/PVAc blend of weight ratio 80/20 has a strength several times higher than that of the original polymer.

Blends of PPC and PVAc were made in a number of different solvents at 10 wt% solids and equal composition (e.g., 50/50 wt% PPC/PVAc). The results are listed in Table 3.6 along with several combinations of PPC with polymers of high commercial use to demonstrate the general immiscibility of PPC with other polymers. Many of the blends are immiscible in solution and generally exhibit gross phase separation upon film casting. Only poly(methyl acrylate) (PMA) exhibited cast films with uniformity approaching that observed for PVAc when blended with PPC. This behavior is critical for cast film uniformity and would relate to performance characteristics when the above blends would be utilized as adhesives, coatings, or sealants applied from solution (1990, **US4912149** A, AIR PROD & CHEM).

3.3.1.4 Cellulose Derivatives

US3668157 A (1972, EASTMAN KODAK CO) discloses a miscible blend of a cellulose ester (60–98 wt%) and an elastomeric block copolymer of polyether-polyester. The cellulose ester is selected from CA, CAB, or cellulose dibenzoate.

EP0105399 A1 (1984) and **DE3314188** A1 (1984) of BAYER AG disclose thermoplastic molding compositions consisting essentially of at least one cellulose ester or cellulose mixed ester (80–97 wt%) and an aliphatic polyester or polyether containing carbonate groups in the polymer chain as linkage (20–3 wt%).

3.3.1.5 Starch

Starch, in particular destructurized starch, is generally hard and brittle in the dried state or even at low water contents (<10%), and cannot be molded at the high temperatures typically employed in thermoforming or molding shaped articles, sheets, or films. The moldability of starch can be increased by adding thermoplastic polymers (fossil fuel–based or renewable-based as well as nonbiodegradable or biodegradable polymers) in order to obtain an extrudable or injection moldable material. However, the synthetic polymers proposed as additions to starch are biodegradable only to a very limited extent or over extremely long periods of time, so that they do not satisfy the biodegradability requirements.

EP327505 A2 (1989, WARNER LAMBERT CO) discloses a polymer blend obtained from a melt comprising a water-containing destructurized starch and at least one essentially water-insoluble synthetic thermoplastic polymer. The ratio of the synthetic polymer to the starch/water component is 0.5–5 wt% to 99.5–95 wt% and preferably 0.5–2 wt% to 99.5–98 wt%. The synthetic thermoplastic polymer is selected from a long list of polymers including polyethylene, polypropylene, PVC, PVAc, ethylene-vinyl alcohol (EVOH), EAA copolymers, ethylene-ethyl acrylate copolymers (EEA), ethylene-methyl acrylate copolymers (EMA), ABS, styrene-acrylonitrile copolymers (SAN), polyacetal, etc.

WO9929733 (1999, RODENBURG VEEVOEDERS BV) discloses the use of nonbiodegradable polymer modifiers in powder or aqueous dispersion for modifying starch. The polymer modifiers are stabilized by protective colloids and/or emulsifiers and contain (1) units derived from one or more of vinyl esters of 1–18C alkylcarboxylic acids, 1–15C alcohol (meth)acrylate esters, dienes, olefins, vinyl aromatics, and/or vinyl halides and optionally (2) 0.1–20.0 wt% units derived from ethylenic comonomers containing carboxy, hydroxy, epoxy, or NH functions. Particularly

TABLE 3.6 Miscibilities of Poly(propylene carbonate) (PPC) with Other Polymers (Mostly Nonbiodegradable) (1990, US4912149 A, AIR PROD & CHEM)

Polymer Blended with PPC	Solvent	Miscibility (10% Solids)	Cast Film
Poly(vinyl acetate) (PVAc)	Methylene chloride, CH_2Cl_2	Miscible	Uniform, transparent
Poly(vinyl acetate) (PVAc)	Chloroform, $CHCl_3$	Miscible	Uniform, transparent
Poly(vinyl acetate) (PVAc)	Acetone, $(CH^3)_2CO$	Miscible	Uniform, transparent
Poly(vinyl acetate) (PVAc)	Ethyl acetate, CH_3COOCH_2CH	Miscible	Uniform, transparent
Poly(vinyl acetate) PVAc	THF, $(CH_2)_4O$	Miscible	Uniform, transparent
Aromatic polycarbonate (PC)	Methylene chloride, CH_2Cl_2	Two phase	Phase separated
Poly(methyl methacrylate) (PMMA)	Chloroform, $CHCl_3$	Two phase	Phase separated
Poly(vinyl chloride) (PVC)	THF, $(CH_2)_4O$	Two phase	Phase separated
Polystyrene (PS)	Methylene chloride, CH_2Cl_2	Two phase	Phase separated
Nitrile rubber (33% An)	Methylene chloride, CH_2Cl_2	Two phase	Phase separated
Chloroprene (CR)	Chloroform, $CHCl_3$	Two phase	Phase separated
Poly(ethyl methacrylate)	Methylene chloride, CH_2Cl_2	Two phase	Phase separated
Poly(vinyl butyral)	Methylene chloride, CH_2Cl_2	Two phase	Phase separated
Polyhydroxy ether of bisphenol A	Methylene chloride, CH_2Cl_2	Two phase	Phase separated
Bisphenol A polyarylate	Methylene chloride, CH_2Cl_2	Two phase	Phase separated
Polysulfone	Methylene chloride, CH_2Cl_2	Two phase	Phase separated
Poly(ethyl acrylate)	Toluene/CH_2Cl_2	Miscible	Phase separated
Nitrocellulose (CN)	THF, $(CH_2)_4O$	Miscible	Phase separated
Cellulose acetate propionate (CAP)	THF, $(CH_2)_4O$	Miscible	Phase separated
Poly(ε-caprolactone) (PCL)	Methylene chloride, CH_2Cl_2	Miscible	Phase separated
Poly(vinylidene fluoride) (PVDF)	DMF, $(CH_3)_2NC(O)H$	Miscible	Phase separated
Poly(2,6-dimethyl-1,4-phenylene oxide)	Chloroform, $CHCl_3$	Two phase	Phase separated
Polychlorostyrene	Methylene chloride, CH_2Cl_2	Two phase	Phase separated
Poly(vinyl methyl ether)	Methylene chloride, CH_2Cl_2	Two phase	Phase separated
Cellulose acetate (CA)	THF, $(CH_2)_4O$	Miscible	Phase separated
Poly(methyl acrylate) (PMA)	Toluene/CH_2Cl_2	Miscible	Uniform, transparent
Styrene/acrylonitrile (30% An)	Methylene chloride, CH_2Cl_2	Two phase	Phase separated
Vinyl acetate/ethylene copolymer	Methylene chloride, CH_2Cl_2	Miscible	Phase separated
Poly(ether-imide): Ultem 1000	Methylene chloride, CH_2Cl_2	Two phase	Phase separated
Polyester: PETG-6763	Methylene chloride, CH_2Cl_2	Two phase	Phase separated
Poly(isobutyl methacrylate)	Methylene chloride, CH_2Cl_2	Two phase	Phase separated
Styrene-ally alcohol copolymer	Methylene chloride, CH_2Cl_2	Two phase	Phase separated

preferred are vinyl ester polymers, such as vinyl acetate polymers, vinyl acetate-ethylene copolymers, vinyl acetate-ethylene-vinyl chloride copolymers, vinyl ester-acrylate copolymers, in particular comprising vinyl acetate and butyl acrylate and/or 2-ethylhexyl acrylate. Most preferred are *N*-methylol-functional vinyl ester polymers, such as vinyl acetate-*N*-methylolacrylamide copolymers and vinyl acetate-ethylene-*N*-methylolacrylamide copolymers.

Numerous other patents disclose the combination of starch and synthetic nonbiodegradable thermoplastic polymers:

1. 10–40 wt% ethylene-vinyl alcohol copolymers (1991, **EP0408503** A2, WARNER LAMBERT CO)
2. 1–30 wt% vinyl alcohol-vinyl acetate copolymers (1990, **EP0404723** A2, WARNER LAMBERT CO)
3. 25–40 wt% vinyl acetate (co)polymers (1992, **DE4038732** A1, HENKEL KGAA)
4. 1–30 wt% poly(4-vinyl pyridine) (1990, **EP0404728** A2, WARNER LAMBERT CO)
5. 10–30 wt% vinyl pyrrolidone copolymer (1991, **EP0407350** A2, WARNER LAMBERT CO)
6. 10–40 wt% polyolefin (1992, **DE4116404** A1, TOMKA IVAN)

WO9116375 A1 (1991, BIOTEC BIOLOG NATURVERPACK) discloses in one of its embodiments a polymer blend, comprising a polyolefin and thermoplastic starch (TPS), obtainable by mixing a polyolefin, such as polyethylene or polypropylene, with 30–70 wt% of TPS having a water content of less than 3.5 wt%. The proportion of TPS is preferably 30–50 wt%. The film produced from this blend exhibits good mechanical properties and good moisture resistance, but the biodegradability is still negatively affected by the proportion of polyolefin (1993, **EP0542155** A2, TOMKA IVAN).

JP2000095898 A (2000, JSR CORP) discloses a biodegradable composition obtained by mixing a biodegradable polymer such as starch, an impact modifier consisting of an epoxidized polyisoprene, and if necessary, a crosslinking agent. The epoxidized polyisoprene (preferably epoxidized *cis*-1,4-polyisoprene 5–75 mol% in epoxidation degree) is obtained, preferably by epoxidation of the C]C double bonds of natural rubber or a polyisoprene containing ≥90% of *cis*-1,4-bond, which is produced by polymerization of isoprene. The biodegradable composition has improved molding processability, extensibility, and ductility, and low cost.

WO2011080623 A2 (2010, KIMBERLY CLARK CO) discloses a polymer blend of multiple inherently incompatible polymer components. The polymer blend comprises a plasticized natural polymer (5–45 wt%), a polyolefin (5–40 wt%), a biodegradable polymer (5–75 wt%), and a compatibilizer (0.5–15 wt%) with both a polar and a nonpolar moiety on the same polymer molecule. The total plasticized natural and biodegradable polymers constitute the majority or predominant phase (≥53 wt%), while the polyolefin forms the minority phase. The polyolefin content is preferably in an intermediate range (e.g., about 10–35, 15–30, 20–40, or 22–37 wt%). It is also recommended not to use an oxidizing agent in the present formulation. The plasticized natural polymer is selected from TPS, thermoplastic plant protein, or thermoplastic algae. The polyolefin is selected from polyethylene, polypropylene, copolymer of ethylene and propylene, polyethylene-*co*-vinyl acetate, and a mixture of two or more polyolefins. The biodegradable polymer is selected from aliphatic polyesters, aliphatic–aromatic polyesters, polyesteramides, or modified PET. The compatibilizer is preferably a polar monomer-grafted polyolefin. The polymer blend is melt extruded into a film.

The concept of the present invention, in part, is illustrated in Figure 3.2, which depicts a change from a polyolefin majority phase (B) to a TPS majority phase (A). (B) depicts a conventional film substrate that is predominately made from a polyolefin (e.g., polyethylene) with a minority phase of TPS. Since polyolefins have the physical characteristics necessary to form a thin film, the resulting blend could be made into a thin film without any complications. (A) depicts a film in which plasticized natural and biodegradable polymers constitute the majority or predominant phase, while the polyolefin forms the minority phase. Previously, efforts of making 60 wt% thermoplastic starch masterbatch and 40 wt% polyolefins have failed to yield a thin film of any utility because the material tended to tear easily, be very brittle, and have low tensile properties. As the amount of biopolymer TPS increases to over 50 vol.% in volume (e.g., 53, 55, 58, or 60 wt%), it forms a majority phase, since TPS or TPS masterbatch does not exhibit the same processability characteristics for making good quality films, pure TPS ordinarily cannot be used to form a thin film of 1–2 mils and is often very rigid and brittle, the resulting polymer blend lacks the required mechanical properties and ability to be processed into thin films. Since the material processability and properties are commonly determined by the continuous phase (most often the majority phase) of the materials, the two proportionate compositions contribute to a difference in mechanism of making films.

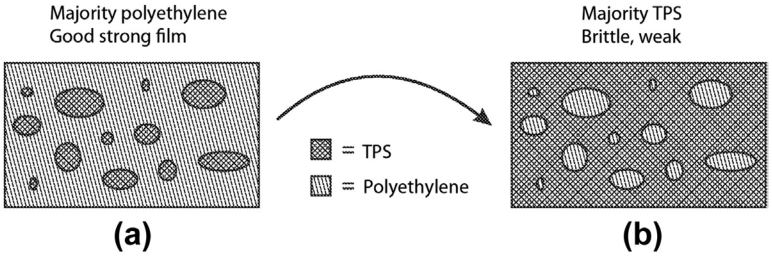


FIGURE 3.2 Schematic representation of the components of a polymer blend within a cast thermoplastic film depicting a change from a polyethylene majority phase (a) to a TPS (thermoplastic starch) majority phase (b) (2010, **WO2011080623** A2, KIMBERLY CLARK CO).

To overcome this problem, **WO2011080623** A2 developed a blend with the addition of the right amount of an additional synthetic biodegradable polymer namely, an aliphatic–aromatic copolyester to the mix even though the copolyester itself has limitation to form a cast film. The overall components were made compatible by one or more compatibilizers. The resulting films were soft, homogeneous, and having balanced mechanical properties desired for the baffle film applications.

The polyolefin and thermoplastic starch molecules are not chemical bonded with each other, nor are starch-polyester graft copolymers included. The polymer blend system is not a water-based suspension. The film casting process does not involve evaporation steps. The starch particles are not crosslinked. It is important to have noncrosslinked starch to form thin films, otherwise the particles are filler and may cause film debonding.

US20050288399 A (2005, CHEN MING-TUNG) discloses a method of producing a biodegradable polymer composition comprising the steps of: (1) providing a composition containing a starch (25–50 wt%), a synthetic biodegradable polyester (10–40 wt%), a synthetic nonbiodegradable polymer with linear alkenes (5–15 wt%), an affinity agent (8–20 wt%), a coupling agent (1–3 wt%), and an additive (1–15 wt%); (2) performing an agitating process; (3) performing a compounding process; and (4) cooling and granulating to form a biodegradable polymer composition. Preferably, the synthetic biodegradable polyester is selected from PLA, PCL, or PBS, and a mixture thereof, in an amount of 15–30 wt%. The synthetic nonbiodegradable polymer with linear alkenes is an alkene copolymer selected from EVAc, EVOH and/or ethylene-acrylic acetate copolymer (EAAc) preferably a mixture of EAAc and EVAc or EVOH in a ratio of 0.1–10. The affinity agent is glycerol or PVOH. It is claimed that more than 90% of the biodegradable polymer composition degrades within 6 months under a compost condition, and then the biodegradable polymer composition degrades completely within 1 year.

Typically, these compositions are obtainable by blending a starch-based component and a synthetic thermoplastic component under conditions that are typical of melting extrusion, in the presence of a limited amount of water or plasticizer (typically 5–40 wt% referred to the starch-water system), at a temperature and pressure sufficient to destroy the crystallinity of starch and obtain a thermoplastic melt. By means of such process, thermoplastic blends have been obtained wherein the starch-based component and the synthetic thermoplastic component form a structure that is interpenetrated or at least partially interpenetrated.

Blends comprising flour are also known. **DE19648616** A1 (1998, INST ETREIDEVERARBEITUNG) discloses the granulation of thermoplastic processable polymer blends containing fractionated cereal flour, aqueous polymer dispersions, such as polyvinyl esters and/or high PVOH and water. Water is required for the granulation and has to be removed in a separate step for obtaining a blend having thermoplastic properties. Furthermore, the PVOH content is high, making the products still water sensitive. Actually the use of a meal or fractionated cereal, but not the use of a flour, is described (2010, **WO2010133560** A1, WACKER CHEMIE AG).

WO2010133560 A1 (2010, WACKER CHEMIE AG) discloses a polymer composition comprising one or more flours (15–60 wt%), two or more polymers, optionally plasticizers (5–30 wt%), optionally fillers and additives, characterized in that at least one of the polymers is a nonbiodegradable polymer in the form of its water-redispersible polymer powder or as aqueous polymer dispersion and that at least one of the polymers is a biopolymer (20–60 wt%), whereby the compositions contain less than 12 wt% of PVOH. Flour generally contains starch, fibers, nonstarch polysaccharides and proteins. Biopolymers are selected from PDLLA, PDLA, PLLA, PGA, PGLA, PCL, poly(L-lactide-*co*-caprolactone-*co*-glycolide), poly(dioxanone) (PDO) poly(trimethylene carbonate), polyglyconate, P3HB, PHBHV, P3HV polysaccharides, modified polysaccharides, PBS, poly(4-butylene adipate) (P4BA), poly(butylene adipate *co*-terephthalate) (PBAT), PBSA, polyanhydrides, polyorthoesters (POE), plasticized starch with PCL, starch-based aliphatic polyesters, polyesteramides, etc. Appropriate nonbiodegradable polymers are based on vinyl esters or (meth)acrylate esters. Preferred vinyl esters are vinyl acetate, vinyl propionate, vinyl butyrate, vinyl-2-ethylhexanoate, vinyl laurate, 1-methylvinyl acetate, vinyl pivalate, and vinyl esters of α-branched monocarboxylic acids having 9–13 carbon atoms. Particularly preferred are vinyl acetate–and methyl acrylate–based polymers.

The inventors of the present patent believe that the use of flour has several advantages compared to starch. Flour is cheaper than starch, while making it gives less waste products and waste water and saves various energy consuming drying steps by skipping all of the starch extraction techniques. Certain constituents of the flour can bring an improvement of the mechanical performance and flexibility of the products due to the presence of fibers, nonstarch polysaccharides, and proteins present in the flour. Particularly, the hydrophobic gluten, lipids, and further proteins present in the flour are believed to add to the resistance to water of the biopolymer, whereas respective products based on starch, e.g., not flour, often result in undesired water sensitivity. These nonstarch components also influence the barrier properties and make stronger materials by having stronger protein glutenin network. Fibrous components are also believed to contribute in terms of mechanical properties acting

TABLE 3.7 Blends of a Major Amount of Biopolymer(s) with Synthetic Nonbiodegradable Polymer(s)

Biopolymer (Major Component)	Minor Component(s)	Other Component(s)	Patent
PLA (99–85 wt%)	s-PP (1–15 wt%)		**JPH10251498** A (1998, KANEBO LTD)
PLA (99.5–40 wt%)	Modified olefin copolymer (0.5–60 wt%)		**JPH09316310** A (1997, KANEBO LTD)
PDLA (25–80 wt%)	PC (20–75 wt%)	Compatibilizer (PLLA/PC copolymer) (0.01–30 pbw)	**US2010056700** A1 (2010, CHEIL IND INC)
PLA (60–97 wt%)	A + B (3–40 wt%) A = ethylene-alkyl (meth)acrylate-maleic anhydride terpolymer or ethylene-alkyl (meth)acrylate-glycidyl methacrylate terpolymer; B = copolymer of ethylene and alkyl (meth)acrylate		**FR2902434** A1 (2007, ARKEMA FRANCE)
PLLA (60–80 wt%) and PDLA, (15–30 wt%)	poly(ethylene-alkyl acrylate-glycidyl methacrylate) (5–10 wt%)		**US2012245292** A1 (2012, HYUNDAI MOTOR CO LTD)
PLA	Epoxidized rubber		**WO9622330** A2 (1996, CARGILL INC)
PLA (50–90 wt%)	PC (50–10 wt%)		**JPH07109413** A (1995, MITSUI TOATSU CHEMICALS)
PLA (60–95 wt%)	PC (40–5 wt%)		**EP0896013** A1 (1999, SHIMADZU CORP)
PDLLA (80–99 wt%)	PC, PET, PS (20–1 wt%)	Polyisocyanate (0.5–5 wt% based on PDLLA)	**JP2000017038** A (2000, KANEBO LTD; RES INST INNOVATIVE TECH EARTH; KANEBO SYNTHETIC FIBERS LTD)
PLA (90–10 wt%)	PC (10–90 wt%)	Multifunctional isocyanate (0.1–5 pbw)	**JP2010143947** A (2010, NAGOYA CITY)
PLA (75–10 wt%)	PC (25–90 wt%)	Glycidyl or acid anhydride grafted polymer (acrylic resin or styrene resin)	**WO2006030951** A1 (2006, TORAY INDUSTRIES)
PLA	PC, ABS, PET (0.1–50 wt%)	Maleic anhydride-grafted polybutadiene	**KR20110064122** A (2010, SAMYANG CORP)
PLA (2–72 wt%)	PC (2–72 wt%) and ABS (2–72 wt%)	PET (1–15 pbw) and ABS (2–15 pbw) and carbodiimide (0.2–3 pbw)	**KR20100079986** A (2010, SAMYANG CORP
PLA (16–82 wt%)	Recycled PET (15–60 wt%), MBS (2–15 wt%)		**KR20110108736** A (2011, SAMYANG CORP)
P3HB, PHBHV	CPE (≤50 wt%), CSPE (≤30 wt%), EVA (≤35 wt%)		**EP0052460** A1 (1982, ICI PLC)
P3HB, PLA (90–50 wt%)	CSPE (10–50 wt%)	MAPE, epoxidized soybean oil, talc, thermostabilizer	**JP2005232232** A (2005, TOSOH CORP)
P3HB, PLA (90–50 wt%)	LLPE (10–50 wt%)	MAPE, epoxidized soybean oil, talc, thermostabilizer	**JP2005232228** A (2005, TOSOH CORP)
PLA (10–90 wt%)	Biobased HDPE (90–10 wt%)	Compatibilizing agent (1–20 wt%)	**WO2013108817** A (2013, NAT INST OF ADVANCED IND SCIEN)

TABLE 3.7 Blends of a Major Amount of Biopolymer(s) with Synthetic Nonbiodegradable Polymer(s)—cont'd

Biopolymer (Major Component)	Minor Component(s)	Other Component(s)	Patent
PHA (30–80, pref. 30–50 wt%) and PLA (10–60, pref. 20–40 wt%)	POM (1–30, pref. 1–10 wt%)	Filler (0–50, pref. 0.5–30) and additive (0–5, pref. 0.5–3.5 wt%)	**CN102181137** A (2011, SHANDONG ECOMANN TECHNOLOGY CO LTD)
PPC (80 wt%)	PVAc (820 wt%)		**US4912149** A (1990, AIR PROD & CHEM)
Starch (25–50 wt%) and aliph. polyester (PLA, PCL, PBS) (10–40 wt%)	EVAc, EVOH, EVAA (5–15 wt%)	Affinity agent (glycerol, PVOH) affinity agent (8–20 wt%); Coupling agent (1–3 wt%); Additive (1–15 wt%)	**US20050288399** A (2005, CHEN MING-TUNG)
Starch	Epoxidized polyisoprene		**JP2000095898** A (2000, JSR CORP)
TPS and PBAT (53 wt%)	Polyethylene (5–40 wt%)	Compatibilizer: polar monomer grafted polyethylene (0.5–15 wt%)	**WO2011080623** A2 (2010, KIMBERLY CLARK CO)

ABS, acrylonitrile-butadiene-styrene copolymer; CPE, chlorinated polyethylene; CSPE, chlorosulfonated polyethylene; EVAc, ethylene-vinyl acetate copolymer; EVAA, ethylene-acrylic acetate copolymer; HDPE, high density polyethylene; MAPE, maleic anhydride polyethylene; PBAT, poly(butylene adipate-*co*-terephthalate); PBS, poly(butylene succinate); PC, aromatic polycarbonate; PCL, poly(ε-caprolactone); PDLLA, poly(D-lactic-*co*-L-lactic acid); PET, poly(ethylene terephthalate); P3HB, poly(3-hydroxybutyrate); PHBHV, poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate); PDLA, poly(D-lactic acid); PLA, poly(lactic acid); PLLA, poly(L-lactic acid); POM, polyoxymethylene; PPC, poly(propylene carbonate); s-PP, syndiotactic polypropylene; TPS, thermoplastic starch.

as functional fillers. Furthermore, flour is produced in fewer processing steps without the use of water, leading to a more sustainable solution. The use of flours will also result in reduced carbon dioxide emission and reduced dependency on fossil fuels. It is thus thought that the life cycle analyses of a flour-based product will be better compared to a starch. Furthermore, it is believed that the combination of the various constituents in flour (being a mixed substrate consisting of carbohydrates and starch) contributes to enhance the biodegradation of the biopolymer products by synergistic effects.

Table 3.7 presents a list of the patents outlined in Section 3.3.1: Biopolymer in majority.

3.3.2 Biopolymer in Minority

Biodegradable polymers are physically blended as additives with synthetic nonbiodegradable polymers in order to promote either degradability[6] or impart flexibility (e.g., PCL) to resulting articles formed from the polymeric materials.

Degradability promoter based on biodegradable polymers is a different approach toward the use of biopolymers. Instead of forming new and different types of polymers, several companies try to render traditional polymers (bio) degradable by mixing them with biopolymer additives without adding much cost. The biopolymer additives are used the same way as colorants and are meant to speed up the degradation process.

3.3.2.1 *Poly(Lactic Acid)*

JPH06263892 A (1994, AGENCY IND SCIENCE TECHN; SHOWA CHEM) discloses a film-forming composition prepared by melt blending an aliphatic polyester (30–50 wt%) and a polyolefin (50–70 wt%) with a graft copolymer having a comb structure as a compatibilizer. The graft copolymer has an acid-modified or epoxy-modified functional group and a group compatible with the polyolefin. A film prepared from this composition is claimed to have high degradability even when the content of the aliphatic polyester is as low as below 50 wt%, mechanical properties equivalent to those of a film made of a general-purpose polymer, and weldability.

JP2008195834 A (2008, RIKEN VITAMIN CO) discloses a film-forming composition comprising a polyolefin, PLA (3–50 wt%) and a carboxylic acid ester of a polyhydric alcohol (0.01–25 wt%). The polyolefin is preferably polyethylene. The carboxylic acid ester of a polyhydric alcohol is preferably glycerol carboxylate. The polymer composition is claimed to have adequate mechanical properties, such as

---

[6] Another system used to promote the degradability of commodity polymers (e.g., polyolefins) involves the use of prodegradants or prooxidants (Niaounakis M. Biopolymers Reuse, Recycling, and Disposal, Chapter 2: Definition and Assessment of (Bio)degradation; Section 2.3: Biopolymers versus Oxodegradable Polymers. Plastics Design Library (PDL). 1st ed: Access Online via Elsevier; 2013. p. 432). These additives accelerate degradation (chain scission and/or crosslinking depending on the polymer type) induced by heat, actinic or ultraviolet (UV) radiation.

tensile modulus and tear strength for practical purposes. A representative example describes a film obtained by kneading PLA and a carboxylic acid ester of a polyhydric alcohol to form a PLA masterbatch, blending the resulting masterbatch with a polyethylene and molding the mixture to form a film.

US2009326152 A1 (2009, FINA TECHNOLOGY) discloses a polymer composition comprising a blend of a polyolefin (52–99 wt%), PLA (1–40 wt%), and a reactive modifier (0.5.15 wt%). Herein, the reactive modifier refers to a polymeric additive that when added to a molten blend of immiscible polymers, such as polypropylene (PP) and PLA or polyethylene and PLA, forms compounds *in situ* that serve to stabilize the blend. The compounds formed *in situ* act as compatibilizers, and the reactive modifiers are precursors to these compatibilizers. The reactive modifier is an epoxy-functionalized polyolefin wherein the epoxy-functionalized polyolefin has a grafting yield of 0.2–15 wt% and is the reaction product of a polyolefin, a multifunctional acrylate comonomer, and an initiator. Examples of suitable epoxy-functionalized polyolefins include epoxy-functionalized polypropylene such as glycidyl methacrylate-grafted polypropylene (PP-*g*-GMA), epoxy-functionalized polyethylene such as polyethylene-*co*-glycidyl methacrylate (PE-*co*-GMA), or combinations thereof. An example of an epoxy-functionalized polyethylene suitable for use in this disclosure includes the commercial product Lotader® AX8840 (Arkema), which is a PE-*co*-GMA containing 8% GMA.

In an embodiment a compatibilized blend PP/PLA may be prepared by the concurrent blending of the reactive modifier with polypropylene and PLA under conditions suitable for the formation of a blended material. Polypropylene, PLA, and the reactive modifier may be dry blended, fed into an extruder, and melted. The mixing may be carried out using a continuous mixer, such as a mixer consisting of an intermeshing corotating twin screw extruder for mixing/melting the components of the compatibilized blend and a single screw extruder or a gear pump for pumping. The compatibilized blend may be further dried in an oven or under vacuum.

It is suggested that the formation of a PP-epoxy-PLA grafted copolymer occurs upon reactive extrusion when at least a portion of the reactive modifier (i.e., epoxy-functionalized polyolefin), which is originally associated with the polypropylene, migrates to the PP/PLA interface. The reactive modifier may contact the PLA molecules at the interface between the polypropylene and PLA phases and react with the PLA to form PP-epoxy-PLA grafted copolymers at the interface. The compatibilizer (i.e., PP-epoxy-PLA copolymer) that is formed *in situ* from reactive extrusion of the reactive modifier (i.e., epoxy-functionalized polyolefin), polypropylene, and PLA) may perform multiple functions. In a molten state, the compatibilizer may decrease the interfacial tension between polypropylene and PLA and improve dispersion of the PLA phase in the polypropylene. Once the PP/PLA blend solidifies, the compatibilizer remains at the interface of polypropylene and PLA, where it may function to chemically interlink polypropylene and PLA. Thus, the compatibilizers form an adhesive or tie layer that serves to improve the interfacial bonding resulting in a compatibilized PP/PLA blend having improved phase dispersions and properties when compared to an uncompatibilized PP/PLA blend.

US2009326130 A1 (2009, FINA TECHNOLOGY) is a modification of the above patent application disclosing that a biaxially oriented film is produced from the PP/PLA blend having a haze of 10–95% and a gloss 45° of 50–125. PLA is present in the PP/PLA blend in an amount of 1–40 wt%, preferably 5–30 wt%, or most preferably 10–20 wt%. The dispersed PLA phases in the PP/PLA blend may function as cavitating agents. Herein, a cavitating agent refers to a compound(s) capable of generating voids in the structure of film during the film-making process. In an embodiment, the PP/PLA blend further comprises a cavitating booster. Herein, a cavitating booster refers to a compound(s) capable of boosting the cavitating efficiency of PLA dispersed phase in the PP/PLA blend, and may broaden the processing window of the PP/PLA blend. The cavitating booster may comprise a functionalized polypropylene, for example, maleic anhydride (MAH) functionalized polypropylene (PP-*g*-MAH).

WO2010047370 A1 (2010, KAO CORP) discloses a method for producing a polymer composition comprising the following steps: (1) melt kneading a raw material (A) that comprises PLA, a crystal nucleating agent, and a plasticizer comprising an ester compound formed from a polycarboxylic acid having a C_{1-7} hydrocarbon group and a mono-alcohol having a C_{1-7} hydrocarbon group, thereby preparing a PLA-containing melt kneaded material having a relative crystallinity degree of 70% or more; (2) melt kneading the PLA-containing melt kneaded material produced in step (1) together with a raw material (B) comprising polypropylene and a compatibilizing agent. The weight ratio PP/PLA in the polymer composition is 90/10–40/60, more preferably 90/10–50/50, and even more preferably 90/10–60/40. Preferred commercial products of PLA are selected from the Lacea® series, NatureWorks® series, and Ecoplastic U'z® series. The polymer composition produced by the process can be used suitably in various industrial applications such as commodities, parts for household electrical appliances, and automotive parts.

WO2013077210 A1 (2013, HITACHI CHEMICAL CO LTD) discloses a method for producing a blend of polypropylene and PLA, comprising a step wherein polypropylene and PLA are melted and kneaded in the presence of a peroxide compound and a carboxylic acid anhydride compound and/or a thermoplastic polymer having a specific functional group that is reactive with PLA (e.g., ethylene-glycidyl-methacrylate-vinyl acetate copolymer). The weight ratio PP/PLA is 90/10–10/90, more preferably 80/20–20/80, and most preferably 70/30–30/70. In most of the provided examples, PLA is in minority.

JP2008038142 A (2008, TORAY INDUSTRIES) discloses a polymer composition produced by compounding PLA (1–60 wt%), a polyolefin (99–40 wt%), and a compatibilizing agent (1–50 wt%). The compatibilizing agent is selected from an ethylene-vinyl acetate copolymer, an ethylene-(meth)acrylate copolymer; a polyolefin having acid anhydride group, carboxyl group, amino group, imino group, alkoxysilyl group, silanol group, silyl ether group, hydroxyl group or epoxy group; an acrylic resin or styrene resin having acid anhydride group, carboxyl group, amino group, imino group, alkoxysilyl group, silanol group, silyl ether group, hydroxyl group or epoxy group; and an ionomer resin. The disclosed polymer composition is claimed to have excellent moldability, impact resistance, and heat resistance.

JPH0543772 A (1993, ASAHI CHEMICAL IND) discloses a blend prepared by adding an aliphatic polyester (10–60 pbw) and a minute amount of formaldehyde (4 pbw) to polyoxymethylene (POM or polyacetal) (100 pbw). A preferred example of the aliphatic polyester is PLA. The formaldehyde is intended to promote the degradation of POM.

WO03014224 A1 (2003, TORAY INDUSTRIES) discloses a blend of PLA (40–50 wt%) with POM (60–40 wt%) and an impact modifier. The impact modifier is preferably a core-shell-type multilayered polymer, composed of an elastomer core and one or more acrylic shell layers.

US2004230001 A1 (2004, DU PONT) discloses also a blend of PLA with POM and an ethylene copolymer impact modifier, which is said to improve the impact resistance of the original biodegradable polymer. The composition is prepared by melt blending POM, PLA, and ethylene copolymer impact modifier until they are homogeneously dispersed to the naked eye and do not delaminate upon injection molding. Other materials (e.g., EVA, ionomers, grafting agents, and other additives) may be also uniformly dispersed in the PLA-ethylene copolymer impact modifier matrix. In the provided examples PLA is used in an amount of 20–50 wt%. The blend may be obtained by combining the component materials using any melt mixing method known in the art. For example: (1) the component materials may be mixed using a melt mixer such as a single or twin screw extruder, blender, kneader, Banbury mixer, roll mixer, etc. to give a resin composition; or (2) a portion of the component materials can be mixed in a melt mixer, and the rest of the component materials subsequently added and further melt mixed until homogeneous.

The miscibility of PLA with POM is a controversial issue since their blends exhibit two T_g*s* (2010, **US2010167048**, FAR EASTERN NEW CENTURY CORPORATION). Nagai et al. [64] investigated the miscibility of POM/PLA blends at various blend ratios and their effect on thermal and mechanical properties. POM and PLA have very similar characteristics, e.g., both are semicrystalline with T_m of about 160 °C and possess almost similar solubility parameters. However, POM is characterized by a very low T_g (about −65 °C to −110 °C), and crystallizes very fast, whereas PLA has a low crystallization rate. Although the POM/PLA blend exhibits two T_gs derived from the POM and PLA phase, respectively, the blend is considered to be miscible, since no phase separation could be detected (see also Table 3.5).

US2013109781 A1 (2013, BIO TEC ENVIRONMENTAL LLC) discloses an additive system for enhancing the degradation of a synthetic polymer when added thereto, comprising a furanone, a glutaric acid, a carboxylic acid compound (e.g., hexadecanoic acid), a biodegradable polymer (e.g., PLA, PGA, PLGA, PCL), and a carrier resin (e.g., PVC, EVA, PMMA, etc.). The additive may also comprise organoleptic chemicals as swelling agents (e.g., natural fibers, cultured colloids, cyclodextrin, etc.).

WO2006038506 A1 (2006, IDEMITSU KOSAN CO) discloses an aromatic polycarbonate-based composition comprising: (1) aromatic polycarbonate (PC) (50–95 wt%) and (2) an aliphatic polyester (50–5 wt%), with (3) carbon nanotubes (0.1–30 wt%) compounded therewith. The aliphatic polyester is preferably PLA (Lacea® H-100, Mitsui Chemicals). The PC-based composition is claimed to have a stabilized phase structure of aromatic polycarbonate/aliphatic polyester, and reaggregation of the polyester during melting and domain orientation during injection molding is reduced. The obtained molding is claimed to be free of layer delamination, showing excellent electrical conductivity (antistatic property), solvent resistance, fluidity, flame retardancy, impact resistance, molding appearance, etc.

3.3.2.2 *Polyxydroxyalkanoates*

EP0052460 A (1982, ICI PLC) discloses, in some of its embodiments, the addition of a minor amount (i.e., ≤50 wt%) of P3HB to a chlorine or nitrile group containing polymer (e.g., PVC, PAN) to assist the processing of the latter. Benefits in processability may be achieved by the addition of a relatively small amount of P3HB, e.g., 0.2–10, particularly 0.5–5 wt%, wherein P3HB acts as a high-molecular-weight processing aid. The addition of P3HB, even in such relatively small amounts, enables polymers containing a major proportion of acrylonitrile, vinyl chloride, or vinylidene chloride units, which are difficult to melt process, to be melt processed more readily. Such polymers are often melt processed at a temperature relatively close to their T_m, and have a narrow processing window. The addition of a small amount of a P3HB causes, inter alia, the melt viscosity to be reduced and assists processability in other respects. To avoid thermal degradation of P3HB, the processing temperature should be below 220 °C. Furthermore, to be effective as a processing aid, P3HB should have a T_m below the processing temperature. Therefore, where the desired processing temperature is very near to, or below, T_m (about 180 °C) of P3HB, a lower melting copolymer such as PHBHV is preferably employed; PHBHV is particularly useful as processing aid for vinyl chloride polymers.

JPS63172762 A (1988, MITSUBISHI RAYON CO) discloses the use of P3HB as an additive to PET in order to improve its crystallization rate. A PET containing a crystallization accelerator added thereto can be used according to purpose. Examples of the crystallization accelerator are talc, sodium stearate, and metal salts of aromatic carboxylic acids.

PHBHV has also been used as an additive (15 wt%) to conventional synthetic binders in paint formulations (1996, **GB2291648** A, ICI PLC). The additive results in more rapid curing and a shorter time before the coating is "tack-free." In this context, it is assumed that as a consequence of a rapid crystallization of PHBHV in the presence of the conventional binder a "quasi-crosslinking" occurs that is responsible for the accelerated physical drying. The physical properties (T_m, T_g, crystallinity) of PHBHV in this case are used in order to improve conventional paint systems based on synthetic binders (curing, drying).

JP2006077063 A (2006, KANEKA CORP) discloses a composition prepared by mixing a polyolefin (100 pbw) with a PHA (1–100, preferably 1–50 pbw) in the presence of a polyolefin containing an acid or epoxy group as compatibilizer (0.1–100, preferably 0.1–50 pbw). Preferred polyolefin and PHA are polypropylene and PHBHx, respectively. The dispersed structure contains a domain of the biodegradable aliphatic polyester polymer surrounded by the matrix of a polyolefin having acid or epoxy group. The composition has well-balanced properties such as impact resistance and flexural modulus.

3.3.2.3 Poly(ε-Caprolactone)

Poly(ε-caprolactone) (PCL), a biodegradable aliphatic polyester derived from fossil fuel–based resources, is known to have a plasticizing effect and impart flexibility on several polymers.

US3632687 A (1972), **US3734979** A (1973), and **US3867324** A (1975) of UNION CARBIDE CORP disclose molded articles, especially, containers, films, and fibers, formed from blends of polyolefins (e.g., polyethylene, polypropylene, polymethylpentene, etc.) and a small amount of PCL. The obtained articles exhibit enhanced stress crack resistance, improved dyeability, low haze, and high gloss. It is suggested that these blends lessen segregation of the two polymers into separate domains, and the negative impact on physical properties that would be associated with such segregation.

US3762979 A (1973, DOW CHEMICAL CO) discloses compositions of vinylidene chloride-vinyl chloride copolymer and 2–6 wt% of PCL (e.g., CAPA®), which is solid at room temperature ($M_n = 11{,}400$–$114{,}000$ g/mol); said compositions are prepared by simple mixing of the two polymers in the powdery or pulverulent state. PCL is compatible with the vinylidene chloride–vinyl chloride copolymer in an amount of up to about 10 wt% based on copolymer weight and exhibits usual plasticizing action with resultant lowering of temperature requirement for the melting of the crystalline copolymer. These compositions are used as adhesive seam materials for the joining of woven or nonwoven fabrics, e.g., by use of dielectric bonding techniques, exhibiting significantly improved bond strength. However, difficulties may be encountered during the preparation of the compositions. The mixing process results disadvantageously in compositions that generally lack homogeneity and, therefore, suffer from a certain lack of reproducibility of their properties (2008, **WO2008028918**, SOLVAY).

To avoid the disadvantages linked to the preparation of these compositions by mixing in the powdery or pulverulent state, an alternative method was proposed by **FR2618441** A1 (1989, SOLVAY) to add the PCL additive during the preparation of a copolymer of vinyl chloride and a particular alkyl acrylate. It is nevertheless well known in the prior art that adding a third substance during the polymerization of vinylidene chloride (VDC) may not only affect the good operation of this but, in addition, have damaging consequences on the remarkable gas and odor barrier properties, characteristic of VDC and not exhibited by vinyl chloride polymers (2008, **WO2008028918**, SOLVAY).

The gas barrier properties of VDC interpolymers find applications in the manufacture of mono- and multilayer blown or cast films. However, due to the proximity of T_g of VDC interpolymer to room temperature (23 °C), these films are susceptible to brittle failure. As such, the improvement in the tear resistance of film made from VDC interpolymer without a significant deterioration in the barrier properties, e.g., oxygen transmission rate, of the film is of continuing interest to the packaging industry.

FR2905378 A1 (2008, SOLVAY) discloses a composition based on a VDC copolymer for the manufacture of controlled-permeability films, comprising 0.1–50 wt% of PCL ($M_n \leq 10{,}000$ g/mol.), which is liquid at room temperature, and 0.1–7 wt% of an epoxidized soybean oil.

WO2008028918 (2008, SOLVAY) discloses that a PCL preformed in a medium other than that of the VDC copolymerization may be added to the copolymer preparation medium. The total amount of PCL is advantageously at most 50 wt% most prefereably 3–15 wt% to the total weight of the composition. Suitable commercial products are selected from the CAPA® series (e.g., CAPA® PL100, 3201, 2403).

These compositions contain, however, relatively large amounts of PCL plasticizer that may give rise to several drawbacks. Furthermore, when PCL is incorporated into the VDC copolymer preparation medium, PCL sometimes has a tendency to degrade due to its sensitivity to the reaction conditions. This incorporation does not therefore make it possible to satisfactorily solve the problems of migration and degradation of the PCL plasticizer incorporated into these compositions (2011, **WO2011110567** A, SOLVAY).

3.3.2.4 Poly(Alkylene Alkanoate)s

WO2013048738 A1 (2013, DOW GLOBAL TECHNOLOGIES LLC) discloses a polymer blend containing VDC interpolymer (80–100 wt%), PBS (≤20 wt%), and optionally at least one additive. A preferred commercial product of PBS is Bionolle® 1010 (Showa High Polymer K.K). The tear resistance of a film (in both the machine- and cross-direction) made from the disclosed blend or composition is improved in comparison with the tear resistance of a film made under similar conditions and from a blend or composition alike in all aspects except that the PBS of the blend or composition is replaced with additional VDC interpolymer.

3.3.2.5 Aliphatic Polycarbonates

US4137280 A (1979, AIR PROD & CHEM) discloses a PVC composition having blended therein from about 5–60 wt%, preferably 10–40 wt%, of a poly(alkylene carbonate) formed by reacting an alkylene oxide and carbon dioxide. The poly(alkylene carbonate) is added to improve the melt flow indices and oxygen barrier characteristics of the PVC.

WO2013007760 A1 (2013, NORNER AS) discloses a blend, useful in e.g., extruded article that is film and molded article, comprising poly(alkylene carbonate) (preferably 10–30 wt%), polyolefin (preferably 50–90 wt%), and compatibilizer. The poly(alkylene carbonate) is selected from PPC, poly(ethylene carbonate) (PEC) or poly(cyclohexene carbonate) (PCHC). The polyolefin is polyethylene (e.g., HDPE) or polypropylene. The compatibilizer is preferably poly(ethylene-*co*-methyl acrylate).

Example: PCHC (QPAC® 100, Empower Materials) was ground with liquid nitrogen and dried at 35 °C for 24 h. The PCHC (10 wt%) was blended with HDPE (FB 1460, Borealis) (90 wt%). A copolymer of ethylene and methyl acrylate (Elvaloy AC 1330, DuPont) was added (5 wt%) and antioxidant (Irganox B 215) and calcium stearate were added as stabilizing agents to give a blend. The output rate was 5 kg/h and the screw speed was 250 rpm. Nitrogen-flushing was applied without vacuum. The set temperature was 130 °C and the logged process temperatures were 136–144–152–159 °C.

WO2014001922 A1 (2014, KIMBERLY CLARK CO) discloses in one of its embodiments a film comprising: 10–20 wt% of at least one polyalkylene carbonate and 80–90 wt% of at least one polyolefin, wherein at least one poly(alkylene carbonate) forms dispersed domains within a continuous phase defined by at least one polyolefin. The polyalkylene carbonate is PPC or PEC. The polyolefin is a copolymer of an α-olefin and ethylene.

3.3.2.6 Cellulose Derivatives

US4770931 A (1988, EASTMAN KODAK CO) discloses immiscible blends of cellulose esters and aromatic polyesters. Shaped articles formed from these blends comprise a continuous PET phase having dispersed therein microbeads of cellulose acetate (CA), which are at least partially bordered by void space, the microbeads of CA being present in an amount of about 10–30 wt% based on the weight of said polyester, said void space occupying about 2–50% vol.% of said shaped article. Such articles are useful as paper substitutes.

3.3.2.7 Starch

The use of starch as a cost-effective additive was developed in the 1970s, but soon it became clear that the normal hydrophilic starch was unsuitable. Addition of starch additives to polyolefins such as polyethylene and polypropylene can enhance the degradability of these polymers without seriously compromising certain properties such as their effectiveness as a moisture barrier; on the other hand, a sacrifice of some other physical properties and color is observed (1992, **US5135966**, SHELL OIL CO). The starch itself decomposes above about 230 °C, and so offers severe limitation in polymer melt processability. Furthermore, such additives do not enable these polymer blends to be classified as compostable in accordance with the definition of compostability in such international standards as EN 13432:2000 or ASTM 6400–12.

A number of processes have been developed for incorporating starch into a polyolefin. **DE2322440** A (1973, COLOROLL LTD) discloses in one of its embodiments a mixture of polyethylene and dispersed therein 5–15 wt% of native starch granules, the surface of said granules being modified by reaction with a compound that reacts with hydroxyl groups to form an ether or an ester. A mixture of polyethylene and starch is processed by mixing at elevated temperatures to give a base material, which is then mixed with polyethylene at room temperature, after which the mixture is injection molded. The process is a multistage one and hence expensive, and furthermore the poor affinity between polyethylene and starch makes it necessary to carry out thorough mixing, which requires a long time at elevated temperatures, and the starch may be damaged by heat (1990, **EP402826** A1, BASF AG).

US4016117 (1977), **US4021388** (1977), and **BE870457** A1 (1979) of COLOROLL LTD disclose compositions consisting essentially of: (1) a vinyl polymer (e.g., polyethylene, polypropylene or PVC); (2) dispersed therein 5–50 wt% of a biodegradable granular filler such as native starch; and (3) up to 5.5 wt% of an auto-oxidizable substance, preferably a fatty acid, which, when in contact with a transition metal salt, undergoes auto-oxidation to generate a peroxide and/or a hydroperoxide that attacks the carbon-to-carbon linkages of the vinyl polymer. Furthermore, about 8 wt% predried starch (0.5% moisture), 90 wt% polyethylene, 1.6 wt% ethyl oleate, and less than 1K oleic acid compositions can be converted to blown films. However, essentially the same composition could not be blown into a satisfactory film if the starch contained as much as 2% moisture. The product became disfigured and weakened by the presence of numerous small bubbles created by the conversion of the free moisture to steam. This limitation on the moisture content imposes requirements for special drying, handling, and storage techniques preparatory to film. It was further found that both gelatinizing the starch and increasing the starch content of film formulations of 5–15 wt% resulted in feel and crease retention properties that are much more paper-like than those of unmodified PE film. Another disadvantage of these materials is that they start to undergo degradation directly after the preparation (1981, **EP0032802** A1, US AGRICULTURE).

Mono- and multilayer films have been prepared using a melt blend of polyolefin and starch. However, the manufacture of such films can be problematic. The hydrophilic nature of starch is inherently incompatible with the hydrophobic nature of a polyolefin. The incompatibility of starch within a polyolefin matrix typically results in the formation of a multiphase morphology having a high interfacial tension that often has a negative impact on the physical and mechanical properties of a resulting polymer film. For example, the presence of starch within a polyethylene film can promote significant reductions in the films gloss, elongation at break, toughness, tear strength, puncture resistance, and clarity. As result of the incompatibility between starch and polyethylene, starch has a tendency to migrate to the surface of the melt stream during melt processing and collect at certain parts of the processing equipment such as the die lips. Starch or oxidized residue thereof deposited on the die lips can then intermittently pick off into passing film causing holes and defects in the resulting film product (2011, **WO2011009165**, TRISTANO PTY LTD); see also Chapter 10: Manufacture of films/laminates; Section 10.3: Laminates.

This led to the development of surface hydrophobic starch, which was then dried to less than 1% moisture content (compared with the 10–12% moisture of normal starch) so that it could be processed in polymer melts above 160 °C. An autooxidant was added to the blend to accelerate degradation. Further development resulted in an additive system called Ecostar™ that claimed to render traditional thermoplastic polymers such as linear low density polyethylene (LLDPE), high density polyethylene (HDPE), polypropylene, or polystyrene, biodegradable [91]. However, while these thermoplastics offer some advantages over other materials, they still incorporate traditional polymers that degrade very slowly or not at all.

BIO-TEC ENVIRONMENTAL LLC developed a biopolymer additive called Bio-Batch®—and purchased from ECM Biofilms—that is not supposed to weaken the properties of the polymer to which is added, and allows the degradation process to proceed only in an environment like a landfill or compost. With further improvements and refinements, Bio-Batch® has evolved into EcoPure®, which is a nonstarch based and nondestructive to the environment additive. EcoPure® is compatible with various types of polymers, including the following: HDPE, LDPE, LLDPE, polypropylene, PET, poly(ethylene terephthalate glycol modified) (PETG), general purpose polystyrene (GPPS), high impact polystyrene (HIPS), nylon, PVC, ethylene-vinyl alcohol (EVOH), and polycarbonate. The newest formulation, EcoPure® G2, is designed for use with clear PET, in such applications as film and bottles. In most applications EcoPure® can be added to polymers at a ratio of 1 wt%. EcoPure® requires the action of certain enzymes for the biodegradation process to begin, so polymers containing EcoPure® will never begin to biodegrade during normal use. EcoPure® performs best in anaerobic environments.

US2008103232 A (2008, BIO TEC ENVIRONMENTAL LLC) discloses an additive material including a biopolymer that is physically blended with a nonbiodegradable polymer to increase the degradation of polymers such as LDPE and LLDPE, PP, polystyrene, and other nondegradable polymers. Combining granular starch mixed with polyethylene together with an unsaturated polymer, a thermal stabilizer, and a transition metal produce a material with increased susceptibility to photooxidation, thermolysis, and biodegradation is obtained. This particular material has also an induction time before degradation may be initiated. The use of starch alone in polyethylene, for example, requires, however, rather large amounts in order to really create an increase in the biodegradation rate.

EP402826 A1 (1990, BASF AG) discloses polymer blends produced by mixing polar ethylene copolymers with native starch or its derivatives (5–90, preferably 20–80, more preferably 40–60 wt%) in an extruder, with no water being added. In **WO9014388** A1 (1990, AGRI TECH IND INC) a polymer blend is produced by mixing native starch with LDPE and adding either ethylene acrylic acid copolymer or glycerol. These polymer blends exhibit relatively poor mechanical properties even in the production of injected moldings and are unsuitable, for example, for the production of films. It appears that the natural structure of the starch is retained in these blends, at least in part, and this obviously detracts from their suitability as engineering plastic. The proportion of ethylene acrylic acid copolymer also accounts for the fact that their biodegradability is very limited (1993, **EP0542155** A2, TOMKA IVAN).

WO2009022195 A1 (2009, CEREPLAST INC) discloses a method of making a polyolefin composition comprising blending a polyolefin (20–80 wt%), a compatibilizer (1–5 wt%), a starch (10–70 wt%, and a plasticizer (3–15 wt%) to form a mixture. In a preferred embodiment (see Table 3.8), the polyolefin and the compatibilizer are blended to form a first blend; the starch and the plasticizer are blended to form a second blend; the first blend is fed into a first feed of an extruder and the second blend is fed into the extruder at a location downstream of the first feed. The second blend is blended with the first blend in the extruder. The blended mixture is extruded to form an extrudate. The polyolefin is selected from the group consisting of polyethylene, polypropylene, polybutene, and combinations thereof. The compatibilizer is selected from the group consisting of maleic anhydride grafted polypropylene, maleic anhydride grafted polyethylene, maleic anhydride grafted polybutene, and combinations thereof. The starch is selected from the group consisting of corn, tapioca, maize, wheat, rice, and combinations thereof. The plasticizer is selected from the group consisting of polyethylene glycol, sorbitol, glycerol, and combinations thereof.

TABLE 3.8 Exemplary Composition of a Polypropylene/Starch Blend (2009, WO2009022195 A1, CEREPLAST INC)

Material Composition	
Materials	Quantity (lbs)
Blend 1	
Polypropylene	80
Maleic anhydride polypropylene	10
Blend 2	
Starch-corn	90
Sorbitol	4
PEG® 8000	10
PEG® 2000	6
Total weight	200

Example: The polypropylene/starch composition was prepared on an L/D=36/1 corotating, intermeshing twin screw extruder of 65-mm diameter, using a temperature profile of between 130°C and 170°C, at screw speeds in the range of 200–400 rpm. Throughput was in the range of 150–250 kg/h, and the compound was water quenched and strand pelletized.

A blend of polypropylene and maleic anhydride grafted polypropylene, and the compatibilizing agent, was prepared in a low shear mixer and fed to the main feeder of a twin screw extruder using a volumetric screw feeder. The starch and starch plasticizers were blended in a high speed mixer and fed into the twin screw extruder through a side feeder using another volumetric screw feeder. The extruder screw and barrel configuration was optimized to handle the large vapor quantity through back venting upstream of the side feeder. This allowed high rates to be achieved with a 50% starch blend going into the side feeder.

US4133784 A (1979, US AGRICULTURE) discloses compositions constituted of starch and an EAA copolymer in an amount of 20–60 wt% and 80–40 wt%, respectively. The compositions are converted into films by casting (spreading), simple extrusion, or rolling (milling) techniques. The produced films are flexible, water resistant, heat sealable, and biodegradable. However, these processes are slow and very expensive. The relatively high processing cost coupled with the high price of EAA compared to polyethylene tend to diminish this composition's potential for achieving large-scale commercial success. Moreover, with certain starch contents, which are necessary to achieve the desired mechanical properties, the degree of biodegradability and the UV stability of the products are greatly compromised (1981, **EP0032802** A1, US AGRICULTURE).

EP0032802 A1 (1981, US AGRICULTURE) discloses (1) adding to the EAA copolymer-starch composition of a quantity of a neutralizing agent, such as ammonia or an amine, sufficient to neutralize some or all of the acid groups of the EAA; (2) adjusting the moisture content of the composition within the range of 2–10%; and (3) blow molding into a film the ammoniated and moisture-maintained composition. The starch is present as a filler within a matrix of the polyethylene that is not biodegradable. Thus, the biodegradability of this material is not satisfactory. While the polymer composition containing EAA has superior water resistance and mechanical properties as compared with the polyethylene-containing material, the biodegradability is less satisfactory. Regarding the EAA-containing material, the composition of the copolymer is not disclosed so that it is not clear whether or not the copolymer is biodegradable. This material has a problem that pin holes are apt to be formed in films obtained therefrom because bubbles are unavoidably formed by vaporization of water during kneading of the raw materials (2004, **EP0535994** A1, AGENCY IND SCIENCE TECHN; RES INST INNOVATIVE TECH EARTH).

EP0400531 A1 (1990) and **EP0400532** A1 (1990) of BUTTERFLY SRL disclose destructurized starch mixed with up to 15 wt% of EAA and/or PVOH. The starch is destructurized by means of a high-boiling plasticizer and a breakdown agent; the plasticizer may be glycerol and the breakdown agent may be urea. Urea and/or polyols are usually added to the EAA copolymer/starch mixture in order to facilitate its preparation and improve the resulting films from the economic and qualitative points of view [82]. The presence of the urea would have the effect of improving the gelling of the starch with small amounts of water and hence of enabling the direct production of a uniform film from semidry compositions (water content of around 16%) as well as of avoiding the need for the EAA copolymer/starch mixture to be mixed with large amounts of water in a mixer before the extrusion process. The addition of glycerol and starch-derived polyols to the EAA copolymer/starch mixture increases the percentage of biodegradable components without affecting the physical properties of the films. Although the use of the plasticizer and the breakdown agent does permit some improvement in the breakdown effect on the native starch, a film produced from the EAA copolymer/starch mixture is not of a quality that is adequate, for example, for it to be used as packing film with high mechanical requirements. Here again the proportion of ethylene-acrylic acid and polyvinyl copolymers has the effect of substantially limiting biodegradability.

WO9925756 A1 (1999, BIOP BIOPOLYMER GMBH) discloses a polymer composition comprising hydrophobic polymer, preferably PVAc, starch (5–15 wt% of PVAc), and an organosilicate component (0.5–15 wt% of PVAc).

WO9106681 A1 (1991, ALLIED SIGNAL INC) discloses a composition of enhanced biodegradability comprising a fossil fuel–based polymer (e.g., HDPE, PVC, PET, etc.) and a biodegradable material such as starch in an amount less than 40 wt%. The composition is treated with a solution containing an enzyme and a nonionic surfactant.

WO0130905 A1 (2001, UCB SA) discloses a water-based polymer composition comprising a biopolymer and a synthetic polymer, characterized in that the biopolymer results from a mechanical thermoplastic processing of a polysaccharide and/or protein starting material using shear forces in the presence of a crosslinking agent, and the synthetic polymer resin consists of a water-based hydrophilic polymer and/or hydrophilic/hydrophobic polymer. The biopolymer is preferably natural or modified starch (e.g., starch-ethers, starch-esters, oxidized starch) from tuber or cereal origin, such as potato, waxy maize, tapioca, or rice, and constitutes preferably 2–50 wt%, more preferably 2–30 wt% of the total dry polymer composition. The water-based polymer is selected from polyurethanes, polyester-urethanes, epoxy-acrylates, polyester-acrylates, urethane-acrylates, polyacrylates, polystyrene-acrylates, styrene-butadiene, and epoxy resin or mixtures thereof.

3.4 COMMERCIAL PRODUCTS

There is a broad range of biopolymer blends in the market nowadays. Representative commercially available biopolymer blends are shown in Table 3.9.

Some exemplary commercial products based on biopolymer blends are [93]:

1. Cereplast Compostable® 3000 film grade for food packaging based on PLA/PBAT (Ecoflex®, BASF) blend; the film has enhanced balance puncture strength, toughness, and can be processed on existing blown film extrusion machines.
2. EcoWorks® of Cortec Corporation, a partially biobased blend of aliphatic and aromatic polyesters for biodegradable film extrusion applications. In addition to the biodegradability, EcoWorks® also contains PLA (Ingeo™, Novamont). Films produced from EcoWorks® are shelf stable and will not degrade prematurely until placed in a proper composting environment.
3. Terraloy™ 20000 series of Teknor Apex, a blend of TPS and PBAT, with TPS content ranging up to 40 wt%. Terraloy 20000 series is designed for blown and cast film, sheet, and thermoformed and injection molded parts intended for composting. Teknor Apex recommends the compounds for replacing polyolefins and polystyrene in applications such as shrink wrap, produce wraps and trays, cosmetics jars and containers, carrier bags, can liners, trays and plates, cutlery, and flower pots.
4. Biolloy™ of JSR, a blend produced by combining a fossil fuel–based thermoplastic with PLA. The product line includes Biolloy™ products, which contain blends of polyolefin-based polymers such as polyethylene,

TABLE 3.9 Commercial Blends of Biopolymers

Blends	Trade Name	Manufacturer	Applications
Co-PBS/PLA (NatureWorks)	BIO-FLEX® series BIO-FLEX® F 1130 BIO-FLEX® F 1110 BIO-FLEX® F 2110 BIO-FLEX® F 6510 BIO-FLEX® A 4100 CL BIO-FLEX® S 1100 BIO-FLEX® S 6540	FKuR Kunststoff GmbH (DE)	BIO-FLEX® F 1130, F 1110 and F 2110: carrier or shopping bags, waste bags, flexible packaging film and air pillows/bubble wrap; agricultural and mulch films; BIO-FLEX® F 2110 and F 1130: fruit and vegetable nets; BIO-FLEX® F 6510: injection molded products, such as writing utensils and other promotional articles
PLA/PBAT (Ecoflex®)	Ecovio® Ecovio® FS shrink film C 2100 (63% bio-based); Ecovio® FS paper C1500 (75% bio-based)	BASF (DE)	Mulch films, carrier bags, waste bags, foam packaging (plates, trays), shrink films, paper coating
PLA/(ABS, PE, PP)	Biolloy™	JSR co. (JP)	Injection molding, blow molding, extrusion and films
Styrene copolymer/30% PLA (Ecodear®)		Toray (JP)	Similar to ABS
Blend of P3HB (Mirel™)	Mvera™	Telles (ADM/Metabolix) (USA)	Can liners, retail bags, yard-waste bags, and stretch wrap
PBS (Bionolle™)/starch, PBS (Bionolle™)/starch/PLA	Starcla™ series	Showa (JP)	Mulch films

TABLE 3.9 Commercial Blends of Biopolymers—cont'd

Blends	Trade Name	Manufacturer	Applications
PLA/PBAT (Ecoflex®)	Cereplast Compostable® 3000 film grade	Cereplast	Films for food packaging
Blend of aliphatic and aromatic polyesters	EcoWorks®	Cortec co.	Film extrusion applications: food packaging, grocery bags, community composting programs, garbage, mulch bags, etc.
Reactive blends of starch/PCL, cellulose esters, zein	Envar	Bioplastics Inc. (USA)	Compost bags, mulch films, paper coatings, etc.
Starch/LLDPE Starch/PP Starch/PBAT Starch/HIPS Starch/LLDPE Starch/PP Starch/PBAT Starch/HIPS	Terraloy™ BP-10001 (≤30% TPS); Terraloy™ BP-13001A (≤30% TPS); Terraloy™ BP-20001A (≤40% TPS); Terraloy™ BP-18003A (≤30% TPS); Terraloy™ MB-10000A (≤50% TPS); Terraloy™ MB-13000A masterbatch (≤50% TPS); Terraloy™ MB-20001A masterbatch (≤50% TPS); Terraloy™ MB-18003A masterbatch (≤50% TPS);	Teknor Apex (USA)	Blown and cast films, sheet; extrusion sheets and coatings; thermoformed and injection molded parts
Starch blends	Mater-BI® Z class; Mater-BI® Y class; Mater-BI® V class;	Novamont (IT)	Mater-BI® Z class: films and sheets (bags, nets, paper lamination, much films, twines, wrapping films; Mater-BI® Y class: rigid and dimensionally stable injection molded items (cutlery, boxes, flowers, pots, seedling, plant trays, gold trees, vending cups, pens; Mater-BI® V class: Rigid and expanded items (loose fillers and packaging foams as a replacement for polystyrene), injection molded items: Soluble cotton swabs, soluble items [92]
(Starch, PLA, PHA, PBS flour)/PVAc (Vinnex®)		Wacker Chemie (DE)	Packaging, catering products, gardening, landscaping
PE blend (based on Baskem's Green PE)	Terralene® LL 1101	FKuR Kunststoff GmbH (DE)	Blown film extrusion and lamination

EVA, ethylene vinyl acetate; HIPS, high impact polystyrene; LDPE, low density polyethylene; LLDPE, linear low density polyethylene; PBAT, poly(butylene adipate-*co*-terephthalate); PBS, poly(butylene succinate); PCL, poly(ε-caprolactone); PE, polyethylene; PHA, polyhydroxyalkanoate; PLA, poly(lactic acid), polylactide; PVAc, poly(vinyl acetate); TPS, thermoplastic starch.

polypropylene, and ABS. Depending on the application, the combination ratio of PLA can range between 5 and 80 wt% allowing users to achieve flowability suitable to their processing method, such as injection molding (for molding complex shapes), blow molding, extrusion, and film.

5. Updated Ecovio® grades of BASF; blends of PLA and PBAT (Ecoflex®) for paper coating and manufacturing shrink films comprising Ecovio® FS Paper, which is 75 wt% biobased, and Ecovio® FS Shrink Film, which is 63 wt% biobased, respectively. Paper and paperboard coated with Ecovio® FS Paper C 1500 have excellent sealability, with temperature stability up to 100 °C and can be repulped. Shrink films made from Ecovio® FS Shrink Film compared to polyethylene shrink films have a linear shrink behavior that leads to a broader shrinkage window; in addition, they have a high tensile strength, medium stiffness, and high puncture resistance.

PATENTS

Patent Number	Publication Date	Family Members	Priority Numbers	Inventors	Applicants	Title
AU4223889 A	19900305	NZ230246 A 19921028; JPH04504731 A 19920820; JP2725870 B2 19980311; CZ8904777 A3 19930113	WO1989US03380 19890804; US19880229896 19880808; US19880229894 19880808; US19890317391 19890301; US19880229939 19880808	SINCLAIR RICHARD G; PRESTON JOSEPH R	BATTELLE MEMORIAL INSTITUTE	Degradable thermoplastic from lactides.
BE870457 A1	19790102	ZA7805208 A 19790829; US4218350 A 19800819; FR2403354 A1 19790413; FR2403354 B1 19850906; US4324709 A 19820413; SE8503650 L 19850731; SE462284 B 19900528; SE462284 C 19900920; SE7809716 A 19790317; NZ188382 A 19800428; NO783106 A 19790319; NL7809320 A 19790320; JPS5490248 A 19790717; IT1109078 B 19851216; IE781873 L 19790316; IE47745 B1 19840613; GB1600496 A 19811014; FI782826 A 19790317; ES473389 A1 19791016; DK407778 A 19790317; DE2839908 A1 19790329; CH644880 A5 19840831; CH644881 A5 19840831; CA1110384 A1 19811006; BR7806072 A 19790417; AU3976278 A 19800320; AU537455 B2 19840628; ATA673778 A 19820315; AT368770 B 19821110; AR223433 A1 19810814; AR230840 A1 1984731	GB19770038772 19770916	GRIFFIN GERALD JOSEPH LOUIS	COLOROLL LTD	Compositions à base de matières plastiques et leur fabrication. “Plasitcs based composition.”
CA2029747 A1	19910515	US5124371 A 19920623; JPH03157450 A 19910705; JPH0662839 B2 19940817; CA2029747 C 19971111	JP19890295765 19891114	TOKIWA YUTAKA; IWAMOTO AKIRA; TAKEDA KIYOSHI	AGENCY IND SCIENCE TECHN; JSP CORP	Biodegradable plastic composition, biodegradable plastic shaped body and method of producing same.

CA2079768 A1	19930405	US5256711 A 19931026; EP0535994 A1 19930407; EP0535994 B1 19960731; DE69212557 T2 19970102; CA2079768 C 20021119	JP19910283847 19911004; JP19910319899 19911107	TOKIWA YUTAKA; KOYAMA MASATOSHI; TAKAGI SIGEYUKI	AGENCY IND SCIENCE TECHN; RES INST INNOVATIVE TECH EARTH	Starch-containing biodegradable plastic and method of producing same.
CN101775199 A	20100714	CN101775199 B 20111130	CN20081217338 20081118	MIN LI; XIANGNAN ZHANG	SHENZHEN ECOMANN BIOTECHNOLOGY	High-rigidity PHAs/PLA blending alloy and preparation method thereof.
CN102181137 A	20110914		CN2011172559 20110324	LUHUA ZHONG; XIAOPING LAN; CHAOYANG OU	SHANDONG ECOMANN TECHNOLOGY CO LTD	High-performance PHAs (polyhydroxyalkanoates)/POM (polyoxymethylene)/PLA (polylactic acid) blending alloy.
CN102504506 A	20120620		CN20111351017 20111109	JIAOLIANG YUAN; BIN YANG	UNIV SHANGHAI JIAOTONG	Method for compatibilizing PLA/PBAT alloy.
DE19648616 A1	19980514	EP0842977 A2 19980520	DE1996148616 19961113	ROTHE THOMAS	INST GETREIDEVER-ARBEITUNG	Zusammensetzung und Verfahren zur Herstellung einer thermoplastisch formbaren Masse. "Composition and process for the manufacture of a thermoplastic mouldable material."
DE2322440 A1	19731129	ZA7302749 A 19741127; NL7306280 A 19731120; JPS4955740 A 19740530; IT986290 B 19750120; FR2184657 A1 19731228; FR2184657 B3 19760423; BE799132 A1 19730831; AU5497273 A 19741031	GB19720023469 19720518	GRIFFIN GERALD JOSEPH LOUIS	COLOROLL LTD	Biologisch Abbaubares material aus Kunststoff. "Biodegradable synthetic material."
DE3314188 A1	19841025	JPS59206815 A 19841122; EP0126261 A1 19841128; EP0126261 B1 19870128; CA1218175 A1 19870217	DE19833314188 19830419	WINGLER FRANK; WANICZEK HELMUT; GEYER OTTO-CHRISTIAN	BAYER AG	Verwendung von Polymerlegierungen auf basis von Celluloseestern in der Augen-Kontaktoptik und aus den Polymerlegierungen hergestellte Kontatlinsen und -schalen. "Use of polyblends based on cellulose esters in optical contact lenses, and contact and scleroid lenses made from these polyblends."

Continued

—Cont'd

Patent Number	Publication Date	Family Members	Priority Numbers	Inventors	Applicants	Title
DE4038732 A1	19920611	WO9210539 A1 19920625; US5439953 A 19950808; JPH06503110 A 19940407; EP0560823 A1 19930922	DE19904038732 19901205	RITTER WOLFGANG; BERGNER RAINER; KEMPF WOLFGANG	HENKEL KGAA	Mit synthetischen Polymerverbindungen modifizierte Werkstoffe und/od Formteile auf Stärkebasis und Verfahren zu ihrer Herstellung. "Starch-based materials and/or molded parts modified by synthetic polymer compounds and process for producing the same."
DE4116404 A1	19921119	WO9220740 A1 19921126; US5314934 A 19940524; JPH06500149 A 19940106; JP3137198 B2 20010219; HUT68437 A 19950628; HU211429 B 19951128; HK1006847 A1 19990319; EP0539544 A1 19930505; EP0539544 B1 19941102; CA2087444 A1 19921119; CA2087444 C 20051129; AU1670592 A 19921230; AT113635 T 19941115	DE19914116404 19910518	TOMKA IVAN	TOMKA IVAN	Polymermischung für die Herstellung von Folien. "Polymer mixture for producing foils."
DE4300420 A1	19940714		DE19934300420 19930109	STERZEL HANS-JOSEF	BASF AG	Polylactide mit erhöhter Flexibilität. "Polylactide with increased flexibility, suitable for film production."
EP0032802 A1	19810729	US4337181 A 19820629; JPS56149444 A 19811119; EP0032802 B1 19850424; CA1171579 A1 19840724	US19800112980 19800117	OTEY FELIX HAROLD; WESTHOFF RICHARD	US AGRICULTURE	Flexible, self-supporting and biodegradable films and their production.
EP0052460 A1	19820526	US4393167 A 19830712; JPH03149255 A 19910625; JPH0470342 B2 19921110; JPS57150393 A 19820917; JPH0615604 B2 19940302; JPS57111349 A 19820710; JPH0469186 B2 19921105; EP0052460 B1 19850206	GB19800036967 19801118	HOLMES PAUL ARTHUR; NEWTON ALAN BRANFORD; WILLMOUTH FRANK MARTIN	ICI PLC	Polymer blends.

EP0105399 A1	19840418	US4506045 A 19850319; EP0105399 B1 19870610	DE19823236521 19821002; DE19833314188 19830419	WANICZEK HELMUT; LINDNER CHRISTIAN; SULING CARLHANS; BARTL HERBERT; UERDINGEN WALTER	BAYER AG	Thermoplastische Formmassen. “Thermoplastic moulding compositions.”
EP0327505 A2	19890809	ZA8900692 A 19891227; RU2026321 C1 19950109; PT89556 A 19891004; PT89556 B 19940729; PL277424 A1 19890904; PL159070 B1 19921130; PH25687 A 19910904; NZ227762 A 19900828; NO890361 A 19890804; NO307521 B1 20000417; MX172659 B 19940106; KR0139046 B1 19980501; JPH0214228 A 19900118; JPH0757827 B2 19950621; IN174313 A1 19941105; IL89096 A 19920906; IE890281 L 19890803; HU206510 B 19921130; GR92300067 T1 19920831; GB2214918 A 19890913; FI890406 A 19890804; FI100977 B 19980331; ES2039315 T1 19931001; ES2039315 T3 19980116; ES2039315 T5 20020601; EP0327505 A3 19901010; EP0327505 B1 19970730; EP0327505 B2 20011114; DK36789 A 19890804; DK174534 B1 20030512; DE327505 T1 19920813; DE68928209 T2 19980903; DE68928209 T3 20020822; CN1036215 A 19891011; CN1034872 C 19970514; CA1334224 C 19950131; BR8900350 A 19890919; AU2887689 A 19890803; AU617411 B2 19911128; AT156166 T 19970815; AR247411 A1 19941229	GB19880002313 19880203	LAY GUSTAV; REHM JOHANNES; STEPTO ROBERT F T; THOMA MARKUS	WARNER LAMBERT CO	Polymeric materials made from destructurized starch and at least one synthetic thermoplastic polymeric material.

Continued

—Cont'd

Patent Number	Publication Date	Family Members	Priority Numbers	Inventors	Applicants	Title
EP0400531 A1	19901205	US5569692 A 19961029; US5462982 A 19951031; PL285384 A1 19910506; NO902347 A 19901203; JPH0324101 A 19910201; JP3040794 B2 20000515; JPH11335401 A 19991207; JP3076797 B2 20000814; IT1234783 B 19920527; HUT54402 A 19910228; HU205954 B 19920728; GR3023869 T3 19970930; FI102760 B1 19990215; ES2163565 T3 20020201; ES2100855 T3 19970701; EP0758669 A2 19970219; EP0400531 B1 19970423; EP0758669 A3 19970502; EP0758669 B1 20010919; DK0758669 T3 20011231; DK0400531 T3 19970721; DE69033806 T2 20020418; DE69030527 T2 19971023; DD297988 A5 19920130; CN1050390 A 19910403; CN1032213 C 19960703; CA2017655 A1 19901130; CA2017655 C 20010508; BR9002601 A 19910820; AU5588190 A 19910124; AU623012 B2 19920430; AT205869 T 20011015; AT152130 T 19970515	IT19890067414 19890530	BASTIOLI CATIA; LOMBI ROBERTO; DEL TREDICI GIANFRANCO; GUANELLA ITALO	BUTTERFLY SRL	A method for the preparation of destructured-starch-based compositions produced thereby.
EP0400532 A1	19901205	US5334634 A 19940802; TR24428 A 19911101; RU2073037 C1 19970210; PL285383 A1 19910506; NO902348 A 19901129; NO179213 B 19960520; KR920010645 B1 19921212; JPH0331333 A 19910212; IT1233599 B 19920406; IL94495 A 19941111; HU205963 B 19920728; ES2062177 T3 19941216; EP0400532 B1 19940105;	IT19890067413 19890530	BASTIOLI CATIA; BELLOTTI VITTORIO; DEL GIUDICE LUCIANO; LOMBI ROBERTO	BUTTERFLY SRL	Polymer compositions for the production of articles of biodegradable plastics material and methods for their preparation.

		DK0400532 T3 19940214; DE69005702 T2 19940601; DD298416 A5 19920220; CZ9002644 A3 19970813; CZ282950 B6 19971112; CN1050391 A 19910403; CN1032919 C 19961002; CA2017654 A1 19901130; BR9002600 A 19910820; AU5588090 A 19901206; AU628175 B2 19920910; AT99719 T 19940115				
EP0402826 A1	19901219	JPH0331328 A 19910212; ES2058682 T3 19941101; EP0402826 B1 19940907; DE3919659 A1 19901220; DK0402826 T3 19941010; CA2016976 A1 19901216; AT111135 T 19940915	DE19893919659 19890616	KLIMESCH ROGER; KOEHLER GERNOT; SCHLEMMER LOTHAR	BASF AG	Verfahren zur Herstellung von mit nichtfasrigen Kohlehydraten gefüllten Ethylen-copolymeren und ihre Verwnedung. "Process for the preparation of ethylene copolymers filled with non-fibrous carbohydrates and their use."
EP0404723 A2	19901227	YU114690 A 19911031; PT94364 A 19910208; PT94364 B 19970430; PL285673 A1 19910408; NZ234018 A 19910827; NO902602 A 19901220; JPH0379645 A 19910404; JPH075788 B2 19950125; IL94587 A 19970415; IE902117 L 19910102; IE902117 A1 19910228; HUT54392 A 19910228; FI102478 B 19981215; EP0404723 A3 19910522; EP0404723 B1 19940810; ES2058868 T3 19941101; DK0404723 T3 19941121; DE69011431 T2 19950126; CN1048552 A 19910116; CA2018785 A1 19901219; BR9002792 A 19910820; AU5703490 A 19901220; AU633928 B2 19930211; AT109813 T 19940815	US19890368486 19890619; US19890431715 19891102	SACHETTO JEAN-PIERRE; LENTZ DAVID JOHN; SILBIGER JAKOB	WARNER LAMBERT CO	Polymer base blend compositions containing destructurized starch.

Continued

—Cont'd

Patent Number	Publication Date	Family Members	Priority Numbers	Inventors	Applicants	Title
EP0404728 A2	19901227	YU117990 A 19911031; PT94383 A 19910208; PL285754 A1 19910422; NZ234091 A 19910827; JPH0379646 A 19910404; EP0404728 A3 19910605; JPH0725936 B2 19950322; IE902174 L 19901222; IE902174 A1 19910102; HUT54393 A 19910228; CN1048551 A 19910116; CA2019084 A1 19901222; BR9002853 A 19910820; AU5750090 A 19910103; AU641603 B2 19930923	US19890369983 19890622; US19890431672 19891102	SILBIGER JAKOB; SACHETTO JEAN-PIERRE; LENTZ DAVID JOHN	WARNER LAMBERT CO	Polymer base blend compositions containing destructurized starch.
EP0407350 A2	19910109	YU126590 A 19920720; PT94542 A 19910320; PL285861 A1 19910225; NZ234315 A 19910827; NO903013 A 19910107; JPH0374444 A 19910329; JPH0725938 B2 19950322; IE902379 A1 19910619; HUT55813 A 19910628; EP0407350 A3 19910605; CN1048549 A 19910116; CA2020150 A1 19910107; BR9003200 A 19910827; AU5806490 A 19910110; AU634123 B2 19930211	US19890376057 19890706; US19890447741 19891208	SACHETTO JEAN-PIERRE; REHM JOHANNES	WARNER LAMBERT CO	Polymer base blend compositions containing destructurized starch.
EP0408503 A2	19910116	PT94594 A 19910320; PT94594 B 19970228; PL285925 A1 19910311; NZ234361 A 19910925; NO902992 A 19910114; NO306471 B1 19991108; JPH03217439 A 19910925; JPH0668041 B2 19940831; IL94966 A 19941128; IE902430 A1 19910619; IE66496 B1 19960110; HU211430 B 19951128; FI102479 B1 19981215;	US19890378536 19890711; US19890449095 19891208	SILBIGER JAKOB; LENTZ DAVID JOHN; SACHETTO JEAN-PIERRE	WARNER LAMBERT CO	Polymer base blend compositions containing destructurized starch.

		ES2058869 T3 19941101; EP0408503 A3 19910612; EP0408503 B1 19940601; DK0408503 T3 19941003; DE69009323 T2 19941006; CN1049020 A 19910206; CA2020405 A1 19910112; CA2020405 C 20030311; BR9003312 A 19910827; AU5868690 A 19910117; AU633936 B2 19930211; AT106431 T 19940615				
EP0444880 A2	19910904	US5206087 A 19930427; JPH05320524 A 19931203; JPH0778167 B2 19950823; EP0444880 A3 19930310; EP0444880 B1 19970507; DE69125965 T2 19970925; CA2037340 A1 19910829; CA2037340 C 20010501	JP19900045725 19900228	TOKIWA YUTAKA; SUZUKI MASAHIRO; KOYAMA MASATOSHI	AGENCY IND SCIENCE TECHN; CHUO KAGAKU KK	Biodecomposable or biodisintegrable moldable material.
EP0535994 A1	19930407	US5256711 A 19931026; US5256711 X6 19931026; EP0535994 B1 19960731; DE69212557 T2 19970102; CA2079768 A1 19930405; CA2079768 C 20021119	JP19910283847 19911004; JP19910319899 19911107	TOKIWA YUTAKA; TAKAGI SIGEYUKI; KOYAMA MASATOSHI	AGENCY IND SCIENCE TECHN	Starch-containing biodegradable plastic and method of producing same.
EP0542155 A2	19930519	US5280055 A 19940118; SG47625 A1 19980417; JPH06207047 A 19940726; HU212708 B 19961028; ES2123533 T3 19990116; ES2123533 T5 20040316; EP0542155 A3 19931013; EP0542155 B1 19980923; EP0542155 B2 20030625; DK0542155 T3 19990614; DK0542155 T4 20030825; DE9219143 U1 19981001; CA2082051 A1 19930515; AU2836392 A 19930520; AT171465 T 19981015	CH19910003320 19911114	TOMKA IVAN	TOMKA IVAN	Biodegradable moulding composition.
EP0896013 A1	19990210	US5952450 A 19990914	JP19970225673 19970806; JP19970246173 19970827	ISHIHARA JIRO; KUYAMA HIROKI; OZEKI EIICHI; ISHITOKU TAKESHI; TANAKA MASAHIDE; SAKAMOTO NAOYA	SHIMADZU CORP	Crosslinked polycarbonate and polylactic acid composition containing the same.

Continued

—Cont'd

Patent Number	Publication Date	Family Members	Priority Numbers	Inventors	Applicants	Title
EP1097967 A2	20010509	US6515054 B1 20030204; EP1097967 A3 20010711; EP1097967 B1 2004122; DE60016878 T2 20051215	JP19990312232 19991102	MATSUSHITA TERUKI; ATSUMI YOSHIKO; ITOH HIROSHI	NIPPONCATALYTIC CHEM IND	Biodegradable resin composition and its molded product.
EP1227129 A1	20020731	WO02072699 A1 20020919; WO02072699 A8 20030116; US2002188071 A1 20021212; US6787613 B2 20040907; NO20033334 A 20030829; NO330519 B1 20110509; JP2004518808 A 20040624; ITTO20010058 A1 20020725; ES2272582 T3 20070501; EP1227129 B1 20060927; DK1227129 T3 20070212; DE60214913 T2 20070906; CN1489616 A 20040414; CN1215119 C 20050817; CA2434763 A1 20020919; CA2434763 C 20110419; AU2002252982 B2 20060629; AT340825 T 20061015	IT2001TO00058 20010125	BASTIOLI CATIA; DEL TREDICI GIANFRANCO; GUANELLA ITALO; PONTI ROBERTO	NOVAMONT SPA	Ternary mixtures of biodegradable polyesters and products manufactured from them.
EP2112199 A1	20091028	WO2009130205 A1 20091029; PT2285890 E 20120119; JP2011518241 A 20110623; ES2376281 T3 20120312; EP2285890 A1 20110223; EP2285890 B1 20111102; CN102027059 A 20110420; CN102027059 B 20130724; AT531757 T 20111115	EP20080154888 20080421	DE VOS SIEBE CORNELIS	PURAC BIOCHEM BV	Polymer composition comprising polylactide.
FR2618441 A1	19890127	US4889892 A 19891226; JPH01103641 A 19890420; FR2618441 B1 19891027; ES2032537 T3 19930216; EP0301632 A1 19890201; EP0301632 B1 19920304; BR8803664 A 19890214	FR19870010613 19870724	MALFROID PIERRE; NGUYEN QUI LONG; BLONDIN JEAN-MARIE; BURNAY JEAN-PAUL	SOLVAY	Compositions souples à base de polymères du chlorure de vinyle comprenant de la poly Epsilon-caprolactone. "Soft compositions based on vinyl chloride polymers containing poly-epsilon-caprolactone."

FR2902434 A1	20071221	WO2007144529 A1 20071221; US2010112357 A1 20100506; PL2032649 T3 20120131; KR20090024709 A 20090309; JP2009540088 A 20091119; JP5174017 B2 20130403; FR2902434 B1 20080801; ES2368093 T3 20111114; EP2032649 A1 20090311; EP2032649 B1 20110803; DK2032649 T3 20111017; CN101495568 A 20090729; CN101495568 B 20120229; AT518912 T 20110815	FR20060052160 20060616	FINE THOMAS; KHUSRAWY MALIHA	ARKEMA FRANCE	Composition d'acide polylactique présentant une résistance aux chocs améliorée. "Poly(lactic acid) composition with improved impact resistance."
FR2905378 A1	20080307	WO2008028915 A1 20080313; US2010135601 A1 20100603; US8324298 B2 20121204; RU2009112385 A 20101020; RU2447101 C2 20120410; FR2905378 B1 20090417; JP2010502801 A 20100128; JP5197604 B2 20130515; EP2064284 A1 20090603; EP2064284 B1 20100303; CN101528844 A 20090909; CN101528844 B 20120829; AT459687 T 20100315	FR20060007798 20060905	DEWAEL PASCAL; FRINGANT CHRISTOPHE; VANDERVEKEN YVES	SOLVAY	Composition d'au moins un polymère du chlorure de vinylidène. "Composition of at least one vinylidene chloride polymer."
FR2918383 A1	20090109	FR2918383 B1 20091016	FR20070056280 20070705	BARBIER JACQUES; DEVER CEDRIC; PICHON THOMAS	CT VALORISATION IND AGRO RESSO	Utilisation d'acide polylactique fonctionnalisé en tant qu'agent compatibilisant. "Use of polylactic acid functionalized by maleic function, as compatibilizing agent."
GB2291648 A	19960131	WO9603468 A1 19960208; JPH10503227 A 19980324; GB2291648 B 19981125; EP0772654 A1 19970514; EP0772654 B1 20010613; DE69521321 T2 20011031; AU3114095 A 19960222	GB19940014922 19940725	TAYLOR PHILIP LOUIS	ICI PLC	Coating compositions containing poly hydroxyalkanoates.

Continued

—Cont'd

Patent Number	Publication Date	Family Members	Priority Numbers	Inventors	Applicants	Title
GB2488811 A	20120912	WO2012120309 A2 20120913; WO2012120309 A3 201304; EP2683773 A2 20140115; CA2828190 A1 20120913; AU2012226557 A1 20130919	GB20110004018 20110309	BAILEY PETER BRADBY SPIROS; HODZIC ALMA; HAYES SIMON ANTHONY	CLEANING AND PAPER DISPOSABLES PLC	
JP2000017038 A	20000118	JP3802680 B2 20060726	JP19980183906 19980630	KUBO TAKAYOSHI; YAMA SHINKO; NAITO HIROSHI; NAKAE TSUNAHIRO	KANEBO LTD; RES INST INNOVATIVE TECH EARTH; KANEBO SYNTHETIC FIBERS LTD	Expandable resin composition having biodegradability.
JP2000095898 A	20000404		JP19980269493 19980924	MIHARA MAKOTO; HASEGAWA TORU; SHIDA HIROTAKA	JSR CORP	Biodegradable material modifier, and biodegradable material composition using the same.
JP2000319446 A	20001121		JP19990127324 19990507	YANO TORU	NISHIKAWA RUBBER CO LTD	Biodegradable rubber composition.
JP2002069279 A	20020308		JP20000256122 20000825	INOUE YOSHIO	DAICEL CHEM	Compatible resin composition.
JP2003096285 A	20030403	JP5157035 B2 20130306	JP20010295915 20010927	KUMAZAWA SADANORI; OOME HIROKAZU; KUMAKI JIRO	TORAY INDUSTRIES	Polyactic acid resin composition, production method thereof and molded article.
JP2003183488 A	20030703		JP20010383513 20011217	ISHIGA SHIGETO; ISODA SHINJI	TECHNO POLYMER CO LTD	Polylactic acid resin composition.
JP2003286401 A	20031010	JP4232377 B2 20090304	JP20020093352 20020328	KUMAZAWA SADANORI; OOME HIROKAZU; KUMAKI JIRO	TORAY INDUSTRIES	Polylactic acid-containing resin composition, molding and film or sheet therefrom.
JP2004010842 A	20040115		JP20020169429 20020611	MATSUO SHIGERU	IDEMITSU PETROCHEMICAL CO	Polylactic acid resin composition.
JP2004143315 A	20040520	JP4154994 B2 20080924	JP20020310928 20021025	ISOBE YASUMITSU; HARA YOSHIO; KAGEYAMA YASUSHI; MORIYAMA TAKESHI; YAMASHITA SEIJI; ODA TOMOKO	TOYOTA MOTOR CORP	Polymer blend and method for producing the same.

JP2005232228 A	20050902	JP4622259 B2 20110202	JP20040039965 20040217	YAMAGUCHI MASAYUKI	TOSOH CORP	Resin composition.
JP2005232232 A	20050902	JP4581420 B2 20101117	JP20040039969 20040217	YAMAGUCHI MASAYUKI	TOSOH CORP	Resin composition.
JP2006077063 A	20060323		JP20040260537 20040908	AOYAMA TAIZO	KANEKA CORP	Composition and its molded article.
JP2007100104 A	20070419	JP4656056 B2 20110323	JP20010095162 20010329; JP20060354318 20061228	KUMAZAWA SADANORI; OOME HIROKAZU; KUMAKI JIRO	TORAY INDUSTRIES	Polylactic acid block copolymer, its preparation process, molded article and polylactic acid composition.
JP2007191625 A	20070802		JP20060012413 20060120	ENDO KOHEI; TOYOHARA KIYOTSUNA; NONOKAWA RYUJI; TO SHIN	TEIJIN LTD; MUSASHINO KAGAKU KENKYUSHO; MUTUAL CORP; KIMURA YOSHIHARU	Polylactic acid.
JP2008038142 A	20080221		JP20060191206 20060712; JP20070172188 20070629	KUMAZAWA SADANORI; ONOE YOSUKE; OOME HIROKAZU	TORAY INDUSTRIES	Resin composition and molded article made thereof.
JP2008063356 A	20080321		JP20060239354 20060904	NONOKAWA RYUJI; TOYOHARA KIYOTSUNA; TO SHIN	TEIJIN LTD	Method for producing a resin composition.
JP2008195834 A	20080828		JP20070032799 20070214	KAMIYA SOICHIRO; MATSUI HITOSHI	RIKEN VITAMIN CO	Resin composition, and packaging film formed by molding the same.
JP2008291268 A	20081204		JP20080176682 20080707	KUMAZAWA SADANORI; OOME HIROKAZU; KUMAKI JIRO	TORAY INDUSTRIES	Polylactic acid block copolymer preparation method.
JP2010143947 A	20100701	JP5309298 B2 20131009	JP20080319129 20081216	HARADA TADASHI; IIDA HIROSHI	NAGOYA CITY	Polylactic acid-based resin composition and its manufacturing method.
JPH05331315 A	19931214	JPH0649276 A 19940222; JP2631050 B2 19970716	JP19910283847 19911004	TOKIWA YUTAKA; KOYAMA MASATOSHI; TAKAGI SIGEYUKI	AGENCY IND SCIENCE TECHN; CHIKYU KANKYO SANGYO GIJUTSU	Biodegradable plastic composition containing gelatinized starch and production thereof.

Continued

—Cont'd

Patent Number	Publication Date	Family Members	Priority Numbers	Inventors	Applicants	Title
JPH0543772 A	19930223		JP19910202933 19910813	YAHIRO SHUJI; MATSUMOTO KATSUO; MATSUZAKI KAZUHIKO	ASAHI CHEMICAL IND	Bio-degradable polyacetal resin composition.
JPH06313063 A	19941108	JP2651884 B2 19970910	JP19930103367 19930430	WADA KENZO; FURUSAWA SACHIKO; KUWABARA JUN	TSUTSUNAKA PLASTIC KOGYO	Biodegradable starch-based composition.
JPH07109413 A	19950425	JP3279768 B2 20020430		KIDO TAKAYASU; YOSHIMURA MASAJI; YODA KAORU	MITSUI TOATSU CHEMICALS	Iridescent resin composition.
JPH07330954 A	19951219	JP3363589 B2 20030108	JP19940127734 19940609	TAKIYAMA EIICHIRO; HATANO YOSHITAKA; FUJIMAKI TAKASHI	SHOWA HIGHPOLYMER	Biodegradable aliphatic polyester composition.
JPH08188671 A	19960723		JP19940319052 19941129	KAMEYAMA HIROKAZU; TOKIWA YUTAKA	AGENCY IND SCIENCE TECHN; CHIKYU KANKYO SANGYO GIJUTSU	Biodegradable plastic molding.
JPH08245866 A	19960924	JP3348752 B2 20021120	JP19950049365 19950309	MATSUI MASAO; KOSEKI HIDEKAZU	SHIMADZU CORP	Plasticized polylactic acid composition and its molded item.
JPH0827362 A	19960130	JP3431042 B2 20030728	JP19940164335 19940715	MIURA MITSUO; ISAHAYA SADANORI; MINE TAKAKIYO; MATSUSHITA HIROYUKI	MITSUBISHI GAS CHEM CO INC	Biodegradable resin composition.
JPH09111107 A	19970428	JP3138196 B2 20010226	JP19950265775 19951013	TERADA SHIGENORI; TAKAGI JUN	MITSUBISHI PLASTICS IND	Biodegradable film or sheet and biodegradable plastic molding.
JPH09316310 A	19971209		JP19960156247 19960527	KANDA TAIJI; ONISHI KATSUMI	KANEBO LTD	Polylactic acid resin composition.
JPH10152602 A	19980609		JP19960313742 19961125	MIURA HITOMI; KIRIE YOZO	SEKISUI CHEMICAL CO LTD	Biodegradable resin composition.
JPH10158485 A	19980616	JP3773335 B2 20060510	JP19970281393 19970929; JP19960283086 19961004	WATANABE ICHIJI; SHIMADA TAKASHI	DAICEL CHEM	Biodegradable aliphatic polyester resin/starch composition.
JPH10251498 A	19980922	JP3666172 B2 20050629	JP19970084417 19970317	KONDO YOSHIKAZU; KAJIYAMA HIROSHI; HINAKO HIDEKI; ICHIHASHI KUNIO	KANEBO LTD	Naturally degradable resin composition and molded product thereof.

JPH10274494 A	19981013		JP19970080273 19970331	TAKAHASHI ISAMU; IGUCHI YUJI; UCHIDA TAKASHI; SUGANO HARUYUKI; KOBAYASHI KAZUHIRO	SHOWA RUBBER; TOKYO ELECTRIC POWER CO	Sponge ball for cleaning heat exchanger.
JPS63172762 A	19880716		JP19870004653 19870112	SAKASHITA KEIICHI TONE SEIJI; MINAMI SHUNSUKE	MITSUBISHI RAYON CO	Polyester resin composition.
KR20100079986 A	20100708	KR101067141 B1 20110922	KR20080138597 20081231	HONG SUNG MIN; RYU SEUNG CHAN; CHO JUNG HWAN; KWON YOUNG DO; CHO SUNG HWAN	SAMYANG CORP	Environmentally friendly resin composition.
KR20110064122 A	20110615		KR20090120581 20091207	SONG JI YOUNG; SHIN KYUNG MOO; CHO SUNG HWAN; KIM DOE	SAMYANG CORP	Method of manufacturing of polylactic acid resin composition.
KR20110108736 A	20111006		KR20100028100 20100329	RYU SEUNG CHAN; OH SEOK BIN; CHOI SEUNG RYUL; CHO SUNG HWAN; KIM DO	SAMYANG CORP	Environment-friendly resin composition.
US2003166748 A1	20030904	US7297394 B2 20071120	US20020087718 20020301	KHEMANI KISHAN; SCHMIDT HARALD; HODSON SIMON K	BIOTEC BIOLOG NATURVERPACK	Biodegradable films and sheets suitable for use as coatings, wraps and packaging materials.
US2003166779 A1	20030904	US2005182196 A1 20050818; US7214414 B2 20070508; US7241832 B2 20070710	US20020087256 20020301	KHEMANI KISHAN; SCHMIDT HARALD; HODSON SIMON K	BIOTEC BIOLOG NATURVERPACK	Biodegradable polymer blends for use in making films, sheets and other articles of manufacture.
US2003204028 A1	20031030	US7265188 B2 20070904	US20030407301 20030404; WO2001US42523 20011005; WO2001US42503 20011005; US20000238572P 20001006	AUTRAN JEAN-PHILIPPE MARIE	PROCTER & GAMBLE	Biodegradable polyester blend compositions and methods of making the same.
US2004230001 A1	20041118	US6943214 B2 20050913	US20040816149 20040401; US20030470083P 20030513; US20040544723P 20040213; US20030471023P 20030516	FLEXMAN EDMUND ARTHUR	DU PONT	Toughened polyoxymethylene-poly(lactic acid) compositions.

Continued

—Cont'd

Patent Number	Publication Date	Family Members	Priority Numbers	Inventors	Applicants	Title
US2005137332 A1	20050623	US7160977 B2 20070109	US20040005587 20041206; US20030531723P 20031222; US20030531599P 20031222	HALE WESLEY R; TANNER CANDACE M	EASTMAN CHEMICAL COMPANY	Polymer blends with improved notched impact strength.
US2005288399 A1	20051229	JP2006009007 A 20060112; TWI248957 B 20060211	TW20040118611 20040625	CHEN MING-TUNG	CHEN MING-TUNG	Biodegradable plastic composition and producing method thereof.
US2007117908 A1	20070524	CN1793198 A 20060628; CN100378138 C 20080402	CN2005117300 20051121	ZHOU QINGHAI; ZHAO XIAOJIANG; WANG XIANHONG; WANG FOSONG; XIONG TAO; GAO FENGXIANG	CHANGCHUN INSTITUTE OF APPLIED CHEMISTRY	Process for improving friability and cold-flow of carbon dioxide epoxy propylane copolymer.
US2008103232 A1	20080501	WO2008055240 A1 20080508; JP2010508425 A 20100318; EP2087033 A1 20090812; CN101589097 A 20091125; AU2007313630 A1 20080508	US20060855430P 20061031	LAKE J A; ADAMS S D	BIO TEC ENVIRONMENTAL LLC	Chemical additives to make polymeric materials biodegradable.
US2009326130 A1	20091231	WO2010002668 A1 20100107; WO2010002668 A8 20110317; US8268913 B2 20120918; US2012296045 A1 20121122; US8444905 B2 20130521; US2012296044 A1 20121122; US8372917 B2 20130212; US8268913 B2 20120918; US2013253121 A1 20130926; US2013197161 A1 20130801; US8546490 B2 20131001; KR20110037928 A 20110413; JP2011526949 A 20111020; EP2296879 A1 20110323; CN101918211 A 20101215	US201313795270 20130312	LI FENGKUI; COFFY TIM J; DAUMERIE MICHEL	FINA TECHNOLOGY	Injection molded article comprising polypropylene and polylactic acid.
US2009326152 A1	20091231	WO2010002669 A1 20100107; US2012080822 A1 20120405; US8362145 B2 20130129; KR20110025730 A 20110311; JP2011526950 A 20111020; EP2297212 A1 20110323; EP2297212 A4 20111012; CN102119178 A 20110706	US20080165051 20080630	LI FENGKUI; COFFY TIM; DAUMERIE MICHEL	FINA TECHNOLOGY	Compatibilized polypropylene and polylactic acid blends and methods of making and using same.

US2010056700 A1	20100304	US8232343 B2 20120731; KR20100027438 A 20100311; KR100989116 B1 20101020; JP2010059423 A 20100318; DE102009029035 A1 20100304; CN101665618 A 20100310; CN101665618 B 20120516	KR20080086359 20080902	CHUNG YOUNG-MI; JUNG CHANG-DO; LEE YOUNG-JUN; PACK JI-WON; KWON YOUNG-CHUL; LEE HYUNG-TAK; CHO JIN-KYUNG	CHEIL IND INC	Environmentally-friendly polylactic acid resin composition.
US2010167048 A1	20100701	US8431218 B2 20130430; US2013211014 A1 20130815; TW201024349 A 20100701; TWI377226 B 20121121	TW20080151890 20081231	KUO CHIH-YING; CHANG LI-LING; WU RU-YU; WANG YIH-WEN	FAR EASTERN NEW CENTURY CORPORATION	Poly(lactic acid) resin composition for preparing transparent and impact-resistant article, article prepared therefrom and preparation process thereof.
US2011152818 A1	20110623	WO2011077304 A3 20111201; WO2011077304 A2 20110630; US8586821 B2 20131119; US2014039435 A1 20140206; MX2012007266 A 20120720; KR20120126066 A 20121120; EP2515817 A2 20121031; EP2515817 A4 20140122; CO6561769 A2 20121115; CN102665635 A 20120912; AU2010334423 A1 20120614	US20090645861 20091223	WANG JAMES H; LEE JAEHONG	KIMBERLY CLARK CO	Melt-processed films of thermoplastic cellulose and microbial aliphatic polyester.
US2012015142 A1	20120119	WO2012007857 A2 20120119 MX2013000379 A 20130221; KR20130100260 A 20130910; EP2593514 A2 20130522; EP2593514 A4 20131218; CN103003362 A 20130327; AU2011277960 A1 20130131	US20100836374 20100714	LEE JAEHONG; WANG JAMES H; WIDEMAN GREGORY	KIMBERLY CLARK CO	Biodegradable blends and films having nano-structural features.
US2012245292 A1	20120927	US8378027 B2 20130219; KR20120108798 A 20121005; DE102011077447 A1 20120927	KR20110027121 20110325	HONG CHAE HWAN; HAN DO SUCK	HYUNDAI MOTOR CO LTD	Manufacturing method of polylactic acid composite composition.
US2013109781 A1	20130502	US2013337530 A1 20131219; US8513329 B2 20130820	US20080113844 20080501; US20070932654 20071031; US20060855430P 20061031	LAKE JOHN ALLEN; ADAMS SAMUEL DAVID	BIO TEC ENVIRONMENTAL LLC	Chemical additives to make polymeric materials biodegradable.
US2014005624 A1	20140102	WO2014001922 A1 20140103	US201213534690 20120627	WANG JAMES HONGXUE; WIDEMAN GREGORY JAMES	KIMBERLY CLARK CO	Film containing a polyalkylene carbonate.

Continued

—Cont'd

Patent Number	Publication Date	Family Members	Priority Numbers	Inventors	Applicants	Title
US3632687 A	19720104		US19690812430 19690401	WALTER EARL RICHARD; KOLESKE JOSEPH VICTOR	UNION CARBIDE CORP	Crystalline polymer alloys comprising a polymer from a cyclic ester and an alkene polymer.
US3668157 A	19720606	US3668157 X6 19720606	US19700057775 19700723	COMBS ROBERT L; BOGAN RICHARD T	EASTMAN KODAK CO	Blend containing at least a cellulose ester and a block copolymer elastomer.
US3734979 A	19730522		US19700102921 19701230	KOLESKE J; WALTER E	UNION CARBIDE CORP	Shaped and molded articles of polymer blends comprising polyolefins and lactone polymer.
US3762979 A	19731002	GB1421233 A 19760114; DE2335348 A1 19750130; BE802562 A1 19740121	US19710173297 19711019	HANEL P BECKER G	DOW CHEMICAL CO	Vinylidene chloride-vinyl chloride copolymer compositions for use as an adhesive seam in fabric construction.
US3867324 A	19750218	CA1011028 A1 19770524	US19720275971 19720728	CLENDINNING ROBERT A; POTTS JAMES E; CORNELL STEPHEN W	UNION CARBIDE CORP	Environmentally degradable-biodegradable blends.
US4016117 A	19770405		US19740527038 19741125; GB19740010267 19740307; GB19720023469 19720518; GB19730055195 19731128; US19730353414 19730423	GRIFFIN GERALD JOSEPH LOUIS	COLOROLL LTD	Biodegradable synthetic resin sheet material containing starch and a fatty material.
US4021388 A	19770503		US19760665418 19760310; GB19740010267 19740307; GB19720023469 19720518; GB19730055195 19731128; US19740527038 19741125	GRIFFIN GERALD JOSEPH LOUIS	COLOROLL LTD	Synthetic resin sheet material.
US4133784 A	19790109	CA1089136 A1 19801104	US19770837491 19770928	OTEY FELIX H; WESTHOFF RICHARD P	US AGRICULTURE	Biodegradable film compositions prepared from starch and copolymers of ethylene and acrylic acid.
US4137280 A	19790130		US19780897627 19780419	DIXON DALE D; FORD MICHAEL E	AIR PROD & CHEM	Polyalkylene carbonates as processing aids for polyvinyl chloride.

US4770931 A	19880913	WO8808869 A1 19881117; US4900654 A 19900213; US4942005 A 19900717; JPH02503324 A 19901011; EP0360818 A1 19900404; DE3882047 T2 19940113; CA1324477 C 19931123	US19870047821 19870505	POLLOCK MARK A; STOWELL WILLIAM J; KRUTAK JAMES J	EASTMAN KODAK CO	Shaped articles from polyester and cellulose ester compositions.
US4912149 A	19900327		US19890313774 19890222	ROBESON LLOYD M; KUPHAL JEFFREY A	AIR PROD & CHEM	Blends of poly(vinyl acetate) and poly(propylene carbonate).
US5135966 A	19920804		US19910798457 19911126	CHATTERJEE ANANDA M; SALANITRO JOSEPH P	SHELL OIL CO	Environmentally degradable polymer composition.
US5883199 A	19990316	US5883199 X6 19990316	US19970825810 19970403	MCCARTHY STEPHEN P; GROSS RICHARD A; MA WENGUANG	UNIV MASSACHUSETTS	Polylactic acid-based blends
WO0130905 A1	20010503	US6818686 B1 20041116; MXPA02004230 A 20021216; JP2003513133 A 20030408; EP1095977 A1 20010502; CN1391596 A 20030115; CN1211424 C 20050720; CA2389245 A1 20010503; AU1854301 A 20010508	EP19990121449 19991028	COLPAERT MARC; BONTINCK DIRK; ROOSE PATRICE	UCB SA	Water based polymer composition comprising a biopolymer and a polymer resin.
WO0170846 A1	20010927	US6803443 B1 20041012; EP1188781 A1 20020320; EP1188781 A4 20030716; EP1188781 B1 20080123; DE60132525 T2 20090129	JP20000080020 20000322	ARIGA TOSHIROU; TAKAHASHI KATSUJI; KAMIKURA MASAO; IMAMURA SHOUJI; MIHARA TAKASHI	DAINIPPON INK & CHEMICALS	Impact modifier and polyester composition containing the modifier.
WO02059199 A1	20020801	US2004068058 A1 20040408; US7067596 B2 20060627; TWI227721 B 20050211; JP2004518781 A 20040624; JP4842502 B2 20111221; ITTO20010057 A1 20020725; ES2305201 T3 20081101; EP1947145 A2 20080723; EP1947145 A3 20080730; EP1947145 B1 20091223; EP1360235 A1 20031112 EP1360235 B1 20080507; AU2002237289 A1 20020806; AT394452 T 20080515; AT452940 T 20100115	IT2001TO00057 20010125	BASTIOLI CATIA; DEL TREDICI GIANFRANCO; GUANELLA ITALO; MILIZIA TIZIANA; PONTI ROBERTO	NOVAMONT SPA	Ternary mixtures of biodegradable polyesters and products manufactured from them.

Continued

—Cont'd

Patent Number	Publication Date	Family Members	Priority Numbers	Inventors	Applicants	Title
WO0216468 A1	20020228	US6573340 B1 20030603; KR20030069984 A 20030827; JP2008255349 A 20081023; JP2004506792 A 20040304; EP2357209 A1 20110817; EP1311582 A1 20030521; EP1311582 A4 20030521; EP1311582 B1 20130515; CN1468273 A 20040114; CN1247658 C 20060329; CA2419574 A1 20020228; CA2419574 C 20110726; BR0113483 A 20030415; BR0113483 B1 20111227; AU4958401 A 20020304	US20000648471 20000823	KHEMANI KISHAN; ANDERSEN PER JUST; SCHMIDT HARALD; HODSON SIMON K	KHASHOGGI E IND	Biodegradable polymer films and sheets suitable for use as laminate coatings as well as wraps and other packaging materials.
WO03014224 A1	20030220	US2007260019 A1 20071108; US2004242803 A1 20041202; US7550541 B2 20090623; US7268190 B2 20070911; EP1445282 A1 20040811; EP1445282 A4 20041124; CN1564848 A 20050112; CN1307259 C 20070328	JP20010236082 20010803; JP20010340948 20011106; JP20020030474 20020207; JP20020014948 20020124; JP20020014949 20020124	OHME HIROYUKI; KUMAZAWA SADANORI; KUMAKI JIRO	TORAY INDUSTRIES	Resin composition and molded article, film and fiber each comprising the same.
WO2004076582 A1	20040910	WO2004076583 A1 20040910; US2010305280 A1 20101202; US7928167 B2 20110419; PT1603987 E 20111110; JP2011140656 A 20110721; JP2006519293 A 20060824; JP5079321 B2 20121121; JP2006518799 A 20060817; JP4724111 B 20110713; HK1084687 A1 20111223; HK1085504 A1 20080620; ES2371069 T3 20111227; ES2297385 T3 20080501;	US20040783995 20040220; US20100851213 20100805; US20030449187P 20030221	WHITEHOUSE ROBERT S	METABOLIX INC	PHA blends.

		EP2241605 A2 20101020; EP2241605 A3 20120321; EP1935945 A1 20080625; EP1603987 A1 20051214; EP1603987 B1 20110803; EP1601737 A1 20051207; EP1601737 B1 20071031; DE602004009764 T2 20080828; AT518932 T 20110815; AT377060 T 20071115				
WO2004085533 A1	20041007	US2006264539 A1 20061123; JP2007524715 A 20070830; JP4277040 B2 20090610; ES2366541 T3 20111021; EP1608700 A1 20051228; EP1608700 B1 20110629 DE10313939 A1 20041014; CN1809611 A 20060726; CN100439439 C 20081203; AT514748 T 20110715	DE2003113939 20030327	MOSSEVELD HENK; WIERER KONRAD ALFONS; KOHLHAMMER KLAUS	WACKER POLYMER SYSTEMS GMBH	Use of polymers for starch modification.
WO2004087812 A1	20041014	US2007032577 A1 20070208; US7718718 B2 20100518; KR20050120675 A 20051222; KR101045446 B1 20110630; JP4600278 B2 20101215; EP1609819 A1 20051228; EP1609819 A4 20060412; EP1609819 B1 20100929; CN1768115 A 20060503; CN1768115 B 20100623; AT482999 T 20101015	JP20030090085 20030328	KANZAWA TAKESHI; KOBAYASHI SADAYUKI; YOSHIDA MINORU; SAKIDA FUMIE; KUMAKI JIRO	TORAY INDUSTRIES	Polylactic acid resin composition, process for producing the same, biaxially stretched polylactic acid film, and molded articles thereof.
WO2005040282 A1	20050506	US2007060687 A1 20070315; EP1679349 A1 20060712; CN1845970 A 20061011	JP20030368611 20031029	KODAMA SAI; INAYAMATOSHIHIRO; MURATA SHIGERU	KYOWA HAKKO CHEMICAL CO LTD	Resin composition.
WO2006030951 A1	20060323	US2011071247 A1 20110324; US8445593 B2 20130521; US2008262151 A1 20081023; US7863382 B2 20110104; KR20070065325 A 20070622; KR101148691 B1 20120525; EP1792941 A1 20070606;	JP20040272620 20040917; JP20050213840 20050725	ISHII HIROMITSU; NAGAO TAKASHI; OHME HIROYUKI	TORAY INDUSTRIES	Resin composition and molded article comprising the same.

Continued

—Cont'd

Patent Number	Publication Date	Family Members	Priority Numbers	Inventors	Applicants	Title
		EP1792941 B1 20110518; CN101942183 A 20110112; CN101942183 B 20130109; CN101942182 A 20110112; CN101942182 B 20120523; CN101023133 A 20070822; CN101023133 B 20111102; AT509985 T 20110615				
WO2006038506 A1	20060413	US2008033097 A1 20080207; US7553900 B2 20090630; TWI378971 B 20121211; JP2006104335 A 20060420; JP4746861 B2 20110810; KR20070073767 A 20070710; KR101139031 B1 20120430; DE112005002471 T5 20070830; CN101035861 A 20070912; CN101035861 B 20100526	JP20040293001 20041005	HAYATA YUSUKE; NODERA AKIO	IDEMITSU KOSAN CO	Aromatic polycarbonate resin composition, process for producing the resin composition, and molded object of the resin composition.
WO2006074815 A1	20060720	US2011269873 A1 20111103; US2008281018 A1 20081113; US8003731 B2 20110823; TWI388592 B 20130311; SI1838784 T1 20081031; MY145412 A 20120215; KR20070094844 A 20070921; JP2011236432 A 20111124; JP2008527120 A 20080724; ES2306273 T3 20081101; EP1838784 A1 20071003; EP1838784 B1 20080618; DK1838784 T3 20081013; BRPI0519835 A2 20090818; AT398655 T 20080715	DE20051001638 20050112; DE20051053069 20051104	SEELIGER URSULA; SKUPIN GABRIEL; STAERKE DIRK	BASF AG	Biologically-degradable polyester mixture.
WO2006103969 A1	20061005	US2009270524 A1 20091029; KR20080000572 A 20080102; JP5076499 B2 20121121; EP1865021 A1 20071212; EP1865021 A4 20090819; CN101151310 A 20080326; CN101151310 B 20110330; AU2006229153 A1 20061005	JP20050092482 20050328; JP20050268023 20050915	OKA YOSHIYUKI; YOSHIOKA TAKAHIDE; OYAMA MASAHIKO	TORAY INDUSTRIES	Polylactic acid foam.

WO2007095708 A1	20070830	US2009082491 A1 20090326; JP2009527593 A 20090730; DOP2007000038 A 20070830; CA2641922 A1 20070830; BRPI0600681 A 20071120; AU2007218992 A1 20070830	BR2006PI00681 20060224	NASCIMENTO JEFTER FERNANDES; PACHEKOSKIWAGNER MAURICIO; AGNELLI JOSE AUGUSTO MARCONDES	PHB IND SA	Environmentally degradable polymeric blend and process for obtaining an environmentally degradable polymeric blend.
WO2008004490 A1	20080110	US2009275692 A1 20091105; US8003721 B2 20110823; EP2045292 A1 20090408; EP2045292 A4 20120530; EP2045292 B1 20140122; JP5291461 B2 20130918; CN101484528 A 20090715; CN101484528 B 20111207	JP20060188004 20060707	SUZUKI YOSHINORI; YAMANE KAZUYUKI; SATO HIROYUKI; WATANABETAKAHIRO	KUREHA CORP	Aliphatic polyester composition and method for producing the same.
WO2008028918 A1	20080313		FR20060007797 20060905	FRINGANT CHRISTOPHE; DEWAEL PASCAL; VANDERVEKEN YVES	SOLVAY	Process for preparing a vinylidene chloride polymer composition and films and packagings obtained from said composition.
WO2008037744 A2	20080403	WO2008037744 A3 20080522; US2010003434 A1 20100107; US8101253 B2 20120124; RU2009114686 A 20101110; JP2010505017 A 20100218; ITMI20061845 A1 20080328; EP2074175 A2 20090701; CN101522797 A 20090902; CA2662105 A1 20080403; AU2007302005 A1 20080403; AU2007302005 B2 20120830	IT2006MI01845 20060927	BASTIOLI CATIA; FLORIDI GIOVANNI; DEL TREDICI GIANFRANCO	NOVAMONT SPA	Biodegradable multiphase compositions based on starch.
WO2008037749 A2	20080403	WO2008037749 A3 20080515; US2009311455 A1 20091217; US8043679 B2 20111025; RU2009114684 A 20101110; PT2202274 E 20120521; JP2010505018 A 20100218; ITMI20061844 A1 20080328; ES2382530 T3 20120611; ES2345518 T3 20100924; EP2202274 A2 20100630;	IT2006MI01844 20060927	BASTIOLI CATIA; FLORIDI GIOVANNI; DEL TREDICI GIANFRANCO	NOVAMONT SPA	Biodegradable compositions based on nanoparticulate starch.

Continued

—Cont'd

Patent Number	Publication Date	Family Members	Priority Numbers	Inventors	Applicants	Title
		EP2202274 A3 20101027; EP2202274 B1 20120229; CN101516997 A 20090826; CN101516997 B 20121128; CA2662446 A1 20080403; BRPI0715276 A2 20130604; AU2007302010 A1 20080403; AU2007302010 B2 20120823; AT547476 T 20120315; AT468372 T 20100615				
WO2008038648 A1	20080403	US2010086718 A1 20100408; EP2080787 A1 20090722; EP2080787 A4 20101222; KR20090054454 A 20090529; KR101118895 B1 20120319; CN101541887 A 20090923; CN101541887 B 20120718	JP20060260540 20060926; WO2007JP68633 20070926	YOSHIKAWA SEISHI; YOSHIDA MITSUHIRO; KOGURE MASAHITO	TOYO SEIKAN KAISHA LTD	Readily degradable resin composition and biodegradable container using the same.
WO2008090590 A1	20080731	US2008182924 A1 20080731; US7732523 B2 20100608; TW200837120 A 20080916; MX2008001089 A 20090224; KR20080070547 A 20080730; EP1950053 A1 20080730; CA2617032 A1 20080726	JP20070016000 20070126; JP20070309928 20071130	MORIMOTO KAZUKI; NISHIOKA YASUHIRO	SEED COMPANY LTD	Elastomer composition, method for producing the same, and eraser using the same.
WO2009022195 A1	20090219	US2014011921 A1 20140109; US2009048368 A1 20090219; EP2178967 A1 20100428	US20070955538P 20070813; US20070838650 20070814	BASH THOMAS F; KELLY WILLIAM E; BAGRODIA SHRIRAM; SCHEER FREDERIC	CEREPLAST INC	Polyolefin compositions comprising bio-based starch materials.
WO2009041518 A1	20090402	US2011015310 A1 20110120; EP2199456 A1 20100623; EP2199456 A4 20130123; CN101809223 A 20100818; CN101809223 B 20130508	JP20070248766 20070926	SHIMIZU TAKEO; TABEYA TOSHIHIRO; SEKI MASAO; TAKEDA KEIJI	TORAY INDUSTRIES	Polyester fiber, process for producing the same, and textile structure employing the same.
WO2009137058 A1	20091112	US2011189414 A 20110804; KR20110008312 A 20110126; EP2285901 A1 20110223; CN102056985 A 20110511; CA2722940 A1 20091112	US20080050896P 20080506; US20080133023P 20080625; US20080199817P 20081120; US20080200619P 20081202; US20080203542P 20081223; US20090166950P 20090406	WHITEHOUSE ROBERT S	METABOLIX INC	Biodegradable polyester blends.

WO2010010696 A1	20100128	US2011124778 A1 20110526; JP5097982 B2 20121212; EP2329961 A1 20110608; EP2329961 B1 20130403; CN102105311 A 20110622; CN102105311 B 20121003	JP20080192173 20080725	MORIMOTO KAZUKI; NISHIOKA YASUHIRO	SEED COMPANY LTD	Abrasive-containing eraser.
WO2010047370 A1	20100429	US2011196076 A1 20110811; US8481620 B2 20130709; EP2345688 A1 20110720; EP2345688 A4 20120328; CN102197067 A 20110921; CN102197067 B 20130814	JP20080274314 20081024	YOSHINO TAIKI; MORI MASAHIRO; TAKENAKA AKIRA	KAO CORP	Process for producing a resin composition.
WO2010051589 A1	20100514	US2012077905 A1 20120329; NZ593179 A 20120525; KR20110095293 A 20110824; JP2012507614 A 20120329; EP2352781 A1 20110810; EP2352781 A4 20130313; CN102282197 A 20111214; CA2742933 A1 20100514; AU2009311259 A1 20100514	AU20080905740 20081106	CHANGPING CHEN; SCHEIRS JOHN	TRISTANO PTY LTD	Biodegradable polymer composition.
WO2010133560 A1	20101125	EP2432830 A1 20120328; EP2432830 B1 20130710; CN102482461 A 20120530; CA2762988 A1 20101125; AU2010251208 A1 20111208; AU2010251208 B2 20130207		TANGELDER ROBERT; WEBER KARL; VAN DER MEIJDEN JACOBUS; PLIJTER JOHANNES; VAN SOEST JEROEN; SCHENNINK GERALDUS	WACKER CHEMIE AG	Bioplastics.
WO2010134454 A	20101125	US2012070679 A1 20120322; US8512852 B2 20130820; TW201105739 A 20110216; KR20120026039 A 20120316; EP2433796 A1 20120328; CN102438832 A 20120502	JP20090123851 20090522	SHIMIZU TOSHIYUKI; UNRININ TOSHIFUMI	TOYO BOSEKI	Polylactic acid resin composition and film.
WO2010139056 A1	20101209	US2012071591 A1 20120322; CA2763986 A1 20101209	US20090213340P 20090601	MOHANTY A K; MISRA M; SAHOO S	UNIV GUELPH	Lignin based materials and methods of making those.

Continued

—Cont'd

Patent Number	Publication Date	Family Members	Priority Numbers	Inventors	Applicants	Title
WO2011002004 A1	20110106		JP20090156063 20090630; JP20090254431 20091105	OGAWA RYOHEI; USUGI SHINICHI; MIZUMA HIROKAZU; TOTANI YOSHIYUKI; TSUJI MASASHI; HASEGAWA AKIRA; HORI HIDESHI	MITSUI CHEMICALS INC	Polylactic acid resin, method for producing polylactic acid resin, polylactic acid resin composition, stereocomplex polylactic acid resin composition, and method for producing stereocomplex polylactic acid resin composition.
WO2011009165 A1	20110127	US2012315416 A1 20121213; TW201121783 A 20110701; SG178083 A1 20120329; NZ597829 A 20131220; MX2012001027 A 20121001; KR20120066005 A 20120621; JP2012533453 A 20121227; EP2456620 A1 20120530; EP2456620 A4 20121205; CN102574374 A 20120711; CA2768708 A1 20110127; AU2010276083 A1 20120209	AU20090903455 20090723	CHANGPING CHEN; SCHEIRS JOHN; LEUFGENS MARKUS	TRISTANO PTY LTD	Multilayer film.
WO2011080623 A2	20110707	WO2011080623 A3 20111117; US2012315454 A1 20121213; MX2012007627 A 20120801; KR20120113220 A 20121012; EP2519567 A2 20121107; CO6551719 A2 20121031; CN102115576 A 20110706; AU2010337977 A1 20120705		WANG JAMES H; WANG YAN; HAO XUEEN GEORGE; ZHANG TONGTONG	KIMBERLY CLARK CO	Natural biopolymer thermoplastic films.
WO2011110567 A	20110915	US2012328806 A1 20121227; JP2013521396 A 20130610; FR2957351 A1 20110916; FR2957351 B1 20130628; EP2545120 A1 20130116; CN102791793 A 20121121	FR20100051731 20100310	DEWAEL PASCAL; CHAPOTOT AGNES; VANDERVEKEN YVES	SOLVAY	Composition based on a vinylidene chloride copolymer.
WO2011157691 A1	20111222	JP2013532209 A 20130815; EP2582757 A1 20130424; CN103003360 A 20130327	EP20100166000 20100615	HILMER KLAUS; BRUENING KAI; FRITZ HANS-GERHARD; ZGAVERDEA ALINA CORINA	BASF SE	Method for producing blends from polylactides(PLA) and thermoplastic polyurethanes (TPU)

WO2012141660 A1	20121018	SK262011 A3 20121105; SG194040 A1 20131129; CN103459498 A 20131218; CA2833131 A1 20121018	SK20110000026 20110411	ALEXY PAVOL; CHODAK IVAN; BAKOS DUSAN; BUGAJ PETER; PAVLACKOVA MIROSLAVA; TOMANOVA KATARINA; BENOVIC FRANTISEK; LAVEC RODERIK; MIHALIK MICHAL; BOTOSOVA MONIKA	USTAV POLYMEROV SAV	Biologically degradable polymeric composition with high deformability.
WO2013007760 A1	20130117		GB20110011929 20110712	HELLAND IRENE; FREDRIKSEN SIW BODIL	NORNER as	Polycarbonate blends.
WO2013048738 A1	20130404		US201161539263P 20110926	JEON HYUN K; BEYER DOUGLAS E	DOW GLOBAL TECHNOLOGIES LLC	Vinylidene chloride interpolymer and poly(butylene succinate) blend.
WO2013077210 A1	20130530		JP20110256387 20111124	NAGAI AKIRA; KAMADA MINOR; INADA TEIICHI; INOUE TAKASHI	HITACHI CHEMICAL CO LTD	Method for producing propylene polymer/lactic acid polymer resin composition, propylene polymer/lactic acid polymer resin composition obtained by said production method, molded body using said resin composition, and component using said molded body.
WO2013108817 A	20130725		JP20120007315 20120117; JP20120193859 20120904	SHIMIZU HIROSHI	NAT INST OF ADVANCED IND SCIEN	Plant-derived plastic blend and a production method thereof.
WO9001521 A1	19900222		US19880229894 19880808; US19880229896 19880808; US19880229939 19880808; US19890317391 19890301; US19890386844 19890731; US19890387670 19890731; US19890387676 19890731; US19890387678 19890731	SINCLAIR RICHARD G; PRESTON JOSEPH R	BATTELLE MEMORIAL INSTITUTE	Degradable thermoplastic from lactides.

Continued

—Cont'd

Patent Number	Publication Date	Family Members	Priority Numbers	Inventors	Applicants	Title
WO9014388 A1	19901129	EP0473726 A1 19920311; EP0473726 A4 19920715; AU5921390 A 19901218	US19890354412 19890519	WOOL RICHARD P; OELSCHLAEGER PETER; WILLETT JULIOS	AGRI TECH IND INC	Injection molded biodegradable starch polymer composite.
WO9106681 A1	19910516		US19890430705 19891102	ALLENZA PAUL; SCHOLLMEYER JULIE	ALLIED SIGNAL INC	Method for enhancing the biodegradation of biodegradable polymeric materials and of articles fabricated therefrom.
WO9116375 A1	19911031	SG50508 A1 19980720; NO914797 A 19911205; JPH04506832 A 19921126; JP3097754 B2 20001010; HUT61791 A 19930301; HU212028 B 19960129; HK1007755 A1 19990423 GR3023472 T3 19970829; ES2103806 T3 19971001; EP0479964 A1 19920415; EP0479964 B1 19970502; DK0479964 T3 19971215; CH680590 A5 19920930; CA2060650 A1 19911027; BR9104633 A 19930427; AU7481591 A 19911111; AU637685 B2 19930603; AT152466 T 19970515	CH19900001426 19900426	TOMKA IVAN	BIOTEC BIOLOG NATURVERPACK	Ein oder Mehrschichtenfolie, teilweise bestehend aus Stärke. "Single or multiple layer foil partially composed of starch."
WO9209654 A2	19920611	WO9209654 A3 19921001; US5900322 A 19990504; US5900322 X6 19990504; US5559171 A 19960924; US5580911 A 19961203; US5599858 A 19970204; US5446079 A 19950829; US6342304 B1 20020129; SG47853 A1 19980417; NZ240799 A 19940126; MX9102312 A 19940131;	US19900620225 19901130; US19910736262 19910723; US19910797512 19911121	BUCHANAN CHARLES M; GARDNER ROBERT M; WHITE ALAN W	EASTMAN CHEM CO	Aliphatic–aromatic copolyesters and cellulose ester/polymer blends.

		KR100245905 B1 20000315; KR100220443 B1 19990915; JP2007138377 A 20070607; JP2006022472 A 20060126; JP2004084156 A 20040318; JP2003221464 A 20030805; JP2003128768 A 20030508; JP3530178 B2 20040524; JP2001354802 A 20011225; JP3393124 B2 20030407; JPH06504558 A 19940526; JP3362040 B2 20030107; IE914155 A1 19920603; HK1041708 A1 20041008; FI20000496 A 20000303; FI932450 A 19930528; ES2278424 T3 20070801 EP0559785 A1 199309 EP0559785 B1 19970312; DE69133554 T2 20071004; DE69132548 T2 20010628; DE69125170 T2 19970619; CN1183429 A 19980603; CN1183428 A 19980603; CN1183427 A 19980603; CN1183433 A 19980603; CN1072245 C 20011003; CN1183423 A 19980603; CN1076358 C 20011219; CN1183426 A 19980603; CN1062740 A 19920715; CN1324891 A 20011205; CN1131281 C 20031217; CA2095536 A1 19920531; CA2095536 C 19990216; BR9107138 A 19940405; AU9105091 A 19920625; AU664831 B2 19951207; AU4557496 A 19960606; AT349476 T 20070115; AT199383 T 20010315; AT150058 T 19970315				

Continued

—Cont'd

Patent Number	Publication Date	Family Members	Priority Numbers	Inventors	Applicants	Title
WO9219680 A1	19921112	SK390192 A3 19941207; SK279993 B6 19990611; RU2095379 C1 19971110; PL297375 A1 19930628; PL174799 B1 19980930; NO925049 A 19921230; LV12151 A 19981020; LV12151 B 19981220; KR960008112 B1 19960620; JPH06502676 A 19940324; JP2527523 B2 19960828; HUT63644 A 19930928; HU216971 B 19991028; GR3024078 T3 19971031; FI925978 A 19921231; FI115138 B 20050315; ES2103943 T3 19971001; EP0539541 A1 19930505; EP0539541 B1 19970709; DK0539541 T3 19970915; DE539541 T1 19970130; DE69220754 T2 19971204; CZ9203901 A3 19931013; CZ285748 B6 19991013; CA2084994 A1 19921104; CA2084994 C 20010904; BR9205258 A 19930727; AU1650992 A 19921221; AU658180 B2 19950406; AT155161 T 19970715	EP19910112942 1991080; IT1991TO00327 19910503; IT1992TO00199 19920310; IT1992TO00282 19920327	BASTIOLI CATIA; BELLOTTI VITTORIO; DEL TREDICI GIANFRANCO; LOMBI ROBERTO; MONTINO ALESSANDRO; PONTI ROBERTO	NOVAMONT SPA	Biodegradable polymeric compositions based on starch and thermoplastic polymers.
WO9411440 A2	19940526	WO9411440 A3 19940707; US5646217 A 19970708; JPH08503500 A 19960416; FI952162 A 19950505; EP0669959 A1 19950906; CA2147857 A1 19940526; AU5426894 A 19940608; AU674361 B2 19961219	GB19920023351 19921106	HAMMOND TIMOTHY	ZENECA LTD	Polymer composition containing polyhydroxyalkanoate and metal compound.
WO9504108 A1	19950209	US5462983 A 19951031; KR100233487 B1 19991201; JPH08502552 A 19960319; JP2742630 B2 19980422; EP0711326 A1 19960515; EP0711326 A4 19960703; EP0711326 B1 20021009; DE69431523 T2 20030626	US19930097563 19930727	BLOEMBERGEN STEVEN; NARAYAN RAMANI	EVERCORN INC	Biodegradable moldable products and films comprising blends of starch esters and polyesters.

WO9615173 A1	19960523	US6018004 A 20000125; US6303677 B1 20011016; US6114042 A 20000905; US6201034 B1 20010313; TW387914 B 20000421; PT792309 E 20030228; PT1074570 E 20040930; PL321599 A1 19971208; NZ289416 A 20000128; NO972226 A 19970714; NO315120 B1 20030714; MX9703538 A 19970830; MX209461 B 20020805; KR977007206 A 19971201; KR100365455 B1 20030418; JPH10508640 A 19980825; JP3411289 B2 20030526; HUT77198 A 19980302; HU222853 B1 20031229; FI20060360 A 20060413; FI118223 B1 20070831; FI972059 A 19970714; FI117510 B1 20061115; ES2183878 T3 20030401; ES2219247 T3 20041201; EP0792309 A1 19970903; EP0792309 B1 20020918; EP1074570 A2 20010207; EP1074570 A3 20010509; EP1074570 B1 20040428; DK792309 T3 20021014; DE4440858 A1 19960523; DK1074570 T3 20040816; CZ9701437 A3 19971112; CZ292145 B6 20030813; CN1170418 A 19980114; CN1071342 C 20010919; CA2205071 A1 v; CA2205071 C 20050111; BR9509685 A 19970916; AU2925395 A 19960606; AU695820 B2 19980820; AT224414 T 20021015; AT265485 T 20040515;	DE19944440858 19941115	WARZELHAN VOLKER; SCHORNICK GUNNAR; BRUCHMANN BERND; SEELIGER URSULA; YAMAMOTO MOTONORI; BAUER PETER	BASF AG	Biodegradable polymers, preparation thereof and use thereof for producing biodegradable moldings.

Continued

—Cont'd

Patent Number	Publication Date	Family Members	Priority Numbers	Inventors	Applicants	Title
WO9622330 A2	19960725	WO9622330 A3 19970130; US5714573 A 19980203; US5922832 A 19990713; US6495631 B1 20021217; EP0804506 A2 19971105; EP0804506 B1 20011212; DE69617905 T2 20020808; AU4856096 A 19960807; AT210702 T 20011215	US19950374893 19950119	RANDALL JED RICHARD; RYAN CHRISTOPHER MICHAEL; LUNT JAMES; HARTMANN MARK HENRY; HALL ERIC STANLEY; KOLSTAD JEFFREY JOHN; WITZKE DAVID ROY	CARGILL INC	Impact modified melt-stable lactide polymer compositions and processes for manufacture thereof.
WO9631561 A1	19961010	US6096809 A 20000801; US6235816 B1 20010522; PT819147 E 20031031; JPH10512010 A 19981117; ES2201173 T3 20040316; EP0819147 A1 19980121; EP0819147 B1 20030604; DK819147 T3 20030929; CN1181098 A 19980506; CA2217541 A1 19961010; AU4952296 A 19961023; AU705499 B2 19990527; AT242295 T 20030615	DE1995113237 19950407; DE1995115013 19950424	LOERCKS JUERGEN; POMMERANZ WINFRIED; SCHMIDT HARALD	BIOTEC BIOLOG NATURVERPACK	Biologically degradable polymer mixture.
WO9925756 A1	19990527	US2002061943 A1 20020523; US6958369 B2 20051025; DE19750846 C1 20000127; EP0961805 A1 19991208; EP0961805 B1 20040414; DK0961805 T3 20040802; AT264355 T 20040415	DE1997150846 19971117	BERGER WERNER; JEROMIN LUTZ; MIERAU UTA; OPITZ GUNTRAM	BIOP BIOPOLYMER GMBH	
WO9945067 A1	19990910	US6235825 B1 20010522; EP0980894 A1 20000223; EP0980894 A4 20020313; EP0980894 B1 20040623; JP3753254 B2 20060308; DE69918233 T2 20050224	JP19980053685 19980305; JP19980053684 19980305	OSHIDA YASUNORI; OBUCHI SHOJI; KITAHARA YASUHIRO; WATANABETAKAYUKI; AIHARA HISASHI; NAKATA TOMOYUKI; SUZUKI KAZUHIKO; AJIOKA MASANOBU	MITSUI CHEMICALS INC	Polylactic acid composition and film thereof.

REFERENCES

[1] Tokiwa Y, Calabia BP, Ugwu CU, Aiba S. Biodegradability of plastics. Int J Mol Sci 2009;10:3722–42.

[2] Yu L, Dean K, Li L. Polymer blends and composites from renewable resources. Prog Polym Sci 2006;31:576–602.

[3] Tri PN, Domenek S, Guinault A, Sollogoub C. Crystallization behavior of poly(lactide)/poly(β-hydroxybutyrate)/talc composites. J Appl Polym Sci 2013;129:3355–65.

[4] Zhang M, Thomas NL. Blending polylactic acid with polyhydroxybutyrate: the effect on thermal, mechanical, and biodegradation properties. Adv Polym Technol 2011;30:67–79.

[5] Park JW, Doi Y, Iwata T. Uniaxial drawing and mechanical properties of poly((R)-3-hydroxybutyrate)/poly(L-lactic acid) blends. Biomacromolecules 2004.

[6] Malinová L, Brožek J. Mixtures poly((R)-3-hydroxybutyrate) and poly(L-lactic acid) subjected to DSC. J Therm Anal Calorim 2011;103:653–60.

[7] Ohkoshi J, Abe H, Dio Y. Miscibility and solid-state structures for blends of poly((S)-lactide) with atactic poly((R,S)-3-hydroxybutyrate). Polymer 2000;41:5985–92.

[8] Kikkawa Y, Suzuki T, Kanesato M, Doi Y, Abe H. Effect of phase structure on enzymatic degradation in poly(L-lactide)/atactic poly(3-hydroxybutyrate) blends with different miscibility. Biomacromolecules 2009;10:1013–8.

[9] Ma P, Spoelstra AB, Schmit P, Lemstra PJ. Toughening of poly(lactic acid) by poly(β-hydroxybutyrate-*co*-β-hydroxyvalerate) with high β-hydroxyvalerate content. Eur Polym J 2013;49:1523–31.

[10] Abdelwahab MA, Flynn A, Chiou B-S, Imam S, Orts W, Chiellini E. Thermal, mechanical and morphological characterization of plasticized PLA–PHB blends. Polym Degrad Stab 2012;97:1822–8.

[11] El-Hadi AM. Effect of processing conditions on the development of morphological features of banded or nonbanded spherulites of poly(3-hydroxybutyrate) (PHB) and polylactic acid (PLLA) blends. Polym Eng Sci 2011;51:2191–202.

[12] Zembouai I, Kaci M, Bruzaud S, Benhamida A, Corre Y-M, Grohens Y. A study of morphological, thermal, rheological and barrier properties of poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate)/polylactide blends prepared by melt mixing. Polym Test 2013;32:842–51.

[13] Ferreira BMP, Zavaglia CAC, Duek EAR. Films of PLLA/PHBV: thermal, morphological, and mechanical characterization. J Appl Polym Sci 2002;86:2898–906.

[14] Gerard T, Butova T. Morphology and molten-state rheology of polylactide and polyhydroxyalkanoate blends. Eur Polym J 2012;48:1110–7.

[15] Nanda MR, Misra M, Mohanty AK. The effects of process engineering on the performance of PLA and PHBV blends. Macromol Mater Eng 2011;296:719–28.

[16] Zhao H, Cui Z, Sun X, Turng L-S, Peng X. Morphology and properties of injection molded solid and microcellular polylactic acid/polyhydroxybutyrate-valerate (PLA/PHBV) blends. Ind Eng Chem Res 2013;52:2569–81.

[17] Modi S, Koelling K, Vodovotz Y. Miscibility of poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate) with high molecular weight poly(lactic acid) blends determined by thermal analysis. J Appl Polym Sci 2012;124:3074–81.

[18] Lim JS, Park K-I, Chung GS, Kim JH. Effect of composition ratio on the thermal and physical properties of semicrystalline PLA/PHB-HHx composites. Mater Sci Eng C 2013;33:2131–7.

[19] Zhao Q, Wang S, Kong M, Geng W, Li RKY, Song C, et al. Phase morphology, physical properties, and biodegradation behavior of novel PLA/PHBHHx blends. J Biomed Mater Res Part B Appl Biomater 2012;100B:23–31.

[20] Broz M, VanderHart D, Washburn N. Structure and mechanical properties of poly(D,L-lactic acid)/poly(ε-caprolactone) blends. Biomaterials 2003;24:4181–90.

[21] Wu D, Yuan L, Laredo E, Zhang M, Zhou W. Interfacial properties, viscoelasticity, and thermal behaviors of poly(butylene succinate)/polylactide blend. Ind Eng Chem Res 2012;51:2290–8.

[22] Yokohara T, Yamaguchi M. Structure and properties for biomass-based polyester blends of PLA and PBS. Eur Polym J 2008;44:677–85.

[23] Jiao L, Huang C-L, Zeng J-B, Wang Y-Z, Wang X-L. Miscibility, crystallization and mechanical properties of biodegradable blends of poly(L-lactic acid) and poly(butylene succinate-*b*-ethylene succinate) multiblock copolymer. Thermochim Acta 2012;539:16–22.

[24] Jiang L, Wolcott MP, Zhang J. Study of biodegradable polylactide/poly(butylene adipate-*co*-terephthalate) blends. Biomacromolecules 2006;7:199–207.

[25] Kim SH. Poly(L-lactic acid) and starch. Korea Polym J 1998;6:422–7.

[26] Jin HJ, Chin IJ, Kim MN, Kim SH, Yoon JS. Blending of poly(L-lactic acid) with poly(*cis*-1,4-isoprene). Eur Polym J 2000;36:165–9.

[27] Ma X, Yu J, Wang N. Compatibility characterization of poly(lactic acid)/poly(propylene carbonate) blends. J Polym Sci Part B Polym Phys 2006;44:94–101.

[28] Luo R, Xu K, Chen G-Q. Study of miscibility, crystallization, mechanical properties, and thermal stability of blends of poly(3-hydroxybutyrate) and poly(3-hydroxybutyrate-*co*-4-hydroxybutyrate). J Appl Polym Sci 2007;105:3402–8.

[29] Godbole S, Gote S, Latkar M, Chakrabarti T. Preparation and characterization of biodegradable poly-3-hydroxybutyrate–starch blend films. Bioresour Technol 2003;86:33–7.

[30] Kumagai Y, Doi Y. Enzymatic degradation and morphologies of binary blends of microbial poly(3-hydroxy butyrate) with poly(ε-caprolactone), poly(1,4-butylene adipate and poly(vinyl acetate). Polym Degrad Stab 1992;36:241–8.

[31] Qiu Z, Ikehara T, Nishi T. Poly(hydroxybutyrate)/poly(butylene succinate) blends: miscibility and nonisothermal crystallization. Polymer 2003;44:2503–8.

[32] Yang DZ, Hu P. Miscibility, crystallization, and mechanical properties of poly(3-hydroxybutyrate) and poly(propylene carbonate) biodegradable blends. J Appl Polym Sci 2008;109:1635–42.

[33] El-Shafee E, Saad GR, Fahmy SM. Miscibility, crystallization and phase structure of poly(3-hydroxybutyrate)/cellulose acetate butyrate blends. Eur Polym J 2001;37:2091–104.

[34] Wang T, Cheng G, Ma S, Cai Z, Zhang L. Crystallization behavior, mechanical properties, and environmental biodegradability of poly(β-hydroxybutyrate)/cellulose acetate butyrate blends. J Appl Polym Sci 2003;89:2116–22.

[35] Dave P, Gross R, Brucato C, Wong S, McCarthy S. Biodegradation of blends containing poly (3-hydroxybutyrate-*co*-valerate). In: Gebelein CG, editor. Biotechnology and polymers. US: Springer; 1991. pp. 53–61.

[36] Tao J, Song C, Cao M, Hu D, Liu L, Liu N, et al. Thermal properties and degradability of poly (propylene carbonate)/poly ([beta]-hydroxybutyrate-*co*-[beta]-hydroxyvalerate)(PPC/PHBV) blends. Polym Degrad Stab 2009;94:575–83.

[37] Reis KC, Pereira J, Smith AC, Carvalho CWP, Wellner N, Yakimets I. Characterization of polyhydroxybutyrate-hydroxyvalerate (PHB-HV)/maize starch blend films. J Food Eng 2008;89:361–9.

[38] Ke T, Sun X. Physical properties of poly(lactic acid) and starch composites with various blending Ratios1. Cereal Chem J 2000;77:761–8.

[39] Shuai X, He Y, Na Y-H, Inoue Y. Miscibility of block copolymers of poly(ε-caprolactone) and poly(ethylene glycol) with poly(3-hydroxybutyrate) as well as the compatibilizing effect of these copolymers in blends of poly(ε-caprolactone) and poly(3-hydroxybutyrate). J Appl Polym Sci 2001;80:2600–8.

[40] Hubbell DS, Cooper SL. The physical properties and morphology of poly-ε-caprolactone polymer blends. J Appl Polym Sci 1977; 21:3035–61.

[41] He Y-S, Zeng J-B, Li S-L, Wang Y-Z. Crystallization behavior of partially miscible biodegradable poly(butylene succinate)/poly(ethylene succinate) blends. Thermochim Acta 2012;529:80–6.

[42] Wang J, Zheng L, Zhu W, Zhang D, Xiao Y, Guan G. Fully biodegradable blends of poly(butylene succinate) and poly(butylene carbonate): miscibility, thermal properties, crystallization behavior and mechanical properties. Polym Test 2012;31:39–45.

[43] Zhou W, Yuan S, Chen Y, Bao L. Morphology and hydrogen-bond restricted crystallization of poly(butylene succinate)/cellulose diacetate blends. J Appl Polym Sci 2012;124:3124–31.

[44] Radano CP, Baker GL, Smith M. Stereoselective polymerization of a racemic monomer with a racemic catalyst: direct preparation of the polylactic acid stereocomplex from racemic lactide. J Am Chem Soc 2000;122:1552–3.

[45] Tsuji H, Hyon SH, Ikada Y. Stereocomplex formation between enantiomeric poly(lactic acid)s. 3. Calorimetric studies on blend films cast from dilute solution. Macromolecules 1991;24:5651–6.

[46] Blümm E, Owen A. Miscibility, crystallization and melting of poly(3-hydroxybutyrate)/poly(L-lactide) blends. Polymer 1995;36:4077–81.

[47] Koyama N, Doi Y. Miscibility of binary blends of poly((R)-3-hydroxybutyric acid) and poly((S)-lactic acid). Polymer 1997;38:1589–93.

[48] Gassner F, Owen A. Physical properties of poly(β-hydroxybutyrate)-poly(ε-caprolactone) blends. Polymer 1994;35:2233–6.

[49] Gada M, Gross R, McCarthy S. Miscible blends of poly (i-hydroxybutyrate-*co-p*-hydroxyvalerate). In: Biodegradable plastics and polymers: proceedings of the third international scientific workshop on biodegradable plastics and polymers, Osaka, Japan, November 9–11, 1993. Elsevier Publishing Company; 1994. p. 176.

[50] Immirzi B, Malinconico M, Orsello G, Portofino S, Volpe MG. Blends of biodegradable polyesters by reactive blending: preparation, characterization and properties. J Mater Sci 1999;34:1625–39.

[51] Parulekar Y, Mohanty AK. Biodegradable toughened polymers from renewable resources: blends of polyhydroxybutyrate with epoxidized natural rubber and maleated polybutadiene. Green Chem 2005;8:206–13.

[52] Jiang L, Liu B, Zhang J. Properties of poly (lactic acid)/poly (butylene adipate-*co*-terephthalate)/nanoparticle ternary composites. Ind Eng Chem Res 2009;48:7594–602.

[53] Li J, Lai MF, Liu JJ. Effect of poly(propylene carbonate) on the crystallization and melting behavior of poly(β-hydroxybutyrate-*co*-β-hydroxyvalerate). J Appl Polym Sci 2004;92:2514–21.

[54] Wu C-S. Physical properties and biodegradability of maleated-polycaprolactone/starch composite. Polym Degrad Stab 2003;80:127–34.

[55] Baumberger S, Lapierre C, Monties B. Utilization of pine kraft lignin in starch composites: impact of structural heterogeneity. J Agric Food Chem 1998;46:2234–40.

[56] Baumberger S, Lapierre C, Monties B, Valle GD. Use of kraft lignin as filler for starch films. Polym Degrad Stab 1998;59:273–7.

[57] Raquez J-M, Narayan R, Dubois P. Recent advances in reactive extrusion processing of biodegradable polymer-based compositions. Macromol Mater Eng 2008;293:447–70.

[58] Nitz H, Semke H, Landers R, Mülhaupt R. Reactive extrusion of polycaprolactone compounds containing wood flour and lignin. J Appl Polym Sci 2001;81:1972–84.

[59] Weihua K, He Y, Asakawa N, Inoue Y. Effect of lignin particles as a nucleating agent on crystallization of poly(3-hydroxybutyrate). J Appl Polym Sci 2004;94:2466–74.

[60] Graupner N. Application of lignin as natural adhesion promoter in cotton fibre-reinforced poly(lactic acid) (PLA) composites. J Mater Sci 2008;43:5222–9.

[61] Li J, He Y, Inoue Y. Thermal and mechanical properties of biodegradable blends of poly(L-lactic acid) and lignin. Polym Int 2003;52:949–55.

[62] Zhang L, Goh SH, Lee SY. Miscibility and crystallization behaviour of poly(L-lactide)/poly(*p*-vinylphenol) blends. Polymer 1998;39:4841–7.

[63] Nijenhuis AJ, Colstee E, Grijpma DW, Pennings AJ. High molecular weight poly(L-lactide) and poly(ethylene oxide) blends: thermal characterization and physical properties. Polymer 1996;37:5849–57.

[64] Nagai S, Itou A, Wongsriraksa P, Yamada K, Leong Y, Hamada H. Miscibility of polyoxyethylene and poly(lactic acid). 69th ANTEC. Boston (MA, USA): SPE; May 1–5, 2011.

[65] Bao D, Liao X, He T, Yang Q, Li G. Preparation of nanocellular foams from polycarbonate/poly(lactic acid) blend by using supercritical carbon dioxide. J Polym Res 2013;20:1–10.

[66] Li Y, Shimizu H. Improvement in toughness of poly(L-lactide) (PLLA) through reactive blending with acrylonitrile–butadiene–styrene copolymer (ABS): morphology and properties. Eur Polym J 2009;45:738–46.

[67] Liu P, Ouyang Y, Xiao R. Fabrication and morphology development of isotactic polypropylene nanofibers from isotactic polypropylene/polylactide blends. J Appl Polym Sci 2012;123:2859–66.

[68] Reddy N, Nama D, Yang Y. Polylactic acid/polypropylene polyblend fibers for better resistance to degradation. Polym Degrad Stab 2008;93:233–41.

[69] Anderson KS, Hillmyer MA. The influence of block copolymer microstructure on the toughness of compatibilized polylactide/polyethylene blends. Polymer 2004;45:8809–23.

[70] Eguiburu JL, Iruin JJ, Fernandez-Berridi MJ, San Roman J. Blends of amorphous and crystalline polylactides with poly(methyl methacrylate) and poly(methyl acrylate): a miscibility study. Polymer 1998;39:6891–7.

[71] Zhang G, Zhang J, Zhou X, Shen D. Miscibility and phase structure of binary blends of polylactide and poly(vinylpyrrolidone). J Appl Polym Sci 2003;88:973–9.

[72] Abbate M, Martuscelli E, Ragosta G, Scarinzi G. Tensile properties and impact behaviour of poly (D(–)3-hydroxybutyrate)/rubber blends. J Mater Sci 1991;26:1119–25.

[73] Greco P, Martuscelli E. Crystallization and thermal behaviour of poly (D(–)-3-hydroxybutyrate)-based blends. Polymer 1989;30:1475–83.

[74] Avella M, Martuscelli E. Poly-D-(–)(3-hydroxybutyrate)/poly (ethylene oxide) blends: phase diagram, thermal and crystallization behaviour. Polymer 1988;29:1731–7.

[75] Avella M, Martuscelli E, Greco P. Crystallization behaviour of poly(ethylene oxide) from poly(3-hydroxybutyrate)/poly(ethylene oxide) blends: phase structuring, morphology and thermal behaviour. Polymer 1991;32:1647–53.

[76] Jin San Y, Chang Soon C, Sung Jai M, Hyoung Jin C, Han-Sup L, Soon Ja C. Miscibility of poly-D(–)(3-hydroxybutyrate) in poly(ethylene oxide) and poly(methyl methacrylate). Eur Polym J 1993;29:1359–64.

[77] Lotti N, Pizzoli M, Ceccorulli G, Scandola M. Binary blends of microbial poly(3-hydroxybutyrate) with polymethacrylates. Polymer 1993;34:4935–40.

[78] Marand H, Collins M. Polym Prepr Am Chem Soc Div Polym Sci 1990;31:552. [CAS].

[79] Xing P, Dong L, An Y, Feng Z, Avella M, Martuscelli E. Miscibility and crystallization of poly(β-hydroxybutyrate) and poly(*p*-vinylphenol) blends. Macromolecules 1997;30:2726–33.

[80] Choe S, Cha Y-J, Lee H-S, Yoon JS, Choi HJ. Miscibility of poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate) and poly(vinyl chloride) blends. Polymer 1995;36:4977–82.

[81] Pingping Z, Haiyang Y, Shiqiang W. Viscosity behavior of poly-ε-caprolactone (PCL)/poly(vinyl chloride) (PVC) blends in various solvents. Eur Polym J 1998;34:91–4.

[82] Otey FH, Westhoff RP, Doane WM. Starch-based blown films. 2. Ind Eng Chem Res 1987;26:1659–63.

[83] Evangelista RL, Sung W, Jane JL, Gelina RJ, Nikolov ZL. Effect of compounding and starch modification on properties of starch-filled low-density polyethylene. Ind Eng Chem Res 1991;30:1841–6.

[84] Bikiaris D, Prinos J, Koutsopoulos K, Vouroutzis N, Pavlidou E, Frangis N, et al. LDPE/plasticized starch blends containing PE-*g*-MA copolymer as compatibilizer. Polym Degrad Stab 1998;59:287–91.

[85] Wang S, Yu J, Yu J. Compatible thermoplastic starch/polyethylene blends by one-step reactive extrusion. Polym Int 2005;54:279–85.

[86] Pachekoski WM, Agnelli JAM, Belem LP. Thermal, mechanical and morphological properties of poly (hydroxybutyrate) and polypropylene blends after processing. Mater Res 2009;12:159–64.

[87] San Yoon J, Choi CS, Maing SJ, Choi HJ, Lee HS, Choi SJ. Miscibility of poly-D(–)(3-hydroxybutyrate) in poly(ethylene oxide) and poly(methyl methacrylate). Eur Polym J 1993;29:1359–64.

[88] Choi HJ, Park SH, Yoon JS, Lee HS, Choi SJ. Rheological study on poly-D(–)(3-hydroxybutyrate) and its blends with poly(ethylene oxide). Polym Eng Sci 1995;35:1636–42.

[89] Ha C-S, Cho W-J. Miscibility, properties, and biodegradability of microbial polyester containing blends. Prog Polym Sci 2002;27:759–809.

[90] Fritz H, Seidenstücker T, Bölz U, Juza M, Schroeter J, Endres H. Study on production of thermoplastics and fibres based on mainly biological materials. EUR 16102. Directorate-General XII Science. Research and Development; 1994.

[91] Maddever WJ, Chapman MG. 47th ANTEC 89. New York (NY, USA): SPE; May 1–4, 1989. pp. 1351–1355.

[92] Bastioli C. Properties and applications of Mater-Bi starch-based materials. Polym Degrad Stab 1998;59:263–72.

[93] Bourg V, Chivrac F, Berthé V. Bioplastic innovation ; October 09, 2012. http://bioplastic-innovation.com/.

Chapter 4

Emulsions/Dispersions/Solutions/Gels

This chapter relates to emulsions, dispersions, solutions, and gels of biopolymers made by other methods than by emulsion, suspension, or solution polymerization.

Emulsions, dispersions, solutions, and gels of biopolymers have being used in broad areas finding applications in paints, coatings, inks, adhesives, and also in clothing, tableware, personal hygiene products (e.g., soaps, detergents, toothpastes, shampoos, rinses, etc.) and cosmetics (e.g., milky lotions, hair dressing agents, perfumes, lotions, ointments, etc.).

4.1 MAKING EMULSIONS AND DISPERSIONS

Emulsions are mixtures of two or more immiscible liquids, wherein one liquid of the two (called the dispersed or noncontinuous phase) is dispersed in the second liquid (called the continuous phase). The most typical continuous phase is water. Aqueous emulsions can be either oil-in-water (O/W) or water-in-oil (W/O) continuous phase mixtures. The emulsions may comprise a liquid dispersion of a polymer dissolved in a hydrophobic solvent or it can be a solvent-free liquid polymer or monomer. Surface active substances (emulsifiers, surfactants) are often used to increase the kinetic stability of emulsions. Although the terms *emulsion* and *dispersion* are often used in literature interchangeably, emulsion implies that both the dispersed and the continuous phases are liquid, while in dispersion the dispersed phase is solid. The term *latex* refers to a stable emulsion or dispersion of polymer droplets or particles of colloidal size, respectively, dispersed in an aqueous medium. It is not always easy, on the basis of the cited patent or article, to discern between an emulsion and a dispersion, i.e., whether the dispersed phase is in liquid or solid phase. Besides, in the same process polymer droplets can be converted to solid particles.

Aqueous emulsions, dispersions, and latices of biopolymers (biodegradable and nonbiodegradable alike) have many advantages meeting current requirements such as easy handling property, safety for operators and working environment as compared with polymer solutions in organic solvents. Most of the aqueous emulsions, dispersions, and latices of plasticizer in very large amount polymers, with the exception of natural rubber, are based on aliphatic polyesters or starch derivatives.

There are described several techniques in the prior art for the preparation of polymer emulsions, dispersions, and latices (1999, **WO9933558** A1, UNIV GENEVE; 2001, **WO0102087** A1, UNIV GENEVE LABORATOIRE DE PHA), which, when suitably modified, can be applied to biodegradable polymers. These techniques can be divided roughly into three main groups: solvent-based, thermomechanical [1], and solvent-free destructuring methods, while there are also numerous combinations of different techniques.

The method of dispersing and stabilizing a polymer depends on its properties. For example, when the polymer is soft and has a low softening point, it can be easily melted and dispersed in water at a high temperature and under high pressure, using a disperser or the like, and the resulting dispersion may be cooled with further stirring. On the other hand, when the polymer is hard and has a low softening point, it is predispersed in water to give a slurry, then the slurry is wet-milled using a ball mill or the like, and additives such as plasticizers are added thereto (1997, **WO9710292** A1, JAPAN CORN STARCH CO LTD).

4.1.1 Solvent-Based Methods

The solvent-based methods include the emulsification-evaporation, (nano)precipitation, salting, and emulsification-diffusion techniques [2], which have in common that they involve the use of an organic solution containing the (nano)particle components and functioning as an internal phase during preparation, and of an aqueous solution containing stabilizers that constitute the dispersion medium for the (nano)particles (1999, **WO9933558** A1, UNIV GENEVE; 2001, **WO0102087** A1, UNIV GENEVE LABORATOIRE DE PHA).

4.1.1.1 Emulsification-Evaporation Technique

According to the emulsification-evaporation technique disclosed in **US4177177** A (1979, EL AASSER MOHAMED S; UGELSTAD JOHN; VANDERHOFF JOHN W) a polymer solution in a water-immiscible organic solvent such as chloroform (trichloromethane) or methylene chloride (dichloromethane)[1] is emulsified in an aqueous phase containing emulsifiers. This crude emulsion is then submitted to a high energy mixing step using a high energy source such as ultrasound, homogenizers, high pressure dispersers,

---

[1] The solubilities of chloroform and methylene chloride in 100 g water are 0.8 and 1.3, respectively at 20 °C.

Biopolymers: Processing and Products. http://dx.doi.org/10.1016/B978-0-323-26698-7.00004-0

colloid mills, or microfluidizers in order to reduce the droplet size. The polymer emulsion resulting from such a treatment is very fine and contains very small droplets (below 0.5 μm in diameter). The emulsification is followed by the removal of the solvent, by vacuum distillation, producing a fine aqueous dispersion of nanospheres. The homogenization step, which is the determining factor in obtaining submicron size particles, requires high energy (1999, **WO9933558** A1, UNIV GENEVE; 2001, **WO0102087** A1, UNIV GENEVE LABORATOIRE DE PHA).

WO9407940 A1 (1994, MONSANTO CO), **WO9721762** A1 (1997, MONSANTO CO), **US5599891** A (1997, ZENECA LTD) and Horowitz and Sanders [3] disclose amorphous polyhydroxyalkanoate (PHA) aqueous dispersions prepared from crystalline polymers by the emulsification-evaporation technique. For example, PHAs such as poly(3-hydroxybutyrate) (P3HB), poly(3-hydroxybutyrate-*co*-3hydroxyvalerate) (PHBHV) and poly(3-hydroxyoctanoate) (PHO) have been prepared as amorphous particles by dissolving the polymer in a solvent of low solubility in water such as chloroform, emulsifying the polymer solution with a solution of aqueous surfactant and heating the emulsion to remove the organic solvent.

The surfactant contains a plurality of repeating units including at least one PHA-compatible unit and at least one hydrophilic unit, wherein the PHA-compatible unit is an aliphatic hydrocarbon, aromatic hydrocarbon, or polyoxyalkylene, and wherein the hydrophilic unit is anionic, cationic, or nonionic.

Example: An aqueous PHA dispersion was prepared by the following steps:

(1) powdered crystalline PHBHV (3HB/3HV = 76.6/23.4 by moles) was dissolved in chloroform to give a 5 wt% solution; (2) the solution was emulsified in an aqueous solution (1 wt%) of Sarkosyl™ (sodium *N*-lauroyl sarcosinate); (3) the chloroform was removed by stirring in a current of nitrogen leaving a dispersion of solid amorphous particles of average diameter 0.56 μm. The aqueous dispersion was concentrated to 6 wt% solids and freed of excess Sarkosyl™ by diafiltration. It was then concentrated to 40 wt% solids by evaporation.

WO9704036 A (1997, PROCTER & GAMBLE) discloses a PHA emulsion having a solid concentration of 2.5 wt% to be used as adhesive in preparing nonwovens. Examples of preferred PHAs include poly(3-hydroxybutyrate-*co*-3-hydroxyoctanoate) (PHBHO) or poly(3-hydroxybutyrate-*co*-hydroxyoctadecanoate). A solution is made of PHA dissolved in 450 g of an organic solvent such as chloroform and emulsified in water with the aid of sonicator. An emulsifier (e.g., ethoxylated oleyl alcohol such as the commercial product Volpo™ 20 of Croda, Inc.) can be used in the mixture to stabilize the emulsion. The organic solvent is subsequently evaporated from the emulsion to obtain a dispersion of the copolymer binder.

JP2003277595 A (2003, MITSUI CHEMICALS INC) discloses a method for preparing an aqueous dispersion of poly(lactic acid) (PLA) by various means, but a specific dispersing means shown in the examples is an aqueous dispersion produced by dissolving PLA in methylene chloride or chloroform, emulsifying the organic solution in an aqueous solution containing poly(vinyl alcohol) (PVOH) or lecithin, stirring and applying heat to evaporate the solvent to get a PLA dispersion.

CN101538400 A (2009, TIANJIN GREEN BIOMATERIAL CO L) discloses a method for making an aqueous dispersion of PHA, wherein the PHA is first dissolved in an organic solvent and the thus obtained organic solution of PHA is dispersed in water containing an emulsifier as well as optionally a dispersant using high speed mixing. Suitable PHAs are PHBHV, poly(3-hydroxybutyrate-*co*-3-hydroxyhexanoate) (PHBHHx), and poly(3-hydroxybutyrate-*co*-4-hydroxybutyrate) (P3HB4HB). Suitable solvents are methylene chloride and ethyl acetate.[2] Suitable emulsifiers are sodium dodecylbenzenesulfonate and fatty alcohol polyoxymethylene. Suitable dispersants are PVOH, methylcellulose, or other cellulose-based modified polymers.

This approach has the disadvantage that the organic solvent has to be removed and then either disposed or recycled, which results in additional process steps and energy consumption. Furthermore, conventional surfactants have been proven to be unsuitable to provide stable dispersions of PHA in water.

JPH10101911 A (1998, MIYOSHI YUSHI KK) discloses a biodegradable polymer emulsion comprising a dispersion of fine particles of PLA prepared as follows: (1) PLA or a copolymer of lactic acid, e.g., with malic acid is mixed with an emulsifier comprising a mixture of an anionic surfactant such as sodium alkylbenzenesulfonate in an amount of at least 80 wt% and a nonionic surfactant such as polyoxyethylene nonylphenyl ether in such a manner that the emulsifier accounts for at most 5 wt% of PLA; (2) the mixture is dissolved in an organic solvent such as methylene chloride or chloroform; and (3) this mixture is emulsified by adding water thereto while being agitated with, e.g., a homomixer to give a PLA emulsion, wherein PLA is emulsified and dispersed in the form of fine particles of a mean particle diameter of 0.05–10 μm and that has a PLA polymer content of 10–70 wt%.

JP2001011294 A (2001, MIYOSHI YUSHI KK) discloses a biodegradable polymer aqueous dispersion prepared by loading a biodegradable polyester such as PLA, a cationic macromolecular compound with a weight average molecular weight $M_w > 300{,}000$ or an anionic macromolecular compound with a $M_w > 1{,}000{,}000$, PVOH,

---

[2] The solubility of ethyl acetate in water is 8.3/100 ml at 20 °C.

ethyl acetate, and water in an autoclave equipped with a stirrer and heated to 100 °C, and removing the organic solvent under reduced pressure. **JP2004099883** A (2004, MIYOSHI YUSHI KK), which is a modification of the method described in **JP2001011294** A (2001), uses a PVOH with a saponification degree ≥95 mol% as dispersing agent. **JP2004323804** A (2004, MIYOSHI YUSHI KK) is another modified version using a PVOH with a saponification degree of about 81% and an oxazoline compound in the aqueous medium.

However, the methods of the aforementioned patent applications have a number of disadvantages. The mixture of cationic or anionic macromolecular compounds and PVOH is nonbiodegradable. Further, it is proposed to add other agents, such as thickeners, flow index modifiers, etc. It is also still obligatory to use as solvent a large excess of volatile organic solvent, which necessitates the use of a subsequent step that strips off under high vacuum a large proportion of this organic solvent. It is, moreover, known that it is not possible to obtain a solvent-free emulsion, save at the risk of breaking the emulsion. This biodegradable emulsion is barely satisfactory, given the number of manipulations to be performed and the fact that a very precise equilibrium of the components needs to be adhered to in order to obtain an industrially advantageous product. Finally, these biodegradable aqueous dispersions are of only limited stability, i.e., they are stable for not more than 1–2 months at 20 °C or at 40 °C, and, as a result, they cannot be used for many applications in which the required stability times are longer (2005, **EP1514891** A1, ROQUETTE FRERES).

JP2001303478 A (2001, TOPPAN FORMS CO LTD) discloses a biodegradable polymer emulsion prepared by dissolving PLA in a fairly volatile organic compound, i.e., ethyl acetate, and then adding an emulsifier chosen from fatty acid salts, carboxylate ethers, alkenyl succinates, and alkyl sulfates. The biodegradable polymer emulsion is used to coat paper, imparting it with mechanical strength, printability, and water-resistance properties, and also stability over time.

This disclosed method is labor intensive and complex, and requires the addition of many ingredients, both into the organic phase and into the dispersing aqueous phase, and still in the presence of volatile organic solvents (2005, **EP1514891** A1, ROQUETTE FRERES).

JP2004204219 A (2004, DAI ICHI KOGYO SEIYAKU CO LTD) discloses a PLA-based aqueous emulsion obtained by the emulsification-evaporation technique using toluene as the water-immiscible organic solvent and 5–30 wt% of a plasticizer, based on PLA, which is a dibasic acid ester of an ethylene oxide adduct of benzyl alcohol and/or an aliphatic alcohol.

JP2003321600 A (2003, ARAKAWA CHEM IND) discloses a method for producing a PLA aqueous emulsion and a coating containing the PLA aqueous emulsion. This PLA aqueous emulsion can be prepared by subjecting to a high pressure emulsification-solvent evaporation a mixture of PLA with a rosin-based resin in water. The high pressure emulsification is carried out as follows: the mixture of PLA and the rosin-based resin forming the dispersion phase is dissolved in benzene, toluene or like solvent; then an emulsifying agent and warm water are added to the solution; the mixture is emulsified by a high pressure emulsifying machine; and, finally, the solvent is distilled off, giving an aqueous dispersion. A stabilized form of rosin is used to improve the compatibility with PLA; triethylene glycol monomethyl ether ester of stabilized rosin is particularly preferred (see also Chapter 13: Coating compositions).

According to **EP1514891** A1 (2005, ROQUETTE FRERES) all the aforementioned patent applications have three major drawbacks:

1. it is indispensable to use volatile organic solvents to dissolve the biodegradable polymers, irrespective of the preparation process used, which therefore does not make it possible to avoid the problems of toxicity, cost premiums, complexity of the steps used, the obligation to install leak-prevention devices, devices for recovering the volatile organic solvents, and their inevitable environmental impact;
2. the use of volatile organic solvents can only lead to aqueous dispersions with a low dry matter content;
3. it is necessary to add various stabilizers, emulsifiers, thickeners, etc., the synthetic nature of which is detrimental to the biodegradability of the aqueous dispersion obtained.

WO2006088241 A1 (2006, TEIJIN LTD; MUSASHINO KAGAKU KENKYUSHO; MUTUAL CORP; YOSHIHARU KIMURA) discloses a method for the preparation of a mixed emulsion of PLA from an aqueous emulsion of poly(L-lactic acid) (PLLA) and an aqueous emulsion of poly(D-lactic acid) (PDLA). The mixed emulsion is suitable for the formation of a stereocomplex PLA (scPLA) by drying (see Chapter 1: Introduction; Section 1.4.1.1.1 Poly(lactic acid)). The weight ratio PLLA/PDLA in the mixed emulsion is preferably 40/60–60/40, more preferably 45/55–55/45. The mixed emulsion has an average particle diameter preferably of 0.05–2 μm, more preferably 0.07–0.5 μm in an O/W form.

It is considered that while PLLA and PDLA are separated from each other by the function of the emulsifier in the state of the mixed emulsion to form micelles that are rarely miscible with each other, when the mixed emulsion is dried, the helices of PLLA and PDLA are interacted with each other by the function of the residual emulsifier to form a stereocomplex when they approach each other.

Example:

1. Preparation of an aqueous emulsion PLLA.
   100 parts of PLLA ($M_w = 20{,}100$) was heated at 100 °C in 400 parts of toluene, dissolved in the toluene for about 1 h, and cooled to 80 °C. Then, 20 parts in terms of solid of a disodium salt of polyoxyethylene alkylether sulfosuccinic acid as an emulsifier and 1000 parts of water were added and stirred intensively at 75 °C for 1 h to carry out preemulsification. Ultrasonic waves were applied to the obtained preemulsified product for 1 h or more to obtain an emulsified product. The toluene contained in the emulsified product was distilled off under reduced pressure by using an evaporator to obtain an aqueous emulsion of PLLA having a solid content of 10% and an average particle diameter of 0.3 µm (solution L1).
2. Preparation of an aqueous emulsion of PDLA.
   The same operation as above was repeated except that PDLA ($M_w = 22{,}200$) was used to obtain an aqueous emulsion of PDLA having a solid content of 10% and an average particle diameter of 0.3 µm (solution D1).
3. Preparation of mixed emulsion.
   The obtained solutions L1 and D1 were mixed together in a weight ratio of 1:1 to obtain a mixed emulsion.
4. Application, drying.
   The mixed emulsion was cast over a substrate and dried at room temperature to obtain a 35-µm-thick film. A wide-angle X-ray diffraction (WAXS) measurement of the film confirmed that scPLA was formed having $M_w = 21{,}000$; the stereocomplex content of the film was 76.1%.

4.1.1.2 (Nano)Precipitation Technique

In the (nano)precipitation technique disclosed in **EP0274961** A1 (1988, CENTRE NAT RECH SCIENT) a polymer and, optionally, a lipophilic stabilizer (e.g., phospholipids) are dissolved in a semipolar water-miscible solvent, such as acetone or ethanol. This solution is poured or injected into an aqueous solution containing a stabilizer (e.g., PVOH) under magnetic stirring. Nanoparticles are formed instantaneously by the rapid diffusion of the solvent, which is then eliminated from the suspension under reduced pressure. The usefulness of this technique is limited to water-miscible solvents in which the diffusion rate is sufficient to produce spontaneous emulsification (1999, **WO9933558** A1, UNIV GENEVE; 2001, **WO0102087** A1, UNIV GENEVE LABORATOIRE DE PHA).

Marchessault et al. [4] also prepared suspensions of amorphous PHO particles by dispersing an acetone solution of the polymer in water and then removing the acetone by distillation. A similar approach is described in **WO9625452** A1 (1996, ZENECA LTD), in which a suspension of amorphous PHBHV is made by mixing a solution of the polymer in 1,2-propanediol at a temperature T of $100\,°\text{C} < T < T_m - 10\,°\text{C}$, wherein T_m is the melting temperature of PHBHV, with water and surfactant, and then removing the organic solvent by diafiltration.

WO0180835 A1 (2001, TANABE SEIYAKU CO) discloses a method for producing biodegradable polymer microspheres, comprising the following steps: (1) adding a polymer solution containing a medicament, a biodegradable polymer, and a good solvent for said polymer which solvent is miscible with water (solvent A) to a homogeneous mixture of a poor solvent for said polymer which solvent is miscible with said solvent A (solvent B) and a poor solvent for said polymer which solvent is immiscible with said solvent A (solvent C), emulsifying the mixture to prepare an emulsion wherein the polymer solution forms a dispersed phase and the homogeneous mixture forms a continuous phase, and then removing solvent A from the dispersed phase. The biodegradable polymer is selected from PLA, poly lactide-*co*-glycolide and poly(2-hydroxybutyric acid-glycolic acid). Solvent A is selected from acetone, tetrahydrofuran, acetonitrile, dimethylformamide, dimethylsulfoxide, dioxane, diglyme, and ethyleneglycol dimethyl ether; solvent B is selected from water and a monovalent alcohol having one to four carbon atoms; and solvent C is glycerol.

JP2002173535 A (2002, UNITIKA LTD) discloses a method for producing an aqueous dispersion of a biodegradable polyester comprising (a) an aliphatic polyester such as PLA, (b) a basic compound such as ammonia or organic amine, (c) an organic solvent such as methyl ethyl ketone,[3] and (d) water comprises a dispersing step, a heating step, an emulsifying step and a cooling step. The whole of the component (a), and the whole or a part of the component (b) and (c) are roughly dispersed in an aqueous medium by stirring at the dispersing step. At the heating step and the emulsifying step, the remaining components are added thereto under stirring before the finish of the emulsifying step, and the resultant mixture is heated to the temperature not less than the higher temperature of 60 °C and the T_g of the component (a). The heated mixture is continuously stirred until the content of coarse particles of the biodegradable polyester, having the particle diameter not less than 20 µm becomes ≤1 wt%.

JP2005008733 A (2005) and **JP2006089687** A (2006) of UNITIKA LTD disclose a PLA aqueous dispersion comprising: (a) a PLA having a D-lactic acid content of 1.5–25 mol%; (b) 1–30 wt%, based on PLA, polyoxyethylene-polyoxypropylene block copolymer as a surfactant; (c) 0.01–20 wt%, based on PLA, ammonia, or an organic amine compound having a boiling point of ≤250 °C; (d) 0–30 wt% water-miscible amphiphilic organic solvent; (e) water; and (f) plasticizer. The PLA particles of the aqueous dispersion have a number average particle diameter

---

[3] The solubility of methyl ethyl ketone (MEK) in water is 27.5 g/100 ml at 20 °C.

of <0.5 µm. The PLA aqueous dispersion is prepared as follows: (1) mixing and heating (>30 °C) components (a)–(e) in a vessel to emulsify PLA; (2) adding the plasticizer (f); and (3) removing the amphiphilic organic solvent. The water-miscible amphiphilic organic solvent is selected from tetrahydrofuran (THF), dioxanoe, acetone, and methyl ethyl ketone; preferably, THF is used.

JP2004002871 A (2004, TOYO BOSEKI) discloses a PLA-based aqueous dispersion obtained by: (1) dissolving PLA in THF; (2) adding water little by little at 60 °C to the solution using sodium stearate as an emulsifier; and (3) removing THF.

WO9812245 A1 (1998, BASF AG) discloses a method for forming an aqueous dispersion from poly(butylene-adipate-*co*-terephthalate) (PBAT), which is a fossil fuel–derived biodegradable polyester. The method includes the added steps of first increasing the molecular weight of the aliphatic-aromatic polyester by reacting it with chain extenders, such as diisocyanates, then dissolving the polymer into an organic solvent followed by dispersion in water, and finally removal of the organic solvent by vacuum distillation. The solvent is selected from methyl ethyl ketone, tetrahydrofuran, or acetone. The patent makes no reference to a method of making an aliphatic-aromatic polyester emulsion in the absence of organic solvent addition. One would further expect that the resultant emulsion would have residual amounts of solvent present in the final latex, and hence contribute to a volatile organic compound (VOC) issue in practical use (2012, **WO2012149407** A1, METABOLIX INC).

4.1.1.3 Salting-Out Technique

The salting-out technique disclosed in **WO8808011** A1 (1988, BINDSCHAEDLER CHRISTIAN; GURNY ROBERT; DOELKER ERIC), and described by Allémann et al. [5] is based on the separation of a totally water-miscible solvent, in particular acetone, from aqueous solutions via the salting-out effect. Typically, the polymer is dissolved in acetone and this solution is emulsified under vigorous mechanical stirring in an aqueous gel containing the salting-out agent (e.g., a mineral salt) and a colloidal stabilizer (e.g., PVOH). This O/W emulsion is diluted with a sufficient volume of water or of aqueous solution in order to enhance the diffusion of acetone into the aqueous phase, thus inducing the formation of nanoparticles. The process does not at any stage require an increase in temperature, unlike methods that utilize an organic solvent evaporation stage or a spray-drying stage. A major drawback of this technique is the use of a high quantity of salt, which gives to the aqueous phase a fixed pH and which must be eliminated in a subsequent purification step. Another drawback is that it is necessary to remove the solvent and a considerable amount of water to obtain a high polymer concentration in the final dispersion. Moreover, the acetone is mixed in the water, which renders recycling of acetone problematic (1999, **WO9933558** A1, UNIV GENEVE; 2001, **WO0102087** A1, UNIV GENEVE LABORATOIRE DE PHA).

JP2000007789 A (2000, DAINIPPON INK & CHEMICALS) discloses a method for the preparation of an aqueous dispersion of self-water dispersible particles made of a biodegradable polyester comprising: (1) a step of reacting a biodegradable aliphatic polyester having hydroxyl groups with a polyvalent carboxylic acid or anhydride or chloride thereof to obtain a biodegradable polyester having acid groups; and (2) a step of dissolving the biodegradable polyester having acid groups obtained in step (1) in an organic solvent, adding a base to the solution with stirring to neutralize to form the salt of the biodegradable polyester having acid groups, and then adding water to the resulting solution or dispersion to undergo phase inversion emulsification.

When water is added to an organic solvent solution of the polyester having a neutralized salt structure with stirring, the solution undergoes phase inversion emulsification leading to the formation of a particulate polyester. During this procedure, an organic solvent solution of the polyester having a neutralized salt structure may be added to water with stirring. Alternatively, an aqueous solution having a base dissolved therein may be added to an organic solvent solution of a polyester having carboxyl groups.

Preferred aliphatic polyesters are PLA and its copolymers. Examples of the base to be used as a neutralizing agent herein include inorganic base such as alkali (e.g., sodium hydroxide and potassium hydroxide, carbonate, and acetate thereof) and aqueous ammonia, and organic base such as alkylamine (e.g., methylamine, dimethylamine, trimethylamine, ethylamine, diethylamine, triethylamine), alkanolamine (e.g., dimethyl ethanolamine, diethanolamine), and alkylammonium hydroxide (e.g., tetramethylammonium hydroxide, tetraethylammonium hydroxide). Examples of the solvent to be used for dissolving the biodegradable polyester having carboxyl groups incorporated therein include chlorine-based organic solvent such as methylene chloride and chloroform, ketone-based organic solvent such as acetone and methyl ethyl ketone, ether-based organic solvent such as tetrahydrofuran, ester-based organic solvent such as ethyl acetate, and alcohol-based organic solvent such as isopropyl alcohol. Since a biodegradable polyester having carboxyl groups incorporated therein is dispersed in water with an organic solvent, the organic solvent preferably has a relatively high affinity for water. Further, since the organic solvent must be removed after dispersion, the organic solvent preferably has a lower boiling point than water.

4.1.1.4 Emulsification-Diffusion Technique

In the emulsification-diffusion technique described by Leroux et al. [6] a partially water-miscible solvent such as benzyl alcohol,[4] previously saturated with water and containing a polymer, is emulsified in an aqueous phase previously saturated with the solvent and containing a stabilizer. The subsequent addition of water to the system causes the solvent to diffuse into the external phase, resulting in the aggregation of polymer in nanoparticles. This method is of interest from a technological point of view, since it does not need comminuting forces as the emulsification-evaporation technique does, it is highly efficient, reproducible and easy to scale up. However, as in the salting-out technique, it is necessary to remove the solvent and a considerable amount of water to obtain a high polymer concentration in the final dispersion (1999, **WO9933558** A1, UNIV GENEVE; 2001, **WO0102087** A1, UNIV GENEVE LABORATOIRE DE PHA).

WO9933558 A1 (2001) and **WO0102087** A1 (2001) of the UNIV GENEVE disclose a method, which is based on the emulsification-diffusion technique, for producing an aqueous colloidal dispersion of biodegradable polymer nanoparticles, comprising the steps of:

1. preparing an organic phase by dissolving a water-insoluble biodegradable polymer, and optionally additional ingredients, in a partially water-soluble organic solvent that preferably is previously saturated with water;
2. preparing an aqueous phase by providing water, and optionally dissolving a stabilizing agent in water, wherein preferably, the water is previously saturated with the same or another partially-water soluble organic solvent;
3. emulsifying the organic phase in the aqueous phase, using a low energy source;
4. removing by vacuum distillation the organic solvent from the O/W emulsion formed in step (3) to cause the formation of nanoparticles, in suspension in the aqueous phase.

The biodegradable polymer is preferably selected from PLA (Medisorb® of Medisorb) and poly(ε-caprolactone) (PCL) (e.g., Tone® 767 of Union Carbide). The partially water-soluble organic solvent is preferably selected from ethyl acetate, methyl acetate, isopropyl acetate, and methyl ethyl ketone (2-butanone).

The disclosed method does not require high shear force for homogenization, does not require the removal of toxic solvent, of stabilizer, of salting-out agent, and/or of a considerable amount of water.

4.1.2 Thermomechanical Methods

WO9606178 A1 (1996, ZENECA LTD) discloses a method for producing an aqueous dispersion of PHA, and especially a PHBHV latex, by heating a slurry of crystalline PHBHV powder in water and surfactant (e.g., sodium dodecyl sulfate) under pressure for 10 min at a temperature $T > T_m$ of the polymer until PHBHV melts and a substantial coalescence of PHA particles occurs, thereby forming a layer of molten PHBHV; separating the layer of PHBHV from the aqueous layer at a high shear rate, thereby forming a fine dispersion of PHBHV; and cooling to form a PHBHV latex.

However, it is not disclosed whether the particles remained in the amorphous state upon cooling, or what the final particle size of the slurry is. This method has the disadvantage that the particle size of the final product is dictated by the size of the powder starting material, which is at least 20–50 μm. Particles of this size crystallize rapidly upon cooling, giving even an initially amorphous suspension a useful shelf-life of less than four days. The duration of the thermal treatment in this case also causes significant further agglomeration of the particles. Suspensions containing large particles are generally unsuitable for film forming applications (1999, **WO9964498** A1, METABOLIX INC).

JPH1192712 A (1999), **WO0196449** A1 (2001), and **JP2002003607** A (2002) of SHOWA HIGHPOLYMER disclose an O/W emulsion prepared by melting and kneading an aliphatic polyester in a twin-screw extruder, and then introducing therein an aqueous emulsifier downstream of the melt, and optionally other additive(s). The mixture is then blended at a temperature $T \leq 100\,°C$ so that the resultant dispersion has a solid concentration of ≥40 wt% and a viscosity at 20 °C of ≥1000 mPa s, preferably of 1500–10,000 mPa s. The aqueous emulsifier has a surface tension, in terms of 1.0 wt% aqueous solution at 20 °C, of ≤63 mN/m. Examples of the biodegradable polymers include poly(butylene succinate) (PBS), poly(butylene succinate-*co*-adipate) (PBSA), poly(ethylene succinate) (PES), poly(ethylene succinate-*co*-adipate) (PESA); reaction products prepared by combining these polyesters with hexamethylene diisocyanate or γ-am inopropyltrimethoxysilane; and PCL, PLA, poly(glycolic acid) (PGA), as well as PHBHV. The emulsifier is PVOH or a nonionic surfactant having a polyoxyethylene chain. Other additives include an adhesive agent, a plasticizer, a filler, a dispersion stabilizer, etc. The disclosed aqueous biodegradable polyester dispersion has a high solid concentration and a high viscosity, which are very advantageous in practical use. The emulsion is claimed to have excellent adhesion and film-forming properties.

Example: Pellets of PBS were continuously fed at a rate of 10 kg/h from a hopper to a corotating twin-screw extruder. Concurrently, 15% aqueous solution of a partially saponified PVOH was continuously injected at a constant temperature of 80 °C and a flow rate of 14 kg/h from an aqueous emulsifier solution supply port of the extruder disposed in a cylinder unit at fourth block from the hopper port using a plunger pump. The resulting mixture was continuously extruded. The PBS used was Bionolle® 1040 (Showa Denko KK)

---

[4] The solubility of benzyl alcohol in water is 4/100 ml at 20 °C.

having a $T_m = 115\,°C$ and a melt flow index, MFI = 46.5. The partially saponified PVOH used was Kuraray Poval™ 220 EG (Kuraray Co Ltd) having a $M_n = 98{,}080$ and a surface tension, in terms of 1 wt% aqueous solution at 20 °C, of 52.0 mN/m. The temperatures in the cylinder were set at 50 °C in a resin pellet supply portion, at 155 °C in a resin melting portion, and at 100 °C between the emulsifier aqueous solution supply portion to the outlet. The viscosity η_o of the resin pellets was 13,000 mPa s at 145 °C, the viscosity η_w of the emulsifier aqueous solution was 1800 mPa s at 80 °C, and the ratio η_o/η_w was 7.2. The product was viscous and milky white, and electric conductance revealed that it was an emulsion having an aqueous phase as a continuous phase. The emulsion cooled to room temperature had a peak particle size of 1.79 μm, a solid concentration of 57.8%, and a viscosity of 183,200 mPa s and exhibited good shelf stability. The emulsion showed a decomposition rate of 70% (35 days) in the biodegradation test.

According to **EP1514891** A1 (2005, ROQUETTE FRERES), the disclosed methods in **JPH1192712** A (1999) and **WO0196449** A1 (2001) have a number of drawbacks:

- If the biodegradable polyester has a $T_m \geq 100\,°C$, it is proposed to increase the working pressure of the extruder or to add plasticizers to lower T_m. However, neither the type, the nature (in terms of solubility parameter values and capacity to form hydrogen bonds), nor the amount of plasticizers to be used is specified. No proposals are given for the said plasticizers.
- The method is aimed only at obtaining very viscous aqueous dispersions, which is the described way, to obtain an emulsion that is stable over time. It is, specifically, a matter of preventing the largest particles from sedimenting out and consequently leading to a lowering of the dry matter content of the emulsion by phase separation. This solution is not satisfactory since it leads to viscous emulsions that are difficult to handle and makes it difficult to obtain thin films. Specifically, excessively viscous solutions lead to thick films, of heterogeneous thickness, which crack and consume a lot of material. A viscous aqueous dispersion also does not promote the coalescence of the polymer particles in suspension during the preparation of films (problem of steric bulk) and reduces the mechanical strength of the films.
- The extrusion operation leads to intense shear of the blended melt, which alters the structure and the intrinsic properties of the polymer. The films made with this aqueous dispersion are mechanically weaker and less rigid. This shear also leads to an increase in hydrophilic end groups and an increase in the mobility of the polymer chains. This increase in hydrophilicity is then reflected by an increase in the diffusion of water into the polymer, which increases the rates of hydrolysis and degradation.

A quite similar process for preparing aqueous dispersions by extrusion, having these same drawbacks, is described in **EP0113443** A2 (1984, DOW CHEMICAL CO). The method described in this patent applies only to cellulose-based biodegradable polymers combined with long-chain fatty acids, and only allows the production of aqueous dispersions with a low dry matter content (~30%).

WO9749762 A1 (1997, POLYMER COREX KUOPIO LTD OY) discloses a dispersion of biodegradable polymers that contains starch ester dispersed in an aqueous phase, and a solvent-free process for manufacturing said aqueous dispersions. The method includes the step of preparing a molten blend, at a temperature of 100–180 °C, of polymers and plasticizers, and then in keeping this blend stirred at high temperature, followed by gradually adding water and dispersants. The plasticizing of the polymer and the dispersion of the mixture in water can be performed in an extruder. The obtained dispersion is homogenized in order to improve its stability.

It is noted, however, again by **EP1514891** A1 (2005, ROQUETTE FRERES) that although the disclosed aqueous biodegradable polymer dispersion has a high solid concentration, this can only be achieved by adding plasticizer in very large amounts, or even in excess relative to the biodegradable polymers (75–175 parts of plasticizer need to be introduced per 100 parts of biodegradable polymers), which necessarily leads to alteration of the properties imparted by said polymers. Moreover, it is stated that the melt phase may be prepared in an extruder, which leads to the same problems of alteration of properties of the polymers used as those mentioned previously in the discussion of **WO0196449** A1 (2001) and **JPH1192712** A (1999).

EP1514891 A1 (2005, ROQUETTE FRERES) attempts to overcome the aforementioned disadvantages by disclosing an aqueous dispersion of one or more biodegradable polyesters comprising an organic phase dispersed in an aqueous dispersing phase and free from volatile organic solvents. The organic phase comprises at least one plasticizer chosen from heavy organic solvents with solubility parameter of 15–28 $(MPa)^{1/2}$ and hydrogen bonding parameter δH of 3.5–16 15–28 $(MPa)^{1/2}$; a preferred plasticizer is glycerol triacetate (triacetin). Particularly preferred biodegradable polyesters are PHA and PLA, and the corresponding commercial products are Nodax® (Procter & Gamble) and Galactic® L68 (Galactic). The aqueous dispersion is formed by melting the polyester in an extruder and then introducing an aqueous emulsifier to the melt. The mixture is blended at a temperature of equal or less than 100 °C. High pressure or a viscosity-reducing agent is to be used in case of high T_m. The disclosed aqueous dispersion is claimed to be stable over time, free of volatile organic compounds, and have high dry matter content and low viscosity.

WO2011024023 A1 (2011, OCV INTELLECTUAL CAPITAL LLC) discloses a similar aqueous dispersion to **EP1514891** A1 formed by mixing an aliphatic polyester, at least one surfactant, at least one plasticizer, and water in a high pressure reactor under a high stirring rate at a temperature above the T_m of the aliphatic polyester for a period of time sufficient to form an aqueous emulsion, and then rapidly cooling said high pressure reactor to avoid recrystallization of said polyester. The aqueous dispersion is used as part of a sizing composition for the treatment of glass fibers.

JPH0978494 A (1997, MITSUI TOATSU CHEMICALS) discloses an aqueous dispersion of PLA for paper coating prepared by: (1) solidifying PLA after melting by heat in a water; (2) stirring with glass beads at a high speed; and (3) pulverizing in order to obtain an aqueous dispersion of fine particles. The composition of the aqueous coating contains (a) particles of a PLA copolymer of a diameter of 0.1–50 µm and weight-average molecular weight, $M_w \leq 50{,}000$, (b) a water-soluble polymer such as PVOH or (carboxy)methylcellulose, and (c) a filler such as kaolin or calcium, in an amount of 5–80 wt% total amount of the component (a) and (c). The composition is applied in an amount of 1–100 g/m^2 to one surface of a substrate containing cellulose fiber and the composition is heat-treated at a temperature $T \geq T_g$ of component (a) so as to form a coated paper.

JP2004018744 A (2004, MITSUI CHEMICALS INC) discloses an aqueous dispersion prepared by emulsifying a molten blend comprising PLA and another biodegradable polyester having a $T_g \leq 30\,°\text{C}$. The ratio of PLA to the biodegradable polyester is 90/10–30/70. The biodegradable polyester is selected from (PBAT), PBS, and PCL. The aqueous PLA dispersion is claimed to have excellent resistance to oil, chemicals, corrosion, low toxicity, high impact strength, and adhesiveness at low temperature.

Example: A blend of PLA (50 pbw) and mixture of PBS and PVOH was subjected to a melting process in an extruder at a temperature of 180 °C, while water was continuously supplied into the extruder. The extruded blend was cooled to 90 °C and then discharged. The discharged material was found to be white or a transparent white solid. The prepared water dispersion was added into warm water for obtaining a white water dispersion, which was later filtered using a metal mesh. The water dispersion was coated on a PLA film, subjected to heat processing at 150 °C.

FR2862310 A1 (2005, ROQUETTE FRERES) discloses an aqueous dispersion prepared by first mixing a biodegradable polymer and a viscosity-reducing agent to prepare a molten organic phase; subsequently the molten organic phase is mixed with an aqueous phase comprising a stabilizer to form an aqueous dispersion of the biodegradable polymer. The biodegradable polymer is selected from PLA, poly(β-malic acid), PHA, PCL, poly(butylene succinate-*co*-adipate), PBAT, polyesteramides, and celluloses or starches that are highly acetylated or rendered hydrophobic by introduction of fixed fatty chains, taken alone or in combination.

4.1.3 Nonsolvent Destructuring Methods

One approach used in the prior art to obtain aqueous dispersions of PHAs is starting directly from the medium obtained from the microbiological process for making PHAs. Such media still contain non-PHA cell material, such as proteins and lipids, which have to be destroyed and residues thereof removed in order to obtain the desired aqueous dispersion of PHAs. According to this method, the bacteria cells containing PHAs are broken open by means of a combined physical, chemical, and enzymatic procedure. In this way, the PHA granules are released from the biomass and an aqueous dispersion is produced, viz a latex. The aqueous PHA dispersion is further purified of cell constituents by means of rinsing steps and centrifugation. Prior art documents representative for this approach of obtaining aqueous colloidal dispersions of PHAs, such as P3HB and PHBHV, directly from the biomass are **WO9113207** A1 (1991, PULP PAPER RES INST; UNIV MCGILL), **WO9624682** A1 (1996, ZENECA LTD), **WO9600263** A1 (1996, STICHTING ONDERZOEK EN ONTWIKKELING NOORD NEDERLAND), **US6024784** A (2000, INST VOOR AGROTECH ONDERZOEK), and **GB2291648** A (1996, ICI PLC).

One principal disadvantage of this technology is that the aqueous dispersion has to be prepared starting from the microbiological process, which is particularly for end users not attractive since they normally do not have the required experience and technology for the microbiological processes. Thus it would be beneficial to have a process for making stable aqueous dispersions of PHAs starting from a powder comprising one or more PHAs (2014, **WO2014023319** A1, SYNTHOMER LTD).

DE4040158 A1 (1992, PCD PETROCHEMIE DANUBIA DEUTSCHLAND) discloses aqueous dispersions of PHA such as P3HB or PHBHV. The dispersions are prepared, for example, by stirring PHA powder, optionally with another thermoplastic powder (e.g., polyethylene, polypropylene, polyamide, paraffin), in water and subsequent homogenization. In a particularly economical method, the PHA dispersion can be obtained directly from the processing of the PHA-storing microorganisms during their biotechnological production. The PHA powder preferably has a mean particle size, $D_{50\%}$-value <25 µm. Such powders can be obtained, for example, by wet-milling of the PHA. A granular P3HB is first slurried in water, then ground and filtered. The wet filter cake having a water content of 40% is optionally dried and dispersed in water using a traditional surfactant such as polyoxyethyleneglycerol monolaureate. However, conventional surfactants have been proven to be unsuitable to provide stable dispersions of PHA in water.

WO2004041936 A (2004, KANEKA CORP) discloses a method for preparing an aqueous dispersion of poly(3-hydroxybutyrate-*co*-3-hydroxyhexanoate) (PHBHx) comprising the steps of: (1) isolating the PHBHx within a microorganism by disrupting the microorganism in an aqueous dispersed state; and (2) separating the PHBHx particles, which are partially agglomerated, from each other by applying mechanical shearing to the aqueous dispersion. Methods of disrupting the microorganisms include use of ultrasonic waves, an emulsifying disperser, a high pressure homogenizer, or a mill. The preparation process provides a stable aqueous dispersion in which the fine particle size of PHBHx produced within the microorganism is maintained considerably without solidifying the resin after melting by heat, without mixing and kneading melted resin and an aqueous solution of an emulsifier or without pulverizing frozen resin. The aqueous dispersion of PHBHx has a solid content concentration of 5–70 wt%. PHBHx has an average particle size of 0.1–50 μm. The composition ratio of PHBHHx is preferably 3-hydroxybutyrate (3HB)/3-hydroxyhexanoate (3HH) = 97–75/3–25 (mol%), more preferably 3HB/3HH = 95–85/5–15 (mol%). The aqueous dispersion of PHBHHx is claimed to have excellent film-forming properties and provide a resin coating film of a flexural modulus of 100–1500 MPa (measured according to JIS K7171),which is flexible, has favorable elongation, and is strong to folding, when applied in coatings, adhesives, fiber processing, sheet film processing, and paper processing. According to a preferred embodiment, the aqueous dispersion is free of conventional anionic or cationic or nonionic surfactants.

WO2014023319 A1 (2014, SYNTHOMER LTD) discloses a method for producing an aqueous dispersion of PHA comprising dispersing a powder containing one or more PHAs in an aqueous medium in presence of a colloidal stabilizer using a high shear disperser at a share rate of 10/s–750,000/s. The PHA is selected from P3HB, poly (4-hydroxybutyrate) (P4HB), PHBHV, P3HB4HB, or PHBHHx. The colloidal stabilizer is selected from PVOH and/or starch or starch derivatives as well as cellulose and cellulose derivatives. These stearic type dispersions stabilizers are biodegradable, easy to handle, readily available, and provide the required long-term stability with a reduced adverse environmental impact compared to conventional surfactants.

Example: 30 g of PVOH (Mowiol® 56-98, Kuraray)—a 4 wt% aqueous solution thereof at 20 °C exhibits a viscosity measured according to DIN 53015 using a No. 2 Ball of 56 mPa s (available from Kuraray)—22 g of water and 0.12 g of an antifoam agent (Foamstopper 101, available from Synthomer Ltd) were added to a reactor containing 40 g of P3HB powder and stirred using a high speed dispersant instrument at a shear rate of 8150/s to obtain a mixture. The mixture was allowed to stir until homogeneous dispersion was formed, and then 0.1 g of a biocide agent (Acticide MBS 5050 10%) was added. The mixture was further stirred for 10 min to obtain 40% solids content aqueous dispersion of P3HB.

Starch dispersions are well-known aqueous starch systems where the granular starch structure has partly or totally been disrupted using sufficient work or heat. In excess of water, the process of starch hydration and granule destruction is known as gelatinization and can be facilitated or impeded by chemical modifications (cf. converted, derivatized, or crosslinked starch) [5]. Pregelatinization yields cold-water dispersible systems. Although there is no need for cooking, pregelatinized starch still requires substantial mechanical energy for dispersion in water. The stability of many starch dispersions over time is an additional problem since the amylose fraction, and to a much lesser extent also the amylopectin fraction, shows a strong tendency toward retrogradation, a process of crystallization resulting in gel formation or precipitation. **US5032683** A (1991, SEQUA CHEMICALS INC) discloses the production of a stable aqueous starch composition having a coatable viscosity, wherein the starch has been gelatinized and reacted at temperatures above 70 °C in the presence of a blocked glyoxal compound. However, converted (thin-boiling) and/or chemically modified starch are the desirable starch materials for these compositions. **US5116890** A (1992, SEQUA CHEMICALS INC) comprises the preparation of water-dispersible, self-crosslink lattices based on a starch hydrolyzate to produce stable emulsions with low viscosity. The process requires undesirable chemicals and is quite laborious.

WO9710292 A1 (1997, NIPPON KOONSUTAAC KK) discloses an aqueous dispersion of a water-insoluble starch derivative having a solid concentration of about 18–28 wt%. The starch derivative is an esterified, vinyl ester-grafted polymer starch. The biodegradable polymer composition further comprises a dispersion stabilizer, a plasticizer, a filler, etc.

WO0069916 A1 (2000, ATO BV) discloses in one of its embodiments the formation of an aqueous dispersion of crosslinked starch nanoparticles. The particles have a narrow particle size distribution with particle sizes below 400 nm, and especially below 200 nm. Prior to dispersion, the starch is processed under high shear forces in the presence of a crosslinking agent. The mechanically treated, crosslinked biopolymer is then formed into a latex by dispersion in a suitable solvent, usually water and/or another hydroxylic solvent such as an alcohol, to a concentration of 4–50 wt%, especially 10–40 wt% (see also Chapter 6: Powdering; Section 6.1: Pelletization).

4.2 MAKING SOLUTIONS

JPH04334448 A (1992, SHIMADZU CORP) discloses a solution of PLA in a volatile organic solvent, which is used to coat the surface of a paper either by spraying or by immersing the paper in the organic solution.

JP2009185108 A (2009, TOYO BOSEKI) discloses a solution of a PLA-based copolymer in an organic solvent. The organic solvent is selected from ester-based solvents, ketone-based solvents, or aromatic solvents (see also, Chapter 2: Properties; Section: 2.1.1.3: Solubility); exemplary solvents are ethyl acetate and butyl acetate. The PLA-based copolymer is characterized by the following features: (1) its D-lactic acid is derived from meso-lactide; (2) the molar ratio (L/D) of L-lactic acid to D-lactic acid is in the range of 1–9; (3) the lactic acid residue content is ≥50 wt%; (4) and the reduced viscosity is 0.2–1.0 dl/g. The PLA solution hardly generates resin precipitates even when stored in low temperatures and has good storage stability.

Although the choice of PLA instead of a synthetic polymer contributes toward the resolution of the problem of biodegradability of the polymers and consequently the packaging, it is not entirely satisfactory. In particular, the use of VOCs as solvents to deposit PLA or its derivatives on the surface of a substrate requires complex and/or delicate handling due to the mandatory safety precautions imposed as a result of the toxicity of the volatile organic solvent (e.g., flammable solvents, risk of explosion, inhalation by the worker, environmental pollution, etc.) (2005, **EP1514891** A1, ROQUETTE FRERES).

WO2006001081 A1 (2006, SHOWA HIGHPOLYMER) discloses a biodegradable polyester solution, which is obtained from a poly(alkylene alkanoate) and a general-purpose halogen-free solvent. The halogen-free solvent is hydrocarbon, ester, ether, acetal, and/or ketone; preferably, ethyl acetate, butyl acetate, toluene, xylene, and/or methyl ethyl ketone. The solution does not gel at temperatures higher than 20 °C and is useful as an adhesive, pressure-sensitive adhesive, coating, ink, etc. The gelation temperature is calculated from specific gravity, volume correction, and molecular weight of the halogen-free solvent and heat of fusion (ΔH), specific gravity, and T_m of the biodegradable polyester by a specific relation.

Example: Dodecane diacid (230.3 g) and 3-methyl-1,5-pentane diol (123.9 g) were heated at 200–210 °C and dehydrated. A product having acid value of 9.9 mg KOH/g was obtained. The obtained product was cooled to 100 °C, and titanium tetraisopropoxide (0.177 g) was added and heated to 200–210 °C. Excess glycol was removed under vacuum and the product was cooled to 180 °C. Further, phosphorous acid (0.08 g) was added and stirred. Hexamethylene diisocyanate (3 g) was added, and a soft biodegradable polyester having $M_w = 213{,}451$, $T_m = -3$ °C, and ΔH = 37.8 mJ/mg, was obtained. The biodegradable polyester (80 g) and *n*-butyl acetate (180 g) were heat dissolved for 3 h, and a biodegradable polyester solution having a gelation temperature of −30.5 °C was obtained.

The extraction or separation of the PHAs from the bacterial biomass often employs large quantities of volatile organic solvents, preferably hydrocarbon solvents such as chloroform, methylene chloride, dichloroethane, trichlorobenzene [7] chloropropane, or other undesirable chemical solvents (1980, **FR2446859** A1 SOLVAY; 1980, **EP0015123** A1, ICI PLC; 1982, **US4324907** A, ICI LTD; 1984, **EP0124309** A2, ICI PLC; 1986, **FR2567149** A1 SOLVAY; 1986, **DD239609** A1, AKAD WISSENSCHAFTEN DDR; 1998, **WO9846782** A1, MONSANTO CO; 1998, **WO9846783** A1, MONSANTO CO). The use of these solvents would not only make the working up of PHAs expensive but also considerably limit the number of possible applications of PHAs. In the process of stripping the solvent, the concentrated PHA solution often forms a very high viscosity fluid or sometimes even a gel, which can be extremely difficult to process. Furthermore, such solvents are potentially harmful to health and environment if not fully removed from the PHA. Consequently, the use of a large amount of such solvents resulting in the formation of highly viscous solutions or gels, especially near the harvesting site, would be undesirable.

In recent years, ionic liquids have been extensively evaluated as environmental-friendly alternatives to conventional organic solvents. Generally speaking, ionic liquids refer to a specific class of molten salts that are liquids at temperatures of 100 °C or below. Ionic liquids have very low vapor pressure and generate virtually no hazardous vapors. Moreover, ionic liquids are composed of charged species, which provide a highly polar medium useful in various applications, such as extraction, separation, catalysis, and chemical synthesis medium.

Ionic liquids can be costly; thus, their use as solvents in many processes may not be feasible. Despite this, methods and apparatuses for reforming and/or recycling ionic liquids have heretofore been insufficient. Furthermore, many processes for producing ionic liquids involve the use of halide and/or sulfur intermediates, or the use of metal oxide catalysts. Such processes can produce ionic liquids having high levels of residual metals, sulfur, and/or halides (2008, **US2008194807**, EASTMAN CHEM CO).

Ionic liquids have been used to dissolve or treat cellulosic materials and starch. Such applications are described in: **US1943176** A (1934, CHEM IND BASEL); **WO03029329** A2 (2003, UNIV ALABAMA); **WO2005017001** A1 (2005, KEMIRA OYJ); **WO2005023873** A1 (2005, KEMIRA OYJ); **WO2005017252** A1 (2005, VIRIDIAN CHEMICAL PTY LTD).

Ionic liquids have also been used to dissolve several other biopolymers. Certain biopolymers that are insoluble or have very limited solubility in water or organic solvents can be dissolved in ionic liquids and extracted from their biological sources with ionic liquids.

US2006241287 A1 (2006, PROCTER & GAMBLE) discloses a method for dissolving biopolymers by mixing a biopolymer with an ionic liquid in its fluid state and in the absence of water to form a mixture. The biopolymer is chitin, chitosan, elastin, collagen, keratin, or PHA. Due to the strong solvating power of the ionic liquid, biopolymers that are insoluble or have limited solubility in organic solvents or water can be dissolved under fairly mild conditions. The dissolution process can be carried out at temperatures from about room temperature (20 °C) to about 100 °C under atmospheric pressure. In some embodiments, the dissolution process is carried out at a temperature of 40–90 °C. Optionally, higher temperatures (up to about 130 °C) may be employed to increase the dissolution rate and reduce the processing time. The dissolution step may take from about 1 min to about 5 h, depending on the temperature. The dissolution step produces a clear, transparent, or translucent solution that comprises the ionic liquid and the biopolymer. In a typical embodiment, the solution comprises 1–50 wt%, preferably 5–45 wt%, and more preferably 10–40 wt% biopolymer.

DE102005062608 A1 (2007, BASF) discloses a solution system based on molten ionic liquid (e.g., imidazolium salt) for dissolving and regenerating carbohydrates (e.g., starch, cellulose, or derivative) in the form of regenerated cellulose fibers. The solution system contains a protic solvent or a mixture of protic solvents, and optionally additives; in case the only protic solvent is water, this is used in the solution system in an amount of more than about 5 wt%.

WO2011056924 A2 (2011, UNIV ALABAMA) discloses a method for dissolving a biopolymer using mixtures of ionic liquids having different cations and/or anions and to compositions comprising the mixtures. The biopolymer is selected from starch, pectin, chitin, chitosan, alginate, silk, elastin, collagen, gelatin, hemicellulose, lignin, or cellulose.

The mixture of ionic liquids comprises two or more ionic liquids having cations selected from: pyridinium (I), pyridazinium (II), pyrimidinium (III), pyrazinium (IV), imidazolium (V), pyrazolium (VI), 1,2,4-triazolium (VII), oxazolium (VIII), 1,2,3-triazolium (IX), thiazolium (X), piperidinium (XI), pyrrolidinium (XII), quinolium (XIII), and isoquinolium (XIV). The mixture of ionic liquids further comprises carboxylate salts, where the carboxylate salt is sodium acetate, potassium acetate, or choline acetate.

In some aspects, the disclosed mixtures perform better at dissolving biomass than single-ionic liquid counterparts. For example, it was found that cellulose displays higher solubility in ternary mixtures of dialkylated imidazolium ionic liquids than in a single ionic liquid of the mixture alone. In a specific example, it was found that an inexpensive 2:1:1 mixture of 1-ethyl-3-methylimidazolium, 1,3-diethylimidazolium, and 1,3-dimethylimidazolium acetate can dissolve up to about 5 wt% cellulose at room temperature and up to about 35 wt% cellulose (when heated) before the solution becomes very viscous, with no decomposition of the ionic liquid mixture observed during the dissolution process.

4.3 MAKING (HYDRO)GELS

The term *gel* as used in the prior art means a three-dimensional network organization swelling in a solvent. When water is the solvent, the gel is defined as "hydrogel." Hydrogels are obtained by crosslinking a water-soluble polymer yielding a three-dimensional network that can contain large amounts of water. When the three-dimensional network is due to polymer chain entanglements, it is called a physical gel, whereas when it is due to chemical bonds it is called a chemical gel.

Hydrogels are frequently used in biomedical applications as delivery systems for proteins and peptides. Proteins can be loaded into the gel by adding the protein to the polymer before the crosslinking reaction is carried out or by soaking a preformed hydrogel in a protein solution. No (aggressive) organic solvents have to be used to load the hydrogels with protein molecules. The release of proteins from hydrogels can be easily controlled and manipulated by varying the hydrogel characteristics, such as the water content and the crosslink density of the gel. However, a major disadvantage of the currently used hydrogel delivery systems is that they are not biodegradable. This necessitates surgical removal of the gel from the patient after the release of the protein in order to prevent complications of inclusion of the empty hydrogel material (wound tissue is frequently formed) (1998, **WO9800170** A1, UNIV UTRECHT).

Biodegradable gels are well known in the art, for example, crosslinked gelatin. Hyaluronic acid has been crosslinked and used as a biodegradable swelling polymer for biomedical applications (1988, **EP0265116** A2, FIDIA SPA). A dextran hydrogel is obtained by coupling glycidyl methacrylate (GMA) to dextran, followed by radical polymerization of an aqueous solution of GMA-derivatized dextran (dex-GMA) [8,9]. Although the described crosslinked dextran hydrogels were expected to be biodegradable, these hydrogels are rather stable under physiological conditions. It is shown among other things that the dissolution time of dextran hydrogels obtained by polymerization of dextran derivatized with glycidyl methacrylate (DS = 4) had a dissolution time of about 100 days. Dextran hydrogels, wherein the dextrans have a higher degree of substitution, did not show any signs of degradation during 70 days, even at extreme conditions.

Another biodegradable hydrogel is disclosed in **US5410016** A (1995, UNIV TEXAS). This material is made from degradable, polymerizable macromers having a water-soluble region, at least one degradable region that is hydrolyzable under in vivo conditions, and free radical polymerizable end groups having the capacity to form additional covalent bonds resulting in macromer interlinking, wherein the polymerizable end groups are separated from each other by at least one degradable region. In preferred embodiments, the macromers include a central backbone of poly(ethylene glycol) (PEG) flanked by biodegradable regions of PCL or PLA, which are in turn flanked by polymerizable vinyl groups.

A primary disadvantage of the macromers and hydrogels disclosed by **US5410016** A (1995) is that they are inflexible in design. PEG has only two groups that are easily modified, the terminal hydroxyl groups, and those groups are modified with the biodegradable and polymerizable groups. Moreover, **US5410016** A does not disclose any ways in which the macromers can be modified or in which the hydrogel can be modified after its formation. Also, the degradable PEG material developed by **US5410016** A exhibits a large degree of swelling in aqueous solutions, which is disadvantageous in many applications (1998, **WO9800170** A1, UNIV UTRECHT).

Poly(vinyl acetate) (PVAc) hydrogels offer many advantages over PEG-based hydrogels. For example, the availability of pendant OH groups along a PVAc backbone adds versatility in terms of the various modifications that could be made to the macromer (e.g., attachment of degradable segments, active agents, hydrophobic groups, etc.). However, a major disadvantage of the PVAc hydrogels that have been developed is that they are not biodegradable.

WO9800170 A1 (1998, UNIV UTRECHT) describes a biodegradable hydrogel consisting of two interpenetrating polymer networks interconnected to each other through hydrolysable spacers. Preferably, the hydrogels are based on water-soluble polymers that contain at least a number of side groups having the capability to form linkers to other polymers, e.g., dextran. In the most preferred embodiment, PGA and/or PLA spacers are introduced between polymerizable methacrylate groups and dextran. When a hydrogel formed of this material is introduced in a physiological environment, the hydrogel becomes biodegradable resulting in dextran, polyhydroxyethylmethacrylate, lactic acid, and/or glycolic acid as degradation products. These degradation products are all biocompatible. Generally, the water-swellable polymers are made hydrolysable by introducing at least one hydrolytically labile unit in the spacers between the main chains of water-soluble polymers and the second polymer chain formed by the crosslinkable units. It is also possible to use polymer chains comprising hydrolytically labile monomer units in the main chain.

JP2011190426 A (2011, SAN DIA POLYMER LTD) discloses water absorptive polymer particles for sanitary products, containing crosslinked polymer comprising water-soluble and/or hydrolysable vinyl monomers and crosslinking agent, and a specific amount of PLA. The PLA exists at the surface of absorptive particles. The hydrogel particles are produced by polymerizing water-soluble or hydrolysable vinyl monomer in presence of cross linking agent, mixing obtained polymer and PLA to produce composite gel of crosslinked polymer and PLA, or mixing vinyl monomer, crosslinking agent, and PLA, and polymerizing.

WO2011047486 A1 (2011, UNIV ALBERTA) discloses gel-forming compositions of block copolymers for use as thermoresponsive, biodegradable hydrogels for sustained delivery of a bioactive agent. The copolymers can comprise block copolymers of PEG and poly(α-benzyl carboxylate-ε-caprolactone) (PBCL), poly(α-carboxyl-ε-caprolactone) (PCCL), or both PBCL and PCCL functionalities, such as poly[(α-carboxyl-ε-caprolactone)-*co*-(α-benzyl carboxylate-ε-caprolactone)].

PATENTS

Patent Number	Publication Date	Family Members	Priority Numbers	Inventors	Applicants	Title
DE102005062608 A1	20070705	CN101346416 A 20090114; CN101346416 B 0130102	DE20051062608 20051223	STEGMANN VEIT; MASSONNE KLEMENS; MAASE MATTHIAS; UERDINGEN ERIC; LUTZ MICHAEL; HERMANUTZ FRANK; GAEHR FRANK	BASF AG	Lösungssystem auf der Basis geschmolzener ionischer Flüssigkeiten, ein Verfahren zu dessen Hertsellung sowie zur Herstellung regenerierter Kohlenhydrate. "Solution system based on molten ionic liquids, process for their production and production of regenerated carbohydrates."
DE4040158 A1	19920617		DE19904040158 19901215	HAEUBL GEORG; SCHEUCHENSTUHL WILLIBALD; ESTERMANN ROBERT; HRABAK OTTO; KROATH HANS	PCD PETROCHEMIE DANUBIA DEUTSCHLAND	Flächenförmiger Gegenstand aus einer mit Polyhydroxyalkanoat-Dispersion beschichteten Trägerschicht. "Flat article obtained by coating carrier sheet with dispersion of polyhydroxyalkanoate."
EP0113443 A1	19840718	US4502888 A 19850305; PH19415 A 19860410; NZ206486 A 19870630; EP0113443 A3 19850522; EP0113443 B1 19910515; JPS59130533 A 19840727; JPH0643516 B2 19940608; CA1219101 A1 19870317; BR8306929 A 19840724; AU2198083 A 19840621; AU572811 B2 19880519	US19820449297 19821213	LENG DOUGLAS ELLIS; SIGELKO WILMER LIST; SOUNDERS FRANK LINWOOD	DOW CHEMICAL CO	Aqueous dispersions of plasticized polymer particles.
EP0265116 A2	19880427	ZA8707559 A 19880413; PT85908 A 19871101; PT85908 B 19900831; PH26025 A 19920129; NZ221994 A 19900726; NO874251 A 19880414; NO175374 B 19940627; NO175374 C 19941005; KR920002702 B119920331 JPS63105003 A 19880510;	IT19860048546 19861013	DELLA VALLE FRANCESCO; ROMEO AURELIO	FIDIA SPA	Cross linked esters of hyaluronic acid.

Continued

—Cont'd

Patent Number	Publication Date	Family Members	Priority Numbers	Inventors	Applicants	Title
		JP2648308 B2 19970827; IT1198449 B 19881221; IN170801 A1 19920523; IL84032 A 19971120; IE872618 L 19880413; HU204858 B 19920228; HUT45734 A 19880829; FI874504 A 19880414; FI96610 B 19960415; FI96610 C 19960725 EP0265116 B1 19980311; DE3752176 T2 19981029; ES2115583 T3 19980701; EP0265116 A3 19890208; EP0265116 B1 19980311; DK536087 A 19880414; CN87106919 A 19880824; CN1025035 C 19940615; CA1317287 C 19930504; AU7960087 A 19880421; AU610087 B2 19910516; AT163942T T 19980315; AR247406 A1 19941229				
EP0274961 A1	19880720	US5049322 A 19910917; JPS63232840 A 19880928; JPH0693998 B2 19941124; GR3004198 T3 19930331; FR2608942 A1 19880701; ES2031529 T3 19921216; CA1293170 C 19911217		FESSI HATEM; PUISIEUX FRANCIS; DEVISSAGUET JEAN-PHILIPPE	CENTRE NAT RECH SCIENT	Process for preparing a colloidal and disperse system in the shape of nanocapsules.
EP1514891 A1	20050316	US2005058712 A1 20050317; US2011237710 A1 20110929; KR20050027060 A 20050317; JP2005089751 A 20050407; JP5138150 B2 20130206; FR2859729 A1 20050318; FR2859729 B1 20060224; EP1514891 B1 20080806; CN1613913 A 20050511; CN100381501 C 20080416; CA2478883 A1 20050312; AT403694 T 20080815	FR20030010743 20030912	SERPELLONI MICHEL; MENTINK LEON; BERNAERTS JOEL	ROQUETTE FRERES	Aqueous dispersions of at least one biodegradable polymer.

JP2001011294 A	20010116	JP4382909 B2 20091216	JP19990189707 19990702	KAMIO KATSUHISA; OKUYA MASAHIRO; KURODA IWAO; HOSODA KAZUO; AMATA YUKIRO	MIYOSHI YUSHI KK	Aqueous dispersion of biodegradable resin and biodegradable composite material.
JP2001303478 A	20011031		JP20000116531 20000418	MINOWA TOSHIYUKI	TOPPAN FORMS CO LTD	Method for producing paper sheet having biodegradable plastic layer.
JP2002003607 A	20020109		JP20000212215 20000713	DOI YUKIO; ISHIOKA RYOJI; OKINO YOSHIRO; IMAIZUMI MITSUHIRO	SHOWA HIGHPOLYMER	Method of manufacturing aqueous dispersion of biodegradable polyester.
JP2002173535 A	20020621		JP20000370106 20001205	YAMADA KAZUNOBU; UEDA KAZUE; KAJIMARU HIROSHI; SHIRASAWA DAISUKE	UNITIKA LTD	Method for producing water dispersion of biodegradable polyester resin.
JP2003277595 A	20031002		P20020084133 20020325	NARUTAKI TOMOMITSU	MITSUI CHEMICALS INC	Aqueous dispersion of poly-lactic acid with improved film-forming property and storage stability.
JP2003321600 A	20031114	JP3775668 B2 20060517	JP20020127744 20020430	TAKAGI YOSHINORI; TSUSHIMA YOSUKE	ARAKAWA CHEM IND	Polylactic acid aqueous emulsion, method for producing the same and coating containing the polylactic acid aqueous emulsion.
JP2004002871 A	20040108		JP20030171002 20030616	SHIBAZAKI SATOKO; MIYAMOTO TAKASHI; ITO TAKESHI; SHINO KATSUYA; HOTTA YASUNARI	TOYO BOSEKI	Biodegradable polymeric aqueous dispersion.
JP2004018744 A	20040122		JP20020177575 20020618	NARUTAKI TOMOMITSU	MITSUI CHEMICALS INC	Aqueous polylactic acid resin dispersion.
JP2004099883 A	20040402		P20030296038 20030820; JP20020240658 20020821	NIIZEKI KOICHI; OKUYA MASAHIRO; KAMIO KATSUHISA	MIYOSHI YUSHI KK	Aqueous dispersion system of biodegradable resin.
JP2004204219 A	20040722		JP20030298019 20030821; JP20020361440 20021212	ISHIHARA KAZUHIKO; SAINAI NAOFUMI	DAI ICHI KOGYO SEIYAKU CO LTD	Polylactic acid plastic emulsion having low temperature film forming property.

Continued

—Cont'd

Patent Number	Publication Date	Family Members	Priority Numbers	Inventors	Applicants	Title
JP2005008733 A	20050113	JP4694110 B2 20110608	JP20030173475 20030618	YAMADA AKIFUMI; OKAMOTO MASASHI; SHIBA YOSHITO; ONISHI HAYAMI	UNITIKA LTD	Polylactic acid resin aqueous dispersion and manufacturing method thereof.
JP2006089687 A	20060406	JP4541085 B2 20100908	JP20040279587 20040927	YAMADA AKIFUMI; OKAMOTO MASASHI; SHIBA YOSHITO	UNITIKA LTD	Method for producing a polylactic acid resin aqueous dispersion.
JP2009185108 A	20090820		JP20080023520 20080204	MIYAMOTO TAKASHI	TOYO BOSEKI	Solution of a polylactic acid based resin.
JP2011190426 A	20110929	JP5264850 B2 20130814	JP20100034270 20100219; JP20100218631 20100929	SUGIYAMA HIROKO; ISHIDA TOSHINOBU	SAN DIA POLYMER LTD	Absorbing resin particle and manufacturing method thereof.
JPH04334448 A	19921120	JP2513091 B2 19960703	JP19910135754 19910510	KOSEKI HIDEKAZU	SHIMADZU CORP	Biodegradable composite material and manufacture thereof.
JPH0978494 A	19970325	JP3523944 B2 20040426	JP19950235165 19950913	TAKAGI MASATOSHI; MINAZU HIROSHI; AJIOKA MASANOBU; YAMAGUCHI TERUHIRO	MITSUI TOATSU CHEMICALS	Composition for aqueous paper coating and coated paper obtained by coating of the same composition.
JPH10101911 A	19980421	JP3616465 B2 20050202	JP19960280339 19961001	KAWASHIMA MASAKI; HOSODA KAZUO; MORIYA MASAFUMI	MIYOSHI YUSHI KK	Biodegradable emulsion.
JPH1192712 A	19990406		JP19970258852 19970924	DOI YUKIO; ISHIOKA RYOJI	SHOWA HIGHPOLYMER	O/W type biologically decomposable emulsion and composition using the same.
US1943176 A	19340109		CHX1943176 19300927	GRAENACHER CHARLES	CHEM IND BASEL	Cellulose solution.
US2006241287 A1	20061026	WO2006116126 A2 20061102; US7763715 B2 20100727; EP1874996 A2 20080109; JP2008535483 A 20080904; CA2602145 A1 20061102; CA2602145 C 20110614	US20060406620 20060419; US20050674131P 20050422	NEAL CHARLES WILLIAM]; FORSHEY PAUL ARLEN; NARASIMHAN KARUNAKARAN; NIEHOFF RAYMOND LOUIS; HECHT STACIE ELLEN; PHAN DEAN VAN; BROOKER ANJU DEEPALI MASSEY; COMBS KATHERINE HELEN	PROCTER & GAMBLE	Extracting biopolymers from a biomass using ionic liquids.

US2008194807 A1	20080814	WO2008100577 A1 20080821; WO2008100569 A1 20080821; WO2008100566 A1 20080821; US8153782 B2 20120410; US2008194834 A1 20080814; US7919631 B2 20110405; US2008194808 A1 20080814; US8148518 B2 20120403; US2012142910 A1 20120607; US2012095207 A1 20120419; KR20090109106 A 20091019; KR20090109107 A 20091019; KR20090109556 A 20091020; EP2118070 A1 20091118; EP2118143 A1 20091118; EP2121766 A1 20091125; JP2010518166 A 20100527; JP2010518245 A 20100527; JP2010518244 A 20100527; CN101657428 A 20100224; CN101657470 A 20100224; CN101657470 B 20120905; CN101668779 A 20100310; CN101668779 B 20131120; CN102603643 A 20120725; CN102675207 A 20120919	US20080030434 20080213; US20070901615P 20070214	BUCHANAN CHARLES MICHAEL; BUCHANAN NORMA LINDSEY	EASTMAN CHEM CO	Reformation of ionic liquids.
US4177177 A	19791204		US19780873067 19780127; US19760670908 19760326	EL AASSER MOHAMED S; UGELSTAD JOHN; VANDERHOFF JOHN W	EL AASSER MOHAMED S; UGELSTAD JOHN; VANDERHOFF JOHN W	Polymer emulsification process.
US5410016 A	19950425		US19930022687 19930301; US19910740703 19910805; US19900598880 19901015; US19920843485 19920228	HUBBELL JEFFREY A; PATHAK CHANDRASHEKHAR P; SAWHNEY AMARPREET S; DESAI NEIL P; HILL JENNIFER L	UNIV TEXAS	Photopolymerizable biodegradable hydrogels as tissue contacting materials and controlled-release carriers.
US5599891 A	19970204		WO1993GB02014 19930928; GB19920020401 19920928; GB19920029447 19920928; GB19930004651 19930308	HOROWITZ DANIEL M; HUNTER BRIAN K; SANDERS JEREMY K M; CLAUSS JOACHIM; GEORGE NEIL	ZENECA LTD	Polymer composition.

Continued

—Cont'd

Patent Number	Publication Date	Family Members	Priority Numbers	Inventors	Applicants	Title
WO0102087 A1	20010111	AU5156799 A 20010122	WO1999EP04677 19990706	QUINTANAR-GUERRERO DAVID; ALLEMANN ERIC; GURNY ROBERT; FESSI HATEM; DOELKER ERIC	UNIV GENEVE LABORATOIRE DE PHA	Method for producing aqueous colloidal dispersions of nanoparticles.
WO0180835 A1	20011101	EP1277465 A1 20030122; CN1430506 A 20030716; CA2405194 A1 20011101; AU4882501 A 20011107	WO2001JP03446 20010423; JP20000122469 20000424	SUZUKI TAKEHIKO; KITAZAWA TAKEO; MATSUMOTO AKIHIRO; SUZUKI AKIRA	TANABE SEIYAKU CO	Process for producing microspheres.
WO0196449 A1	20011220	JP2001354841 A 20011225; AU6429901 A 20011224; EP1302502 A1 20030416; EP1302502 A4 20041020; EP1302502 B1 20060830; US2003181630 A1 20030925; US6716911 B2 20040406; KR20030016294 A 20030226; DE60122732 T2 20061221; CN1441823 A 20030910; CN1239579 C 20060201	JP20000181574 20000616	DOI YUKIO; ISHIOKA RYOJI; OKINO YOSHIRO; IMAIZUMI MITSUHIRO	SHOWA HIGHPOLYMER	Process for producing aqueous dispersion of biodegradable polyester.
WO03029329 A2	20030410	WO03029329 A3 20030731; ZA200402610 A 20041223; US2003157351 A1 20030821; US6824599 B2 20041130; PL206185 B1 20100730; NZ532076 A 20050930; NO20041774 A 20040430; MXPA04003029 A 20050620; KR20040065550 A 20040722; KR100778793 B1 20071128; JP2009079220 A 20090416; JP2005506401 A 20050303; IL161124 A 20100328; HK1076120 A 20081128; ES2371756 T3 20071128; EP2325246 A2 20110525; EP2325246 A3 20050303; EP1458805 A2 20040922; EP1458805 B1 20110831; EA008535 B1 20070629;	US20010326704P 20011003	SWATLOSKI RICHARD PATRICK; ROGERS ROBIN DON; HOLBREY JOHN DAVID	UNIV ALABAMA; PG RES FOUNDATION INC	Dissolution and processing of cellulose using ionic liquids.

		DK1458805 T3 20111003; CN101007853 A 20070801; CN101007853 B 20121003; CN1596282 A 20050316; CN100365050 C 20080130; CA2462460 A1 20030410; CA2462460 C 20090519; BR0213106 A 20060523; AU2002347788 A1 20030414; AU2002347788 B2 20060713; AT522571 T 20110915				
WO2004041936 A1	20040521	US2006258833 A1 20061116; US7491754 B2 20090217; JP4553733 B2 20100929; EP1566409 A1 20050824; CA2503590 A1 20040521; BR0315787 A 20050913; AU2003277546 A1 20040607	JP20020325984 20021108	SENDA KENICHI; MIKI YASUHIRO	KANEKA CORP	Aqueous dispersion of biodegradable polyester and method for production thereof.
WO2005017001 A1	20050224	US2008023162 A1 20080131; FI20031156 A 20050216; FI115835B B1 20050729; EP1654307 A1 20060510; CA2532989 A1 20050224; BRPI0413435 A 20061010	FI20030001156 20030815	MYLLYMAEKI VESA; AKSELA REIJO	KEMIRA OYJ	Dissolution method for lignocellulosic materials.
WO2005017252 A1	20050224	US2007215300 A1 20070920; EP1654415 A1 20060510; BRPI0413559 A 20061017; CA2534619 A1 20050224; CN1836068 A 20060920	AU20030904323 20030813	UPFAL JONATHAN; MACFARLANE DOUGLAS R; FORSYTH STEWART A	VIRIDIAN CHEMICAL PTY LTD	Solvents for use In the treatment of lignin-containing materials.
WO2005023873 A1	20050317	US2007073051 A1 20070329; FI20031301 A 20050312; FI116142 B1 20050930; ES2343326 T3 20100728; EP1664125 A1 20060607; EP1664125 B1 20100324; CA2533553 A1 20050317; BRPI0413432 A 20061010; AT461942 T 20100415	FI20030001301 20030911	MYLLYMAEKI VESA; AKSELA REIJO	KEMIRA OYJ	Starch esterification method.
WO2006088241 A1	20060824	US2008161505 A1 20080703; KR20070105990 A 20071031; EP1849833 A1 20071031; EP1849833 A4 20100811; CN101124280 A 20080213; CA2598470 A1 20060824	JP20050080382 20050220	KIMURA YOSHIHARU	TEIJIN LTD; MUSASHINO KAGAKU KENKYUSHO; MUTUAL CORP; YOSHIHARU KIMURA	Method of manufacturing polyactic acid.

Continued

—Cont'd

Patent Number	Publication Date	Family Members	Priority Numbers	Inventors	Applicants	Title
WO2011024023 A1	20110303		WO2009IB07047 20090831	MOIREAU PATRICK; CRETU ADINA M	OCV INTELLECTUAL CAPITAL LLC	Process for preparing aqueous emulsions of biodegradable polyesters.
WO2011047486 A1	20110428		US20090254478P 20091023	LAVASANIFAR AFSANEH; SAFAEI-NIKOUEI NAZILA	UNIV ALBERTA	Biodegradable thermoresponsive hydrogels.
WO2011056924 A2	20110512	WO2011056924 A3 20110929; US2012216705 A1 20120830	US20090257992P 20091104	ROGERS ROBIN D; DALY DANIEL T; GURAU GABRIELA	UNIV ALABAMA	Methods for dissolving polymers using mixtures of different ionic liquids and compositions comprising the mixtures.
WO8808011 A1	19881020	US4968350 A 19901106; NO885570 A 19890214; NO174208 B 19931220; NO174208 C 19940330; KR960002225 B1 19960213; JPH01502991 A 19891012; JP2564386B B2 19961218; IE62111 B1 19941214; IE881026 L 19881016; GR3006969 T3 19930630 FI885767 A 19881213; FI96219 B 19960215; FI96219 C 19960527; ES2035949 T3 19930501; EP0363549 A1 19900418; EP0363549 B1 19921209; DK698688 A 19881215 DK173005B B1 19991101; DE3877678 T2 19931007; CA1340020 C 19980901; BR8806902 A 19891031; AU1680688 A 19881104; AU610594 B2 19910523; AT84806 T 19930215	CA19880580702 19881020; CH19870001497 19870416	BINDSCHAEDLER CHRISTIAN; GURNY ROBERT; DOELKER ERIC	BINDSCHAEDLER CHRISTIAN; GURNY ROBERT; DOELKER ERIC	Process for preparing a powder of water-insoluble polymer which can be redispersed in a liquid phase, the resulting powder and utilization therof.

WO9407940 A1	19940414	NO951158 A 19950327; JPH08502088 A 19960305; JP3667754 B2 20050706; FI951452 A 19950327; FI114027 B 20040730; EP0662097 A1 19950712; EP0662097 B1 20020522; DK0662097 T3 20020909; DE69331952 T2 20030109; CA2144449 A1 19940414; CA2144449 C 20080909; BR9307130 A 19990330; AU4829693 A 19940426; AU675664 B2 19970213; AT217894 T 20020615	GB19920020447 19920928; GB19920020401 19920928; GB19930004651 19930308	CLAUSS JOACHIM; HOROWITZ DANIEL MARK; HUNTER BRIAN KEITH; SANDERS JEREMY KEITH MORRIS; GEORGE NEIL	MONSANTO CO	Polymer composition.
WO9606178 A	19960229	US5952460 A 19990914; NO970738 A 19970411; MX9701249 A 19980331; JPH10504459 A 19980506; FI970679 A 19970416; EP0776371 A1 19970604; CA2197782 A1 19960229; AU3188295 A 19960314	GB19940016691 19940818; GB19950002980 19950216	LIDDELL JOHN MACDONALD; GEORGE NEIL; HALL ALAN	ZENECA LTD	Production of polymers of hydroxyalkanoic acids.
WO9624682 A1	19960815	US5977250 A 19991102; JPH11500613 A 19990119; EP0808373 A1 19971126; EP0808373 B1 19990506; DE69602351 T2 19991125; AU4631196 A 19960827; AT179757 T 19990515	GB19950002531 19950209; GB19950009857 19950516; GB19950002521 19950209; GB19950002522 19950209	GEORGE NEI; HAMMOND TIMOTHY; LIDDELL JOHN MACDONALD; SATGURUNATHAN RAJASINGHAM; TURNER PETER DERYCK	ZENECA LTD	Latex of polyhydroxyalkanoate.
WO9625452 A1	19960822	US5891936 A 19990406; JPH11500476 A 19990112; FI973364 A 19971015; FI117898 B1 20070413; EP0809669 A1 19971203; EP0809669 B1 19990421; DE69602176 T2 19991118; AU4668996 A 19960904; AT179196 T 19990515	GB19950002980 19950216; GB19950026281 19951221	LIDDELL JOHN MACDONALD; GEORGE NEIL; TURNER PETER DERYCK	ZENECA LTD	Production of a polymer composition.
WO9704036 A1	19970206	MX9800592 A 19981129; KR100266488 B1 20000915; JPH11510194 A 19990907; JP4113989 B2 20080709; ES2162088 T3 20011216; EP0839170 A1 19980506;	US19950001274P 19950720	NODA ISAO	PROCTER & GAMBLE	Nonwoven materials comprising biodegradable copolymers.

Continued

—Cont'd

Patent Number	Publication Date	Family Members	Priority Numbers	Inventors	Applicants	Title
		EP0839170 B1 20011017; EP1132446 A2 20010912; EP1132446 A3 20030604; EP1132446 B1 20060823; DE69636485 T2 20070419; DE69616067 T2 20020711; CA2226864 A1 19970206; CA2226864 C 20030520; AU6499896 A 19970218; AT207104 T 20011115; AT337382 T 20060915				
WO9710292 A1	19970320	US5993530 A 19991130; JPH0977910 A 19970325; JP2997995 B2 20000111; EP0850988 A1 19980701; EP0850988 A4 20010214; EP0850988 B1 20050302; DE69634410 T2 20060316; AU6890796 A 19970401; AU710136 B2 19990916; AT290047 T 20050315	JP19950235675 19950913	TANAKA HIDEYUKI; HOSOKAWA NOBUHIRO; SUGIURA NOBUYUKI; TAKAHARA MASATO	JAPAN CORN STARCH CO LTD	Aqueous dispersion of biodegradable resin composition.
WO9721762 A1	19970619	MX9804764 A 19981031; JP2000502375 A 20000229; JP3920924 B2 20070530; EP0866829 A1 19980930; EP0866829 B1 20030326; DE69627013 T2 20031204; CA2239980 A1 19970619; CA2239980 C 20050816; AU1333397 A 19970703; AT235531 T 20030415	GB19950025390 19951212	GEORGE NEIL	MONSANTO CO	Dispersions of polyhydroxyalkanoate in water.
WO9749762 A1	19971231	US2002032254 A1 20020314; US6656984 B1 20031202; FI962627 A 19971226 FI108038 B1 20011115; ES2221053 T3 20041216; EP0907681 A1 19990414; EP0907681 B1 20040428; DK907681 T3 20040830; DE69728875 T2 20050609; AU3264297 A 19980114; AT265493 T 20040515	FI19960002627 19960625	HAASMAA KRISTIINA; PARONEN TIMO PETTERI; URTTI ARTO OLAVI; PELTONEN SOILI; HEIKKILAE MAIJA ELINA; VUORENPAEAE JANI	POLYMER COREX KUOPIO LTD OY	Hydrophobic polymer dispersion and process for the preparation thereof.

WO9800170 A1	19980108	US2002131952 A1 20020919; US6497903 B1 20021224; PT910412 E 20030930; JP2000515853 A 20001128; JP4625548 B2 20110202; ES2198579 T3 20040201; EP0910412 A1 19990428; EP0910412 B1 20030423; DK0910412 T3 20030811; DE69721265 T2 20040506; AU3360197 A 19980121; AT238068T T 20030515	EP19960201821 19960701; US19960031671P 19961122	HENNINK WILHELMUS EVERHARDUS; VAN DIJK-WOLTHUIS WENDELMOED N	UNIV UTRECHT	Hydrolysable hydrogels for controlled release.
WO9846782 A1	19981022	US6043063 A 20000328; EP0975788 A1 20000202; AU6971598 A 19981111	US19970043017P 19970415	KURDIKAR DEVDATT L; STRAUSER FRED E; SOLODAR A JOHN; PASTER MARK D; ASRAR JAWED	MONSANTO CO	Methods of PHA extraction and recovery using non-halogenated solvents.
WO9846783 A1	19981022	US6087471 A 20000711; EP0973930 A1 20000126; EP0973930 B1 20070613; DE69837914 T2 20080221; AU6974398 A 19981111; AT364708 T 20070715	US19970043018P 19970415	KURDIKAR DEVDATT L; STRAUSER FRED E; SOLODAR A JOHN; PASTER MARK D	MONSANTO CO	High temperature PHA extraction using PHA-poor solvents.
WO9933558 A1	19990708	AU5860798 A 19990719	WO1997EP07308 19971229	QUINTANAR-GUERRERO DAVID; LLEMANN ERIC; GURNY ROBERT; FESSI HATEM; DOELKER ERIC	UNIV GENEVE	Method for producing an aqueous colloidal dispersion of nanoparticles.
WO9964498 A1	19991216	US2001024631 A1 20010927; US2001023274 A1 20010920; US6605262 B2 20030812; US6323276 B2 20011127; US6228934 B1 20010508; MXPA00011963 A 20030422; JP2002517582 A 20020618; JP4368525 B2 20091118; EP1086164 A1 20010328; EP1086164 B1 20060816; DE69932818 T2 20070118; CA2333005 A1 19991216; AU4429399 A 19991230; AU746769 B2 20020502; AT336537 T 20060915	US19980088565P 19980609	HOROWITZ DANIEL; GERNGROSS TILLMAN U	METABOLIX INC	Methods and apparatus for the production of amorphous polymer suspensions.

Continued

—Cont'd

Patent Number	Publication Date	Family Members	Priority Numbers	Inventors	Applicants	Title
WO2006001081 A1	20060105	JP4653098 B2 20110316	WO2004JP09485 20040629	DOI YUKIO; ISHII AKIRA; NISHIIKE HARUKI; NOGAMI HISASHI; ISHIOKA RYOUJI	SHOWA HIGH-POLYMER	Solution of biodegradable polyester.
WO2014023319 A1	20140213		WO2012EP03423 20120810	BESCOND GWENAELLE; NENOV NIKOLAY	SYNTHOMER LTD	Method for producing an aqueous dispersion of poly(hydroxyalkanoates).
FR2862310 A1	20050520	WO2005052075 A 20050609; US2007088099 A1 20070419; NO20062798 A 20060615; KR20070008522 A 20070117; JP2007511631 A 20070510; JP5138224 B2 20130206; EP1685201 A1 20060802; CA2546107 A1 20050609	FR20040005038 20040510; FR20030013429 20031117	MENTINK LEON; BOUVIER FREDERIC; CLABAUX PIERRE PHILIPPE; BERNAERTS JOEL	ROQUETTE FRERES	Utilisation d'une dispersion aqueuse d'au moins un polymère biodégradable contenant au moins un agent stabilisant, pour la préparation d'une composition filmogène aqueuse. "Use of an aqueous dispersion of at least one biodegradable polymer containing at least one stabilizing agent, for the preparation of an aqueous film-forming composition."
CN101538400 A	20090923		CN2008152463 20080318	KAITIAN XU; GUOQIANG CHEN; WEICHUAN LU; XIAOJUAN WANG; JIAOYU PAN; ZHIFEI CHEN; WENFU ZHU	TIANJIN GREEN BIOMATERIAL CO L	Polyhydroxyalkanoates-containing aqueous emulsion, preparation method and application thereof.
JP2000007789 A	20000111	US6190773 A 20010220; JP3861500 B2 20061220	JP19990081359 19990325; JP19980113343 19980423	IMAMURA AKIYUKI; WATANABE YASUYUKI; TSUKUDA KAZUAKI; HIROKAWA TAKASHI; ARIGA NAGARO	DAINIPPON INK & CHEMICALS	Self-water dispersible particle made of biodegradable polyester and process for the preparation thereof.
WO9113207 A1	19910905	US5451456 A 19950919; CA2076038 A1 19910822; CA2076038 C 20010327	WO1990CA00058 19900221; CA19902076038 19900221	MARCHESSAULT ROBERT H; LEPOUTRE PIERRE F; WRIST PETER E	PULP PAPER RES INST; UNIV MCGILL	Poly-β-hydroxyalkanoates for use in fibre constructs and films.

WO9812245 A1	19980326	US6103858 A 20000815; US6103858 X6 20000815; NO991356 A 19990520; NO322142 B1 20060821; JP2001501652 A 20010206; EP0927219 A1 19990707; EP0927219 B1 20010228; DE19638686 A1 19980326; DK0927219 T3 20010326	DE1996138686 19960920	YAMAMOTO MOTONORI; WARZELHAN VOLKER; SEELIGER URSULA; KIM SON NGUYEN; SCHUMACHER KARL-HEINZ; HUMMERICH RAINER; BEIMBORN DIETER BERNHARD; PAGGA UDO	BASF AG	Wässrige Dispersion eines biologisch abbaubaren Polyesters sowie deren Verwendung. "Aqueous dispersion of a biodegradable polyester and its use thereof."
WO2012149407 A1	20121101	US2013225761 A1 20130829	US201161481027P 20110429	WHITEHOUSE ROBERT S	METABOLIX INC	Process for latex production by melt emulsification.
JP2004099883 A	20040402		JP20030296038 20030820; JP20020240658 20020821	NIIZEKI KOICHI; OKUYA MASAHIRO; KAMIO KATSUHISA	MIYOSHI YUSHI KK	Aqueous dispersion system of biodegradable resin.
JP2004323804 A	20041118		JP20030124646 20030430	NIIZEKI KOICHI; OKUYA MASAHIRO; KAMIO KATSUHISA	MIYOSHI YUSHI KK	Biodegradable resin aqueous dispersion.
WO9600263 A1	19960104	US5958480 A 19990928; US6410096 B1 20020625; NO965492 A 19961223; NL9401037 A 19960201; EP0766719 A1 19970409; AU2684095 A 19960119	NL19940001037 19940623	EGGINK GERRIT; NORTHOLT MARTIN DINANT	STICHTING ONDER-ZOEK EN ONTWIKKELING NOORD NEDERLAND	Method for producing a biologically degradable polyhydroxyalkanoate coating with the aid of an aqueous dispersion of polyhydroxyalkanoate.
US6024784 A	20000215	NL1008497 C2 19990907	NL19981008497 19980305	BUISMAN GODEFRIDUS JOHANNES HE; CUPERUS FOLKERT PETRUS; WEUSTHUIS RUUD ALEXANDER; EGGINK GERRIT	INST VOOR AGROTECH ONDERZOEK	Poly(3-hydroxyalkanoate) paint and method for the preparation thereof.
GB2291648 A	19960131	WO9603468 A1 19960208; JPH10503227 A 19980324; GB2291648 B 19981125; EP0772654 A1 19970514; EP0772654 B1 20010613; DE69521321 T2 20011031; AU3114095 A 19960222	GB19940014922 19940725	TAYLOR PHILIP LOUIS	ICI PLC	Coating compositions containing poly hydroxyalkanoates.

Continued

—Cont'd

Patent Number	Publication Date	Family Members	Priority Numbers	Inventors	Applicants	Title
EP0124309 A2	19841107	US4562245 A 19851231; EP0124309 A3 19850619; JPS59205992 A 19841121; AU2727884 A 19841101	GB19830011677 19830428	STAGEMAN JOHN FREDERICK	ICI PLC	Extraction of hydroxybutyrate.
US4324907 A	19820413		GB19790015858 19790508	SENIOR PETER J; WRIGHT LEONARD F; ALDERSON BARRY	ICI LTD	Extraction process
FR2446859 A1	19800814	US4310684 A 19820112; JPS5599195 A 19800728; JPS6254475 B2 19871116; FR2446859 B1 19810130; EP0014490 A1 19800820; EP0014490 B1 19821013	FR19790001862 19790122	VANLAUTEM NOEL; GILAIN JACQUES	SOLVAY	Procédé de séparation de poly-bêta-hydroxybutyrates d'une biomasse. "Process for the separation of poly-beta-hydroxybutyrates from a biomass."
FR2567149 A1	19860110	US4705604 A 19871110; JPS6135790 A 19860220; JPH0581239 B2 19931111; FR2567149 B1 19861205; EP0168095 A1 19860115; EP0168095 B1 19880120	FR19840010921 19840706	VANLAUTEM NOEL; GILAIN JACQUES	SOLVAY	Procédé pour l'extraction de poly-bêta-hydroxybutyrates au moyen d'un solvant à partir d!une suspension aqueuse de microorganismes. "Process for the extraction of poly-beta-hydroxybutyrates with a solvent from an aqueous suspension of microorganisms."
DD239609 A1	19861001		DD19850278981 19850726	SCHMIDT JOACHIM; SCHMIECHEN HELMUTH; REHM HELGA; TRENNERT MARIKA	AKAD WISSENSCHAFTEN DDR	Verfahren zur Gewinnung Von Poly-Beta-Hydroxybuttersaeure Aus Getrockneten Bakterienbiomassen. "Process for obtaining poly-beta-hydroxybutyrate from dried bacterial biomas."
EP0015123 A1	19800903	EP0036699 B1 19830202; EP0036699 B2 19870902; EP0036699 A1 19810930; ES8103169 A1 19810516; EP0015123 B1 19821222; DK73380 A 19800822; AU5560680 A 19800828; AU529981 B2 19830630	GB19790006076 19790221; GB19790006077 19790221; GB19790015858 19790508	HOLMES PAUL ARTHUR; WRIGHT LEONARD FEREDRICK	ICI PLC	Extraction of poly-beta-hydroxybutyric acid.

US5032683 A	19910716	EP0405918 A1 19910102	US19890371512 19890626	DRAGNER LOUIS R; FLOYD WILLIAM C; RAMP JAMES W	SEQUA CHEMICALS INC	Glyoxal modified aqueous starch dispersion and method.
US5116890 A	19920526		US19910718500 19910620; US19890371493 19890626	FLOYD WILLIAM C; DRAGNER LOUIS R	SEQUA CHEMICALS INC	Non-formaldehyde self-crosslinking latex.
WO0069916 A1	20001123	US6677386 B1 20040113; MXPA01007503 A 20020621; MX220923 B 20040611; KR20010108128 A 20011207; KR100451527 B1 20041008; JP2002544335 A 20021224; JP3946958 B2 20070718; ES2209813 T3 20040701; EP1159301 A1 20011205; EP1159301 B1 20031015; DE60005932 T2 20040812; CN1337969 A 20020227; CN1293100 C 20070103; CA2361722 A1 20001123; CA2361722 C 20090421; BR0007703 A 20020827; BR0007703 B1 20101019; AU2467300 A 20001205; AU760508 B2 20030515; AT252114 T 20031115	JP19990200203 19990125	GIEZEN FRANCISCUS EGENIUS; JONGBOOM REMIGIUS OENE JULES; FEIL HERMAN; GOTLIEB KORNELIS FESTER; BOERSMA ARJEN	ATO BV	Biopolymer nanoparticles.

REFERENCES

[1] Vähä-Nissi M, Laine C, Talja R, Mikkonen H, Hyvärinen S, Harlin A. Aqueous dispersions from biodegradable/renewable polymers. In: 13th European place conference, Bregenz, Austria; 2011.

[2] Quintanar-Guerrero D, Allémann E, Fessi H, Doelker E. Preparation techniques and mechanisms of formation of biodegradable nanoparticles from preformed polymers. Drug Dev Ind Pharm 1998;24:1113–28.

[3] Horowitz DM, Sanders JK. Phase separation within artificial granules from a blend of polyhydroxybutyrate and polyhydroxyoctanoate: biological implications. Polymer 1994;35:5079–83.

[4] Marchessault R, Morin F, Wong S, Saracovan I. Artificial granule suspensions of long side chain poly (3-hydroxyalkanoate). Can J Microbiol 1995;41:138–42.

[5] Allémann E, Gurny R, Doelker E. Preparation of aqueous polymeric nanodispersions by a reversible salting-out process: influence of process parameters on particle size. Int J Pharm 1992;87:247–53.

[6] Leroux J-C, Allemann E, Doelker E, Gurny R. New approach for the preparation of nanoparticles by an emulsification-diffusion method. Eur J Pharm Biopharm 1995;41:14–8.

[7] Lafferty R, Korsatko B, Korsatko W. Microbial production of poly-β-hydroxybutyric acid. Biotechnol VCH Weinh 1988;6B:135–76.

[8] van Dijk-Wolthuis WNE, Franssen O, Talsma H, van Steenbergen MJ, Kettenes-van den Bosch JJ, Hennink WE. Synthesis, characterization, and polymerization of glycidyl methacrylate derivatized dextran. Macromolecules 1995;28:6317–22.

[9] De Smedt SC, Lauwers A, Demeester J, Van Steenbergen MJ, Hennink WE, Roefs SPFM. Characterization of the network structure of dextran glycidyl methacrylate hydrogels by studying the rheological and swelling behavior. Macromolecules 1995;28:5082–8.

Chapter 5

Compounding and Additives

5.1 GENERAL

The biopolymers are usually mixed with various additives used in plastics industry, the type and amount of which are properly selected in order to obtain desired processing and performance characteristics. A skilled person can select from many different types of additives for inclusion into a biopolymer [1]. With the purpose of functional improvement or addition of a new function, additives may be incorporated into a biopolymer in any proportions during any stage of polymerization or processing.

An important issue in the compounding of biopolymers with additives/fillers is their mutual compatibility, which affects the dispersibility of the additives/fillers in the polymer matrix. In cases of limited compatibility, the mechanical and thermal resistance of the compounded product will be limited, rendering it difficult to use in some applications. In order to diminish, or even eliminate, the compatibility problem, it is common practice to either treat the surface of fillers with an energy source and/or with a suitable surface or coupling agent. As far as the surface or coupling agents are concerned, they are based on nonrenewable resources, are often not biodegradable, can be noxious or toxic, and are relatively expensive.

Other important issues affecting the dispersibility of the additives/fillers are the shape (for fibers, the aspect ratio) and size of the particles. Fillers have the tendency to aggregate/agglomerate and as the particle size decreases toward the nanoregion, the dispersibility is deteriorated. To date, an efficient and widely accepted way of dispersing nanofillers in a polymer matrix has not been invented (see Chapter 12: Manufacture of (bio)composites; Section 12.1: General).

The various compounding methods can be categorized in two main groups: (1) compounding by shear and heat, and (2) compounding in liquid or solution. In both groups the additives are added to the biopolymer as powders, dispersions, solutions, or masterbatches.

Furthermore, the additives can be dispersed in a biopolymer using any known techniques, such as batch and continuous compounding. Batch compounding is typically used when production quantities are small, strict quality control is needed, or the composition changes frequently. Continuous compounding is typically used for high production rates, combinations of multiple process streams, or to eliminate batch-to-batch variations. The type of compounding process is selected and/or adjusted according to the requirements of the particular combination of polymer matrix and additive.

5.2 COMPOUNDING BY SHEAR AND HEAT

This type of compounding includes solid state shear compounding and melt compounding. Melt compounding, which is the most representative method of this category, involves intense mixing with heat and shear at temperatures equal or above melting. One problem of using this process is the sensitive nature of the biopolymers, which are prone to degradation during melting. On the other hand, compounding at temperatures below melting and/or at lower shear rates has the benefit of not causing any degradation, but the dispersion of the additives is less efficient.

The equipment used for compounding the various additives in a biopolymer may be a twin screw corotating extruder, a twin screw counter-rotating extruder, a single screw extruder, a Banbury mixer, etc. A standard screw extruder typically has three zones: a feed zone, a compression zone, and a metering zone. Material from a hopper enters at the feed zone where it is moved forward to the compression zone by the rotation of the screw(s). In the compression zone the material is subjected to elevated temperatures and pressures caused by the screw action and external heaters (e.g., electrical heaters). The material melts and is moved forward to the metering zone and finally through a die. The die may create a strand of the compounded material. As it cools off, the strand may be fed through a pelletizer in order to create granules. The additives are usually fed into the melted polymer stream through the hopper, or, optionally, through one or several side feeders.

5.2.1 Compounding with Inorganic Compounds

JP2003313307 A (2003, SUZUKI MOTOR CO) discloses a method of compounding poly(lactic acid) (PLA) with a layered clay mineral comprising the steps of: (1) mixing layered clay mineral with methanol; (2) drying resulting material to a solid and; (3) melt compounding the dry layered clay mineral in an amount of 5–40 wt% with PLA in an extruder. By blending methanol to the layered clay mineral, the layered clay mineral becomes compatible with

Biopolymers: Processing and Products. http://dx.doi.org/10.1016/B978-0-323-26698-7.00005-2

PLA, and the heat deflection temperature (HDT) under load of the polymer is improved. A preferred clay mineral is talc.

JP2004244457 A (2004, TOYO SEIKAN KAISHA LTD) discloses a biodegradable polymer composition of improved heat resistance formed by melt compounding in a Banbury mixer an inorganic filler and a crystalline aliphatic polyester such as PLA so that the interparticle distance is 30 μm or less. The inorganic filler is preferably talc of an average particle size of 15 μm and is used in an amount of about 40 wt%.

JP2004027136 A (2004, YAMAGATA UNIV RES INST) discloses a PLA composition obtained by mixing a phyllosilicate preliminarily swelled with water or a water-based solvent with PLA in a shearing mixer and kneading the composition at a temperature, T, of $0\,°\mathrm{C} < T < T_\mathrm{m}$ of PLA. The shearing mixer is preferably a biaxial mixing extruder having at least one vent. The manufacturing method is claimed to improve the dispersibility of the layered silicate and provide a PLA composition having excellent heat resistance, mechanical property, biodegradability, and moldability. Advance of hydrolysis is suppressed, and mixing is carried out at a low temperature.

JP2004204143 A (2004, UNITIKA LTD) discloses a biodegradable polyester composition comprising 100 pbw of an aliphatic polyester composed at least 50 wt% of PLA and 0.1–20 pbw of hectorite or saponite in which a primary-quaternary ammonium ion or a phosphonium ion is bonded between the layers. The aliphatic polyester and the layered silicate are melt-kneaded, preferably in a twin screw extruder at a temperature $T < T_\mathrm{m} + 80\,°\mathrm{C}$, preferably $T < T_\mathrm{m} + 50\,°\mathrm{C}$. The composition has a haze of 25% or below determined at a thickness of 1 mm and an HDT of 90 °C or higher under a load of 0.98 MPa. The biodegradable polyester composition is claimed to have excellent transparency, moldability, and heat resistance. It is used for the manufacture of sheets, pipes, containers, lids of tableware, etc.

WO2012086192 A1 (2012, KAO CORP) discloses a method for producing a PLA composition by kneading PLA (100 pbw) and a surface-treated inorganic powder (20–200 pbw), using a mutual meshing engagement-type twin screw extruder (see Figure 5.1). The outer diameter (D) of the screw is 200 mm or less. The ratio L/D of the screw is 30–60. The extruder has a primary temperature-determining zone, a secondary temperature-determining zone, and primary and secondary kneading portions. The ratio of discharge amount (Q) (kg) of kneaded material from the twin screw extruder and screw speed (N) (rpm) is 0.2–1.5 kg/rpm. The PLA composition further contains a plasticizer (3–50 pbw) and a crystal nucleating agent (0.05–10 pbw). The inorganic powder contains metal hydroxide, metal hydrate, and/or layered silicate. The powder preferably contains aluminum hydroxide, magnesium hydroxide, calcium hydroxide, calcium aluminate hydrate, tin oxide hydrate, zinc nitrate hexahydrate, and nickel-nitrate hexahydrate. Alternately, inorganic powder contains talc, smectite, kaolin, mica, and/or montmorillonite. A PLA composition having excellent heat resistance and flexibility can be obtained.

The mutual meshing engagement-type twin screw extruder satisfies requirements 1–3: (1) being provided with: a first temperature-determining zone, said first temperature-determining zone being formed so as to include an area at least 6.3 D–13 Dmm apart from the center position of a starting material-supply port of a barrel, setting the barrel temperature to $(T_\mathrm{m} + 50) - (T_\mathrm{m} + 80)\,°\mathrm{C}$, and being provided with screws to which conveyance elements are attached; and a second temperature-determining zone, said second temperature-determining zone being formed so as to include an area at least 19.3 Dmm or greater apart from the center position of the starting material-supply port of the barrel and setting the barrel temperature to $(T_\mathrm{m} - 20) - (T_\mathrm{m} + 40)\,°\mathrm{C}$; (2) being provided with a first kneading part, said first kneading part having a length of 1 D–4 Dmm and being provided with screws

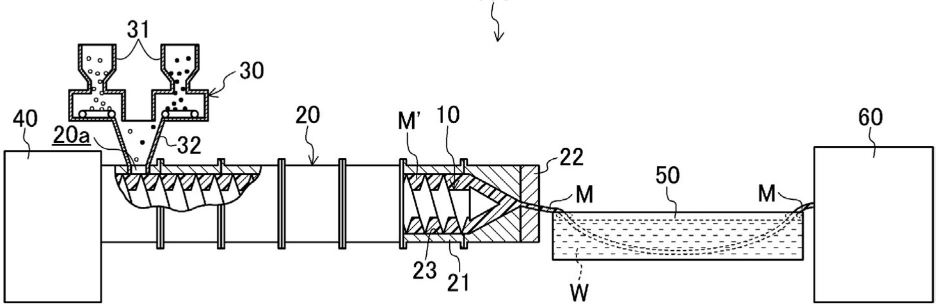


FIGURE 5.1 Intermeshing engagement-type twin screw extruder (2012, **WO2012086192** A1, KAO CORP). 100, Mutual meshing engagement-type twin screw extruder; 10, Screw; 111, Conveyance element; 112, Kneading element; 12, Rotating shaft; 20, Barrel; 20a, Raw material supply port; 21, Barrel unit; 22, Die; 23, Screw penetration hole; 30, Material supply part; 31, Feeder(s); 32, Hopper; 40, Rotational drive part; 50, Cooling bath; 60, Pelletizing part nm; M, Kneaded material; M′, Resin mixture; W, Water.

having kneading elements attached thereto, in an area 13 D–20.9 Dmm apart from the center position of the starting material-supply port of the barrel; (3) being provided with a second kneading part, said second kneading part having a length of 1 D–4 Dmm and being provided with screws having kneading elements attached thereto, in an area of 20.9 Dmm or greater apart from the center position of the starting material-supply port of the barrel.

5.2.2 Compounding with Organic Compounds

WO2008012981 A1 (2008, YOSHINO KOGYOSHO CO LTD) discloses a method of compounding poly(L-lactic acid) (PLLA) with a functional filler comprising D-lactic acid in an extrusion or injection molding machine. The addition of a functional filler comprising D-lactic acid into PLLA, which is a crystalline polymer having low melt viscosity, renders its melt viscosity into a range suitable for blow molding and contributes to the formation of a stereocomplex (see Chapter 1: Introduction; Section 1.4.1.1.1: Poly(lactic acid)). The thus formed stereocomplex affects the crystallization behavior of PLLA and contributes to the promotion of the crystallization, and improves the heat resistance of a shaped body formed thereof. The amount of the functional filler compounded is preferably 5–20 wt%, more preferably 10 wt% of PLLA. If the functional filler is added in an amount of not less than 30 wt%, the viscosity in the injection molding becomes low and hence there is a problem caused in the workability of the secondary shaping. Moreover, the formation of the stereocomplex between the functional filler and PLLA occurs when the amount of the filler compounded is 5 wt%, 10 wt%, or 20 wt%. As a PLLA the following commercial grades are used: Lacea® H440, Lacea® H400 (Mitsui Chemicals, Inc.), and NatureWorks® 7000D, 7032D (NatureWorks LLC). The functional filler is preferably obtained by graft polymerization of a compound having two to four hydroxyl groups with 30–50 molecules of D-lactic acid. The compound in the functional filler is preferably selected from polysaccharides and oligosaccharides. Examples of polysaccharides are starch and cyclodextrin; an example of oligosaccharides is pentasaccharide. In a further preferable embodiment the compound in the functional filler is an inorganic compound such as silica nanoparticles, or an organic compound selected from polyethylene glycol, trimethylolpropane, and pentaerythritol.

For the purpose of improving the heat stability of poly(glycolic acid) (PGA) in melt processing, KUREHA CORP discloses a series of patents (2003, **WO2003037956** A1; 2003, **WO2006095526** A1; 2007, **US2007100037** A1; 2012, **US2012259047**) wherein various phosphoric or phosphorous acid esters are compounded with PGA, followed by melt kneading, to produce a PGA composition having improved melt stability and crystallinity.

Although the phosphoric acid ester improves the thermal stability of PGA, there is no evidence that the resultant PGA composition has been effectively improved in moisture resistance. Commercially available phosphoric acid esters usually contain a relatively high moisture content. For use in the PGA composition, such a phosphoric acid ester is added in an amount as small as several hundreds of ppm with respect to the whole composition. Thus, moisture contained in the phosphoric acid ester has been presumed to have no influence on the quality, such as moisture resistance, of the PGA composition. However, this assumption has been challenged by **US2012259047** A1 (2012, KUREHA CORP).

US2012259047 A1 (2012, KUREHA CORP) discloses a method for producing an aliphatic polyester composition, wherein an aliphatic polyester such as PGA is melt kneaded with a phosphoric acid ester having a reduced moisture content of 1.5 wt% or less. As a result, an aliphatic polyester composition having an improved moisture resistance is provided. The present invention was based on the findings that an extremely small amount of moisture contained in a phosphoric acid ester influences the moisture resistance of the aliphatic polyester composition; the control of the moisture content to below a specific value allows production of an aliphatic polyester composition having particularly stable moisture resistance among other properties; and further reduction of the moisture content allows further improvement in moisture resistance as ever. Incidentally, it has already been shown that a moisture content in an aliphatic polyester resin composition is related to its moisture resistance. Moisture in phosphoric acid ester used as a component in the composition may be presumed to also affect the moisture resistance.

CN1417256 A (2003, CAS CHANGCHUN APPLIED CHEM INST) discloses a method of melt blending a first component of poly(3-hydroxybutyrate) (P3HB) or poly(3-hydroxybutyrate-3-*co*-hydroxypentanoate) (PHBHP) with a second component of *p*-*tert*-butylphenol, bisphenol A, bisphenol S or 2,4,6-tri(2′-hydroxy-4′-butoxy phenyl)-1,3,5-triazine; and an optional component including plasticizer. The weight ratio between the first component and the second component is 70–90 to 10–30 and the optional component is 0–30 wt% of the first component. By means of melt blending, modified material of enhanced toughness may be obtained.

WO2012012064 A1 (2012, ARCHER DANIELS MIDLAND CO) discloses in one of its embodiments a method of melt compounding a polyhydroxyalkanoate (PHA), such as P3HB with an acid compound having a pKa of 3–10. PHA powder or PHA pellets are mixed with the acid compound (either neat or in solution) in a vessel on a shaker or tumbler. The PHA mixed with the acid compound is extruded at 180 °C and pelletized. The acid compound is present in the composition at an amount of 0.01–10 wt%, and is selected from the group consisting of citric acid, poly(acrylic acid), stearic acid, palmitic acid, lactic acid, a derivative of any thereof, and combinations of any thereof.

The PHA composition has an increased thermal stability as compared to a PHA without dispersed acid. The present invention was based on the finding that the caustic digestion of PHA resulted in a product that is primarily crotonic acid, which is a product of the thermolysis of PHA. It was also found that the strong acid digestion of a PHA such as P3HB resulted in a product that was primarily 3-hydroxybutyric acid. Based on these findings, it was established that the presence of a weak acid, with a high enough pKa that would not promote the hydrolysis of the ester, reduced the tendency of PHA to undergo thermal degradation. Enhancing the thermal stability of the PHA will make this biopolymer more amenable to processing techniques used with plastics, including melt compounding, extrusion, melt extrusion, molding, injection molding, coating, spinning, casting, and/or calendering operations.

5.3 COMPOUNDING IN LIQUID OR SOLUTION

This type of compounding involves mixing the various additives in liquid or solid form with a biopolymer solution or liquid at ambient or elevated temperatures.

5.3.1 Compounding in Liquid or Solution with Inorganic Compounds

US2012289618 A1 (2012, KOREA INST SCI & TECH) discloses a method of preparing a biodegradable nanobiocomposite including the following steps: (1) putting two kinds of single-phase biodegradable polymers—namely, poly(ᴅ-lactic acid) (PDLA) and PLLA—a clay, and a small amount of organic solvent into a reactor; (2) injecting a supercritical fluid into the reactor and applying a predetermined temperature and pressure; (3) uniformly mixing the single-phase polymers and clay to form a stereocomplex (or stereoisomeric) composite and cause a dispersion reaction of the clay; and (4) collecting the PLA/clay nanocomposite. The nanosized clay used as a filler is preferably a clay mineral having a layered structure in which oxide layers having a negative charge are laminated to each other, and may be a natural clay or synthetic clay having a thickness of about 1 nm, a length of about 2180 Å, and an aspect ratio of about 2000 for each layer. More specifically, the clay compound may be a phyllosilicate having a negative charge made of aluminum silicate or magnesium silicate layers, or potassium or sodium phyllosilicates filled with sodium ions (Na^+) or potassium ions (K^+) between phyllosilicate layers. The phyllosilicates are preferably selected from montmorillonite, hectorite, saponite, beidellite, nontronite, vermiculite, volkonskoite, sauconite, fluorohectorite, magadite, kaolinite, and halloysite. The PLA/clay nanocomposite has the form of a particle or porous foam (see Chapter 12: Manufacture of biocomposites; Section 12.3.3: Nanobiocomposites).

Example: PLLA (0.84 g) of average molecular weight 50,000 and PDLA dissolved at 1/1 into 3.89 ml of dichloromethane, respectively, were injected into a 40-ml high pressure reactor, and 16.8, 50.4, and 84 mg of fluorinated clay (self-made) corresponding to a weight ratio of 1%, 3%, and 5 wt% to total weight of polymer were injected herein. The weight ratio of the total amount of PLAs to the total amount of solvent (supercritical carbon dioxide and dichloromethane in a weight ratio 70/30) was 5/100. Then, carbon dioxide was pressurized and injected into the high pressure reactor using a high pressure liquid pump. The reactor was gradually heated and pressurized to reach an internal temperature 65 °C and an internal pressure of 350 bar, respectively. When the temperature and pressure became constant, they were stirred for 5 h to carry out the reaction, and when the reaction was completed, the reactor was immediately opened to obtain a PLA/clay stereocomplex nanocomposite in the form of a powder. An X-ray diffraction analysis showed that PLA/clay stereocomplex nanocomposite was well formed with respect to various amounts of clays.

5.3.2 Compounding in Liquid or Solution with Organic Compounds

CN1417256 A (2003, CAS CHANGCHUN APPLIED CHEM INST) discloses in one of its embodiments a method of solution blending a first component of P3HB or PHBHP with a second component of *p-tert*-butylphenol, bisphenol A, bisphenol S or 2,4,6-tri(2′-hydroxy-4′-butoxy phenyl)-1,3,5-triazine; and an optional component including plasticizer. All the components are dissolved in the same solvent (e.g., chloroform) and mixed with steering. The disclosed method is a modification of the previously described melt blending method in Section 5.2.2.

WO2012012064 A1 (2012, ARCHER DANIELS MIDLAND CO) discloses in one of its embodiments (see also Section 5.2.2) a method of mixing a PHA solution in chloroform ($CHCl_3$) with an acid compound having a pKa of 3–10 (e.g., citric acid) dissolved in methanol. The chloroform was subsequently removed. The acid compound is present in the composition at an amount of 0.01–10 wt%. The PHA composition has an increased thermal stability as compared to a PHA without dispersed acid. The disclosed method is a modification of the melt blending method described in Section 5.2.2.

Table 5.1 summarizes the previously described compounding techniques and formulations.

TABLE 5.1 Representative Compounding Techniques and Formulations of Biopolymers

Biopolymer	Compounding Type	Additive(s)	Patent
PLA	Melt compounding in extruder	CH_3OH-treated clay (e.g., talc), 5–40 wt%	**JP2003313307** A (2003, SUZUKI MOTOR CO)
PLA	Melt compounding in Banbury mixer	Talc (40 wt%, 15 μm)	**JP2004244457** A (2004, TOYO SEIKAN KAISHA LTD)
PLA	Shear compounding in twin screw extruder at $T < T_m$	Water-swelled phyllosilicate	**JP2004027136** A (2004, YAMAGATA UNIV RES INST)
PLA	Melt compounding in twin screw extruder at $T < T_m + 50\,°C$	Hectorite or saponite (0.1–20 pbw)	**JP2004204143** A (2004, UNITIKA LTD)
PLA	Melt compounding in twin screw extruder	Surface-treated inorganic powder, e.g., $Al(OH)_3$ (20–200 pbw); plasticizer (3–50 pbw); and crystal nucleating agent (0.05–10 pbw)	**WO2012086192** A1 (2012, KAO CORP)
PHA	Melt compounding using a tumbler and an extruder	Citric acid (0.01–10 wt%)	**WO2012012064** A1 (2012, ARCHER DANIELS MIDLAND CO)
PLA	Melt compounding in twin screw extruder	*p-tert*-butylphenol, bisphenol A, bisphenol S, 2,4,6-tri(2′-hydroxy-4′-butoxy phenyl)-1,3,5-triazine; opt. plasticizer	**CN1417256** A (2003, CAS CHANGCHUN APPLIED CHEM INST)
scPLA	Solution-compounding (CH_2Cl_2/ $scCO_2$)	Clay (e.g., phyllosilicate)	**US2012289618** A1 (2012, KOREA INST SCI & TECH)
P3HB, PHBHP	Solution compounding ($CHCl_3$)	*p-tert*-butylphenol, bisphenol A, bisphenol S, 2,4,6-tri(2′-hydroxy-4′-butoxy phenyl)-1,3,5-triazine; opt. plasticizer	**CN1417256** A (2003, CAS CHANGCHUN APPLIED CHEM INST)
PHA	Solution compounding ($CHCl_3$)	Citric acid	**WO2012012064** A1 (2012, ARCHER DANIELS MIDLAND CO)

$Al(OH)_3$, aluminum hydroxide; CH_2Cl_2, dichloromethane; CH_3, chloroform; CH_3OH, methanol; P3HB, poly(3-hydroxybutyrate); PHA, polyhydroxyalkanoate; PHBHP, poly(3-hydroxybutyrate-3-*co*-hydroxy pentanoate); $scCO_2$, supercritical carbon dioxide; scPLA, stereocomplex PLA (PLLA/PDLA = 1/1).

5.4 MAKING MASTERBATCHES

The masterbatch technique involves the addition of predetermined amounts of various additives to a polymer carrier to produce a concentrated composition (masterbatch or concentrate). The masterbatch is diluted with a polymer (preferably based on the same polymer carrier) during the manufacture of end articles usually in a loading of a few percent, wherein an improved dispersibility of the additive(s) is achieved.

Masterbatching is a favorable way of incorporating various additives into a polymer. A masterbatch provides a convenient way of handling small amounts of critical ingredients, like specialized additives in higher concentration than those occurring in a normal mixture for subsequent dilution with the remainder of the ingredients.

When making a color masterbatch, the concentration of colorant, e.g., pigment, into a carrier is significant because of the relative cost of the colorant ingredient(s) and the need for that color to consistently and precisely mix and disperse into the carrier and then to consistently and precisely dilute into the polymer and other compound ingredients during "letdown" of the concentrate in mixing equipment prior to formation of the product. Letdown ratios depend on the concentration of colorant in the color concentrate and whether the final molded product is intended to be opaque, translucent, or transparent **WO2011040905** A1 (2012, POLYONE CORP).

JP2000086965 A (2000, DAINICHISEIKA COLOR CHEM; SHOWA DENKO KK; SHOWA HIGHPOLYMER) discloses a colorant masterbatch capable of coloring an aliphatic polyester simultaneously with molding. This colorant masterbatch contains an aliphatic polyester (30–99.98 wt%) having a weight-average molecular weight $M_w \geq 60{,}000$, a pigment (0.01–60 wt%) and a dispersing agent (0.01–40 wt%) composed of an aliphatic polyester having low molecular weight. The dispersing agent is an aliphatic polyester having a number-average molecular weight (M_n) of 500–30,000 and a M_w of 1000–60,000 and selected from low-molecular polycaprolactone (PCL), low-molecular poly(ethylene succinate) (PES), low-molecular poly(butylene succinate) (PBS), and low-molecular poly(butylene succinate-*co*-adipate) (PBSA), or their mixtures. The colorant composition is melt kneaded in an extruder to form colored pellets. The pellets are mixed with an aliphatic polyester in an extruder or an injection molding machine at 120–240 °C to give colored moldings having smooth surface and good appearance in which the colorant is uniformly dispersed in the aliphatic polyester.

JP2002179891 A (2002, DAINICHISEIKA COLOR CHEM) is a modification of the previous patent application that discloses a colorant masterbatch containing an aliphatic polyester (30–99.97 wt%), a pigment (0.01–60 wt%), a polyether additive (0.01–40 wt%), and a wax dispersant (0.01–40 wt%).

JP2005248139 A (2005, TOYO BOSEKI) discloses a colorant masterbatch obtained by dispersing an inorganic pigment and/or an organic pigment in PLA having reduced viscosity 0.1–1.0 dl/g. The acid value of PLA is preferably 10–80 eq/10^6 g of the pigment masterbatch. The pigment masterbatch is used for coloring biodegradable polyesters providing improved dispersibility of the pigment.

JP2005248062 A (2005, TOYO INK MFG CO) discloses a colorant masterbatch comprising 40–90 wt% of a pigment (A) and 10–60 wt% of a sulfonic acid metal salt-copolymerized PLA. The colorant masterbatch facilitates the dispersion of the pigment in a biodegradable polyester matrix and provides a biodegradable polymer molded product having a smooth surface, without causing bleeding or stickiness, and having a beautiful appearance.

Example: An amorphous PLA (Vyloecol BE-410, Toyobo, JP) (50 wt%)) with $M_w = 50{,}000$, $M_n = 30{,}000$ and sodium sulfate group concentration of 20 eq/10^6 g and C.I. Pigment Blue 15:3 (50 wt%) were mixed to form a masterbatch. The masterbatch (1 wt%) was mixed with PLA (99 wt%) to form a biodegradable polymer composition. The obtained composition was subjected to injection molding. The obtained plate had a smooth surface and was easily decomposed by microorganisms.

JP2010070621 A (2010, NEW JAPAN CHEM CO LTD) discloses a masterbatch of a trimesic acid amide compound suitable for manufacturing molded articles of a PLA having stable quality. The masterbatch is prepared by mixing 100 pbw of PLA and 1–20 pbw of trimesine acid amide compound. The mixing process is controlled so that the maximum particle diameter of the fed trimesic acid amide is ≤70 μm, the mixing temperature is $T_g \leq T \leq 200$ °C, and the mixing time is within a period of time when the maximum particle diameter of the trimesic acid amide reaches 100 μm. Especially preferred trimesic acid amide compounds are trimesic acid tri(methylcyclohexylamide), trimesic acid tri(*t*-butyl amide), and trimesic acid tri(cyclohexyl amide).

JP2011111541 A (2011, JAPAN POLYPROPYLENE CORP) discloses a PLA-based masterbatch containing the following components (a) to (d), and produced through compounding steps (I) and (II). Component (a) is polypropylene; component (b) is an acid-modified polyolefin and/or a hydroxy-modified polyolefin; component (c) is PLA; and component (d) is an epoxy-modified polyolefin. The step (I) involves melt compounding of component (c) with the component (d); and step (II) involves melt compounding the product of step (I) with the component (a) and component (b). The PLA-containing masterbatch has good moldability (fluidity), forming a molded product having balanced physical properties such as flexural modulus and impact strength, improved commercial productivity (reducing production cost of the molded product), and being partially biodegradable and/or partially obtainable from renewable resources.

CN102372911 A (2012, KINGFA SCI & TECH CO LTD; SHANGHAI KINGFA SCI & TECH CO; ZHUHAI WANTONG CHEMICAL CO LTD) discloses a colorant masterbatch for biodegradable polymer, comprising: (a) biodegradable polyester (10–80 wt%), (b) pigment (1–80 wt%), (c) lubricant (0.1–10 wt%), (d) high temperature–resistant agent (0.1–5 wt%), and (e) hydration-resistant agent (0.1–5 wt%). The preparation method of the colorant masterbatch comprises the following steps: (1) mixing the components in a high speed mixer; (2) adding the mixture into melting-compounding equipment for compounding and plastifying; and (3) extruding, granulating, and drying. The biodegradable polyester (a) is an aliphatic polyester or aliphatic/aromatic copolyester, preferably PLA, PBS, PCL, PHA, and poly(butylene succinate-*co*-terephthalate) (PBST). The pigment (b) is inorganic or organic and has an average grain size of less than 400 nm. The lubricant (c) is stearic acid or its salt, wax, amide and/or *N*,*N′*-ethylenebis(stearamide). The high temperature–resistant agent (d) is epoxy acrylic acid copolymer having 2–15 epoxy groups in molecule. The hydration-resistant agent (e) is carbodiimide.

JP2002179898 A (2002, RIKEN TECHNOS CORP) discloses a masterbatch obtained by melt compounding an aliphatic polyester having a glass transition temperature $T_g \leq 30$ °C and a metal salt comprising a cation that is an alkali metal or an alkaline earth metal and an ion-dissociable anion, and, as necessary, an organic compound having a group -$[O(AO)_n]$- (wherein, A denotes a 2–4C alkylene group; *n* denotes an integer of 1–7). The masterbatch is mixed with PLA. The aliphatic polyester is preferably selected from PBSA (e.g., Bionolle® 3020 of Showa High Polymer Co. Ltd., JP) and PCL (e.g., Celgreen® PH7 of Daicel Chemical Industries, JP). The metal salt is preferably selected from $LiClO_4$, $NaClO_4$, $KClO_4$, and $LiCF_3SO_3$. A preferred organic compound is dibutoxyethoxyethyl adipate (Sankonol® 0862 of Sanko Chemical Industry Co. Ltd.).

The PLA-based composition has good antistatic properties and is useful for the preparation of packaging material for parts of electronic and electrical instruments.

JP2008195834 A (2008, RIKEN VITAMIN CO) discloses a polymer composition comprising a polyolefin, PLA (3–50 wt%) and a carboxylic acid ester of a polyhydric alcohol (0.01–25 wt%). The polyolefin is polyethylene. The carboxylic acid ester of a polyhydric alcohol is a glycerol carboxylate or a polyglycerol carboxylate. A masterbatch was prepared by compounding PLA and a carboxylic acid ester of a polyhydric alcohol. The masterbatch was blended with a polyethylene and extruded to a film (see also Chapter 3: Blending; Section 3.3.2: Biopolymer in minority).

Example: A PLA masterbatch was obtained by mixing 25 pbw of a glycerol fatty acid ester (Rikemal® PL-019 of Riken Vitamin Co., Ltd.) with 100 pbw of PLA (Lacea® H440 of Mitsui Chemicals, Inc.) in a twin screw extruder at 185 °C and extruding the mixture through a strand die. The strand was cooled, cut, and dried at 80 °C for 3 h.

EP2065435 A1 (2009, SUKANO MAN & SERVICES AG) discloses a polyester masterbatch composition comprising a biodegradable polyester such as PLA and a metal alkyl sulfonate (0.1–5 wt%), where the glycerol fatty acid esters are excluded from the composition. Preferably, the polymer carrier is added in the extruder via the main hopper, and the metal alkyl sulfonate additive is incorporated into the polymer melt via a side feeder. The molten homogeneous material obtained is then preferably strand pelletized. The masterbatch polyester pellets are mixed with a biodegradable polyester and molded. The addition of the metal alkyl sulfonate as an impact modifier via a masterbatch to a biodegradable polyester, preferably PLA, during the manufacture of end-articles, ensures optimal dispersion, which is crucial for the impact and transparency performance of the end application.

WO0100730 A1 (2001, MITSUI CHEMICALS INC) discloses an aliphatic polyester composition for masterbatch production comprising an aliphatic polyester (100 pbw) and an antiblocking agent (0.1–40 pbw). Preferably, the aliphatic polyester is PLA. The antiblocking agent is preferably an inorganic particle selected from titanium dioxide, magnesium carbonate, barium sulfate, magnesium silicate, silica, talc, and kaolin—more preferable is silica. The antiblocking agent preferably has an average particle diameter of 0.007–0.05 μm. Optionally, the composition contains 0.1–10 pbw, per 100 pbw of aliphatic polyester, of a dispersing agent as a third component. An exemplary dispersing agent is a compound selected from a polyhydric alcohol ester, a polybasic carboxylic acid ester, and a hydroxy-polyvalent carboxylic acid ester. The aliphatic polyester composition for the masterbatch is preferably obtained by conducting compounding, melt extrusion, and pelletization at 150–230 °C, and then heat treatment at 40–100 °C for 2–10 h. The production under such conditions can control crystallinity in the range of 10–60%. The obtained masterbatch is suitable for producing an aliphatic polyester film improved in filler dispersion, blocking resistance, transparency, stability in molding, and slip properties.

JP2005200600 A (2005, MITSUI CHEMICALS INC) discloses a PLA masterbatch comprising 0.07–10 pbw of a crystalline inorganic compound containing ≥30 wt% silicic acid (SiO_2) as a crystal-nucleating agent and 100 pbw PLA. The composition was mixed, dry blended, extruded, and melt kneaded to obtain masterbatch pellets. The masterbatch pellets were diluted 5–30 times with PLA pellets in a blow molding machine. The inorganic compound is talc, kaolin, clay, and/or silica, and the PLA used is Lacea® H440 (Mitsui Chemicals, Inc.).

US6156929 A (2000, CORTEC CORP) discloses a masterbatch obtained by mixing a suitable biodegradable polyester with selected vapor phase corrosion inhibitors in relatively high percentages, such as 10–20 wt%. The vapor phase corrosion inhibitor is selected from amine salts, ammonium benzoate, triazole derivatives, alkali dibasic acid salts, alkali nitrites, tall oil imidazolines, alkali metal molybdates, and mixtures thereof. The biodegradable polyester is selected from PLA, PCL, PBSA, and blends thereof. The masterbatch is further blended with a suitable polyester to provide finished product such as a film containing 1–3 wt% corrosion inhibitor.

Example: PBSA (Bionolle® 3001, Showa Denko) is extruded with a selected corrosion inhibitor (see Table 5.2) to produce a masterbatch of about 15 wt% corrosion inhibitor, balance polyester. This masterbatch is further blended with more of this polyester and extruded as a film. Films made with this polyester have a higher softening

TABLE 5.2 Representative Formulation of a Corrosive Inhibitor Composition (2000, US6156929 A, CORTEC CORP)

Formulation	
Component	**wt%**
Cyclohexylammonium benzoate	25
Ethanol ammonium benzoate	5
Benzotriazole	6
Sodium sebacate	60
Sodium nitrite	4

temperature and find utility where more heat resistance is needed.

JP2006083262 A (2006, TOYO BOSEKI) discloses a method for preparing a conductive masterbatch comprising electroconductive fine powder such as carbon black and PLA having preset reduced viscosity. The masterbatch facilitates the dispersion by melt compounding of the conductive fine powder in a PLA matrix. The conductive-PLA composition is used for making planar heating elements.

EP2028218 A1 (2009, TOTAL PETROCHEMICALS RES FELUY) discloses a method for preparing a carbon nanotube–containing masterbatch, comprising melt blending an aliphatic polyester such as PLA with carbon nanotubes to form a composite. The carbon nanotube–containing masterbatch is used as a compatibilizer to blend carbon nanotubes into polyolefins such as polypropylene. Blends of carbon nanotubes and aliphatic polyesters are surprisingly homogeneous. It appears that the polarity of the nanotubes is more similar to aliphatic polyesters than to polyolefins. Therefore, a carbon nanotube/PLA composite is more homogeneous than if the carbon nanotube was blended directly into polypropylene. Using a biodegradable polyester to disperse carbon nanotubes into polyolefins has the added benefit of providing a composition that is at least partially biodegradable and/or partially obtainable from renewable resources.

CN101469072 A (2009, SHENZHEN ECOMANN BIOTECHNOLOGY CO LTD) discloses a method for the preparation of a biodegradable nanocomposite comprising the steps of:

1. mixing PHA with a grafting monomer (e.g., maleic anhydride or acrylamide), and an initiator (e.g., dicumyl peroxide or dibenzoyl peroxide) in a high speed mixer, and then reactive melt blending in double-screw extruder for reactive extrusion, at a temperature of 140–190 °C, to obtain a graft-modified PHA;
2. melt compounding the graft-modified PHA with an organically modified montmorillonite to prepare a highly filled masterbatch; and
3. mixing the highly filled masterbatch with PHA by melting to obtain the biodegradable nanocomposite (see Chapter 12: Manufacture of biocomposites; Section 12.3.3: Nanobiocomposites).

CN102167894 A (2011, CHANGCHUN APPLIED CHEMISTRY) discloses a method of preparing a nanobiocomposite, comprising the steps of: (1) dispersing a graphene oxide in water for acquiring a graphene oxide dispersion; (2) adding a PLA solution to the graphene oxide dispersion under stirring conditions, letting the uniformly stirred mixed solution stand for layering and filtering for obtaining a masterbatch; and (3) mixing the masterbatch with PLA for obtaining the graphene/PLA composite material, wherein the graphene oxide accounts for 0.1–5 wt% of PLA. Experiments show that the graphene/PLA composite has a tensile strength up to 79 MPa, a tensile elastic modulus up to 3100 MPa, a notch impact strength up to 12 kJ/m^2 and a HDT up to 95 °C (see Chapter 12: Manufacture of biocomposites; Section 12.3.3: Nanobiocomposites).

JP2005060689 A (2005, TORAY INDUSTRIES) discloses a blowing agent masterbatch prepared by melt compounding a biodegradable polymer such as PDLA and chemical blowing agent (e.g., azodicarbonamide) at a temperature less than the decomposition temperature of the foaming agent (see Chapter 9: Foaming and foamed products; Section: Chemical blowing agents: 9.1.2).

CN101503521 A (2009, UNIV SHANGHAI JIAOTONG) discloses a masterbatch prepared by melt mixing PBS and cellulose fibers in a two-roll mixing mill in a weight ratio of 1/1–1/2. The masterbatch (5–20 pbw) is then added together with poly(3-hydroxybutrate-*co*-3-hydroxyvalerate) (PHBHV) (50–80 pbw) and PBS (50–20 pbw) to a homomixer for evenly mixing, and the mixture is transferred to a Banbury mixer for melt mixing to obtain a biocomposite.

EP1659149 A1 (2006, DING SHAOZHONG) discloses the preparation of a biodegradable masterbatch comprising the following steps: (1) powdering and dehydrating 100 parts starch and 0.2–1 parts anticoagulant agent; (2) mixing the dehydrated starch with 3–12 parts of a coupling agent, and extruding with 5–20 parts dispersant, 30–90 parts aliphatic polyester (e.g., PLA, PGA, PCL, or PHA), 12–35 parts plasticizer, 3–18 parts chemical degradation promoter, and 0.2–1.2 parts co-oxidant, wherein, the coupling agent is selected from titanate or diisocyanate, and the dispersing agent is selected from glycerol, corn oil, or clean oil. The dehydration of the starch is very critical since the starch contains massive hydrophilic groups, and thus a comparatively higher water containment to compromise the molding results. The obtained biodegradable masterbatch has a comparatively lower unit production cost (approximately at US$1.5), that is three to four-fold of cost reduction when compared to that of the existing PCL masterbatch.

WO2008011668 A1 (2008, BIOGRADE HONG KONG PTY LTD; TRISTANO PTY LTD) discloses a method of preparing a masterbatch comprising melt mixing in the presence of a transesterification catalyst (0.1–1 wt%), a polysaccharide (20–70 wt%), a first biodegradable polyester (20–70 wt%), and a polymer having pendant carboxylic acid groups (5–50 wt%). The polysaccharide is selected from starch, glycogen, chitosan, and cellulose. The first biodegradable polyester is selected from PCL, PLA, P3HB, PES, PHBHV, PBS, poly(butylene adipate-*co*-terephthalate) (PBAT), poly(butylene adipate) (PBA), cellulose acetate butyrate (CAB), and cellulose acetate propionate (CAP). The polymer having pendant carboxylic acid groups is selected from ethylene acrylic acid copolymer (EEA), poly(ethylene acrylic acid-*co*-vinyl alcohol), poly(acrylic acid), poly(methacrylic acid), ethylene-methacrylic acid copolymers, and poly(acrylamide-*co*-acrylic acid); preferably, EEA is used. The polymer having pendant carboxylic acid groups facilitates transesterification between the polysaccharide and the biodegradable polyester during preparation of the masterbatch. The transesterification reaction product between the polysaccharide and the first biodegradable polyester is to be understood as taking the dual role of both agent and carrier. In other words, as used herein the term *masterbatch* is to be construed such that it embraces the situation where aforementioned carrier polymer and agent is in fact a reaction product between the polysaccharide, the biodegradable polyester, and possibly the polymer having pendant carboxylic acid groups. Such components within the masterbatch are in turn believed to function as a compatibilizer and reduce the formation of multiphase morphology when the masterbatch is melt mixed with a second biodegradable polyester. The second biodegradable polyester may be the same as or different from the first biodegradable polyester.

WO2010051589 A1 (2010, TRISTANO PTY LTD), which is a modification of the previous patent application, discloses a method of preparing a biodegradable polymer composition, said method comprising melt mixing together a masterbatch and constituents (a) that comprise one or more biodegradable polyesters and polyepoxide; wherein the masterbatch has been formed by melt mixing together constituent (b) that comprises one or more biodegradable polyesters, polysaccharide, polymer having pendant carboxylic acid groups, and transesterification catalyst, and wherein constituents (a) and/or (b) further comprise fatty acid sodium salt.

Some representative masterbatches of biopolymers disclosed in patents are presented in Table 5.3.

5.5 ADDITIVES AND MODIFIERS

Biopolymers are rarely used on their own to make biodegradable articles. A variety of additives and modifiers commonly used in the plastics compounding industries are generally included in the compound of biopolymers to obtain useful performance properties that approach those of conventional polymers. Additives are used, among other things, to enhance melt strength, thermal stability, and melt lubricity of a biopolymer during processing. Other additives are used to improve the performance of the biopolymers, especially impact strength, heat resistance, flame resistance, gas barrier properties, antifogging properties, etc. Additives are also used to modify the appearance or to reduce the cost of the final product. Nonlimiting examples of additives include plasticizers, impact modifiers, colorants (dyes and pigments), antioxidants, light and UV stabilizers, antistatic agents, releasing agents, denesting agents, matting agents, antiaging agents, fluorescent brighteners, dispersants, lubricants, thickeners, chain extenders, coupling agents, crosslinking agents, nucleating agents, heat stabilizers, viscosity stabilizers, antifogging agents, antistatic agents, foaming agents, mildew proof agents, antibacterial agents (fungicides, and mildewcides), drying agents (desiccants), flame retardants, various fillers, etc. [2]. Most of these additives are included in masterbatches, which make the introduction of the additives into the polymer matrix easier, due to better dispersion.

5.5.1 Processability Boosters

5.5.1.1 Melt Strength Enhancers

Melt strength enhancers are added to improve the processing of biopolymers. Paraloid™ BPMS 250 (Rohm and Haas[1]) is a melt strength enhancer that improves the processing of PLA and its blends. Biostrength® 700 (Arkema) is a melt strength improver/rheology modifier. CESA®-extend chain extender (Clariant) is an epoxy-functional styrene/acrylic oligomer masterbatch that can be used to relink polymer chains that have broken due to thermal, oxidative, and hydrolytic degradation; it has shown encouraging results with PLA. Processing Aide of DaniMer is a renewable-based additive that enables improved processing efficiencies such as higher operating speeds, increased throughput, and reduced defects. The DaniMer processing aide also provides “de-nest” characteristics and reduces the material’s adherence to metal during processing. Terraloy™ MB-90001A1 masterbatch (Teknor Apex) is a melt strength enhancer that broadens the processing window of PLA in cast film and sheet for packaging and other applications.

BioAdimide™ 500 XT (Rhein Chemie[2]) acts as a chain extender that can increase the melt viscosity of an extruded PLA by 20–30% compared to an unstabilized grade, allowing for consistent and easier processing. In addition, it improves the hydrolytic stability of PLA.

5.5.1.2 Heat Stabilizers

Heat stabilizers are antioxidants that are used to reduce the degrading effects of heat generated during processing of the biopolymer composition under severe conditions (shearing, temperature, and oxygen). These packages of stabilizers can present several components and are generally developed by companies specialized in polymer additives, such as PolyOne and Clariant.

---

[1] Rohm and Haas was acquired by The Dow Chemical in 2009.

[2] Rhein Chemie Rheinau GmbH has been presented with the 2011 Frost & Sullivan Global New Product Innovation Award in the Bioplastic Additives Market for its BioAdimide® product.

TABLE 5.3 Representative Masterbatches of Biopolymers

Biopolymer Carrier of the Masterbatch	Additive(s)	Polymer Matrix	Patent
Aliphatic polyester (30–99.98 wt%) of $M_w \geq 60{,}000$	Pigment (0.01–60 wt%); aliphatic polyester of $M_w \leq 60{,}000$ (0.01–40 wt%) as dispersing agent	Aliphatic polyester	**JP2000086965** A (2000, DAINICHISEIKA COLOR CHEM; SHOWA DENKO KK; SHOWA HIGHPOLYMER)
Aliphatic polyester (30–99.97 wt%)	Pigment (0.01–60 wt%); polyether additive (0.01–40 wt%); wax dispersant (0.01–40 wt%);	Aliphatic polyester	**JP2000086965** A (2000, DAINICHISEIKA COLOR CHEM; SHOWA DENKO KK; SHOWA HIGHPOLYMER)
PLA	Inorg. and/or org. pigment	Aliphatic polyester (e.g., PLA, PCL)	**JP2005248139** A (2005, TOYO BOSEKI)
Sulfonic acid metal salt-copolymerized PLA (10–60 wt%)	Pigment (40–90 wt%)	PLA	**JP2005248062** A (2005, TOYO INK MFG CO)
PLA	Trimesine acid amide (1–20 pbw) of ≤70 μm	PLA	**JP2010070621** A (2010, NEW JAPAN CHEM CO LTD)
PLA (>50 wt%)	PP; maleic acid anhydride modified-polypropylene; ethylene-glycidylmethacrylate copolymer	PP	**JP2011111541** A (2011, JAPAN POLYPROPYLENE CORP)
PLA, PBS, PCL, PHA, PBST	Pigment (1–80 wt%), lubricant (0.1–10 wt%); epoxy acrylic acid copolymer (0.1–5 wt%); carbodiimide (0.1–5 wt%)	Biodegradable polymer	**CN102372911** A (2012, KINGFA SCI & TECH CO LTD; SHANGHAI KINGFA SCI & TECH CO; ZHUHAI WANTONG CHEMICAL CO LTD)
PBSA, PCL	Metal salt ($LiClO_4$, $NaClO_4$, $KClO_4$, $LiCF_3SO_3$); dibutoxyethoxyethyl adipate	PLA	**JP2002179898** A (2002, RIKEN TECHNOS CORP)
PLA (100 pbw)	Glycerol fatty acid ester (25 pbw)	PE	**JP2008195834** A (2008, RIKEN VITAMIN CO)
PLA	Metal alkyl sulfonate (0.1–5 wt%)	PLA	**EP2065435** A1 (2009, SUKANO MAN & SERVICES AG)
PLA	Anti-blocking agent, e.g., silica (0.1–40 pbw)		**WO0100730** A1 (2001, MITSUI CHEMICALS INC)
PLA	Crystal-nucleating agent (0.07–10 pbw) contg. SiO_2 (≥30 wt%)	PLA	**JP2005200600** A (2005, MITSUI CHEMICALS INC)
PLA, PCL, PBSA	Corrosion inhibitor (10–20 wt%)	PCL, PBSA	**US6156929** A (2000, CORTEC CORP)
PLA	Electroconductive fine powder (e.g., carbon black)	Aliphatic polyester	**JP2006083262** A (2006, TOYO BOSEKI)
PLA	Carbon nanotubes	PP	**EP2028218** A1 (2009, TOTAL PETROCHEMICALS RES FELUY)
Graft-modified PHA (P3HB, PHBHV, P3HB4HB)	Org. modified montmorillonite	PHA	**CN101469072** A (2009, SHENZHEN ECOMANN BIOTECHNOLOGY CO LTD)
PLA solution	Aq. dispersion of graphene oxide	PLA	**CN102167894** A (2011, CHANGCHUN APPLIED CHEMISTRY)
PDLA	Blowing agent (e.g., azodicarbonamide)	PLA	**JP2005060689** A (2005, TORAY INDUSTRIES)
PBS	Natural fiber	PHBHV (50–80 wt%) and PBS (50–20 wt%)	**CN101503521** A (2009, UNIV SHANGHAI JIAOTONG)

TABLE 5.3 Representative Masterbatches of Biopolymers—cont'd

Biopolymer Carrier of the Masterbatch	Additive(s)	Polymer Matrix	Patent
Modified starch (100 pbw) and PCL (30–90 pbw)	Coupling agent (3–12 pbw); dispersant (5–20 pbw); plasticizer (12–35 pbw); chemical degradation promoter (3–18 pbw); co-oxidant (0.2–1.2 pbw)	Biodegradable polymer	**EP1659149** A1 (2006, DING SHAOZHONG)
1st biodegradable polyester (PCL, PLA, P3HB, PES, PHBHV, PBS, PBAT, PBA, CAB, CAP); and EEA	Polysaccharide (20–70 wt%); and transesterification catalyst (0.1–1 wt%)	2nd biodegradable polyester (PCL, PLA, P3HB, PES, PHBHV, PBS, PBAT, PBA, CAB, CAP)	**WO2008011668** A1 (2008, BIOGRADE HONG KONG PTY LTD; TRISTANO PTY LTD)
1st biodegradable polyester (PCL, PLA, P3HB, PES, PHBHV, PBS, PBAT, PBA, CAB, CAP); and EEA	Polysaccharide (20–70 wt%); and transesterification catalyst (0.1–1 wt%)	2nd biodegradable polyester (PCL, PLA, P3HB, PES, PHBHV, PBS, PBAT, PBA, CAB, CAP); and polyepoxide; and fatty acid sodium salt	**WO2010051589** A1 (2010, TRISTANO PTY LTD)

CAB, cellulose acetate butyrate; CAP, cellulose acetate propionate; EEA, ethylene-acrylic acid copolymer; P3HB, poly(3-hydroxybutyrate); PHBHV, poly(3-hydroxybutyrate-*co*-hydoxyvalerate); P3HB4HB, poly(3-hydroxybutyrate-*co*-4-hydroxybutyrate); PBA, poly(butylene adipate); PBAT, poly(butylene adipate-*co*-terephthalate); PBSA, poly(butylene succinate-*co*-adipate); PBST, poly(butylene succinate-*co*-terephthalate); PBS, poly(butylene succinate); PCL, poly(ε-caprolactone); PE, polyethylene; PDLA, poly(D-lactic acid); PES, poly(ethylene succinate); PHA, polyhydroxyalkanoate; PLA, poly(lactic acid); PP, polypropylene.

5.5.1.3 Plasticizers

Although plasticizers are analyzed in following Section 5.5.2.1, as performance boosters, they can also be considered as processability boosters. In other words, plasticizers not only modify the physical properties but can also improve processing characteristics of biopolymers. Plasticizers can influence processability by inducing lower viscosity, easier filler incorporation and dispersion, lower powder demand and less heat generation during processing, better flow, improved release, and enhanced building tack. The ease or difficulty of processing biopolymers can be influenced by the type and amount of plasticizer [3].

5.5.1.4 Lubricants

As a complementary cooperative function, aiming at reducing shearing and consequently the degradation of the biopolymer, it is possible to use secondary co-stabilizers, of the processing aid type (internal lubricant, external lubricant, and flow modifiers). Lubricants are used in trace quantities and do not bring any significant changes to the polymer's properties (e.g., T_g) as opposed to plasticizers.

Lubricants are usually constituted of mixtures of metallic soaps of alkaline, earth alkaline and transition metals, organic phosphonates, and fatty amides. Slip/antiblocking, antistatic, denesting and mold-release agents are added to biopolymers during processing to control or eliminate sticking of biopolymers to themselves and metal surfaces. OnCap™ BIO additives (PolyOne) is a range of additive concentrate products designed to provide optimum properties of the current biodegradable biopolymers, including slip, antiblock, antistatic, and denesting agents.

5.5.1.5 Nucleating Agents

Nucleating agents are compositions, compounds, etc., that induce the formation of polymer crystals (i.e., regulate and control crystallinity). For the thermodynamic and kinetic control of the crystallization process (nucleation and growth) of crystallizable biopolymers, nucleating agents are used in a combined form with the cooling gradient imposed to the biopolymer during its final processing stage, according to the desired crystalline morphology and degree of crystallinity. Typical nucleating agents for aliphatic polyesters, such as PLA and PHAs, include talc, boron nitride, calcium carbonate, magnesium carbonate, or titanium oxide (1996, **JPH083432** A), MITSUBISHI CHEM CORP); amide compounds of a specific formula (1998, **JPH1087975** A, NEW JAPAN CHEM CO LTD); sorbitol derivatives of specific formula (1998, **JPH10158369** A, MITSUI CHEMICALS INC); phosphoric acid ester metal salts and/or basic inorganic aluminum compounds (2003, **JP2003192883** A, ASAHI DENKA KOGYO KK; TOYOTA MOTOR CORP), and the like. These nucleating agents can improve the crystallization rate and the degree of crystallinity. Boron nitride is commonly known as the best available nucleating agent for P3HB.

WO2005097894 A1 (2005, NISSAN CHEMICAL IND LTD) discloses a PLA composition that contains a crystal nucleating agent suitable for accelerating crystallization of PLA. The PLA composition comprises a PLA and a metal salt of a phosphorus compound of specific formula; representative examples of nucleating agents are magnesium phenylphosphonate, sodium phenylphosphonate, zinc phenylphosphonate, and disodium 4-*t*-butylphenylphosphonate.

WO2005066256 A1 (2005, METABOLIX INC) discloses nucleating agents for aliphatic polyesters comprising nitrogen-containing heteroaromatic core (e.g., pyridine, pyrimidine, pyrazine, pyridazine, triazine, or imidazole); representative examples of nucleating agents are cyanuric acid (1,3,5-triazine-2,4,6-triol), uracil, thymine, and nitroimidazole. The aliphatic polyesters are selected from P3HB, PLA, PGA, poly(4-hydroxybutyrate) (P4HB), PBS, and PCL.

JP2009242520 A (2008, RIKEN VITAMIN CO) discloses a PLA composition comprising PLA, a crystallization nucleating agent, and a glycerol fatty acid ester or a polyglycerol fatty acid ester, wherein the crystallization nucleating agent is at least one kind selected from clay minerals (e.g., talc), fatty acid amides, and a compound group of organometallic complex.

WO2013131649 A1 (2013, HUHTAMAEKI OYJ; PURAC BIOCHEM BV) discloses a nucleating composition for use in a PLLA thermoformable composition comprising talc, lamellar clay mineral (e.g., kaolin), and PDLA or stereocomplex PLA (scPLA). The disclosed nucleating system is claimed to provide not only a sufficient high rate of crystallization combined with a thereof independent, broad window for thermoforming and consequently a sufficient high thermoforming speed with short cycle times but also a sufficiently high resistance against deformation up to a temperature of 100 °C by maintaining sufficient stiffness for the use of containers, preferably of cups, that are produced by thermoforming the PPLA composition containing the nucleating combination.

A list of representative nucleating agents disclosed in patents is given in Table 5.4.

5.5.1.5 *Drying/Desiccant Agents and Hydrolysis-Suppressing Agents*

Desiccants are compounds that attract and absorb substances that promote degradation, such as moisture and degradation products (e.g., acidic groups). Drying/desiccant agents eliminate the need for pre-drying the polymer before processing and also to help to protect metal tools from oxidation. They are particularly recommended in applications where high moisture levels negatively influence processability. Desiccant compounds are particularly useful for stabilizing disposable materials during processing stages, such as packaging manufacture, when the materials are exposed to high temperatures and/or water. Preferred desiccant compounds are essentially not volatile at the temperatures at which polymer formation or packaging occurs. Desiccant compounds can also be used to absorb moisture into the disposable material from the environment, such as rainfall in a landfill.

Suitable desiccant compounds include water grabbers, alkaline compounds capable of neutralizing acid, dry mineral fillers, and mixtures thereof. Suitable water grabbers include dry silica, talc, clays, calcium sulfate, calcium chloride, sodium sulfate, carbodiimides, and mixtures thereof. Suitable alkaline desiccant compounds include sodium bicarbonate, sodium acetate, sodium phosphate, and mixtures thereof. Preferred desiccant compounds include dry silica gel and calcium sulfate.

CESA®-dry MB 1 (Clariant) is a desiccant masterbatch of specific active substances in a polyethylene carrier that can be used to facilitate processing of recycled polymers, polymers containing biodegradable starch, and other high-moisture-level polymers.

Hydrolysis-suppressing agents, also known as functional group-capping agents, are compounds that cap functional terminal groups for improving the moisture resistance of biodegradable biopolymers. Hydrolysis-suppressing agents exhibit reactivity with active hydrogen contained in the biodegradable biopolymers. An active hydrogen means hydrogen bonded with oxygen or nitrogen (an O–H or N–H bond). This hydrogen is higher in reactivity than hydrogen in the carbon-hydrogen bond (C–H). More specifically, such active hydrogen is present in a carboxylic group (–COOH), a hydroxy group (–OH), an amino group ($-NH_2$), or in an amido linkage (–NHCO–) in the biodegradable biopolymer. By adding these suppressing agents, it becomes possible to reduce the amount of active hydrogen in the biodegradable biopolymer, thus preventing the molecular chain from being catalytically hydrolyzed by the active hydrogen. As a result, the hydrolysis of the biodegradable polymer is delayed and the mechanical properties of the material, such as tensile strength and impact strength, are maintained for a prolonged period of time.

Compounds that have reactivity to the active hydrogen in a biodegradable biopolymer are carbodiimides, isocyanates, and oxazolines. In particular, the carbodiimide compound (–N=C=N–) is preferred since this compound may be melted and kneaded with a biodegradable high molecular weight biopolymer; it is sufficient to add a small amount thereof to suppress hydrolysis more effectively. The carbodiimide controls the hydrolysis in the initial reaction after the addition by reacting with the hydroxyl or carboxyl groups remaining in the biodegradable biopolymer, or after that, by bonding to the linkages of a biodegradable polymer cleaved by hydrolysis, thus recombining them.

TABLE 5.4 Nucleating Agents for Aliphatic Polyesters

Biopolymer	Nucleating Agent(s)	Patent
PLA	Inorg. particles (0.5–5 wt%) compr. talc having a mean particle diameter $f \leq 5$ µm and/or boron nitride having a mean particle diameter ≤30 µm	**JPH083432** A (1996, MITSUBISHI CHEM CORP)
PLA	Inorg. particles (0.1–10 pbw) contg. ≥30% silicic acid (SiO_2)	**JP2005200600** A (2005,MITSUI CHEMICALS INC)
PLA	Phosphate metal salt (e.g., ADK STAB NA-10, NA-11, NA-21, NA-30, NA-35 of ASAHI DENKA CO, LTD) and basic inorg, aluminum cpd. (0.01–5.0 pbw)	**JP2003192883** A (2003, ASAHI DENKA KOGYO KK; TOYOTA MOTOR CORP)
PLA (75–95 wt%) and PCL (25–5 wt%)	Inorg. particles (0.1–15 pbw) contg. ≥50% silicic acid (SiO_2)	**JPH08193165** A (1996, MITSUI TOATSU CHEMICALS)
PLA	Magnesium phenylphosphonate, sodium phenylphosphonate, zinc phenylphosphonate, disodium 4-*t*-butylphenylphosphonate	**WO2005097894** A1 (2005, NISSAN CHEMICAL IND LTD)
PLLA	Nucleating system: Talc, lamellar clay mineral (e.g., kaolin) and PDLA or scPLA	**WO2013131649** A1 (2013, HUHTAMAEKI OYJ; PURAC BIOCHEM BV)
PLA	Clay minerals (e.g., talc), fatty acid amides, organometallic complex	**JP2009242520** A (2008, RIKEN VITAMIN CO)
PLA	Calcium lactate, sodium benzoate (5 wt%)	**WO9204413** A1 (1992, BATTELLE MEMORIAL INSTITUTE)
PLA	Trimesic acid (*t*-butylamide), 1,4-cyclohexane dicarboxylic acid dianilide and 2,6-naphthalene dicarboxylic acid dicyclohexylamide (0.01–5.0 pbw)	**JPH1087975** A (1998, NEW JAPAN CHEM CO LTD)
PLA, PBS, PBSL	Sorbitol deriv.: bis benzylidene sorbitol, bis (*p*-methybenzylidene) sorbitol, bis (*p*-ethylbezylidene) sorbitol and bis (*p*-chlorobenzylidene) sorbitol	**JPH10158369** A (1998, MITSUI CHEMICALS INC)
PLA	Sorbitol deriv. (e.g., EC-1 of EC Chemical Co., Ltd; GEL All MD, GEL All DH of New Japan Chemical Co, LTD; NC-4 of Mitsui Toatsu; AL-PTBBA of Shell Chemical Co, Ltd); Phosphate metal salts (e.g., ADK STAB NA-10, ADK STAB NA-11, ADK STAB NA-21 of Asahi Denka Kogyo KK) (0.05–5 pbw)	**JP2001226571** A (2001, C I KASEI CO LTD)
PLA	PGA	**DE4007882** A1 (1991, BOEHRINGER INGELHEIM KG)
P3HB, P3HB4HB (11% 4HB), PHBHHx (5% HH), PHBHV (8% HVL), P4HB, PLA, P3HB4HB (11% 4HB), PBS	• Boron nitride • Cyanuric acid (1,3,5-triazine-2,4,6-triol) • methylbenzylidene sorbitol (Millad® 3940, of Milliken Chemicals) • Dimethylbenzylidene sorbitol (Millad® 3988 of Milliken chemicals) • Aluminum hydroxy diphosphate	**WO2005066256** A1 (2005, METABOLIX INC)

P3HB, poly(3-hydroxybutyrate); P3HB4HB, poly(3-hydroxybutyrate-*co*-4-hydroxybutyrate); PHBHHx, poly(3-hydroxybutyrate-*co*-3-hydroxyhexanoate) or poly(hydroxybutyrate-*co*-hydroxyhexanoate); PHBHV, poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate); P4HB, poly(4-hydroxybutyrate); PBS, poly(butylene succinate); PBSL, poly(butylene succinate-*co*-lactate); PCL, poly(ε-caprolactone); PDLA, poly(D-lactic acid); PGA, poly(glycolic acid); PLA, poly(lactic acid); PLLA, poly(L-lactic acid); scPLA, stereocomplex PLA.

Other compounds and techniques to cap functional groups of biodegradable polymers are described in Biopolymers: Reuse, Recycling and Disposal [4].

BioAdimide™ 100 additive (Rhein Chemie) is especially suited to improve the hydrolysis resistance of biobased polyesters, specifically PLA, and to expand its range of applications. According to Rhein Chemie, the BioAdimide™ 100 grade improves the hydrolytic stability up to seven times that of an unstabilized grade, thereby helping to increase the service life of the polymer.

5.5.2 Performance Boosters

5.5.2.1 Plasticizers

Plasticizers are compounds that are incorporated into a polymer during, or after, polymerization to improve its processability and flexibility by lowering the polymer's T_g. Introduction of plasticizers into a thermoplastic polymer can reduce the melt viscosity of the polymer and lower the temperature, pressure, and shear rate required to form the polymer. Plasticizers introduce pliability, flexibility, and toughness into a polymer to an extent not typically found in a material containing only a polymer or copolymer as such. Plasticizers can also affect the degradation rate of the polymer. Plasticizers are used in a much higher quantity than in any other additive (typically 5–20% wt), significantly contributing to the end product cost.

Plasticizer molecules are thought to embed themselves between the chains of polymers, spacing the polymer molecules apart (e.g., increasing the "free volume"), and thus lowering the T_g of the polymer while making it softer. The more plasticizer is used, the lower the polymer's T_g becomes. In general, the plasticizer stays in the polymer chains, impairing its crystallization. This lower crystallization rate contributes to the reduction of the processing temperature of the material. The lower crystallinity further contributes to a higher flexibility of the chains, making the polymer less rigid and less fragile. In general, the plasticizers present a maximum concentration that can be used in a polymer. Concentrations above this limit result in exudation of the plasticizer (a phenomenon known as "bleeding," "blooming," or "leaching"), jeopardizing the operations of surface finishing, including printing on the product (2007, **WO2007095709** A1, PHB IND SA).

Plasticizers, which are effective in modifying properties of biopolymer products, should be completely miscible or compatible with the biopolymer, nonvolatile, and should not migrate to the surface of the polymer composition, as might be desirable with a processing aid. The bleeding of the plasticizer to the surface of a food packaging made of PLA could be a source of contamination of the food or beverage in contact with the packaging, or may possibly regain the initial brittleness of pure PLA [5]. An obvious requirement of plasticizers to be used with biopolymers is that they are biodegradable. Plasticizers derived from renewable resources are especially preferred.

PLA and certain PHAs such as P3HB and to a lesser degree PHBHV are excessively brittle and difficult to form, thereby limiting their industrial applications. One of the early examined techniques for reducing the brittleness of these biopolymers involves the addition of a plasticizer. Numerous references discuss the modification of properties of biodegradable polymers with plasticizers and lubricants. Those references, however, offer little guidance in selecting suitable compounds to be used for mass-marketed, biodegradable polymers.

Plasticizers for PLA reported in the literature [5–20], and summarized by Wypych [21] include:

- phthalate esters; e.g., dimethyl-, diethyl-, dipropyl-, dibutyl-, dihexyl-, diheptyl-, dioctyl-, etc.;
- aliphatic esters: dimethyl- and diethylsuccinate and related esters; glycerol mono-, di- and triacetate (triacetin); glycerol mono-, di-, and tripropionate; glycerol mono-, di-, and tributanoate (tributyrin); glycerol mono-, di-, and tristearate [12–15]; glucose monoesters; citrate esters: triethyl, tri-*n*-butyl citrate, and acetyl tri-*n*-butyl citrate [6,19,20]; adipate esters [18]: dioctyl adipate[3]; partial fatty acid esters [19]: oleic acid esters; ricinoleic acid esters, erucic acid esters;
- lactide, lactic acid, lactic acid oligomers [6,9];
- alkylene glycols: ethylene glycol, diethylene glycol, triethylene glycol, tetraethylene glycol, propylene glycol, poly(ethylene glycol) [7,8,10,11,19], poly(propylene glycol) [16], poly(1,3-propanediol), poly(butylene glycol);
- alkane diols; e.g., 1,3-propanediol, 2,2-dimethyl-1,3-propanediol, 1,3-butanediol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, 2,2,4-trimethyl-1,6-hexanediol, 1,3-cyclohexanedimethanol, 1,4-cyclohexanedimethanol, 2,2,4,4-tetramethyl-1,3-cyclobutanediol;
- epoxidized vegetable oils (soybean oil [22,23], linseed oil, castor oil).

Traditional plasticizers for PLA films and articles have tended to migrate from within the polymer to the outer surface. Once at the surface, some plasticizer molecules are volatile enough to evaporate into the surrounding atmosphere at a rate dependent, in part, on the surrounding temperature. With the bleeding of some plasticizers, PLA films can experience a decrease in their initial flexibility and can become increasingly oily and slippery to the touch. Additionally, properties such as tensile strength, modulus, tear strength, and elongation to break can be adversely affected and tend to justify the characterization of such films as exhibiting poor age stability (2011, **WO2011082052** A1, 3M INNOVATIVE PROPERTIES CO).

One of the oldest patents to plasticize PLA and increase its flexibility and tear strength is **US1995970** A (1935, DU PONT), which discloses the addition of dibutylphthalate and nitrocellulose to PLA. Another old patent, **US3636956** A (1972, ETHICON INC) discloses the use of 2-methoxyethyl phthalate for the plasticization of PLA and poly(lactic acid-*co*-glycolic acid) (PLGA). **US3498957** A (1970, ETHICON INC) discloses a polymerization method for making

---

[3] Also called bis(2-ethylhexyl) adipate (DEHA).

PLA characterized by the addition of a nonpolymerizable ester plasticizer to an L-lactide containing reaction mixture before polymerization is initiated. The plasticizer is derived from an aliphatic saturated carboxylic acid and an aliphatic saturated hydrocarbon alcohol that can contain ether oxygen linkages; a representative example of plasticizer is triacetin; triacetin is virtually odorless, has a relatively high boiling point (258 °C), is biodegradable, and is commercially available at a reasonable cost. Furthermore, when triacetin is compounded with PLA at levels of about 15 wt%, this can drop the T_g of PLA by 30 °C (i.e., $T_g = 30$ °C).

JPH07177826 A (1995, MITSUI TOATSU CHEMICALS) discloses also the use of triacetin for the plasticization of a PLA-based agricultural film.

EP226061 A2 (1987, ALLIED CORP) discloses a PLA composition containing a biocompatible plasticizer as an application to biomaterials. Biocompatible plasticizers include triethyl citrate, tri-n-butyl citrate, acetyl triethyl citrate, acetyl tri-n-butyl citrate, and triacetin. In particular, triethyl citrate has been found to be useful.

In addition, **DE3734223** A1 (1989, BOEHRINGER INGELHEIM KG) discloses a PLA composition that contains an ester acetate (e.g., ethyl acetate) as a plasticizer that is useful for plasticizing biomaterials such as medical films and rods for implanting in the body.

JPH04335060 A (1992, MITSUI TOATSU CHEMICALS) discloses a composition containing PLA and a general-purpose plasticizer. The plasticizer is selected from phthalic acid esters, aliphatic dibasic acid esters, phosphates, hydroxy polyvalent carboxylates, fatty acid esters, polyvalent alcohol esters, epoxy plasticizers, and polyester plasticizers, or a mixture thereof.

JPH08199053 A (1996) and **JPH08245866** A (1996) of SHIMADZU CORP disclose plasticized PLA compositions obtained by compounding PLA with an ester of aliphatic dicarboxylic acid and/or chain molecular diol having a molecular weight lower than 2000 such as dioctyl adipate or an aliphatic polyester containing these as its major constituents. The plasticized PLAs are claimed to have controllable biodegradability, good flexibility, transparency and gloss, and less surface stain owing to bleeding out of the plasticizer without excessive loss of crystallinity and heat resistance.

JPH09296103 A (1997, SHIMADZU CORP) discloses a PLA composition containing a plasticizer selected from triacetin, tributyrin, and butylphthaloyl butyl glycolate. The PLA composition has a softening near the human body temperature (T_g of 30–37 °C), and it is used for body-contacting material such as sticking plasters, tapes, ear pads, nose pads, sheet covers, pillows, and glass rims.

JPH11323113 A (1999, SHIMADZU CORP) discloses a PLA composition containing a plasticizer selected from the derivatives of ether-ester, glycerol, phthalic acid, glycolic acid, citric acid, and adipic acid.

Although PLA can be softened with the above plasticizers, it still has numerous shortcomings including decrease of the heat resistance of plasticized PLA, the absence of impact strength, cracking during bending, and a decrease in the molecular weight of the PLA during compounding. In addition, vaporization of the plasticizer during processing and the problem of bleeding out cannot be avoided in the case of these low-molecular-weight plasticizers. These problems can be noticed at room temperature and can become more pronounced at elevated temperatures (e.g., ≥40 °C).

JP2002080703 A (2002) and **JP2003020390** A (2003) of RIKEN VITAMIN CO disclose biodegradable polyester compositions comprising PLA acid as main component and a diglycerol acetate (mono-, di-, tri-, and tetraacetate) with an acetylation rate not less than 50% as plasticizer.

JP2005036104 A (2005, DAI ICHI KOGYO SEIYAKU CO LTD) discloses a biodegradable plasticizer that can be mixed in any proportion with a biodegradable polymer such as PLA. The plasticizer is selected from a group containing butyl diglycol adipate, methyl diglycol adipate, methyl diglycol benzoate adipate, and the like. A biodegradable composition is prepared by mixing a plasticizer emulsion with a PLA emulsion.

Example: A nonionic surfactant (Noigen EA-177 of Daiichi Kogyo Seiyaku Co Ltd) (3 pbw) and ethylene glycol (3 pbw) were dissolved in distilled water (9.5 pbw). A biodegradable plasticizer (methyl diglycol benzyl adipate) (100 pbw) was added in the mixture for 1 h and stirred. Stirring was further continued for 30 min, and the mixture was diluted with water (43.2 pbw). A white liquid emulsion with 64.9% of solid content and average particle diameter of 0.63 μm was obtained. The obtained emulsion (2.3 pbw) and PLA emulsion (15 pbw) were mixed. The mixture was applied on a glass plate, dried at 25 °C for 24 h and at 70 °C for 30 min. A transparent and flexible film was obtained. The film had tensile strength of 17.7 MPa and elongation at break of 485%.

JP2004359892 A (2004, SAKAMOTO YAKUHIN KOGYO CO LTD) discloses a biodegradable polyester such as PLA plasticized with a polyglycerol fatty acid ester composed of a polyglycerol having an average polymerization degree of 2–3 and a 2–12C straight- or branched-chain saturated fatty acid (excluding single use of a 2C straight-chain saturated fatty acid) and having ≥50% esterification degree. A preferred plasticizer is diglycerol tetra caprylic acid ester.

JP2008069299 A (2008, TAIYO KAGAKU KK; UNIV OSAKA) discloses a PLA composition comprising 1–20 pbw polyglycerol fatty acid ester or polyglycerol condensed hydroxy fatty acid ester per 100 pbw PLA.

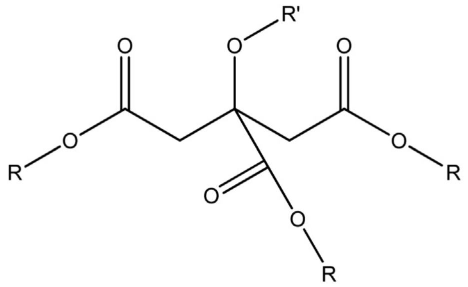
The polyglycerol fatty acid ester preferably has mean polymerization degree of 2–10 and ≥50% fatty acid esterification ratio. The fatty acid, which is a structural component of the polyglycerol fatty acid ester, is two or more types of palmitic acid, stearic acid, and oleic acid. The fatty acid of the polyglycerol condensation hydroxy fatty acid ester is condensed ricinoleic acid. The disclosed plasticizers impart flexibility to PLA without impairing its thermal properties.

Example: PLA (Lacea® H-900 of Mitsui Chemicals, Inc. having $M_w = 123{,}000$ and $M_n = 61{,}000$) and polyglycerol fatty acid ester (Chirabazol VR-01 of Taiyo Kagaku Co., Ltd. having an average polymerization degree of polyglycerol of 10 and esterification degree of 69%, and containing oleic acid) were mixed in a weight ratio of 97/3 to obtain a PLA composition. The PLA composition was extruded into a film claimed to have excellent flexibility.

JP2010260900 A (2010, TOHCELLO CO LTD) discloses a film obtained from a PLA composition comprising: 80–95 wt% of a scPLA made of PLLA (45–55 wt%) and PDLA (55–45 wt%); and 5–20 wt% of a polyglycerol fatty acid ester. The polyglycerol is diglycerol and/or decaglycerol. The esterification degree of polyglycerol fatty acid ester is at least 50%.

WO2011082052 A1 (2011, 3M INNOVATIVE PROPERTIES CO) discloses a composition that includes PLA and a plasticizer, the plasticizer having the chemical formula shown in Scheme 5.1.

Example: Various samples were prepared by mixing PLA with each of the plasticizers (15 wt%) of Table 5.5 in a Brabender batch mixer at 75 rpm, 180 °C for 5 min. The 5-min mixing time was sufficient to disperse the plasticizer uniformly within PLA. The composition was transferred to a press and compressed to form 5-mil-thick sheets. Age stability of each plasticizer in PLA was assessed by measuring the weight of the PLA sheets over time as they were exposed to elevated temperatures (65 °C). Temperatures were maintained using convection ovens. Data is presented in Table 5.5 as fractional weight loss over a 4-week time period. The cause of the weight loss for each sample was investigated using 1H NMR and was found to be caused by plasticizer evaporation and not from degradation of PLA. Table 5.5 includes an additional observation to note whether the surface of the aged sheet was "oily" due to plasticizer collected on the surface of the sheet—indicated in Table 5.5 by a "+."



SCHEME 5.1 Acetyl trialkyl citrate plasticizer (2011, **WO2011082052** A1, 3M INNOVATIVE PROPERTIES CO). R may be the same or different and wherein at least one R is a branched alkyl group having a carbon chain length of C_5 or greater; R′ is H or an acyl group. Preferred plasticizers are compounds (4)–(9) of Table 5.5.

WO2013154255 A1 (2013, LG HAUSYS LTD) discloses a biodegradable polymer composition comprising an aliphatic polyester and a benzoate-based plasticizer. The aliphatic polyester is PLA, PGA, PCL, or P3HB. The benzoate-based plasticizer is selected from 2-(2-(2-phenylcarbonyloxy ethoxy)ethoxy)ethylbenzoate, glycerol tribenzoate, trimethylolpropane tribenzoate, isononyl benzoate, 1-methyl-2-(2-phenylcarbonyloxy propoxy) ethylbenzoate, 2,2,4-trimethyl-1,3-pentanediol

TABLE 5.5 Experimental Results of the Tested Plasticizers Including Examples 4–9 and Comparative Examples C3–C5 (2011, WO2011082052 A1, 3M INNOVATIVE PROPERTIES CO)

Control	Plasticizer	% Weight Loss (4 weeks, 65 °C)	Oily
C3	Acetyl tri-*n*-butyl citrate (Citroflex® A-4)[1]	0.9	–
C4	Acetyl triphenyl citrate	5.4	–
C5	Acetyl trihexyl citrate	2.1	+
4	Acetyl tri-3-methylbutyl citrate	1.6	+
5	Acetyl tri-2-ethylhexyl citrate (Citrofol® AHII)[2]	3.0	–
6	Acetyl tri-2-octyl citrate	0.4	–
7	Acetyl tri-3-methylbutyl:butyl (1:2) citrate	3.3	–
8	Acetyl tri-2-ethylhexyl:butyl (1:2) citrate	1.7	–
9	Acetyl tri-2-octyl:butyl (1:2) citrate	1.8	–

[1] *Vertellus™ Performance Materials, USA.*
[2] *Jungbunzlauer, CH.*

dibenzoate, *n*-hexyl benzoate and/or trimethylolpropane tribenzoate; phthalate-based plasticizer is not used. The disclosed plasticizers are biodegradable compared to non-biodegradable phthalate-based plasticizers, and they do not have the disadvantages of the low plasticization rate of citrate-based plasticizers.

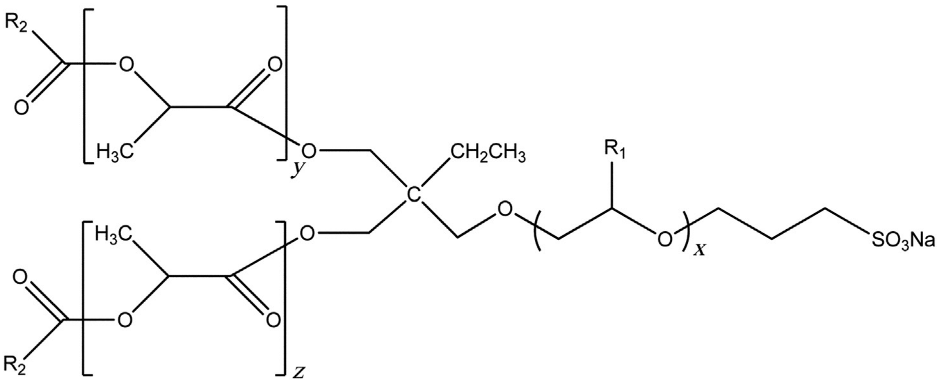
JP2007246707 A (2007, SANYO CHEMICAL IND LTD) discloses a plasticizer for PLA comprising the salt of an alkylene oxide addition product of an aliphatic (1–18C) active hydrogen compound, and preferably having M_n of 200–10,000. The aliphatic active hydrogen compound (a) is an aliphatic alcohol; preferably, an alkylcarbonyl-alkylene oxide sulfonate salt is used.

TW201043661 A (2010, IND TECH RES INST) discloses a plasticizer for PLA of the formula depicted in Scheme 5.2.

US5076983 A (1991, DU PONT) discloses a method for manufacturing a self-supporting film of PLA in which lactic acid oligomers are used as plasticizing agents. **WO9204413** A1 (1992, BATTELLE MEMORIAL INSTITUTE) discloses the use of residual lactic acid monomer or lactic acid oligomers to plasticize PLA, with plasticizer levels of 2–60 wt%. **US5180765** A (1993, BIOPAK TECHNOLOGY LTD) discloses a method for softening PLA by adding lactic acid, D-lactide, L-lactide, *meso*-D,L-lactide, racemic D,L-lactide, oligomers of lactic acid, oligomers of lactide, derivatives of oligomers of lactic acid, or various mixtures thereof. Particularly advantageous is the sequential incorporation of plasticizer into PLA to obtain a blended composition by melt blending with PLA a first plasticizer selected from the group consisting of oligomers of lactic acid, oligomers of lactide, and mixtures thereof; and melt blending with the blend of a second plasticizer selected from the group consisting of lactic acid, L-lactide, D-lactide, *meso* D,L-lactide, racemic D,L-lactide, and mixtures thereof. This procedure allows the blending of the first plasticizer at a first temperature and the blending of the second plasticizer at a second temperature lower than the first temperature. Similarly, **JPH06306264** A (1994, MITSUI TOATSU CHEMICALS) discloses a method to soften PLA or poly(D-lactic acid-L-lactic acid) (PDLA) by adding a cyclic oligomer of lactic acid to PLA or PDLA. **WO2009092825** A1 (2009, ARA PATRIZIA MARINA; ARA MARCO PAOLO) discloses also the plasticization of PLA with mixtures of lactic acid oligomers. PLA films plasticized with lactic acid oligomers are claimed to have better flexibility in comparison to PLA films plasticized with commercial polyadipate plasticizers known commercially under the name of Glyplast 206/3. Overall, the use of a plasticizer such as lactide, lactic acid, or its oligomers is considered to be useful for pliable films and other packaging applications made of PLA conventionally served by polyethylene and other nondegradable thermoplastic polymers.

On the other hand, the use of monomers and oligomers of hydroxy acids such as lactic acid and/or esters thereof such as lactide, though biodegradable, are known to have some drawbacks. The end groups in the lactic acid monomers and oligomers (carboxyl groups or equally the final free hydroxyl groups) can cause premature degradation in PLA. Although lactide has no end groups because it is a cyclic ester, lactide is highly volatile and can migrate to the surface of the film, thereby causing processing problems, such as lactide condensation on equipment, and undesirable alterations in the mechanical properties of a PLA film (1999, **US5908918** A, CHRONOPOL INC). According to **WO9204413** A1 (1992) residual monomer can deposit out on rollers during processing. **US5076983** A (1991) also comments that excessive levels of plasticizer can cause unevenness in films and may separate and stick to and foul drums used for casting such films.

FR2973386 A1 (1993, BIOPAK TECHNOLOGY LT) discloses the use of a lactide oligomer, obtained by a process comprising at least one step of polymerization of the lactide via ring opening in the presence of a functional agent chosen from fatty acids and fatty alcohols, as a plasticizer for formulations based on biodegradable polymers and/or vegetable flours (e.g., mixture of PLA and wheat flour). The difunctional agent is diol or diacid compound, succinic acid, adipic acid, and/or 1,4-butanediol.



SCHEME 5.2 Alkylene oxide sulfonate salt-type plasticizer (2010, **TW2010431661** A, IND TECH RES INST). *x* is 1–50; when *x*-1, R_1 is hydrogen or methyl; when $x>1$, among R_1, a portion thereof are hydrogen, a portion thereof are methyl, wherein the hydrogen and methyl have a ratio of 5/1–10/1; R_2 is C_{1-6} alkyl group (no hydroxyl group containing); $y+z=5-300$.

Apart from these, a softening agent for aliphatic polyesters such as PLA and its copolymers that have a poly(vinyl ether) structure, such as, e.g., poly(isobutyl vinyl ether) (1993, **EP1312642** A, KYOWA YUKA KK) has been known. **WO2005040282** A1 (2005, KYOWA HAKKO CHEMICAL CO LTD) discloses in one of its embodiments a method for softening PLA by blending it with a poly(ethyl vinyl ether)-based polyurethane. Although they are excellent in optical transparency, compositions containing the disclosed softening agent are still susceptible to improvement typically in elongation.

Other high-molecular-weight plasticizers have also been reported, including polyesters such as PCL and polyethers. **JPH08283557** A (1996, SHIMADZU CORP) discloses that a poly(alkylene dicarboxylate) polyester is useful as a plasticizer used for the purpose of softening polymers consisting primarily of PLA. **JPH08199052** A (1996, SHIMADZU CORP) discloses that a poly(alkylene ether) such as polyethylene glycol, polypropylene glycol, poly(butylene ether), or their mixture with $M_n \geq 2000$ is useful as plasticizer of PLA.

In all of these cases, however, the amount of plasticizer that can be added is only able to slightly improve the impact strength of PLA, and when an attempt is made to considerably increase softness, it causes a decrease in the heat-resistance temperature and bleed out in the same manner as the case of a low-molecular-weight plasticizer, while transparency also decreases depending on the type and amount of plasticizer added. In addition, although elasticity can be given, there are disadvantages consisting of weakness to impacts and low crazing resistance.

Several patents and literature documents also describe the plasticization of PHAs, and especially P3HB or PHBHV, with a number of plasticizers. Plasticizers reported in literature [3,24] are dibutyl phthalate, dioctyl phthalate, triethyl citrate, dioctyl adipate, triacytyl glycerol (triglyceride), polyadipate, soybean oil, and epoxidized soybean oil. Triethyl citrate or dibutyl phthalate presented better plasticizing effects than soybean oil and epoxidized soybean oil for PHBHV [25]. However, these plasticizers do not substantially improve the flexibility of P3HB remarkably. They also lower the properties of the polymer such as modulus, tensile strength, and gas barrier.

WO2006012917 A1 (2006, COGNIS BRASIL LTDA; P3HB IND SA; COGNIS DEUTSCHLAND GMBH) discloses the use of C_6–C_{30} fatty alcohols and glycerol esters of C_6–C_{24} fatty acids as plasticizers in P3HB and its copolymer compositions to improve the processability and physical–mechanical properties. The plasticizers are incorporated in the P3HB and its copolymers by mixing in a dry blend system.

WO2007095708 A1 (2007); **WO2007095709** A1 (2007); **WO2007095711** A1 (2007); and **WO2007095712** (2007) of PHB IND SA disclose methods for producing a biodegradable biopolymer composition comprising the steps of: (1) mixing P3HB or PHBHV, or their blends with PLA or PCL, in powder form with 2–30 wt% (preferably 5–10 wt%) of a plasticizer based on vegetable oils and fatty acids of animal and vegetable origin that is distilled and hydrogenated; (2) adding to the biopolymer mixture 0.01–2 wt% of a thermal stabilizer additive, a nucleating agent, and a flow aid additive; and (3) extruding the obtained composition so as to promote, in the melt state, the incorporation of the additives in the matrix of P3HB or PHBHV and its subsequent granulation. The vegetable oils used for the production of plasticizers are soybean, corn, castor, palm, coconut, peanut, linseed, sunflower, babasu palm, palm kernel, canola, olive, carnauba wax, tung, jojoba, grape seed, andiroba, almond, sweet almond, cotton, walnuts, wheatgerm, rice, macadamia, sesame, hazelnut, cocoa (butter), cashew nut, cupuacu, poppy, and their possible hydrogenated derivatives.

WO2013016444 A2 (2013, POLYONE CORP) attempts to solve the problem of bleeding by using crosslinkable bioplasticizers. These crosslinkable bioplasticizers comprise a mixture of an epoxy-functional bioderived plasticizer (e.g., epoxidized methyl soyate) and an aromatic dianhydride (e.g., pyromellitic dianhydride). When heated, the mixture crosslinks, which can be accelerated by the addition of a Lewis acid metal catalyst. The crosslinked bioplasticizer can be melt compounded into a thermoplastic polymer or can be formed in situ in the thermoplastic polymer. The crosslinking of the bioplasticizer can reduce bleeding of the bioplasticizer to the surface of a plastic article made by extrusion, molding, calendering, or thermoforming techniques.

Plasticizers and/or swelling agents (e.g., water) are also used for the destructure of native starch. Destructurized starch behaves as a thermoplastic polymer (TPS) and can be processed by conventional techniques (see Chapter 1: Introduction; Section 1.11.2: Starch). Products derived therefrom by the use of water as "plasticizer" tend to have the problem of rapidly losing water to the environment by evaporation. As a result, this type of material tends to become brittle with age. These materials are also highly water sensitive, which is undesirable for the majority of applications of thermoplastic products.

Example of plasticizers for starch are: dimethyl sulfoxide (DMSO), glycerol, ethylene glycol, propylene glycol, xylitol, sorbitol, mannitol, pentaerythritol, diglyceride, diglycol ether, succinic acid anhydride, formamide, *N*,*N*-dimethylformamide, *N*-methylformamide, dimethylacetamide, *N*-methylacetamide *N*,*N*′-dimethylurea, glycerol mono-, di-, or triacetate (triacetin), sodium diethylsulfosuccinate, and/or alcohol-amines such as, e.g., ethanol amine or propanol amine, and the like. Processability and moldability of starch can be enhanced by plasticizers like glycerol being able to reduce the T_m of starch below its decomposition temperature as described in **US5362777** A (1994, TOMKA I). However, resulting products will be unstable and properties will diminish in time due to migration or even loss of plasticizers during storage and use. Furthermore, products will remain highly water and humidity sensitive.

A representative list of biopolymer/plasticizer systems disclosed in patents is given in Table 5.6.

TABLE 5.6 Representative Biopolymer/Plasticizer Systems

Biopolymer	Plasticizer	Patent
PLA	Dibutylphthalate and nitrocellulose	**US1995970** A (1935, DU PONT)
PLA, PGLA	2-methoxyethyl phthalate	**US3636956** A (1972, ETHICON INC)
PLA	Triacetin[1]	**US3498957** A (1970, ETHICON INC)
PLA	Triacetin	**JPH07177826** A (1995, MITSUI TOATSU CHEMICALS)
PLA	Triethyl citrate	**EP226061** A2 (1987, ALLIED CORP)
PLA	Ethyl acetate	**DE3734223** A1 (1989, BOEHRINGER INGELHEIM KG)
PLA	Phthalic acid esters, aliphatic dibasic acid esters, phosphates, hydroxy polyvalent carboxylates, fatty acid esters, polyesters	**JPH04335060** A (1992, MITSUI TOATSU CHEMICALS)
PLA	Ester of aliphatic dicarboxylic acid and/or chain molecular diol of mol. wt < 2000 (e.g., dioctyl adipate); aliphatic polyester containing these as its major constituents	**JPH08199053** A (1996); **JPH08245866** A (1996, SHIMADZU CORP)
PLA	Triacetin, tributyrin, butylphthaloyl butyl glycolate	**JPH09296103** A (1997, SHIMADZU CORP)
PLA	Ether-ester derivatives, glycerol, phthalic acid, glycolic acid, citric acid, adipic acid	**JPH11323113** A (1999, SHIMADZU CORP)
PLA	Diglycerol acetate	**JP2002080703** A (2002); **JP2003020390** A (2003); **EP1270659** A1 (2003, RIKEN VITAMIN CO)
PLA	Butyl diglycol adipate, methyl diglycol adipate and methyl diglycol benzoate adipate	**JP2005036104** A (2005, DAI ICHI KOGYO SEIYAKU CO LTD)
PLA	Diglycerol tetra caprylic acid ester	**JP2004359892** A (2004, SAKAMOTO YAKUHIN KOGYO CO LTD)
PLA	Polyglycerol fatty acid ester (e.g., Chirabazol VR-01 of Taiyo Kagaku Co., Ltd.; polymn. degree of polyglycerol 10 and esterification degree 69%, and containing oleic acid)	**JP2008069299** A (2008, TAIYO KAGAKU KK; UNIV OSAKA)
scPLA (PLLA/PDLA = 45–55/55–45 wt%)	Polyglycerol fatty acid ester	**JP2010260900** A (2010, TOHCELLO CO LTD)
PLA	Acetyl tri-3-methylbutyl citrate, Acetyl tri-2-ethylhexyl citrate (Citrofol® AHII), Acetyl tri-2-octyl citrate, Acetyl tri-3-methylbutyl:butyl (1:2) citrate, Acetyl tri-3-methylbutyl:butyl (1:2) citrate, Acetyl tri-2-ethylhexyl:butyl (1:2) citrate, Acetyl tri-2-octyl:butyl (1:2) citrate	**WO2011082052** A1 (2011, 3M INNOVATIVE PROPERTIES CO)
PLA, PGA, PCL or P3HB	Benzoate-based plasticizer (e.g., glycerol benzoate, trimethylolpropane tribenzoate and isononyl benzoate)	**WO2013154255** A1 (2013, LG HAUSYS LTD)
PLA	Lactic acid oligomers	**US5076983** A (1991, DU PONT)

Continued

TABLE 5.6 Representative Biopolymer/Plasticizer Systems—cont'd

Biopolymer	Plasticizer	Patent
PLA	Lactic acid or lactic acid oligomers	**WO9204413** A1 (1992, BATTELLE MEMORIAL INSTITUTE)
PLA	Mixt. of two plasticizers 1st plasticizer: oligomers of lactic acid, oligomers of lactide; 2nd plasticizer: lactic acid, L-lactide, D-lactide, meso D,L-lactide, racemic D,L-lactide	**US5180765** A (1993, BIOPAK TECHNOLOGY LTD)
PLA, PDLA	Cyclic oligomer of lactic acid	**JPH06306264** A (1994, MITSUI TOATSU CHEMICALS)
PLA	Lactic acid oligomers	**WO2009092825** A1 (2009, ARA PATRIZIA MARINA; ARA MARCO PAOLO)
PLA/wheat flour	Lactide oligomer (e.g., L-lactide/succinic acid oligomer)	**FR2973386** A1 (1993, BIOPAK TECHNOLOGY LT)
PLA	Polyvinyl ether (e.g., polyisobutyl vinyl ether)	**EP1312642** A (1993, KYOWA YUKA KK)
PLA	Poly(ethyl vinyl ether)-based polyurethane	**WO2005040282** A1 (2005, KYOWA HAKKO CHEMICAL CO LTD)
PLA	Poly(alkylene dicarboxylate)	**JPH08283557** A (1996, SHIMADZU CORP)
PLA	Polyethylene glycol, polypropylene glycol, poly(butylene ether)	**JPH08199052** A (1996, SHIMADZU CORP)
PLA	Triacetin, glycerol tripropionate, polymeric adipate	**WO9732929** A1 (1997, NESTE OY)
PLA	Triacetin, glycerol tripropionate	**JPH0834913** A (1996); **US6136905** A (2000, MITSUI CHEMICALS INC)
PLA	Triacetin, methyl ricinolate, dihexyl phthalate, PCL diol or PCL triol (typically of $M_{\mathrm{n}} < 1000$), acetyl tri-*n*-butyl citrate	**WO9734953** A1 (1997, PROCTER & GAMBLE)
Epoxidized soybean oil modified PLA	Acetyl tri-*n*-butyl citrate, triethyl citrate	**US5359026** A (1994, CARGILL INC)
P3HB	C_6–C_{30} fatty alcohols and glycerol esters of C_6–C_{24} fatty acids	**WO2006012917** A1 (2006, COGNIS BRASIL LTDA; P3HB IND SA; COGNIS DEUTSCHLAND GMBH)
P3HB, PHBHV	Vegetable oils and fatty acids of animal and vegetable origin that is distilled and hydrogenated	**WO2007095708** A1 (2007); **WO2007095709** A1 (2007); **WO2007095711** A1 (2007); **WO2007095712** A1 (2007, PHB IND SA)
Starch	Glycerol	**US5362777** A (1994, TOMKA I)
Any polymer	Crosslinkable bioplasticizer: mixt. of epoxy-functional bioderived plasticizer (e.g., epoxidized methyl soyate) and aromatic dianhydride (e.g., pyromellitic dianhydride)	**WO2013016444** A2 (2013, POLYONE CORP)

P3HB, poly(3-hydroybutyrate); PCL, poly(ε-caprolactone); PLGA, poly(lactic acid-glycolic acid); PLA, poly(lactic acid); PHBHV, poly(3-hydroxybutyrate-co-3-hdrpxyvalerate); scPLA, stereocomplex PLA.

[1]*glycerol triacetate.*

5.5.2.2 Impact Modifiers

Impact modifiers improve toughness and reduce brittleness of end-products. Most impact modifiers are based on elastomer polymers (see Chapter 3: Blending; Section: 3.3.1: Biopolymer in Majority). It is known that the addition of core–shell impact modifiers, for instance, composed of elastomer core and acrylic shell, can significantly improve the impact strength of brittle materials. However, such core–shell impact modifiers are typically not biodegradable themselves, and their use in biodegradable polymers for the manufacture of compostable articles seems contradictory. With a minimal loading in the end product of 5%, they would prevent certification of the end product as being compostable by not meeting the stringent requirements in accordance with the norm EN 13432:2000, which only tolerates up to 1% of nonbiodegradable additives in compostable articles. Moreover, core–shell impact modifiers are typically accompanied by a strong decrease of the transparency and/or need a high loading (5–10 wt%). Furthermore, such core–shell impact modifiers are typically expensive, rendering them economically unsuitable (2009, **EP2065435** A1, SUKANO MAN & SERVICES AG).

There are biodegradable polymers, such as aliphatic-aromatic copolyesters (e.g., Ecoflex® of BASF), starch- or cellulose-based polymers, which may be effective in improving the flexibility and brittleness of PLA. However, these may typically cause an alteration of PLA's transparency rendering it very hazy and almost opaque. PCL, which acts as a plasticizer for PLA by improving the flexibility and brittleness of PLA, induces a lowering of PLA's T_g increasing its softness and potentially leading to deformation of the article (**EP2065435** A1, SUKANO MAN & SERVICES AG).

Nonpolymeric impact modifiers used in biodegradable polyester compositions include, for example, combinations of PLA, glycerol monostearate, and sodium alkyl sulfonate (2004, **US2004024141** A1, RIKEN VITAMIN CO; 2009, **EP2065435** A1, SUKANO MAN & SERVICES AG), which are also known for their good antistatic properties (see following Section 5.5.2.11: antistatic additives). Yet, glycerol fatty acid derivatives such as glycerol monostearate act as a plasticizer for the majority of polyesters and thus reduce the T_g of the base polymer and, therefore, the HDT of the articles produced thereof, limiting their final use. In addition, glycerol fatty acid derivatives may also be acting as an internal lubricant, causing a decrease of the melt viscosity of the carrier, and thus potentially leading to difficulties in processability, such as in sheet production or in extrusion blow molding process, where a high melt strength is required. Further, their addition may also enhance the migration of additives out of the polymer matrix, which is highly detrimental for food contact approvals and organoleptics properties of the end use article when intended for food packaging applications. Additive migration to the surface of the final article may in addition decreases the surface energy of the polymer and eventually deteriorate the printability of end use articles (2009, **EP2065435** A1, SUKANO MAN & SERVICES AG).

Alternatively, the impact modifier may be a mineral filler like EMforce® Bio additive (Specialty Minerals), which is a high aspect ratio, calcium-based synthetic mineral product. EMforce® Bio additive provides a simple, cost-effective method for improving the impact resistance of biopolymers while maintaining stiffness and compostability.

Biomax® Strong 120 (DuPont Packaging) is an ethylene copolymer designed to modify PLA for improved toughness properties in packaging and industrial applications without sacrificing product clarity. Similarly, Plamate® PD-150 (DIC Co) is a modifying agent that improves flexibility and impact resistance of PLA while at the same time preserves PLA's characteristic transparency. OnCap™ BIO Impact T (PolyOne) is a transparent impact modifier for PLA and is available as a compound, a solid, or a liquid concentrate. Paraloid™ BPM-500 (Rohm and Haas[4]) is an acrylic PLA impact modifier. Biostrength® additives (Arkema, Inc.) include impact modifiers such as Biostrength® 280 and Biostrength® 150, respectively targeted for transparent and opaque applications of PLA. In addition, Terraloy™ 90,000 series masterbatches (Teknor Apex) for use with PLA increase impact strength 10–20 times while providing excellent clarity for flexible and thermoformed packaging, extrusion coating, and food service disposables. The masterbatches are formulated with Biostrength® impact modifier (Arkema, Inc.) and carrier polymers consisting of Ingeo™ PLA (NatureWorks LLC). Teknor Apex recommends adding the masterbatch to PLA at 5–10% levels.

5.5.2.3 *Flame Retardants*

Flame retardants increase fire resistance, especially by reducing the ease with which a polymer burns. Some of the conventional flame retardants are the halogen-based flame retardants. They are characterized by high flame retardancy, small amounts of use, and good mechanical strength and other properties. A halogen-based flame retardant such as a bromine compound suppresses a burning reaction when a halogen-based gas component generated by a thermal decomposition traps radicals emitted from the polymer in a gaseous phase and thereby suppresses a burning reaction. However, halogen-based flame retardants may generate harmful gases during combustion. Furthermore, the use of halogen-based flame retardants is now being prohibited in Europe since there is a concern that polymer containing the halogen-based flame retardants may generate dioxin when it is disposed and incinerated. The environmental hazards, and toxicity associated with halogen-based retardants, make them less viable candidates in biopolymer compositions.

Nonhalogenated flame retardants are more preferred as they do not suffer from these issues. Nonhalogenated flame retardants include inorganic compounds (e.g., metal hydroxides, metal sulfates, metal nitrates, carbonate compounds, tin compounds, titanium compounds, zirconium compounds, and molybdenum compounds), silica compounds, some phosphorous compounds, boric acid–containing compounds, organic compounds, and nitrogen compounds.

The phosphorous-based flame retardants show high flame retardancy to some extent. The phosphorus-based flame retardants facilitate the formation of a carbonized (charred) layer by burning, and this charred layer blocks

---

[4] See footnote 1.

oxygen and radiation heat, whereby it is considered that burning is suppressed.

JP2004190025 A (2004, TORAY INDUSTRIES) discloses a PLA composition comprising PLA and at least two flame retardants selected from among bromine- and chlorine-based flame retardants, phosphorus-based flame retardants, nitrogen compound–based flame retardants, silicone-based flame retardants, and other inorganic flame retardants or at least two flame retardants selected from among phosphorus-based flame retardants, nitrogen compound–based flame retardants, silicone-based flame retardants, and other inorganic flame retardants. The phosphorus-based flame retardant is at least one flame retardant selected from among a condensed phosphoric ester, a polyphosphate, and red phosphorus.

WO2012043219 A1 (2012, TORAY INDUSTRIES) discloses a PLA composition comprising PLA and a mixture of two flame retardants (b1) and (b2); b1 is selected from melamine phosphate and/or melamine pyrophosphate and/or melamine polyphosphate; b2 is selected from piperazine phosphate and/or piperazine pyrophosphate and/or piperazine polyphosphate.

JP2013043959 A (2013, UNITIKA LTD) discloses a PLA composition comprising PLA, phosphazene compounds (5–25 pbw) and melamine phosphates; wherein, the weight ratio of phosphazene compounds/melamine phosphates is in the range of 90/10–50/50.

JP2003192925 A (2003) and **JP2005162871** A of SONY CORP disclose biodegradable polymer compositions comprising at least one biodegradable polymer (e.g., PLA, PCL, P3HB, PES, PBS, PBA), a flame-retardant additive comprising metal hydroxide(s), a phosphorus-containing compound, and at least one hydrolysis inhibitor for the biodegradable polymer. The metal hydroxide(s) include at least one of aluminum hydroxide, magnesium hydroxide, and calcium hydroxide. The phosphorus-containing compound is, for example, triphenyl phosphate, phosphinic acid salt (phosphinate), or red phosphorus; and the flame-retardant additive preferably also contains a nitrogen compound.

While the phosphorus compounds generally plasticize PLA easily and are very effective in improving its fluidity, it is required to be mixed with the polymer at a high mixing ratio to achieve the same flame retardancy as that of the halogen-based flame retardants. For this reason, a PLA composition that contains a phosphorus-based flame retardant tends to be inferior in mechanical properties and heat resistance, in particular, HDT (2005, **WO2005061626** A1, NEC CORP). Furthermore, among the phosphorous-based flame retardants, phosphates tend to bleed out from the polymer composition in storage at a high temperature and a high humidity or in a long-term storage. A concern is paid to the toxicity of phosphates that are discharged to the environment. Red phosphorus is highly flame retardant due to a high phosphorus concentration; however, on incomplete combustion, it generates highly toxic phosphine (phosphane) gas. It also has the risk of spontaneous ignition by friction or impact (2006, **EP1674551** A1, SHINETSU CHEMICAL CO).

Environment protection, occupational health and the safety considerations have restricted the appropriate flame retardants for biopolymers to metal hydroxides, silicone-based compounds, and ammonium polyphosphate.

JP2013079356 A (2013, UNITIKA LTD) discloses a PLA composition comprising PLA, an ammonium polyphosphate (16–65 pbw), and an organic sulfonic acid metal salt (0.1–5 pbw).

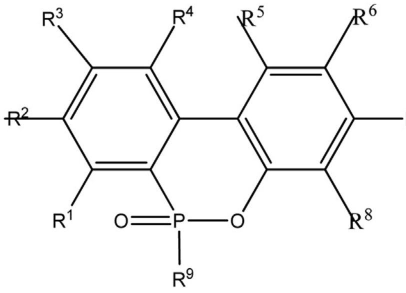
The metal hydroxides and ammonium polyphosphate involve some problems when used as the flame retardants for biodegradable polymers such as PLA. One problem is associated with the addition of a metal hydroxide to biopolymers. Metal hydroxides show an insufficient flame retardancy, even when metal hydroxides and silicone-based flame retardants are added to a biopolymer. For a metal hydroxide to obtain a sufficient flame retardant effect, the metal hydroxide such as aluminum hydroxide is required to be added in a large quantity. The mixing ratio of the flame retardant depends on the required flame retardancy, and it may be over 50 wt%. The addition of such a large amount of a metal hydroxide degrades the fluidity of the biopolymer such as PLA, and alters substantially its properties (2011, **WO2011122080** A1, NEC CORP). The other problem is associated with the addition of ammonium polyphosphate to biopolymers. If the ammonium polyphosphate has not been surface treated, it is poorly dispersible in the polymer and less resistant to water, to a degree that allows phosphoric acid to leach out, promoting quick degradation of the biopolymer with time. Although ammonium polyphosphate is often coated with melamine-formaldehyde resins, the timed release of formaldehyde is undesirable. Alternatively, silane coupling agents, titanium-based coupling agents, and aluminum-based coupling agents are used to coat the surface of ammonium polyphosphate.

JP2005120118 (2005) and **JP2005120119** A (2005) of MITSUBISHI PLASTICS IND disclose flame retardant injection molded products having both flame retardancy and durability, containing a PLA, a metal hydroxide surface treated with a silane coupling agent, and an aromatic carbodiimide. A preferred silane coupling agent is epoxysilane, and there are only examples using an epoxy-silane coupling agent. Use of a metal hydroxide surface treated with an epoxy-silane coupling agent, however, achieves insufficient effects (2009, **WO2009125872** A1, KAO CORP; NEC CORP).

WO2009125872 A1 (2009, KAO CORP; NEC CORP) discloses instead a PLA composition comprising PLA and a metal hydrate surface treated with at least one silane coupling agent selected from an amino-silane coupling agent, a mercapto-silane coupling agent, and an isocyanate-silane coupling agent, wherein the content of an alkali metal component in the metal hydrate is not more than 0.2 wt%. Silane coupling agents, titanium-based coupling agents, and aluminum-based coupling agents are unsuitable to cover the entire surface of ammonium polyphosphate, leading to insufficient dispersion, water resistance, and flame retardancy (2006, **EP1674551** A1, SHINETSU CHEMICAL CO).

WO2011122080 A1 (2011, NEC CORP) discloses a flame retardant for PLA comprising one, two or more components selected from a group consisting of: (b1) a phosphorus compound having a phosphaphenanthrene skeleton and a hydroxy group; (b2) a phosphazene compound and a metal hydroxide (b3), the flame retardant comprising at least 1 pbw of the phosphorus compound (b1). The phosphorus compound having a phosphaphenanthrene skeleton and a hydroxy group (b1) is depicted in Scheme 5.3.

WO2006054493 A1 (2006, PANASONIC CORP) discloses a biodegradable polymer composition obtained by melt compounding a silica-magnesia catalyst as a flame-retardant component with a biodegradable polymer such as PLA and PBS. Also, a silica-alumina (SiO_2/Al_2O_3), La_2O_3, and CeO catalysts may be used. It is considered that these catalysts significantly contribute to the flame retardation of the biopolymer by degrading it into molecules of low molecular weights so that a total molecular weight of combustible gases is emitted by thermal decomposition. In other words, assuming that a polymer is broken at predetermined times, as the polymer is broken into molecules of lower molecular weights, an amount of gases as a fuel is reduced by just that much and combustion energy is lowered compared with the case where the polymer is broken into molecules of higher molecular weights. As a result, the combustion energy in the burning field is reduced, and radiant heat is lowered, whereby the thermal decomposition of the polymer is suppressed. It is considered that, by repeating this, the combustion cycles cannot be continued, and the flame retardation of the resin is achieved. This flame-proofing mechanism is different from those of halogen-based and phosphorus-based flame retardants. For example, in the case of halogen-based flame retardants represented by bromine-based flame retardants, halogen-containing gas components generated by thermal decomposition capture radicals released from a polymer in the vapor phase, thereby suppressing combustion reactions. As mentioned earlier, the phosphorous-based flame retardants facilitate the formation of a carbonized (char) layer during the combustions, which blocks oxygen and radiation heat, thereby suppressing the combustion. **WO2013046487** A1 (2013) of PANASONIC CORP discloses an outer casing for an electric device, comprising a molded article that is made up of the previously described biodegradable polymer composition comprising ≥50 wt% of PLA or its copolymer, and silica-magnesia catalyst particles as flame retardants.



SCHEME 5.3 Phosphorus compound having a phosphaphenanthrene skeleton and a hydroxy group as part of a flame retardant system for PLA (2011, **WO2011122080** A1, NEC CORP).

A representative list of biopolymer/plasticizer systems disclosed in patents is given in Table 5.7.

5.5.2.4 Antioxidants

Antioxidants are used to protect the biopolymers during processing and use of the biopolymer. Typical antioxidants include hindered phenol type compounds, phosphite-type compounds, thioether-type compounds, and the like.

5.5.2.5 Light and UV Stabilizers

Light and ultraviolet (UV) stabilizers are used to protect biopolymers from discoloration and premature degradation by inhibiting initiation of the degradation process via preferentially absorbing incident UV radiation. Typical light and UV absorber stabilizers include benzophenone-type compounds, benzotriazole-type compounds, aromatic benzoate–type compounds, oxalic acid anilide–type compounds, cyanoacrylate-type compounds, hindered amine–compounds, and the like. The light and UV stabilizers are added in the polymer either by direct mixing or by means of a color concentrate used to color the polymer. When this optional additive is included in the color concentrate it adds value to that concentrate as a masterbatch in polymer compounding because the UV stabilizer also helps protect the polymer from adverse effects arising from exposure to the ultraviolet rays. Being included in a masterbatch as an additive makes the introduction of the stabilizer easier, due to better dispersion (2012, **WO2011040905** A1, POLYONE CORP).

PolyOne and Clariant have developed biobased UV stabilizer masterbatches that protect the contents of transparent biopolymer packaging. The CESA®-light UV stabilizers of Clariant include three major classes of UV stabilizers: UV absorbers, nickel quenchers, and hindered amine light stabilizers (HALS).

5.5.2.6 Heat Deflection Temperature Modifiers

Heat deflection temperature modifiers improve heat deflection of a biopolymer. DaniMer provides a renewable additive that improves the heat deflection of PLA to 88 °C (190 F), enabling PLA to provide the performance characteristics

TABLE 5.7 Representative Flame Retardant Systems Used in Biodegradable Polymers

PLA	Mixt. of 2 Flame Retardants: Bromine-, Chlorine-, Phosphorus-, Nitrogen- and Silicone-Based Flame Retardants; the Phosphorus-Based Flame Retardant Is Selected from Condensed Phosphoric Ester, Polyphosphate, and Red Phosphorus	**JP2004190025** A (2004, TORAY INDUSTRIES)
PLA	Ammonium polyphosphate (15–5 pbw) and an organic sulfonic acid metal salt (0.105 pbw)	**JP2013079356** A (2013, UNITIKA LTD)
PLA	Phosphazene compounds and melamine phosphates (5–25 pbw; mass ratio phosphazene compounds/(melamine phosphates = 90/10–50/50)	**JP2013043959** A (2013, UNITIKA LTD)
PLA	Mixt. of ≥2 flame retardants (b1 + b2): (b1) melamine phosphate and/or melamine pyrophosphate and/or melamine polyphosphate; (b2) piperazine phosphate and/or piperazine pyrophosphate and/or piperazine polyphosphate	**WO2012043219** A1 (2012, TORAY INDUSTRIES)
PLA	Metal hydrate (e.g., aluminum hydroxide) contg. ≤0.2% of an alkali metal-based substance ≥44.5% and ≤80%)	**WO2005061626** A1 (2005, NEC CORP)
PLA, PCL, P3HB, PHV, PNS, PBS, PBA, cellulose, starch, chitin, chitosan, dextran	Phosphorous-contg. cpd.: Triphenyl phosphate, phosphinic acid salt (phosphinate), red phosphorus); and metal hydroxide(s): aluminum hydroxide, magnesium hydroxide, calcium hydroxide	**JP2003192925** A (2003); **JP2005162871** A (2005, SONY CORP)
PLA	Metal hydroxide surface treated with a silane coupling agent (is epoxy-silane)	**JP2005120118** (2005); **JP2005120119** A (2005, MITSUBISHI PLASTICS IND
PLA	Metal hydrate surface treated with at least one silane coupling agent (amino-silane, mercapto-silane, isocyanate-silane)	**WO2009125872** A1 (2009, KAO CORP; NEC CORP)
PLA	Ammonium polyphosphate surface treated with an organosilicon condensate (5–100 pbw) and flame retardant coagent (talc, graphite, melamine cyanurate) (1–80 pbw)	**EP1674551** A1 (2006, SHINETSU CHEMICAL CO)
PLA	Phosphorus cpd. having a phosphaphenanthrene skeleton and a hydroxy group	**WO2011122080** A1 (2011, NEC CORP)
PLA	Silica-magnesia (SiO_2/MgO) catalyst particles (0.5–40 wt%; 1–10 μm)	**WO2006054493** A1 (2006); **WO2013046487** A1 (2013, PANASONIC CORP)

for many thermoformed and injection molded articles. This material is not transparent and will produce some increased opacity dependent upon the percent of additive utilized.

5.5.2.7 Heat Stabilizers

DuPont™ Biomax® Thermal 300 (DuPont) is a renewable heat stabilizer that allows PLA-thermoformed packaging to withstand elevated temperatures. PLA-thermoformed packages can be stored shelf stable, shipped normally, and even reheated in the microwave without deformation.

5.5.2.8 Compatibilizers, Coupling Agents

Compatibilizers are used to improve the mixing of incompatible polymers. CESA®-mix (Clariant) compatibilizer enables different polymers to form a homogeneous structure.

Coupling agents improve the interaction and compatibility of mixed polymers. For instance, starch and PLA do not have readily reactive functional groups, so their mutual compatibility is poor. To overcome this shortcoming, a chemical with isocyanate functional groups such as methylene diisocyanate (MDI) is reactively blended with the starch and PLA.

5.5.2.9 Fillers

Fillers are often added to biodegradable biopolymers to either improve the mechanical properties or reduce cost. Typical fillers include calcium carbonate (most common), magnesium carbonate, titanium dioxide, talc, and silicon dioxide. To improve the compatibility between fillers and biopolymer matrix, it is preferred to use surface-treated fillers. Since fillers are generally inorganic, they have the potential to accumulate over time in soil or other disposal environments.

5.5.2.10 Colorants

Colorants, including pigments and dyes, are used to alter the color or improve the aesthetics of a biopolymer. The choice of colorants depends on the ultimate color desired by the designer for the polymer article. Like other additives, colorants must not be toxic and harmful to the environment. Commercial sources for pigments and dyes include multinational companies such as Polyone, Clariant, BASF, Bayer, Danimer, Color-Chem International, Sun Chemical, Zhuhai Skyhigh Chemicals, and others identified at Internet websites.

Table 5.8 lists eight commercially available pigment colorants in a variety of primary and secondary colors, five chromatics, two blacks, and one white as listed by **WO2011040905** A1 (2012, POLYONE CORP).

TABLE 5.8 Eight Commercial Pigment Colorants (2012, WO2011040905 A1, POLYONE CORP)

Raw Material Name	CI Name	Family	Color	FDA[1]
Tioxide R-FC6 White	Pigment White 6	Inorganic	White	Y
Regal 660R Black Powder	Pigment Black 7	Organic		N
MPC Channel Black	Pigment Black 7	Organic		Y
Heliogen Blue K7090	Pigment Blue 15:3	Organic	Blue	Y
Heliogen Blue K6903	Pigment Blue 15:1	Organic	Blue	Y
34L2000 Azure Blue	Pigment Blue 28	Inorganic	Blue	Y
Sicotan Yellow 2001 FG	Pigment Brown 24	Inorganic	Yellow	Y
Sicotan Yellow K 1011	Pigment Yellow 53	Inorganic	Yellow	Y

[1] *As published by the commercial producer or as tested by PolyOne or both.*

Table 5.9 lists 14 commercially available dye colorants as listed by **WO2011040905** A1 (2012, POLYONE CORP).

In addition to the traditional colorants, biobased colorants are now industrially available [26,27]. Renol®-compostable product line of Clariant includes masterbatches based on over 80 different pigments, which can be incorporated in several biopolymers (PLA, PHA, and starch based). Derived from natural resources, the colors include red, orange, yellow, green, and blue. Orange is derived from the root of the turmeric spice plant. Yellow comes from a tropical flower, green from chlorophyll and other plant sources, and carmine red from the cochineal insect. Some of them boast excellent clarity, but their lightfastness may be limited [28].

The OnColor™ BIO Colorants of Polyone range of masterbatches are based on sustainable materials and can be used with commercially available biodegradable polymers including starch, PLA, PHA, PHBHV, PBS, PBAT, and their blends. Teknor Color Company has three series of color concentrates for use in PLA and its blends that are suitable for injection, extrusion, and blow molding processes. The three series of colorants differ in terms of their carrier resins, which are either PLA or polyesters compatible with PLA and thus readily blended into it. Ampacet markets a series of color masterbatches, including organic-based pigments from renewable resources for a broad range of biopolymers. DaniMer offers also a wide range of colorants compounded with PLA.

5.5.2.11 Antistatic Additives

Antistatic agents are used to reduce the effects of static electricity generated on the surfaces of hydrophobic polymers such as electric discharge during molding, attraction of dust or dirt, and office-automation equipment malfunction. Antistatic agents are additives whose efficiency is measured either by determining the surface resistivity or the static decay. Without antistatic agents, the surface resistivity of polymer is typically of 10^{14}–$10^{15}\,\Omega$.[5] Antistatic additives will lower the surface resistivity of 10^{9}–$10^{12}\,\Omega$. In order to achieve a higher conductivity, conductive fillers such as carbon black or carbon fibers or powdered metal must be added to the polymer [29]. There are two types of antistatic agents, one of which is a coating type and the other of which is a kneading type. Examples of a coating type of antistatic agents in which biodegradable polyester is used as its main constituent include the following: one composed of saccharose lauric acid ester and a water-soluble polymer (2000, **JP2000280410** A; 2000, **EP1041105** A2 CHUO KAGAKU KK); a fluorine-based compound having a perfluoroalkyl group and a perfluoroalkenyl group in molecules (1998, **JPH1086307** A, MITSUI PETROCHEMICAL IND); a specified anion-based surfactant and a specified nonion

---

[5] Often in practice, surface resistivity is given in units of ohms/square.

TABLE 5.9 Fourteen Commercial Dye Colorants (2012, WO2011040905 A1, POLYONE CORP)

Raw Material Name	CI Name	Family	Color	FDA
Lambdaplast Blue NL	Solvent Blue 59	Anthraquinone	Blue	N
Macrolex Blue RR Granular	Solvent Blue 97	Anthraquinone	Blue	N
Macrolex Green G Granular	Solvent Green 28	Anthraquinone	Green	N
Macrolex Green 5B Granular	Solvent Green 3	Anthraquinone	Green	N
Macrolex Orange G Granular	Disperse Orange 47	Polymethine	Orange	N
Macrolex Orange 3G Granular	Solvent Orange 60	Perinone	Orange	N
Macrolex Red EG Granular	Solvent Red 135	Perinone	Red	N
Macrolex Red E2G Granular	Solvent Red 179	Perinone	Red	N
Thermoplast Red 454	Solvent Red 195	Anthraquinone	Red	N
Violet R Granular	Disperse Violet 26	Anthraquinone	Violet	N
Macrolex Violet B Granular	Solvent Violet 13	Anthraquinone	Violet	N
Macrolex Violet 3R Granular	Solvent Violet 36	Anthraquinone	Violet	N
Key Plast Yellow 3G	Solvent Yellow 93	Pyrazolone	Yellow	N
Key Plast Yellow AG	Solvent Yellow 114	Quinophthalone	Yellow	N

surfactant (2002, **JP2002012687** A, UNITIKA LTD). However, these coated-type antistatic agents have problems such as decreased transparency, deterioration of sustainability or durability, development of sticky film, and frequent occurrence of intrafilm blocking (2004, **US2004024141** A1; **WO2004069930** A1, RIKEN VITAMIN CO).

The kneading-type antistatic agents may be listed: (a) general surfactants; (b) anion-based surfactants, for example, a fatty acid amine system and an alkyl sulfate system, etc.; (c) cation-based surfactants such as quaternary ammonium salt, etc.; (d) nonion-based surfactants such as sorbitan fatty acid ester, glycerol fatty acid ester, etc.; and (e) amphoteric surfactants such as alkylbetaine base. In particular, anion-based surfactants such as metal alkylsulfate metal, metal alkylbenzenesulfonate, etc. are effective as an antistatic agent of aromatic polyesters such as PET. However, there are some rather serious side effects in that biodegradable fatty acid polyesters are colored with anion-based surfactants, cation-based surfactants, and amphoteric surfactants, and the physical properties of molded articles are deteriorated.

A large number of nonion-based surfactants have been tried with PLA including polyhydric alcohol such as ethylene glycol, diethylene glycol, triethylene glycol, glycerol, trimethylolpropane, pentaerythyritol, sorbitol; polyethylene glycol; and polyethylene glycol adduct or a polypropylene glycol adduct of a higher alcohol, a polyhydric alcohol, and an alykylphenol (**JP2002114900** A (2002, MITSUBISHI PLASTICS IND; SHIMADZU CORP).

Glycerol fatty acid esters have also been used with some success with PLA, in particular, glycerol fatty acid monoesters such as glycerol monopalmitate, glycerol monostearate, glycerol monoolate, glycerol monolinoleate, and glycerol monobehenate (2002, **WO02087877** A1, TRESPAPHAN GMBH; 1998, **JPH1036650** A, MITSUI PETROCHEMICAL IND. However, unless the glycerol fatty acid ester is mixed with PLA in an amount of 3.5–7.5 parts, no antistatic effect can be brought about. In addition, since the added amount is large, the physical properties of a molded article may deteriorate, and, further, the sustainability of the antistatic performance is not sufficient (1998, **JPH1036650** A, MITSUI PETROCHEMICAL IND). Although polyalcohol fatty acid esters such as ethylene glycol, diethylene glycol, trimethylolpropane, sorbitol, etc. are effective for PLA (1997, **JPH09221587** A, MITSUBISHI PLASTICS IND; SHIMADZU CORP; 2002, **JP2002114900** A, MITSUBISHI PLASTICS IND, SHIMADZU CORP), the esters are less effective for biodegradable fatty acid polyesters such as PBS, etc.

JPH08231837 A (1996, SHIMADZU CORP) discloses a PLA mixed with an antistatic agent comprising a block copolymer of an aliphatic polyester with a polyalkylene ether.

Riken Vitamin offers Rikemal® and Rikemaster®, which are general-purpose antistatics based on glycerol fatty acid esters. Clariant offers the CESA®-stat antistatic masterbatches that can be used with virtually any polymer.

5.5.2.12 Miscellaneous Additives

Antifog agents are used to control moisture fogging of the interior surfaces of transparent biobased packaging. **JP2000280410** A (2000) and **EP1041105** A2 (2000) of CHUO KAGAKU KK disclose antifogging sheets for single use transparent food packaging containers comprising a transparent substrate, and an antifogging layer provided on one side of said transparent substrate. The antifogging layer consists of 50–80 wt% of sucrose lauric acid ester with an Hydrophile-Lipophile Balance (HLB) of 14–16 and 50–20 wt% of a water-soluble polymer. Furthermore, a silicone layer is provided on the other side of said transparent substrate. The transparent substrate can be made of PLA and the water-soluble polymer can be made of PVOH.

OnCap™ BIO of PolyOne is an additive concentrate range including also antifog agents. Clariant offers the CESA®-nofog additive masterbatches that can be used with virtually any polymer.

Antislip agents are used to improve stackability by roughening the surface of a biopolymer film, reducing its slip properties.

Corrosion inhibitors are added to packaging film to protect the appearance and extend the service life of metal parts and components. CESA®-cor anticorrosion concentrates of Clariant are nitrite-free corrosion inhibitors that have a neutral odor, and when extruding a polymer film with CESA®-cor, the active inhibitors are vaporized and well dispersed. The film protects the packaged part by condensing on the surface of the metal.

Antimicrobials protect films, fibers, and molded products against bacterial growth, fungi, mold and mildew, and prevent unpleasant odors, discoloration, and surface degradation of polymer parts. There are two major types of antimicrobials: organic antimicrobials consisting of substances that migrate within the polymer matrix, spreading over the surface of the materials where their antimicrobial action has effect. Inorganic antimicrobials incorporate substances containing silver in ionic form, bound to inorganic compounds that regulate the diffusion of ions within the polymer mass. The silver ion is the active ingredient that interacts with bacteria. Clariant offers a wide range of CESA®-antimicro masterbatches for every type of polymer.

Several more additives are used by manufacturers and product designers to handle the inherent weaknesses of biopolymers. While most of these additives stabilize biopolymers under various conditions so they can be used in many applications, at the same time they compromise the biodegradability of a biopolymer.

Except additives that are used to protect the biopolymer during processing and/or service life, there are also other additives that can accelerate the degradation of the biopolymer after disposal. Most of these additives are either incorporated directly into the biodegradable polymers or in capsules that degrade in the presence of water and acid, or coated onto the surface of the biodegradable polymer. Additives that can promote the (bio)degradation rate include: enzymes and microbial nutrients; compounds that can initiate and/or propagate depolymerization; and especially selected additives, e.g., (nano)particles acting as degradation agents [4].

PATENTS

Patent Number	Publication Date	Family Members	Priority Numbers	Inventors	Applicants	Title
CN101469072 A	20090701	CN101469072 B 20120502	CN20081142367 20080812	XIANGNAN ZHANG; MIN LI; CHAOQUN LI	SHENZHEN ECOMANN BIOTECHNOLOGY	Preparation of polyhydroxyalkanoate/montmorillonite intercalation type nano composite material.
CN101503521 A	20090812		CN2009147049 20090305		UNIV SHANGHAI JIAOTONG	Preparation of high-strength high-ductility biodegradable composite material.
CN102167894 A	20110831	CN102167894 B 20130102	CN2011125309 20110124	PENGYANG DENG; YUAN YIN; CHUNBAI ZHENG	CHANGCHUN APPLIED CHEMISTRY	Graphene/polylactic acid composite material and preparation method thereof.
CN102372911 A	20120314		CN20111362280 20111116	JIAN JIAO; RENXU YUAN; YUKE ZHONG; WEI ZHAO; YIBIN XU; XIANGBIN ZENG; TONGMIN CAI; SHIYONG XIA	KINGFA SCI & TECH CO LTD; SHANGHAI KINGFA SCI & TECH CO; ZHUHAI WANTONG CHEMICAL CO LTD	Efficient color master batch composition special for biodegradable plastic and preparation method thereof.
CN1417256 A	20030514	CN1176997 C 20041124	CN2002156420 20021216	FEI BIN; DONG LISONG; CHEN CHENG	CHANGCHUN APPLIED CHEMISTRY	Toughening method of poly(3-hydroxybutyrate) and poly(3-hydroxybutyrate-3-hydroxypentanoate).
DE3734223 A1	19890420	ZA8807535 A 19900627; PT88703 A 19881101; PT88703 B 19921231; PH30236 A 19970205; NZ226514 A 19900226; NO884474 A 19890410; NO176304 B 19941205; NO176304 C 19950322; JPH02117 A 19900105; JP2763303 B2 19980611;	DE19873734223 19871009	STRICKER HERBERT; ENTENMANN GUENTHER; KERN OTTO; MIKHAIL MICHEL DR; ZIERENBERG BERND	BOEHRINGER INGELHEIM KG	Implantierbares, biologisch abbaubares Wirkstofffreigabesystem. “Implantable biodegradable drug delivery system.”

		KR970006082 B1 19970423; IL87973 A 19920818; IE883040 L 19890409; IE62505 B1 19950208; FI884604 A 19890410; FI100302 B 19971114; EP0311065 A1 19890412; ES2061589 T3 19941216; DK561588 A 19890410; DK175252 B1 20040719; CA1333770 C 19950103; AU2352288 A 19890413; AU609194 B2 19910426; AT101035 T 19940215				
DE4007882 A1	19910919	JPH04220456 A 19920811; EP0446852 A2 19910918; EP0446852 A3 19920819	DE19904007882 19900313	BIELZER RAFFAEL; ENTENMANN GUENTHER; OFFERGELD HEINZ	BOEHRINGER INGELHEIM KG	Verwendung von Polyglycolsäure und ihrer Derivate als Nucleierungsmittel. “Use of polyglycolic acid and its derivatives as nucleating agent.”
EP0226061 A2	19870624	US5358475 A 19941025; JPS62144663 A 19870627; JPH0552749 B2 19930806; EP0226061 A3 19880720; EP0226061 B1 19940216; DE3689650 T2 19940526	US19850809978 19851217	MARES FRANK C O ALLIED CORPORA; TANG REGINALD TING-HONG C O AL; CHIU TIN-HO C O ALLIED CORPORA; LARGMAN THEODORE C O ALLIED CO	ALLIED CORP	High molecular weight bioresorbable polymers and implantation devices thereof.
EP1029890 A2	20000823	US6544607 B1 20030408; TW574309 B 20040201; KR20000058110 A 2000092; EP1029890 B1 20040728; DE60012381 T2 20050504	JP19990039449 19990218	KUROKI T; IKADO S; IWATA M; WANIBE HIROTAKA	MITSUI CHEMICALS INC	Aliphatic polyester composition and stretched film obtained from said composition.
EP1041105 A2	20001004	EP1041105 A3 20020102	JP19990092397 19990331; JP19990092488 19990331	WATANABE AKIHITO; SUZUKI MASAHIRO; KOYAMA MASATOSHI; KAMEYAMA HIROKAZU	CHUO KAGAKU KK	Anti-fogging sheet and container using same.

Continued

—Cont'd

Patent Number	Publication Date	Family Members	Priority Numbers	Inventors	Applicants	Title
EP1270659 A1	20030102	US2003083440 A1 20030501; US6720374 B2 20040413; TWI294444 B 20080311; KR20020096888 A 20021231; KR100806985 B1 20080225; JP2003073532 A 20030312; JP3748832 B2 20060222; EP1270659 B1 20060222; DE60209310 T2 20061109; CN1392197 A 20030122; CN1300247 C 20070214	JP20010184795 20010619; JP20020109231 20020411	SASHITA KAZUYUKI; HASEBE TADASHI	RIKEN VITAMIN CO	Aliphatic polyester composition and flexible products.
EP1312642 A1	20030521	US2003119959 A1 20030626; US2004225065 A1 20041111; JP2003138140 A 20030514; CN1417239 A 20030514; CN1261466 C 20060628	JP20010339023 20011105	INAYAMA TOSHIHIRO; MURATA SHIGERU; NIIMI TATSUO	KYOWA YUKA KK	Softening agent.
EP1659149 A1	20060524	WO2004076550 A1 20040910; WO2004076550 A8 20050224; US2009156713 A1 20090618; JP2006518780 A 20060817; EP1659149 A4 20070627; CN1524897 A 20040901; CN1230466 C 20051207; AU2004215733 A1 20040910	WO2004CN00143 20040224; CN2003105343 20030225	DING SHAOZHONG	DING SHAOZHONG	A fully-biodegradable plastic masterbatch and its preparation process.
EP1674551 A1	20060628	US2006142421 A1 20060629; TWI389972 B 20130321; JP2006176731 A 20060706; JP4548591 B2 20100922; EP1674551 B1 20100728; CN1807505 A 20060726; CN1807505 B 20110831	JP20040374114 20041224	IHARA TOSHIAKI; TANAKA MASAKI; MATSUMURA KAZUYUKI	SHINETSU CHEMICAL CO	Flame retardant resin composition.
EP1728818 A1	20061206	US2006276575 A1 20061207; JP2006335874 A 20061214; CN1872902 A 20061206	JP20050162189 20050602	KAO CORP	KAO CORP	Plasticizer for biodegradable resin.
EP2028218 A1	20090225	US2011184115 A1 20110728; KR20100044232 A 20100429; JP2010536973 A 20101202; WO2009027357 A1 20090305; EP2181142 A1 20100505; CN101784588 A 20100721; CN101784588 B 20120718	EP20070114921 20070824	DEBRAS GUY; LUIJKX ROMAIN	TOTAL PETROCHEMICALS RES FELUY	Reinforced and conductive resin compositions comprising polyolefins and poly(hydroxycarboxylic acid).
EP2065435 A1	20090603	US2009162683 A1 20090625; JP2009144152 A 20090702	EP20070405339 20071129; EP20080405294 20081128	GUILLAUME DOUARD	SUKANO MAN & SERVICES AG	Biodegradable polyester compositions.

FR2973386 A1	20121005	WO2012131252 A1 20121004; FR2973386 B1 20130426	FR20110052525 20110328	BARBIER JACQUES; DEVER CEDRIC	VALAGRO CARBONE RENOUVELABLE POITOU CHARENTES	Utilisation d'un oligomère de lactide biodégradable comme plastifiant. "Use of a biodegradable lactide oligomer as plasticizer."
JP2000086965 A	20000328		JP19980259662 19980914	NATSUME TATSUYA; SANO TOSHIMICHI; NODA MITSUO; IMAIZUMI MITSUHIRO; SUZUKI ATSUSHI	DAINICHISEIKA COLOR CHEM; SHOWA DENKO KK; SHOWA HIGHPOLYMER	Coloring agent composition.
JP2000280410 A	20001010		JP19990092397 19990331	WATANABE AKITO; KOYAMA MASATOSHI; KAMEYAMA HIROKAZU	CHUO KAGAKU KK	Anti-fogging sheet material and anti-fogging food packaging container.
JP2000302956 A	20001031	JP3383256 B2 20030304	JP20000024209 20000201; JP19990039449 19990218	KUROKI T; IMON S; IWATA M; WANIBE HIROTAKA	MITSUI CHEMICALS INC	Aliphatic polyester composition and oriented film therefrom.
JP2001226571 A	20010821	JP4583537 B2 20101117	JP20000035811 20000214	TAYA NAOKI; SATANI SHOICHI; TAYAUCHI MASATO	C I KASEI CO LTD	Polylactic acid based resin material and heat-shrinkable film.
JP2002012687 A	20020115	JP3415103 B2 20030609	JP20000194698 20000628	TSURUSAKI YOSHIYUKI	UNITIKA LTD	Polylactic acid-based biaxially oriented film with excellent antistaticity and method for producing the same.
JP2002080703 A	20020319		JP20010184795 20010619; JP20000184035 20000620	SASHITA KAZUYUKI; HASEBE TADASHI	RIKEN VITAMIN CO	Polyester resin composition, and material for agriculture or material for packaging.
JP2002114900 A	20020416	JP3597809 B2 20041208	JP20010308484 20011004	TAKAGI JUN; TERADA SHIGENORI	MITSUBISHI PLASTICS IND; SHIMADZU CORP	Antistatic polylactic acid-based composition.
JP2002179891 A	20020626	JP3506425 B2 20040315	JP20000379951 20001214	NAGAO KEN; NATSUME TATSUYA; YAMASHITA ROKUYA	DAINICHISEIKA COLOR CHEM	Colorant composition and colored resin molded product.
JP2002179898 A	20020626	JP4629217 B2 20110209	JP20000376823 20001212	OGOSHI IKUO	RIKEN TECHNOS CORP	Antistatic polylactic acid resin composition.

Continued

—Cont'd

Patent Number	Publication Date	Family Members	Priority Numbers	Inventors	Applicants	Title
JP2003020390 A	20030124		jP20020109161 20020411; JP20000184035 20000620	SASHITA KAZUYUKI-HASEBE TADASHI	RIKEN VITAMIN CO	Polyester resin composition and material for agriculture or wrapping.
JP2003192883 A	20030709		JP20010400252 20011228	NAKAZAWA KENJI; HIDA ETSUO; KONO TOSHINORI; URAYAMA YUJI; KANAMORI KENJI; OKUYAMA HISATSUGU	ASAHI DENKA KOGYO KK; TOYOTA MOTOR CORP	Polylactic acid-based resin composition, molded article and method for producing the molded article.
JP2003192925 A	20030709		JP20020121890 20020424; JP20010316361 20011015	YAMADA SHINICHIRO; FUJIHIRA HIROKO; MORI HIROYUKI; NOGUCHI TSUTOMU	SONY CORP	Biodegradable flame-retardant composite composition and method for producing the same.
JP2003313307 A	20031106		JP20020121858 20020424	ITO FUMIO	SUZUKI MOTOR CO	Manufacturing method of polylactic acid resin.
JP2004027136 A	20040129		JP20020189066 20020628	OTOMO TAKASHI; INOUE TAKASHI; KURIYAMA TAKU	YAMAGATA UNIV RES INST	Polylactic acid-based resin composition, process for producing the same and processed product using polylactic acid-based resin composition as stock material.
JP2004190025 A	20040708		JP20030400748 20031128; JP20020349061 20021129	OOME HIROKAZ; ISHII HIROMITSU; KUMAZAWA SADANORI; NAGAO TAKASHI; KUMAKI JIRO	TORAY INDUSTRIES	Resin composition and molded article made thereof.
JP2004204143 A	20040722		JP20020377073 20021226	KOGAMI AKINOBU; UEDA KAZUE; YOSHIMURA KAZUKO	UNITIKA LTD	Biodegradable resin composition having transparency and manufacturing method thereof.
JP2004244457 A	20040902	JP4348960 B2 20091021	JP20030033592 20030212	ITO TAKURO	TOYO SEIKAN KAISHA LTD	Polyester resin composition, stretched molded article and method for producing stretched molded article.

JP2004359892 A	20041224		JP20030162388 20030606	NAKAMURA RIKIYA; IMANISHI JUN; IMAMURA HIDEAKI; NARIBAYASHI IKUYA	SAKAMOTO YAKUHIN KOGYO CO LTD	Polyester resin composition.
JP2005036104 A	20050210	JP4071683 B2 20080402	JP20030274377 20030714	ISHIHARA KAZUHIKO; SAINAI NAOFUMI	DAI ICHI KOGYO SEIYAKU CO LTD	Plasticizer emulsion, method for producing the same and biodegradable resin composition using the same.
JP2005060689 A	20050310	JP4910270 B2 20120404	JP20040221739 20040729; JP20030204417 20030731	KUMAZAWA SADANORI; OOME HIROKAZU	TORAY INDUSTRIES	Foam and its producing method.
JP2005120118 A	20050512	JP4659351 B2 20110330; CN1867630 A 20061122; CN100434475 C 20081119	JP20030353128 20031014	TANAKA KAZUYA; TAKAGI JUN	MITSUBISHI PLASTICS IND	Flame-retardant injection-molded body.
JP2005120119 A	20050512	JP4777606 B2 20110921	JP20030353129 20031014	TANAKA KAZUYA; TAKAGI JUN; KATO YUKIO	MITSUBISHI PLASTICS IND	Flame-retardant injection-molded body.
JP2005162871 A	20050623	CN1914278 A 20070214	JP20030403475 20031202	HORIE TAKESHI; YAMADA SHINICHIRO; FUJIHIRA HIROKO; MORI HIROYUKI; NOGUCHI TSUTOMU	SONY CORP	Resin composition, molded product, electrical product, and method for producing the resin composition.
JP2005200600 A	20050728		JP20040010325 20040119	YAMADA TAKAYUKI; WATANABE TAKAYUKI; KITAHARA YASUHIRO; SUGI MASAHIRO	MITSUI CHEMICALS INC	Lactic acid-based polymer composition.
JP2005248062 A	20050915		JP20040061879 20040305	SAKAI TAKASHI; FUKAWA SOJI	TOYO INK MFG CO	Color molding biodegradable resin composition and molded product.
JP2005248139 A	20050915		JP20040026324 20040203; JP20040127958 20040423	SHIGA KENJI	TOYO BOSEKI	Pigment masterbatch and resin composition and molded product composed of the same.

Continued

—Cont'd

Patent Number	Publication Date	Family Members	Priority Numbers	Inventors	Applicants	Title
JP2006083262 A	20060330		JP20040268262 20040915	TACHIKA HIROSHI; SHIGA KENJI	TOYO BOSEKI	Electroconductive resin composition, method for producing the same and planar heating element using the same.
JP2007246707 A	20070927		JP20060072692 20060316	YOSHIDA KAZUNORI; MAEDA NOBORU	SANYO CHEMICAL IND LTD	Plasticizer for polylactic acid.
JP2008069299 A	20080327	JP4942436 B2 20120530	JP20060250484 20060915	UYAMA HIROSHI; DOI MIKIO; TAKASE YOSHIHIKO; OKUBO TSUTOMU	TAIYO KAGAKU KK; UNIV OSAKA	Plasticized polylactic acid composition.
JP2008195834 A	20080828		JP20070032799 20070214	KAMIYA SOICHIRO; MATSUI HITOSHI	RIKEN VITAMIN CO	Resin composition, and packaging film formed by molding the same.
JP2009242520 A	20091022		JP20080089383 20080331	MATSUI HITOSHI; KAMIYA SOICHIRO	RIKEN VITAMIN CO	Polylactic acid resin composition and molded article obtained by molding the same.
JP2010070621 A	20100402		JP20080238697 20080917	IWASAKI SHOHEI; YOSHIMURA MASAFUMI	NEW JAPAN CHEM CO LTD	Masterbatch and method for manufacturing the same.
JP2010260900 A	20101118		JP20090110709 20090430	NARITA JUNICHI	TOHCELLO CO LTD	Polylactic acid film and method for manufacturing the same.
JP2011111541 A	20110609		JP20090269648 20091127	SUZUKI AKIHIRO; FUKUNAGA SHOICHI; ADACHI MINORU	JAPAN POLYPROPYLENE CORP	Polylactic acid-containing master batch, method for producing the same, polylactic acid-containing propylene-based resin composition and molded product thereof.
JP2013043959 A	20130304		JP20110184205 20110826		UNITIKA LTD	Polylactic acid resin composition and molding.
JP2013079356 A	20130502		JP20110207372 20110922; JP20110270172 20111209		UNITIKA LTD	Polylactic acid-based resin composition.

JPH04335060 A	19921124	JP3105020 B2 20001030	JP19910105673 19910510	AJIOKA MASANOBU; ENOMOTO TSUYOSHI; YAMAGUCHI TERUHIRO; SHINODA NORIMASA	MITSUI TOATSU CHEMICALS	Degradable thermoplastic polymer composition.
JPH06263892 A	19940920	JP3353117 B2 20021203	JP19920348377 19921228	TOKIWA YUTAKA; FUJII KIYOTOSHI	AGENCY IND SCIENCE TECHN; SHOWA CHEM	Microbially degradable thermoplastic resin film.
JPH06306264 A	19941101	JP3290496 B2 20020610	JP19930094056 19930421	AJIOKA MASANOBU; HIGUCHI CHOJIRO; YAMAGUCHI TERUHIRO; SUZUKI KAZUHIKO	MITSUI TOATSU CHEMICALS	Thermoplastic polymer composition.
JPH07177826 A	19950718	JP3347440 B2 20021120	JP19930323740 19931222	SUGA KEIKO; IMON SHUHEI; MORIYA SHINOBU; KUROKI TAKAYUKI; SHINODA NORIMASA	MITSUI TOATSU CHEMICALS	Agricultural film.
JPH08193165 A	19960730	JP3359764 B2 20021224	JP19940313009 19941216; JP19930327858 19931224; JP19940280810 19941115	SUZUKI KAZUHIKO; NAKADA TOMOYUKI; WATANABE TAKAYUKI; KITAHARA YASUHIRO; AJIOKA MASANOBU	MITSUI TOATSU CHEMICALS	Heat-resistant lactic acid polymer molding.
JPH08199052 A	19960806	JP3391133 B2 20030331	JP19950011724 19950127	MATSUI MASAO; INOKAWA YASUSHI	SHIMADZU CORP	Plasticized polylacitc acid and its molded item.
JPH08199053 A	19960806	JP3419127 B2 20030623	JP19950011725 19950127	MATSUI MASAO; KOSEKI HIDEKAZU	SHIMADZU CORP	Plasticized polylactic acid and its molded item.
JPH08231837 A	19960910	JP3387255 B2 20030317	JP19950041035 19950228	MATSUI MASAO; INOKAWA YASUSHI	SHIMADZU CORP	Antistatic polylactic acid and molded product thereof.
JPH08245866 A	19960924	JP3348752 B2 20021120	JP19950049365 19950309	MATSUI MASAO; KOSEKI HIDEKAZU	SHIMADZU CORP	Plasticized polylactic acid and its molded item.

Continued

—Cont'd

Patent Number	Publication Date	Family Members	Priority Numbers	Inventors	Applicants	Title
JPH08283557 A	19961029		JP19950087152 19950412	MATSUI MASAO; KOSEKI HIDEKAZU	SHIMADZU CORP	Plasticized polylactic acid composition and its molded item.
JPH083432 A	19960109	JP3334338 B2 20021015	JP19940139023 19940621	NOGUCHI HIROSHI; KASAI ATSUSHI; OTA TAKAYUKI; MIYAZAKI KEIKO; ISHII YUKIKO	MITSUBISHI CHEM CORP	Polylactic acid resin composition.
JPH0834913 A	19960206	JP3472644 B2 20031202	JP19950108450 19950502; JP19940105232 19940519; US19950434540 19950504	SUZUKI KAZUHIKO; WATANABE TAKAYUKI; KITAHARA YASUHIRO; AJIOKA MASANOBU; IMON SHUHE	MITSUI TOATSU CHEMICALS	L-lactic acid polymer composition, molded product and film.
JPH09221587 A	19970826	JP3592819 B2 20041124	JP19960026416 19960214	TAKAGI JUN; TERADA SHIGENORI	MITSUBISHI PLASTICS IND; SHIMADZU CORP	Antistatic polylactic acid film and sheet.
JPH09296103 A	19971118	JP3674152 B2 20050720	JP19960134260 19960430	OTA MASAAKI; KUYAMA HIROKI	SHIMADZU CORP	Polylactic acid composition.
JPH10158369 A	19980616		JP19960319190 19961129	KAWAGUCHI TATSUYA; OBUCHI SEIJI; NAKADA TOMOYUKI; WATANABE TAKAYUKI; KITAHARA YASUHIRO; SUZUKI KAZUHIKO; AJIOKA MASANOBU	MITSUI CHEMICALS INC	Resin composition and molding product thereof.
JPH1036650 A	19980210		JP19960190488 19960719	NAKADA TOMOYUKI; WATANABE TAKAYUKI; KITAHARA YASUHIRO; OBUCHI SEIJI; SUZUKI KAZUHIKO; AJIOKA MASANOBU	MITSUI PETROCHEMICAL IND	Polymer composition.

JPH1086307 A	19980407	JP3439621 B2 20030825	JP19970095927 19970414; JP19960096616 19960418; JP19960105125 19960425	KOBAYASHI NAOKI; IMON SHUHEI; KOUNO AKIRA; KUROKI TAKAYUKI; WANIBE HIROTAKA	MITSUI PETROCHEMICAL IND	Aliphatic polyester coating film.
JPH1087975 A	19980407	JP3671547 B2 20050713	JP19960265326 19960913	IKEDA NAOKI; YOSHIMURA MASAFUMI; KIMURA YOSHIHARU	NEW JAPAN CHEM CO LTD	Polylactic acid-based resin composition.
JPH11323113 A	19991126	JP3707240 B2 20051019	JP19980125762 19980508	ISHIHARA JIRO; KANAMORI KENJI; HORIBE YASUMASA; KOSEKI HIDEKAZU	SHIMADZU CORP	Polylactic acid composition.
TW201043661 A	20101216		TW20090119885 20090615; TW20090134480 20091012	WAY TUN-FUN; HWANG SHI-KUANG; HUA JIAN-LIN	IND TECH RES INST	Plasticizers for modifying polylactic acid by blending with polylactic acid and fabrication method thereof.
US1995970 A	19350326		US19310527854 19310404	LOWRANCE DOROUGH GEORGE	DU PONT	Polymeric lactide resin.
US2004024141 A1	20040205	TWI302550 B 20081101; KR20040014193 A 20040214; JP2004067801 A 20040304; JP3955245 B2 20070808; EP1388562 A1 20040211; EP1388562 B1 20061122; DE60309787 T2 20070913; CN1473875 A 20040211; CN1324082 C 20070704	JP20020227323 20020805	HASEBE TADASHI; SASHITA KAZUYUKI	RIKEN VITAMIN CO	Biodegradable polyester resin composition and films, sheets and other molded articles thereof.
US2007100037 A1	20070503	US7501464 B2 20090310; JP2007126653 A 20070524; JP5089133 B2 20121205; EP1790677 A1 20070530; CN1974660 A 20070606; CN1974660 B 21 20110921	US20050731260P 20051031; US20060588341 20061027	SATO HIROYUKI; AKUTSU FUMIO; KOBAYASHI FUMINORI; HOKARI YUKI	KUREHA CORP	Process for producing aliphatic polyester composition.
US2012259047 A1	20121011	JP2012229404 A 20121122	JP20110087315 20110411; JP20120085606 20120404	AKUTSU FUMIO; HAYASHI NAOKI; SATO HIROYUKI; SHIBATA MASUMI; WATANABE AKIKO	KUREHA CORP	Aliphatic polyester resin composition and process for production thereof.

Continued

—Cont'd

Patent Number	Publication Date	Family Members	Priority Numbers	Inventors	Applicants	Title
US2012289618 A1	20121115	KR20120126769 A 20121121	KR20110044812 20110512	JUNG YOUNGMEE; KIM SOO HYUN; KIM SANG-HEON; PURNAMA PURBA	KOREA INST SCI & TECH	Preparation method of clay/polymer composite using supercritical fluid-organic solvent system.
US3498957 A	19700303		US19650487295 19650914	JACOBSON HENNING W	ETHICON INC	Polymerization of cyclic carboxylic esters in the presense of a nonpolymerizable ester plasticizer.
US3636956 A	19720125	ZA7100808 A 19711124; US3636956 X6 19720125; SE361599 B 19731112; NO132784 B 19750929; NO132784 C 19760107; NL7103263 A 19711116; JPS4936597 B1 19741002; FR2088548 A1 19720107; FR2088548 B1 19750926; FI52523 B 19770630; FI52523 C 19771010; DE2062604 A1 19711125; CH573752 A5 19760331; CA982007 A1 19760120; BE758156 A4 19710428	US19700036797 19700513	SCHNEIDER ALLAN K	ETHICON INC	Polylactide sutures.
US5180765 A	19930119		US19900579005 19900906; US19880229896 19880808; US19890387678 19890731	SINCLAIR RICHARD G	BIOPAK TECHNOLOGY LTD	Biodegradable packaging thermoplastics from lactides.
US5359026 A	19941025	WO9504097 A1 19950209; US5998552 A 19991207; US5594095 A 19970114; US5798435 A 19980825; US6291597 B1 20010918; NZ271513 A 19970526; JPH09501456 A 19970210; JP3369185 B2 20030120; FI960433 A 19960130; FI112083 B 20031031;	US19930100550 19930730	GRUBER PATRICK RICHARD; KOLSTAD JEFFREY JOHN; WITZKE DAVID ROY; HARTMANN MARK HENRY; BORSCH ANDREA	CARGILL INC	Viscosity-modified lactide polymer composition and process for manufacture thereof.

		EP0711314 A1 19960515; EP0711314 B1 20021002; EP0711314 B9 20030402; ES2186689 T3 20030516; DK0711314 T3 20030210; DK0711314 T5 20030818; DE69431483 T2 20030731; CA2168041 A1 19950209; CA2168041 C 20071009; BR9407212 A 19960917; AU684303 B2 19971211; AU7516294 A 19950228; AT225378 T 20021015				
US5908918 A	19990601	US5756651 A 19980526	US19980084563 19980526; US19960682095 19960717	CHEN XIAOMAO; SCHILLING KEVIN H; KELLY JR WILLIAM E	CHRONOPOL INC	Impact modified polylactide.
US6136905 A	20001024	US5763513 A 19980609; EP0683207 A2 19951122; EP0683207 A3 19960221; EP0683207 B1 19990331	US19970996477 19971222; US19950434540 19950504; JP19940105232 19940519	SUZUKI KAZUHIKO; WATANABE TAKAYUKI; KITAHARA YASUHIRO AJIOKA MASANOBU; IKADO SHUHEI	MITSUI CHEMICALS INC	L-lactic acid polymer composition, molded product and film.
US6156929 A	20001205	EP1116746 A2 20010718; EP1116746 A3 20011212; CA2298327 A1 20010714; CA2298327 C 20081014	US20000483482 20000114; US19980164887 19981001	CHANDLER CHRISTOPHE; MIKSIC BORIS A; AHLBRECHT ARTHUR H; CURRIER JUDE	CORTEC CORP	Biodegradable film.
WO0100730 A1	20010104	US6462105 B1 20021008; TWI255837 B 20060601; EP1108751 A1 20010620; EP1108751 B1 20071024; DE60036845 T2 20080521	JP19990179241 19990625; JP20000122041 20000424	KUROKI TAKAYUKI; IKADO SHUHEI	MITSUI CHEMICALS INC	Aliphatic polyester composition for masterbatch and process for producing aliphatic polyester film with the composition.
WO02087877 A1	20021107	US2004161622 A1 20040819; US7144634 B2 20061205; EP1385700 A1 20040204; EP1385700 B1 20050727; AU2002338496 B2 20070426; AT300423 T 20050815	DE2001121153 20010430	OSENBAUM SONJA; HAEDE PETRA; BUSCH DETLEF	TRESPAPHAN GMBH	Polylactic acid (PLA) film having good antistatic properties.

Continued

—Cont'd

Patent Number	Publication Date	Family Members	Priority Numbers	Inventors	Applicants	Title
WO03011959 A1	20030213	US2003100645 A1 20030529; US7910645 B2 20110322; PT1412425 E 20070131; JP2004536941 A 20041209; ES2274996 T3 20070601; EP1412425 A1 20040428; EP1412425 B1 20061018; DE60215511 T2 20070606; CN1537140 A 20041013; CN100379803 C 20080409; BR0211556 A 20040713; AU2002324595 B2 20070628; AT342936 T 20061115	US20010309318P 20010801	AHMED SHARF U; EMIRU ANDUALEM W	FULLER H B LICENSING FINANC	Breathable biodegradable hot melt composition.
WO2003037956 A1	20030508	WO03037956 A9 20040521; US2003125431 A1 20030703; US6951956 B2 20051004; US2003125508 A1 20030703; JP2009030068 A 20090212; JP4704456 B2 20110615; JP4256779 B2 20090422; EP1449864 A1 20040825; EP1449864 A4 20050420; EP1449864 B1 20091202; EP1914258 A1 20080423; EP1914258 B1 20101124; CN1827686 A 20060906; CN1827686 B 20100512; CN1608093 A 20050420; CN1280333 C 20061018; CA2710098 A1 20030508; CA2710098 C 20121023; CA2464635 A1 20030508; CA2464635 C 20110322; AU2002343784 B2 20080131; AU2002343784 C1 20080911; AT489415 T 20101215; AT450556 T 20091215	US20020132578 20020425; JP20020007839 20020116; JP20010335443 20011031	YAMANE KAZUYU KIMIURA HIROMITSU; ONO TOSHIHIKO; NAKAJIMA JUNJI; ITOH DAISUKE	KUREHA CHEMICAL IND CO LTD	Crystalline polyglycolic acid, polyglycolic acid composition and processes for production of both.

WO2004069930 A1	20040819	US2008214713 A1 20080904; JP2004262971 A 20040924; KR20060010716 A 20060202; KR101010385 B1 20110121; JP4628649 B2 20110209; EP1605017 A1 20051214; EP1605017 A4 20060412; EP1605017 B1 20090107; CN1748003 A 20060315; CN100419023 C 20080917	JP20030031856 20030210	ASEBE TADASHI; KAMIYA SOICHIRO; SASHITA KAZUYUKI	RIKEN VITAMIN CO	Antistatic method for biodegradable polyester resin composition and products thereof.
WO2005040282 A1	20050506	US2007060687 A1 20070315; EP1679349 A1 20060712; CN1845970 A 20061011	JP20030368611 20031029	KODAMA SAI; INAYAMA TOSHIHIRO; MURATA SHIGERU	KYOWA HAKKO CHEMICAL CO LTD	Resin composition.
WO2005061626 A1	20050707	US2008071015 A1 20080320; US7790069 B2 20100907; US2010311886 A1 20101209; US8202450 B2 20120619; JP2011168798 A 20110901; JP4894263 B2 20120314; CN1914279 A 20070214; CN1914279 B 20100505	JP20030422239 20031219	KIUCHI YUKIHIRO; YANAGISAWA TSUNENORI; TANAKA SYUKICHI; SOYAMA MAKOTO; INOUE KAZUHIKO; IJI MASATOSHI	NEC CORP	Flame resistant thermoplastic resin composition.
WO2005066256 A1	20050721	US2011178213 A1 20110721; US2010130652 A1 20100527; US2005209377 A1 20050922; US8003719 B2 20110823; US7718720 B2 20100518; JP2007517126 A 20070628; HK1097412 A1 20090123; ES2315737 T3 20090401; EP1964879 A1 20080903; EP1964879 B1 20120613; EP1704180 A1 20060927; EP1704180 A4 20070221; EP1704180 B1 20080910; CN1922255 A 20070228; CN1922255 B 20110119; CA2550009 A1 20050721; CA2550009 C 20130514; BRPI0418339 A 20070502; AU2004312517 A1 20050721; AU2004312517 B2 20100708; AT407967 T 20080915	US20030533640P 20031230; US20040783995 20040220	PADWA ALLEN R	METABOLIX INC	Nucleating agents.

Continued

—Cont'd

Patent Number	Publication Date	Family Members	Priority Numbers	Inventors	Applicants	Title
WO2005097894 A1	20051020	US2007299170 A1 20071227; US7531585 B2 20090512; KR20070009584 A 20070118; KR101152973 B1 20120611; JP4973848 B2 20120711; ES2379361 T3 20120425; EP1736510 A1 20061227; EP1736510 A4 20080521; EP1736510 B1 20111221; CN1938378 A 20070328; CN100384937 C 20080430; AT538176 T 20120115	JP20040097361 20040330	OZAWA MASAAKI; KAWAMURA YASUO; KASAI MIKIO	NISSAN CHEMICAL IND LTD	Polylactic acid resin composition.
WO2006012917 A1	20060209	US2008139702 A1 20080612; PT1781798 E 20100616; MX2007001297 A 20080304; JP2008509234 A 20080327; ES2344951 T3 20100910; EP1781798 A1 20070509; EP1781798 B1 20100602; CN101035902 A 20070912; CN101035902 B 20120704; CA2575273 A1 20060209; CA2575273 C 20121016; BRPI0418990 A 20071211; AU2004322084 A1 20060209; AU2004322084 B2 20091126; AT469977 T 20100615	WO2004EP08874 20040806	BUENO DE ALMEIDA WANDERSON; SILVA BIZZARRI PABLO; SERTORI DURAO ANTONIO; DO NASCIMENTI JEFTER FERNANDES	COGNIS BRASIL LTDA; PHB IND SA; COGNIS DEUTSCHLAND GMB	Use of fatty alcohols as plasticizer to improve the physical–mechanical properties and processability of phb and its co-polymers.
WO2006054493 A1	20060526	US2008194739 A1 20080814; US2011101566 A1 20110505; KR20070095875 A 20071001; JP2012162724 A 20120830; JP5054978 B2 20121024; EP1816169 A1 20070808; EP2333016 A1 20110615; EP1816169 A4 20090916; EP1816169 B1 20120111; CN102161832 A 20110824; CN102161832 B 20130626; CN101056948 A 20071017; CN101056948 B 20110413	JP20040336012 20041119	YAMASHITA TAKEHIKO; TAKEDA KUNIHIKO	PANASONIC CORP	Flame-retardant resin composition, process for producing the same, method of molding the same.

WO2006095526 A	20060914	US2008167409 A1 20080710; US8293826 B2 20121023; EP1860153 A1 20071128; EP1860153 A4 20090415; EP1860153 B1 20110406; CN101133121 A 20080227; CN101133121 B 20110713; AT504630 T 20110415	JP20050063668 20050308	HOKARI YUKI; IKEDA TSUKASA; YAMANE KAZUYUKI	KUREHA CORP	Aliphatic polyester resin composition.
WO2007095708 A1	20070830	US2009082491 A1 20090326; JP2009527593 A 20090730; DOP2007000038 A 20070830; CA2641922 A1 20070830; BRPI0600681 A 20071120; AU2007218992 A1 20070830	BR2006PI00681 20060224	NASCIMENTO JEFTER FERNANDES; PACHEKOSKI WAGNER MAURICIO; AGNELLI JOSE AUGUSTO MARCONDES	PHB IND SA	Environmentally degradable polymeric blend and process for obtaining an environmentally degradable polymeric blend.
WO2007095709 A1	20070830	US2009018235 A1 20090115; JP2009527594 A 20090730; DOP2007000034 A 20070915; CA2641924 A1 20070830; BRPI0600683 A 20071120; AU2007218993 A1 20070830	BR2006PI00683 20060224; WO2007BR00045 20070223	NASCIMENTO JEFTER FERNANDES; PACHEKOSKI WAGNER MAURICIO; AGNELLI JOSE AUGUSTO MARCONDES	PHB IND SA	Environmentally degradable polymeric composition and process for obtaining an environmentally degradable polymeric composition.
WO2007095711 A1	20070830	US2009030112 A1 20090129; JP2009527596 A 20090730; DOP2007000032 A 20070915; CA2641926 A1 20070830; BRPI0600783 A 20071120; AU2007218995 A1 20070830	BR2006PI00783 20060224	NASCIMENTO JEFTER FERNANDES; PACHEKOSKI WAGNER MAURICIO; ARENA DAWSON BUIM; COELHO ANA CRISTINA	PHB IND SA; LOGOS QUIMICA LTDA	Biodegradable polymeric composition and method for producing a biodegradable polymeric composition.
WO2007095712 A1	20070830	US2009023836 A1 20090122; JP2009527597 A 20090730; DOP2007000036 A 20070915; CA2641927 A1 20070830; BRPI0600787 A 20071120; AU2007218996 A1 20070830	BR2006PI00787 20060224	NASCIMENTO JEFTER FERNANDES; PACHEKOSKI WAGNER MAURICIO; AGNELLI JOSE AUGUSTO MARCONDES	PHB IND SA	Environmentally degradable polymeric composition and method for obtaining an environmentally degradable polymeric composition.
WO2008011668 A1	20080131	US2009312456 A1 20091217; US2011086950 A1 20110414; US8067485 B2 20111129; US8232348 B2 20120731; TW200831601 A 20080801; NZ575069 A 20100930; KR20090054434 A 20090529; JP2009544826 A 20091217; IL196761 A 20130228;	AU20060904095 20060728	CHANGPING CHEN	BIOGRADE HONG KONG PTY LTD; TRISTANO PTY LTD	Masterbatch and polymer composition.

Continued

—Cont'd

Patent Number	Publication Date	Family Members	Priority Numbers	Inventors	Applicants	Title
		EP2052030 A1 20090429; CN102167890 A 20110831; CN101516996 A 20090826; CN101516996 B 20111012; CA2659123 A1 20080131; BRPI0715054 A2 20130528; AU2007278752 A1 20080131; AR062138 A1 20081015				
WO2008012981 A1	20080131	US2009226655 A1 20090910; KR20090023737 A 20090305; KR101039649 B1 20110609; JP2008030306 A 20080214; EP2047967 A1 20090415; CN101495290 A 20090729; CN101495290 B 20120725; CA2658794 A1 20080131; AU2007277961 A1 20080131; AU2007277961 B2 20100527	JP20060206473 20060728	SUGAI MASAHIRO; SUZUKI MASATO; SHIMURA HIROMI; CHIBA JUNICHI	YOSHINO KOGYOSHO CO LTD	Heat-resistant poly(L-lactic acid) preform.
WO2009092825 A1	20090730	US2011054099 A1 20110303; US8084551 B2 20111227; JP2011510148 A 20110331; EP2256149 A1 20101201; EP2256149 A4 20120321; CN101970547 A 20110209; CA2712709 A1 20090730	WO2008ES00038 20080125	FIORI STEFANO; ARA PAOLO	ARA PATRIZIA MARINA; ARA MARCO PAOLO	Method for plasticizing lactic acid polymers.
WO2009125872 A1	20091015	KR20100131482 A 20101215; EP2264103 A1 20101222; EP2264103 A4 20130918; CN101990565 A 20110323		KISHIMOTO HIROAKI; TAKENAKA AKIRA; KIUCHI YUKIHIRO; YANAGISAWA TSUNENORI; INOUE KAZUHIKO; IJI MASATOSHI; SERIZAWA SHIN	KAO CORP; NEC CORP	Polylactic acid resin composite.
WO2010051589 A1	20100514	US2012077905 A 120120329; NZ593179 A 20120525; KR20110095293 A20110824; JP2012507614 A 20120329; EP2352781 A1 20110810; EP2352781 A4 20130313; CN102282197 A 20111214; CA2742933 A1 20100514; AU2009311259 A1 20100514	AU20080905740 20081106	CHANGPING CHEN; SCHEIRS JOHN	TRISTANO PTY LTD	Biodegradable polymer composition.

WO2011040905 A1	20110407	US2012165422 A1 20120628; CN102575076 A 20120711; CA2775703 A1 20110407	WO2009US58812 20090929	VERNON GARY; ROSENDALE DAVID	POLYONE CORP	Polyester articles having simulated metallic or pearlescent appearance.
WO2011050479 A1	20110505	WO2011050480 A1 20110505; CA2776948 A1 20110505; CA2776946 A1 20110505; US2012302671 A1 20121129; EP2493979 A1 20120905; EP2493978 A1 20120905; AU2010312244 A1 20120517; AU2010312243 A1 20120517; US2013131225 A1 20130523	US20090256167P 20091029; US20090256177P 20091029	REID TOBY SIMON OLIVER; TAHERI KAMBIZ; DADDEY ERNEST OHENE KORANTENG; STAMBOULIDES CHRISTOS	SOLE GEAR DESIGN INC	Compositions comprising polylactic acid, bentonite, and gum arabic.
WO2011082052 A1	20110707	US2012270978 A1 20121025; KR20120109571 A 20121008; JP2013515822 A 20130509; EP2519579 A1 20121107; CN102892820 A 20130123	US20090290356P 20091228	MYERS SASHA B; JENNEN JAY M; AUSEN RONALD W; SPAWN TERENCE D; ANDERSON KELLY S; FRANK JOHN W	3M INNOVATIVE PROPERTIES CO	Plasticized polylactide.
WO2011122080 A1	20111006	US2013012631 A1 20130110; CN102834458 A 20121219	JP20100077915 20100330	SERIZAWA SHIN; KIUCHI YUKIHIRO; IJI MASATOSHI	NEC CORP	Flame-retardant polylactide resin composition, molded object made therefrom, and manufacturing method thereof.
WO2012012064 A1	20120126	US2013093119 A1 20130418	US20100360062P 20100630	HAGBERG ERIK	ARCHER DANIELS MIDLAND CO	Processes for producing thermostable polyhydroxyalkanoate and products produced thereof.
WO2012043219 A1	20120405	US2012329920 A1 20121227; US8440748 B2 20130514; EP2524945 A1 20121121; EP2524945 A4 20121121; EP2524945 B1 20131113; KR20120116995 A 20121023; JP4962662 B2 20120627; CN102869724 A 20130109	JP20110121494 20110531; JP20100216644 20100928	SATO DAISUKE; ONOUE YOSUKE; KUMAZAWA SADANORI	TORAY INDUSTRIES	Thermoplastic resin composition and molded item formed from same.
WO2012086192 A1	20120628	JP2012131072 A 20120712; CN103260840 A 20130821	JP20100283537 20101220	KISHIMOTO HIROAKI; TAKENAKA AKIRA	KAO CORP	Method for producing polylactic resin composition.

Continued

—Cont'd

Patent Number	Publication Date	Family Members	Priority Numbers	Inventors	Applicants	Title
WO2012141660 A1	20121018	US2014039096 A1 20140206; SK262011 A3 20121105; SG194040 A1 20131129; CN103459498 A 20131218; CA2833131 A1 20121018	SK20110000026 20110411	ALEXY PAVOL; CHODAK IVAN; BAKOS DUSAN; BUGAJ PETER; PAVLACKOVA MIROSLAVA; TOMANOVA KATARINA; BENOVIC FRANTISEK; PLAVEC RODERIK; MIHALIK MICHAL; BOTOSOVA MONIKA	USTAV POLYMEROV SAV	Biologically degradable polymeric composition with high deformability.
WO2013016444 A2	20130131	WO2013016444 A3 20130711	US201161512330P 20110727	AVAKIAN ROGER W; HU LING	POLYONE CORP	Crosslinkable bioplasticizers.
WO2013046487 A1	20130404	US2013169127 A1 20130704; CN103124768 A 20130529	JP20110208585 20110926	NAGASHIMA TAKASHI; NAKAO SUGURU	PANASONIC CORP	Casing for electronic equipment.
WO2013131649 A1	20130912		EP20120001550 20120307	HOEKSTRA AAD; SCHENNINK GERALD G J; DE VOS SICCO	HUHTAMAEKI OYJ; PURAC BIOCHEM BV	An essentially biobased, thermoformable composition and containers formed thereof.
WO2013154255 A1	20131017	TW201341448 A 20131016; KR20130114344 A 20131018	KR20120036606 20120409	NAM SEUNG BAIK; SON JONG-SEOK	LG HAUSYS LTD	Biodegradable resin composition containing eco-friendly plasticizer, and biodegradable resin product using same.
WO9204413 A1	19920319	JPH06504799 A 19940602; FI930992 A 19930305; EP0548284 A1 19930630; CA2091185 A1 19920307; BR9106821 A 19930713; AU8660191 A 19920330	US19900579465 19900906; US19900579005 19900906; US19900579460 19900906; US19900579000 19900906	SINCLAIR RICHARD G; PRESTON JOSEPH R	BATTELLE MEMORIAL INSTITUTE	Packaging thermoplastics from lactic acid.

WO9732929 A1	19970912	US6117928 A 20000912; JP2000506204 A 20000523; FI961022 A 19970906; FI961022 A 19970906; FI105040 B 20000531; ES2170364 T3 20020801; EP0885261 A1 19981223; EP0885261 B1 20011219; DE69709320 T2 20020718; DK0885261 T3 20020325; AU2097097 A 19970922; AT211157 T 20020115		HILTUNEN ELINA; SELIN JOHAN-FREDRIK; SKOG MARIA	NESTE OY	Polylactide films.
WO9734953 A1	19970925	CA2231568 A1 19970925; AU5316296 A 19971010	WO1996US03738 19960319; CA19962231568 19960319	WNUK ANDREW JULIAN; MELIK DAVID HARRY; YOUNG TERRILL ALAN	PROCTER & GAMBLE	Biodegradable polymeric compositions and products thereof.
WO9945067 A1	19990910	US6235825 B1 20010522; JP3753254 B2 20060308; EP0980894 A1 20000223; EP0980894 A4 20020313; EP0980894 B1 20040623; DE69918233 T2 20050224	JP19980053685 19980305; JP19980053684 19980305	YOSHIDA YASUNORI; OBUCHI SHOJI; KITAHARA YASUHIRO; WATANABE TAKAYUKI; AIHARA HISASHI; NAKATA TOMOYUKI; SUZUKI KAZUHIKO; AJIOKA MASANOBU	MITSUI CHEMICALS INC	Polylactic acid resin composition and film thereof.

REFERENCES

[1] Flick EW. Plastics additives database. William Andrew, Incorporated// Plastics Design Library; 2004.

[2] Corporation R. Chemical additives for the plastics industry: properties, applications, toxicologies. New Jersey (USA): Radian Corporation, Noyes Publications; 1987.

[3] Vieira MGA, da Silva MA, dos Santos LO, Beppu MM. Natural-based plasticizers and biopolymer films: a review. Eur Polym J 2011;47:254–63.

[4] Niaounakis M. Biopolymers reuse, recycling, and disposal. Chapter 7: Degradability on Demand. Plastics Design Library (PDL). 1st ed. Oxford: William Andrew Publishing; 2013. pp.193–241. Access online via Elsevier.

[5] Lemmouchi Y, Murariu M, Santos AMD, Amass AJ, Schacht E, Dubois P. Plasticization of poly(lactide) with blends of tributyl citrate and low molecular weight poly(d,l-lactide)-b-poly(ethylene glycol) copolymers. Eur Polym J 2009;45:2839–48.

[6] Martin O, Avérous L. Poly(lactic acid): plasticization and properties of biodegradable multiphase systems. Polymer 2001;42:6209–19.

[7] Hu Y, Rogunova M, Topolkaraev V, Hiltner A, Baer E. Aging of poly(lactide)/poly(ethylene glycol) blends. Part 1. Poly(lactide) with low stereoregularity. Polymer 2003;44:5701–10.

[8] Hu Y, Hu YS, Topolkaraev V, Hiltner A, Baer E. Crystallization and phase separation in blends of high stereoregular poly(lactide) with poly(ethylene glycol). Polymer 2003;44:5681–9.

[9] Sinclair RG. The case for polylactic acid as a commodity packaging plastic. J Macromol Sci Part A 1996;33:585–97.

[10] Hu Y, Hu YS, Topolkaraev V, Hiltner A, Baer E. Aging of poly(lactide)/poly(ethylene glycol) blends. Part 2. Poly(lactide) with high stereoregularity. Polymer 2003;44:5711–20.

[11] Younes H, Cohn D. Phase separation in poly(ethylene glycol)/poly(lactic acid) blends. Eur Polym J 1988;24:765–73.

[12] Ljungberg N, Wesslén B. Tributyl citrate oligomers as plasticizers for poly (lactic acid): thermo-mechanical film properties and aging. Polymer 2003;44:7679–88.

[13] Ljungberg N, Andersson T, Wesslén B. Film extrusion and film weldability of poly(lactic acid) plasticized with triacetine and tributyl citrate. J Appl Polym Sci 2003;88:3239–47.

[14] Ljungberg N, Wesslén B. The effects of plasticizers on the dynamic mechanical and thermal properties of poly(lactic acid). J Appl Polym Sci 2002;86:1227–34.

[15] Anderson KS, Schreck KM, Hillmyer MA. Toughening polylactide. Polym Rev 2008;48:85–108.

[16] Piorkowska E, Kulinski Z, Galeski A, Masirek R. Plasticization of semicrystalline poly(l-lactide) with poly(propylene glycol). Polymer 2006;47:7178–88.

[17] Jacobsen S, Frintz HG. Plasticizing polylactide – the effect of different plasticizers on the mechanical properties. Polym Eng Sci 2004;39:1303–10.

[18] Martino VP, Jiménez A, Ruseckaite RA. Processing and characterization of poly(lactic acid) films plasticized with commercial adipates. J Appl Polym Sci 2009;112:2010–8.

[19] Jacobsen S, Fritz HG. Plasticizing polylactide – the effect of different plasticizers on the mechanical properties. Polym Eng Sci 1999;39:1303–10.

[20] Labrecque LV, Kumar RA, Davé V, Gross RA, McCarthy SP. Citrate esters as plasticizers for poly(lactic acid). J Appl Polym Sci 1997;66:1507–13.

[21] Wypych G. In: Wypych G, editor. Handbook of plasticizers. William Andrew; 2004. p. 312.

[22] Ali F, Chang Y-W, Kang SC, Yoon JY. Thermal, mechanical and rheological properties of poly (lactic acid)/epoxidized soybean oil blends. Polym Bull 2009;62:91–8.

[23] Xu Y-Q, Qu J-P. Mechanical and rheological properties of epoxidized soybean oil plasticized poly(lactic acid). J Appl Polym Sci 2009;112:3185–91.

[24] Baltieri RC, Innocentini Mei LH, Bartoli J. Study of the influence of plasticizers on the thermal and mechanical properties of poly (3-hydroxybutyrate) compounds. Macromol Symp 2003;197:33–44.

[25] Choi JS, Park WH. Effect of biodegradable plasticizers on thermal and mechanical properties of poly(3-hydroxybutyrate). Polym Test 2004;23:455–60.

[26] Markarian J. Biopolymers present new market opportunities for additives in packaging. Plastics, Addit Compd 2008;10:22–5.

[27] Sherman LM. Enhancing biopolymers: additives are needed for toughness, heat resistance & processability. Online article can be found in http://wwwptonlinecom/articles/enhancing-biopolymers-additives-are-needed-for-toughness-heat-resistance-processability [accessed 16.02.14]. Plastics Technology.

[28] Naitove M. Additives and colorants score dramatic advances. Plastics technology March 2008. http://www.ptonline.com/articles/additives-and-colorants-score-dramatic-advances.

[29] Clariant masterbatches. CESA® additive masterbatches antistat, antifog; September 2013. http://www.masterbatches.com/C12575E4001FB2B8/vwLookupDownloads/Additives_Brochure_Short_ClariantMB_en.pdf/$FILE/Additives_Brochure_Short_ClariantMB_en.pdf.

Chapter 6

Powdering

This chapter relates only to methods of preparing particles from preformed biopolymers.

Conventional methods for producing fine polymer particles can be roughly divided into two types: (1) building-up processes such as emulsion polymerization, and (2) top-down processes such as pulverization (e.g., by mechanical crushing), pelletization (e.g., by melt kneading), dissolution-deposition, and emulsion-precipitation. The major building-up processes are beyond the scope of this chapter.

Biodegradable polymer particles have a multitude of uses. They are mainly used in medical applications as delivery carriers for the controlled release of therapeutic compositions and contrast or imaging agents in the human body. Biodegradable polymer particles also find uses in cosmetics, agriculture, paints, and coatings in genera.

6.1 PELLETIZATION

In the case of obtaining various forms, such as filament, film, and sheet, an ordinary thermoplastic polymer is generally melted, cooled, solidified, and pelletized to obtain a particulate forming resin material, which is then supplied for various forming processes.

Poly(lactic acid) (PLA) pellets can be manufactured in a similar way by: (1) melting PLA in an extruder at a temperature of about 190 °C; (2) extruding the PLA melt into strands; and (3) cooling in a water bath (water temperature is about 10 °C to room temperature). After leaving the water bath, part of the water that has adhered on the strands is removed by blowers and the strands are pelletized. If necessary, the pellets can further be subjected to a crystallization step to crystallize and/or dry the PLA. The shape of pellets obtained by this method is cylindrical. However, the cylindrical-shaped PLA pellets are agglomerated frequently when carrying out the following crystallization and/or drying steps, making the production difficult. In another aspect, the water content of the PLA pellets obtained after the crystallization step is very high (>800 ppm), and the pellets generally require further drying in order to reduce the hydrolysis of the PLA. Accordingly, such production method results have a high energy demand. More specifically, the process of rapid cooling from the high temperature of melt to a low temperature and then raising the temperature again results in mass energy consumption (2011, **US2011130513** A1, CHI MEI CORP).

In an alternative manufacturing method of PLA pellets, the outlet of a die used to extrude the polymer melt is positioned underwater, and the water is at a low temperature (e.g., 10 °C). The PLA melt is immediately cut into pellets by cutters outside the outlet of the die when extruded therefrom, and crystallization and/or drying can be further carried out depending on needs. The appearance of the pellets obtained by such a manufacturing method is slightly bead shaped (see Figure 6.1) showing a concave (81) in the surface of a pellet (80). However, the PLA pellets obtained by this method tend also to agglomerate and have a high water content (>600 ppm) (2011, **US2011130513** A1, CHI MEI CORP).

In an attempt to solve the aforementioned problems, **US2011130513** A1 (2011, CHI MEI CORP) provides a method for the preparation of bead-shaped PLA pellets, comprising a die-face cutting step (see Figure 6.2), a dewatering step, and a crystallization step, wherein the die-face cutting step is carried out by immersing the PLA melt under water at a temperature of 50–90 °C; the dewatering step is carried out in an atmosphere at a temperature of 80–150 °C; the crystallization step is carried out in an atmosphere at a temperature of 80–150 °C; the bead-shaped pellets finally obtained have a water content of 10–400 ppm, and smooth surfaces with no concaves.

The cooling with water step has also been considered impractical for some highly hydrolyzable biopolymers such as poly(glycolic acid) (PGA). This is because PGA is hydrolyzed in a stage when a melt thereof is introduced into water to be cooled, thus resulting in a PGA of a lower molecular weight having deteriorated properties. For this reason, the cooling subsequent to melting for formation of particulate forming material of PGA has been effected by air cooling. However, when a melt-extrudate (strand) of PGA is solidified by air cooling, for example, the strands after solidification are distorted and, when pelletized (e.g., into cylindrical pellets) by means of a cutter, etc. provide a particulate product having a broad particle size distribution, which is inconvenient for a subsequent product-forming step. Further, when the number of strands is increased in order to increase the productivity, inconveniences, such as entanglement and adhesion of the strands, are liable to occur (2007, **WO2007034805** A1, KUREHA CORP).

According to **WO2007034805** A1 (2007, KUREHA CORP) the above-mentioned hydrolysis of molten PGA in the water cooling step is associated with the glycolide

Biopolymers: Processing and Products. http://dx.doi.org/10.1016/B978-0-323-26698-7.00006-4

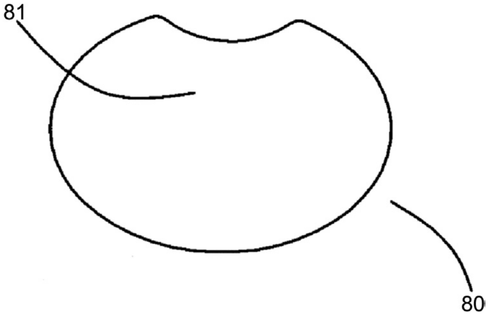


FIGURE 6.1 Schematic representation of the surface of a PLA pellet containing a concave (2011, **US2011130513** A1, CHI MEI CORP). 80: Pellet, 81: Concave.

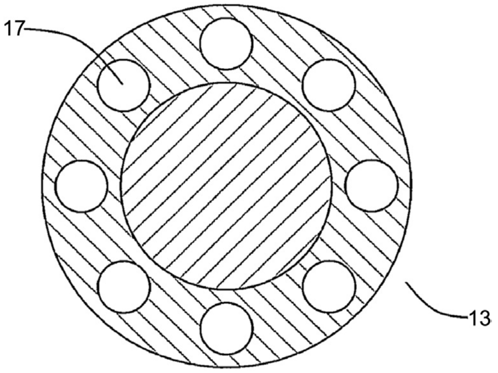


FIGURE 6.2 Schematic representation of an outlet portion of the die in the die-face cutting step (2011, **US2011130513** A1, CHI MEI CORP). 13: Outlet of die, 17: Small holes.

content in the molten PGA, and, if the glycolide content is suppressed to a certain level or below by an appropriate means, the hydrolysis and lowering in moisture resistance of the PGA during water cooling can be suppressed within a tolerable extent, and it becomes also possible to obtain a narrow particle size distribution of the particulate product. **WO2007034805** A1 (2007, KUREHA CORP) discloses a method for producing a granular PGA composition, based on the above findings, comprising cooling a PGA composition having a residual glycolide content of at most 0.6 wt% in the molten state, by contact with an aqueous cooling medium to solidify the composition, followed by pelletization.

WO0069916 A1 (2000, ATO BV) discloses a process for producing biopolymer nanoparticles, which in main embodiment are starch nanoparticles. In the process, the starch is plasticized in an extruder using shear forces, and a crosslinking agent (e.g., glyoxal) is added during the processing. The extrudate leaves the extruder through a five-hole die (diameter of holes 3 mm) and is subsequently granulated. The granules are cryogenically ground and sieved to obtain starch particles having an average particle size of less than 400 nm. After the processing, the starch nanoparticles can be dispersed in an aqueous medium.

WO2008022127 A2 (2008, ECOSYNTHETIX INC) discloses a modified version of the previous process for producing starch nanoparticles. The temperatures in the intermediate section of the extruder are preferably kept above 100 °C. The screw configuration includes two or more steam seal sections, each steam seal section having an upstream pressure generating section and an adjacent downstream mixing section. When the temperatures in the process exceed 100 °C, the steam seals prevent water from flashing to steam and back venting to the feed opening. This is done by gradually increasing the pressure in the extruder faster than the vapor pressure of water increases due to the increasing temperature used to cook and break down the starch for viscosity control. In the process, starch feedstock and a plasticizer are preferably added separately to the feeding zone of the extruder, and a crosslinking agent is added to the extruder downstream of the feed zone. An extrudate is formed through an extrusion die. The extrudate is transported to a hammer mill, where it is milled into smaller sized particles. The modified process can produce larger quantities of starch nanoparticles.

6.2 PULVERIZATION

Pulverization refers to the production of polymer particles by mechanical crushing, grinding, or shredding.

The extrudates of the last two patent applications in the previous section are ground or milled to obtain starch nanoparticles.

JP2007197602 A (2007, ASAHI CHEMICAL CORP) discloses a method for the preparation of PLA powder in which cylinder-shaped pellets having a crystallinity content of at least 20% and containing PLA having a molar ratio (L/D) of L-lactic acid to D-lactic acid of 90/10 that are heat treated at 80–160 °C for 80 min and pulverized at 40–100 °C. The pulverized mixture is cooled to obtain fine particles having an average particle diameter of 1–1000 μm. The obtained particles have a PLA content of 99% or more and a low-molecular-weight organic compound content of 0.05% or less. The obtained fine particles have favorable grindability and spike property, and can be used as scrub agent for cosmetics for hair cleaning, abrasive, coating, and toner.

JP2001288273 A (2001, KANEBO LTD) discloses a method for the preparation of PLA powder, comprising cooling chips or massive lumps of PLA at a low temperature of from −50 °C to −180 °C, and grinding and classifying them. The PLA powder is suitably used as a raw material for an aqueous dispersion adhesive. However, this technique requires freezing of the polymer. This leads to a larger energy cost, and the resulting crushed particles generally have random shapes.

WO2012133039 A1 and **WO2012133037** A1 (2012) of KUREHA CORP disclose methods for producing aliphatic polyester particles, particularly PGA, PLA, or particles of a mixture thereof, by pulverizing the aliphatic polyester at a temperature $T < T_g$ of the aliphatic polyester. The aliphatic polyester particles have an average particle size of 5–500 µm and are suitable for making pharmaceutical tablets. In a modified version of the aforementioned patents, **WO2012121296** A1 (2012, KUREHA CORP) discloses an aliphatic polyester particulate composition formed by adding an antiblocking agent to an aliphatic polyester particulate having an average particle size of 0.01–1000 µm.

WO2012098340 A (2012, ARKEMA FRANCE) discloses a method for the preparation of an aliphatic polyester powder comprising the following steps: (1) supplying an aliphatic polyester, preferably PLA, having an inherent viscosity of less than 0.5 dl/g; and (2) grinding the polyester, so as to obtain a polyester powder having a volume median diameter of less than 30 µm. Polyesters having a number-average molecular weight $M_n > 30{,}000$ g/mol are compounded with 0.1–20 wt%, preferably 1–15 wt% of a compound selected from alcohols, preferably polyols, and/or carboxylic acids, and subjected to depolymerization by melting and/or kneading, to achieve an optimal inherent viscosity of less than 0.5 dl/g, in order to obtain particles of average diameter less than 30 µm. The polyester powder is used for the production of cosmetic, pharmaceutical, and perfume products.

US2011287105 A1 (2011, MICRO POWDERS INC) discloses a method for micronizing PLA pellets to make them suitable for use in topical applications such as cosmetic and personal care compositions. The large PLA pellets can be processed to the required size according to methods generally known in the art, including grinding cryogenically on a disk mill (mechanical grinding) or air jet milling.

However, biopolymer-based microparticles produced by the pulverization methods have several problems. In particular, the grinding of PLA or PGA generates a substantial amount of fine particles, which is detrimental to the quality of the powder. The handling property of the fine particles is poor, and the overall surface area of the powder becomes large, affecting the degradation rate, which is increased. In the case of PGA, hygroscopicity is increased as result of a larger surface area (2012, **WO2012017832** A1, KUREHA CORP). Furthermore, particles produced by pulverization are not spherical in shape, particle diameter does not become smaller, particle diameter distribution is broad, and, in some cases, it is impossible to keep the particles in a round shape because of fiber-shaped ones or the like. Often, such particles have rough and/or jagged surfaces. Particularly, in the technical fields of cosmetics, where great importance is attached to feeling of touch and impression, or paints, where it is important to control rheology, effects produced by adding such microparticles were not sufficient hitherto.

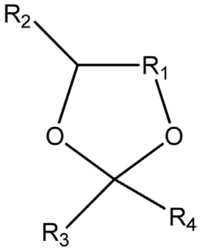
6.3 DISSOLUTION-DEPOSITION

In the dissolution-deposition method, the polymer is heated in the presence of an organic solvent up to a high temperature to form a polymer solution, which is then cooled to produce fine particles. In this technique, however, the output depends on the solubility of the polymer in the solvent, and in many cases, it is disadvantageous in terms of productivity deposition of the polymer. In an alternative variation, deposition is performed by adding a poor solvent to the polymer solution.

DE3218151 A1 (1983) and **DE3428640** A1 (1986) of AKZO GMBH disclose a method for the preparation of microporous PLA powder comprising the steps of: (1) heating, preferably at a temperature above 150 °C, and dissolving PLA in xylene or diethyl phthalate; (2) slowly cooling the resulting clear and bright solution; (3) subjecting the resulting suspension to filtering; and (4) removing the remaining solvent, either by evaporation or extraction. The recovered microporous powder can take up a multiple of its own weight of active material and is especially suitable for applying thereto therapeutically active substances for controlled release therefrom, and is particularly appropriate for utilization in veterinary and human medicine.

JPH1135693 A (1999, MITSUI CHEMICALS) discloses a method for the preparation of powdered aliphatic polyester such as PLA, poly(butylene succinate) (PBS), or copolymer of PLA and PBS (PLA-*co*-PBS), comprising mixing an organic solvent solution of the polyester with an aromatic hydrocarbon having a substituent group at a temperature lower than 60 °C and subjecting the deposited solid material to solid–liquid separation. Preferred organic solvents are aliphatic halogenated hydrocarbons such as dichloromethane or aromatic hydrocarbons such as pyridine. Hydrocarbons having an alkyl group or a halogen such as toluene or chlorobenzene are preferred as the substituent group-containing aromatic hydrocarbons.

WO0168890 A2 (2001, MONSANTO TECHNOLOGY LLC) discloses a method of extracting polyhydroxyalkanoate (PHA) such as poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate) (PHBHV) from a solution comprising a solvent and the PHA, involving the steps of: (1) providing the solution at a first temperature; (2) cooling the solution to a second temperature effective to precipitate PHA, and concurrently shearing the solution, to yield a precipitated PHA substantially free of gelation; and (3) recovering the precipitated PHA. Another embodiment relates to a method of extracting PHA from a solution of PHA and biomass involving: (1) providing biomass having intracellular PHA; and (2) dissolving the PHA using a solvent at a first temperature effective for dissolving the PHA. The solvent is selected from the group consisting of amyl alcohol, 2-methyl-1-butanol, hexyl alcohol, ethylene glycol diacetate, 2-heptanone, butyl butyrate, other alcohols, esters or dioxanes; preferably, amyl alcohol is used.



SCHEME 6.1 General formula of compound used to dissolve the biodegradable polyester. R_1 is a 1-3C alkylene; R_2 is H, methyl or ethyl; R_3, R_4 are each H or a 1-5C alkyl or an allyl.

JP2005200663 A (2005, TRIAL CORP) discloses a method for the preparation of a biodegradable spherical single powder comprising the steps of: (1) heating and mixing a biodegradable thermoplastic polymer such as PLA (PLA4031DK of Unitika Co., Ltd.) with a dispersion medium (e.g., polyethylene glycol) that is incompatible with the thermoplastic polymer up to a temperature not less than the melting temperature (T_m) of the thermoplastic polymer to disperse the polymer into fine particles; (2) cooling down the obtained fine particles of the thermoplastic polymer to a temperature not more than its T_m to make them into roughly spherical single powders whose average particle size is more than 0.01 µm and less than 1000 µm. The biodegradable spherical single powder contains a filler (e.g., ZnO or TiO_2) inside or on its surface for improving the mechanical, electrical, or thermal properties.

JP2005002302 A (2005, TOHO CHEM IND CO LTD) discloses biodegradable polyester particles of average particle size of 50 nm to 500 µm by dissolving the biodegradable polyester in a compound expressed by general formula of Scheme 6.1, and then adding a poor solvent while agitating. An exemplary aliphatic polyester is PLA (Lacea® H-100 of Mitsui Chemicals Co.). Examples of good solvent and poor solvent are 1,3-dioxolane and water, respectively.

In the preparation of particles for which a large amount of the organic solvent is required, there is concern that the organic solvent may remain in the polymer (2012, **WO2012017832** A1, KUREHA CORP).

6.4 EMULSION-PRECIPITATION

In the emulsion-precipitation method, the polymer is dissolved in an organic solvent or the polymer is melted, and the resulting solution or melt is combined with water to provide an emulsion, which is subsequently processed into polymer particles while maintaining the shape. Precipitation of the polymer can be performed either by evaporation of the organic solvent [1] or by the addition of a poor solvent to the polymer emulsion.

EP0330180 A1 (1989, BIOMATERIALS UNIVERSE INC) discloses a method for the preparation of microsphere comprising PLA and a water-soluble physiologically active substance, comprising the steps of: (1) preparing a solution of the water-soluble physiologically active substance and PLA uniformly dissolved in a mixed solvent comprising a hydrophilic organic solvent and water or in an organic acid; (2) mixing the solution with a poor solvent immiscible with said mixed solvent or organic acid to give an "oil-in-oil" (O/O) type or "water-in-oil" (W/O) type emulsion, and (3) subjecting the emulsion to solvent evaporation drying. The PLA-based microspheres of this invention are advantageous in that the active substance can be uniformly incorporated into the microspheres without loss of the activity, and can gradually release the active substance for a long time period of more than 1 week.

FR2608988 A1 (1988, CENTRE NAT RECH SCIENT) discloses in one of its embodiments the preparation of dispersible colloidal systems of a film-forming polymer in the form of spherical particles and of a size less than 500 nm, comprising:

1. the preparation of a liquid phase consisting essentially of a solution of a film-forming polymer, such as PLA in an amount of 1–10 wt%, preferably 0.2–2 wt%, and a biologically active substance in a solvent or in a mixture of solvents to which one or more surfactants may be added;
2. the preparation of a greater volume of a second liquid phase consisting essentially of a nonsolvent or a mixture of nonsolvents of the film-forming polymer to which one or more surfactants may be added; the nonsolvent or the mixture of nonsolvents for the substance being miscible in all proportions with the solvent or mixture of solvents for the film-forming polymer;
3. the addition of one of the liquid phases prepared in (1) or (2) to the other with moderate agitation so as to produce a colloidal suspension of nanoparticles of the film-forming polymer, and
4. if desired, the removal of all or part of the solvent or the mixture of solvents and of the nonsolvent or the mixture of nonsolvents so as to give rise to a colloidal suspension of nanoparticles of the desired concentration or to lead to a powder of nanoparticles having a diameter of about 200 nm.

Example: 125 mg of PLA are dissolved in 25 ml of acetone. 125 mg of poly(ethylene oxide)-*b*-poly(propylene oxide) copolymer (Pluronic™ F68 or Poloxamer™ 188), a nonionic surfactant, are dissolved in 50 ml of purified water. The acetone phase is added to the aqueous phase with magnetic stirring (100 rpm.). The mixture immediately becomes opalescent as a result of the formation of nanoparticles of PLA. The mean diameter of the nanoparticles is about 200 nm with a dispersion index of 0.5. The acetone is removed under reduced pressure (water pump vacuum) and the suspension is concentrated to the desired volume, for example, 10 ml, under the same conditions. The concentrated suspension of nanoparticles is filtered through a glass frit (pores 9–15 μm) or through a membrane filter (pores 5 μm).

US2011245456 A1 (2011, REGEN BIOTECH INC) discloses a method for the preparation of biodegradable polyester microparticles comprising the steps of: (1) dissolving a biodegradable polyester in dimethyl sulfoxide (DMSO); (2) spraying the solution in a low temperature hydrocarbon solution to provide frozen DMSO microparticles; (3) adding the microparticles in a low temperature salt aqueous solution to dissolve DMSO, and removing salt. The biodegradable polyester is selected from the group consisting of PLA, PGA, poly(lactic acid-*co*-glycolic acid) (PLGA), poly(ε-caprolactone) (PCL), poly(3-hydroxybutyrate) (P3HB), and poly(3-hydroxyvalerate) (PHV).

WO0076483 A1 (2000, SAMYANG CORP) discloses a method for the preparation of biodegradable polymer microspheres containing a physiologically active agent, comprising the steps of: (1) dissolving a biodegradable polymer in a water-miscible organic solvent to give a polymer solution, and dissolving or suspending said physiologically active agent in the polymer solution to give a polymer solution containing the physiologically active agent; (2) emulsifying the polymer solution containing the physiologically active agent into a water-miscible alcohol containing an emulsion stabilizer to provide an O/O emulsion; and (3) adding the O/O emulsion to a neutral or alkaline aqueous solution, and precipitating biodegradable polymeric microspheres containing the physiologically active agent from the aqueous solution. The biodegradable polymer is selected from the group consisting of an aliphatic polyester such as PLA, PLGA, poly(lactide-*co*-caprolactone) (PLCL), a copolymer of lactide and 1,4-dioxane-2-one, a copolymer of caprolactone and glycolide, a polyorthoester, polyanhydride, polyphosphoamide, poly(amino acid), etc. The water-miscible organic solvent is selected from the group consisting of acetic acid, lactic acid, formic acid, acetone, acetonitrile, dimethylformamide, dimethyl acetamide, dimethyl sulfoxide, dioxane, N-methyl pyrrolidone, and a mixture thereof. The water-miscible alcohol is a member selected from the group consisting of methanol, ethanol, propanol, isopropanol, ethylene glycol, diethylene glycol, triethylene glycol, propylene glycol, glycerol, and a mixture thereof.

JP2004269865 A (2004, DAICEL CHEM) discloses a method for the preparation of spherical biodegradable polymer particles with homogenous particle size distribution. The biodegradable polymer particles are produced by preparation of a dispersion of a biodegradable polymer component (A) and a water-soluble adjuvant component (B) followed by elution of the adjuvant component (B). The biodegradable polymer component (A) may be composed of a polyester such as an aliphatic polyester, a polyether, a poly(vinyl alcohol) (PVOH), and a cellulose derivative. The adjuvant component (B) is composed of an oligosaccharide (B_1) composed of tetroses and a water-soluble plasticizer component (B_2) to plasticize the oligosaccharide composed of sugars or a sugar alcohol. The weight ratio of the biodegradable polymer component (A) and the adjuvant component (B) may be at 55/45 to 1/99 and the weight ratio of the oligosaccharide (B_1) and the plasticizer component (B_2) may be at 99/1 to 50/50.

EP0479043 A1 (1992, DANUBIA PETROCHEM POLYMERE) discloses a method of recovering P3HB after precipitating P3HB in the form of floc, which comprises extracting P3HB from P3HB-containing cells in organic solvents, which are not miscible with water and have the boiling point of below 100 °C, such as methylene chloride, chloroform, and trichloroethylene, under water-containing condition while heated and stirred, and pouring said organic phase containing the extracted P3HB into hot water. This technology is one of the crystallizing technologies of P3HB but does not agglomerate P3HB substantially. Additionally, this technology comprises very complicated processes, therefore has difficulties for an industrial application. Moreover, 10 to 30 times weight of the organic solvent relative to that of dried microbial cell is required. Furthermore, since the use of organohalogen compounds tends to be limited for protection of the environment, it is not desirable to use them (2005, **WO2004033700** A1, KANEKA CORP).

The emulsion-precipitation method, however, has the feature that the resulting particles have the same diameter as that of the emulsion particles. This emulsion particle diameter depends on the stirring power, viscosity, and interfacial tension, and the particle diameter distribution is large in most cases. Furthermore, evaporation and spray drying are expensive techniques that demand the use of large quantities of (usually organic, volatile) solvents.

WO0040617 A1 (2000, INST VOOR AGROTECH ONDERZOEK) discloses a method for the preparation of starch particles using a two-phase system comprising at least the following steps:

1. preparation of a first phase comprising a dispersion of starch in water;
2. preparation of a dispersion or emulsion of the first phase in a second liquid phase with the proviso that the second phase is not water;
3. crosslinking of the starch present in the first phase;
4. separating the starch particles thus formed.

According to a first aspect of the invention, the second phase consists of a hydrophobic liquid and step (2) consists in forming an oil-in-water (O/W) emulsion, which is then inverted to a W/O emulsion. According to a second aspect of the invention, the second phase consists of a water-miscible nonsolvent for starch such as acetone, or preferably ethanol. In step (4) separation of the particles can be effected by means of lowering the temperature, as a result of which the W/O emulsion is destabilized. Separation can also be achieved by adding nonpolar solvents, preferably a nonpolar alcohol, more preferably cyclohexanol or cyclooctanol. The resulting starch particles are small and controllable in the range of 50 nm to 100 μm in diameter.

6.5 COAGULATING DISPERSIONS

PHAs are in the form of fine particles having a diameter of not more than 1 μm as they are produced in microbial cells. In many cases, it is more difficult to separate such fine particles from a liquid medium as compared with the case of particles having larger diameter, while their handling requires special care. Fine particles are considered to have a risk of causing dust explosion due to their low required energy for the explosion and can be accumulated in lungs in the case of being aspirated, thus care should be taken for handling.

Several technologies for agglomerating fine PHA particles have been developed, including agglomeration by heating or an alkaline metal salt. As far as the technology of agglomerating fine particles of PHA by heating is concerned, there is a method that comprises heating a suspension containing P3HB to the vicinity of the T_m of P3HB [2].

WO9402622 A1 (1994, ZENECA LTD) discloses a method in which the fine particles of PHA, for example, P3HB and PHBHV, in suspension in a liquid are agglomerated by maintaining the suspension at a temperature above 80 °C, and more preferably 40–70 °C below the T_m of PHA for a time sufficient to cause substantial agglomeration. Suitable temperatures in the case of PHBHV containing up to 25%, for example, 5–20% of hydroxyvaleric acid residues, the balance being substantially all hydroxybutyric acid residues, are in the range 120–160 °C. In general, a considerable amount of agglomeration can be achieved with such materials in about 1 min at 130 °C. The method may be carried out by the direct injection of steam at a suitable temperature and pressure into a flowing stream of the suspension. This has the advantage that the suspension can be agglomerated continuously. On the other hand, since the treatment is carried out at a considerably high temperature, there is a possibility of causing the decrease in molecular weight. Moreover, this technology requires special equipment capable of high temperature heating and incubation, and further having pressure resistance (2004, **WO2004033700** A1, KANEKA CORP).

As far as the technology of agglomerating fine particles of PHA by adding an alkali metal salt is concerned, a known method has used a bivalent cation [3]. Particularly, there have been reports of a technology of separating P3HB by adding calcium chloride, magnesium sulfate, magnesium chloride, and magnesium acetate to a P3HB suspension to agglomerate P3HB (1991, **CA2083697** A1, INNOVATIVE TECH CENTER). However, this technology makes metal salts mixed into a polymer, therefore, it may not be preferable depending on the products (2004, **WO2004033700** A1, KANEKA CORP).

WO2004033700 A1 (2004, KANEKA CORP) claims to overcome the disadvantages of the prior art by providing a method of obtaining PHA agglomerates of high purity and handling easiness, while inhibiting the decrease in molecular weight. PHA agglomerates are obtained by suspending fine PHA particles in a hydrophilic solvent or a mixture comprising water and a hydrophilic solvent, and stirring the obtained suspension at a temperature of not more than the boiling point of said suspension. A particularly preferred PHA is poly(3-hydroxybutyrate-*co*-3-hydroxyhexanoate) (PHBHHx). The hydrophilic solvent is one selected from the group consisting of alcohols (e.g., methanol, ethanol), ketones (e.g., acetone), nitriles (e.g., aetonitrile), amides (e.g., dimethylformamide), and ethers (e.g., tetrahydrofuran). According to the disclosed method, since impurities contained in a PHA (e.g., lipid) can be dissolved and removed, the purity of the PHA can be enhanced. Moreover, conditions such as high temperature and high pressure that require special equipment are not necessarily needed.

DE19924772 A1 (2000, BUNA SOW LEUNA OLEFINVERB GMBH) discloses a method for the preparation of an agglomerate on the basis of fine-particle, biodegradable starch esters that after a short period can be redispersed in water. According to said method, a starch ester with a particle size of 1–50 μm and a solids content of 5–16 wt% is dehydrated to a water content of 50–70 wt%, and the resulting moist, pasty mass granulated or agglomerated is then carefully dried at a temperature of 20–60 °C. To improve the stability of said agglomerates, a water-soluble, biodegradable polymer can be added to the moist mass. The agglomerates are useful as carriers for active agents (e.g., pharmaceuticals or agrochemicals such as slow-release fertilizers) or for microorganisms (e.g., for use in waste water purification).

6.6 SUPERCRITICAL FLUID TECHNOLOGY

Supercritical fluid (SCF) technology has also been employed for the formation of particles from biodegradable polymers. Numerous variations of the SCF technology have been applied to obtain biodegradable polymer micro- or nanoparticles using SCF either as solvent, such as in the “rapid expansion of supercritical solutions” (RESS) process, or as antisolvent in the “supercritical antisolvent” (SAS) process (also called “gas antisolvent,” GAS) (2012, **WO2011120155**, UNIV ALBERTA).

Several researchers investigated the RESS [4–10] and SAS [4,11,12] processes for the formation of poly(L-lactic acid) (PLLA) micro- and nanoparticles. Sane and Thines [5] used RESS to precipitate PLLA nanoparticles from a PLLA solution of carbon dioxide and tetrahydrofuran (cosolvent). Tom and Debenedetti [6] used chlorodifluoromethane to obtain PLA nanoparticles dispersed with either microparticles or agglomerates of micro- and nanoparticles. Montes et al. [4] applied REES and SAS processes to obtain PLLA particles that were as small and spherical as possible in order to use them in drug delivery devices. Particle morphology was improved from irregular blocks to spherical microparticles on applying the SAS precipitation. Dichloromethane was the best of the chlorinated solvents investigated.

Kluge et al. [13,14] applied the "supercritical fluid extraction of emulsions" process, which is related to SAS, to obtain composite nanoparticles of amorphous PLGA and an anti-inflammatory drug (Ketoprofen™), finding that the PLGA concentration in the emulsion affected particle size and particle size distribution.

WO2005073285 A1 (2005, JAPAN SCIENCE & TECH AGENCY) discloses a method for producing fine polymer particles that comprises a step of dissolving or dispersing a polymer such as PLA in a high pressure fluid containing a SCF and an added solvent as an entrainer, and a step of spraying the resultant high pressure fluid into a poor solvent to allow the fluid to expand rapidly. The method permits the production of fine polymer particles or fine coating particles having a controlled average particle diameter. The SCF is carbon dioxide, ammonia, methane, ethane, ethylene, and/or butane. The entrainer is generally selected from poor solvents, such as ethanol, and may be the same with the poor solvent. The poor solvent is water, methanol, ethanol, propanol, acetone, and/or liquid nitrogen.

Example: Ethanol (200 ml) and PLA (5 g) of molecular weight 10,000 were taken in a high pressure cell, and water was added as porous solvent. Carbon dioxide was supplied to the high pressure cell, and reaction was performed, to obtain PLA microspheres having a uniform average particle diameter.

WO2011120155 A1 (2011, UNIV ALBERTA) discloses micro-and nanosized particles, agglomerates, and fibers generated from high-molecular-weight water-soluble biopolymers such as gums and polysaccharides by applying the SAS process. A method of producing micro- or nanoparticles from an aqueous solution of a high-molecular-weight biopolymer includes the step of spraying the aqueous solution together with a mixture of a compressible gas and a water-soluble cosolvent/antisolvent into a pressurized chamber. The method may be adapted to impregnate the micro- or nanoparticles with a bioactive material. The compressible gas comprises carbon dioxide, carbon dioxide and ethanol, nitrogen, or mixtures thereof. The water-soluble cosolvent/antisolvent comprises ethanol, acetone, or isopropanol, or mixtures thereof.

PATENTS

Patent Number	Publication Date	Family Members	Priority Numbers	Inventors	Applicants	Title
CA2083697 A1	19911126	US5334520 A 19940802; JPH05507410 A 19931028; FI925333 A 19921124; EP0535065 A1 19930407; AU7996291 A 19911231	US19900528549 19900525	DENNIS DOUGLAS E	INNOVATIVE TECH CENTER	Production of poly-beta-hydroxybutyrate in transformed *Escherichia coli*.
DE19924772 A1	20001130	WO0073380 A1 20001207	DE1999124772 19990529	KAKUSCHKE ROLF; STOYE HARTMUT; RAPTHEL INNO	BUNA SOW LEUNA OLEFINVERB GMBH	Verfahren zur Herstellung von in Wasser redispergierbaren Agglomeraten aus biologisch abbaubaren Stärkeestern. “Method for producing agglomerates of biodegradable starch esters which can be redispersed in water.”
DE3218151 A1	19831117	US4471077 A 19840911; JPS58206637 A 19831201; EP0094536 A2 19831123; EP0094536 A3 19840926; EP0094536 B1 19861126	DE19823218151 19820514	LANGE WOLFGANG	AKZO GMBH	Microporous polylactide powders and a process for their preparation.
DE3428640 A1	19860206	US4645664 A 19870224; JPS6142531 A 19860301; EP0171603 A1 19860219; EP0171603 B1 19890125; DE3428640 C2 19881215	DE19843428640 19840803	LANGE WOLFGANG	AKZO GMBH	Microporous powdery polylactides.
EP0330180 A1	19890830	US5100669 A 19920331; JPH01216918 A 19890830; JP2670680 B2 19971029; EP0330180 B1 19930113; EP0330180 B2 19990303; DE68904326 T2 19930527; DE68904326 T3 19990715	JP19880042459 19880224	HYON SUONG-HYU; IKADA YOSHITO	BIOMATERIALS UNIVERSE INC	Polylactic acid type microspheres containing physiologically active substance and process for preparing the same.
EP0479043 A1	19920408	US5213976 A 19930525; JPH04264125 A 19920918; GR3018034 T3 19960229; ES2078406 T3 19951216; DK0479043 T3 19951211; AT130035 T 19951115; AT395319 B 19921125	DANUBIA PETROCHEM POLYMERE	BLAUHUT WILFRIED; GIERLINGER WOLGANG; STREMPEL FRIEDRICH	DANUBIA PETROCHEM POLYMERE	Process for the production of a polyhydroxyalkanoate from the cell material of a microorganism and polyhydroxyalkanoate flocks.

FR2608988 A1	19880701	US5118528 A 19920602; JPS63240936 A 19881006; JP2739896 B2 19980415; FR2608988 B1 19910111; EP0275796 A1 19880727; EP0275796 B1 19920325; EP0275796 B2 19950906; CA1292168 C 19911119; ES2031151 T3 19921201; ES2031151 T5 19921201; GR3004152 T3 19930331; GR3018122 T3 19960229	FR19860018446 19861231	FESSI HATEM; DEVISSAGUET JEAN-PHILIPPE; PUISIEUX FRANCIS; THIES CURT	CENTRE NAT RECH SCIENT	Procédé de préparation de systèmes coloidaux dispersibles d'une substance sous forme de nanoparticules. "Process for the preparation of dispersible colloidal systems of a substance in the form of nanoparticles."
JP2001288273 A	20011016	JP4635292 B2 20110223	JP20000102653 20000404	TANIYAMA YOICHI; YOSHIDA KOJI	KANEBO LTD	Polylactic acid-based resin powder, method for preparing it, and adhesive produced therefrom.
JP2004269865 A	20040930		JP20040040366 20040217; JP20030038847 20030217	ITO HISAYOSHI	DAICEL CHEM	Production process of biodegradable resin particle.
JP2005002302 A	20050106	JP4570855 B2 20101027	JP20030196770 20030611	AKIMOTO MIKIO; NAGASAWA KAZUYUKI	TOHO CHEM IND CO LTD	Biodegradable polyester-based resin fine particle and method for producing the same.
JP2005200663 A	20050728	JP3759155 B2 20060322	JP20050105635 20050401	SUGANO GEN	TRIAL CORP	Preparation process of biodegradable spherical single powder.
JP2007197602 A	20070809	JP5093834 B2 20121212	JP20060019003 20060127	FUJIMOTO KATSUHIRO; KOBAYASHI AKIO	ASAHI CHEMICAL CORP	Biodegradable resin powder and method for producing the same.
JPH1135693 A	19990209		JP19970191488 19970716	MORI YUKIKO; IKEDA YOSHI; WATANABE KATSUJI GOTO KENICHI; TAMAI MASAJI	MITSUI CHEMICALS INC	Production of powdery polyester having biodegradability.
US2011130513 A1	20110602	W201119826 A 20110616	TW20090141246 20091202	CHIANG HENG-BO; HUANG CHEN-PAO	CHI MEI CORP	Method for producing bead-shaped polylactide pellets.

Continued

—Cont'd

Patent Number	Publication Date	Family Members	Priority Numbers	Inventors	Applicants	Title
US2011287105 A1	20111124	WO2011149689 A1 20111201; JP2013527204 A 20130627; EP2575771 A1 20130410	US20100800804 20100524	GITTLEMAN DAVID	MICRO POWDERS INC	Composition comprising biodegradable polymers for use in a cosmetic composition.
WO0040617 A1	20000713	US6755915 B1 20040629; NL1010926 C2 20000703; MXPA01006641 A 20040421; MX226463 B 20050225; KR20010108052 A 20011207; KR100652533 B1 20061201; JP2012111955 A 20120614; JP2002543220 A 20021217; JP4977292 B2 20120718; ES2200586 T3 20040301; EP1155041 A1 20011121; EP1155041 B1 20030604; DE69908655 T2 20040701; CN1335857 A 20020213; CN1226307 C 20051109; CA2357032 A1 20000713; CA2357032 C 20090217; BR9916691 A 20020319; BR9916691 B1 20101130; AU3081700 A 20000724; AU765200 B2 20030911; AT242272T T 20030615	NL19981010926 19981230	VAN SOEST JEROEN JOHANNES GERA; STAPPERS FRANK H M; VAN SCHIJNDEL RENEE JOSIE GIDE; GOTTLIEB KORNELIS FESTER; FEIL HERMAN	INST VOOR AGROTECH ONDERZOEK	Method for the preparation of starch particles.
WO0069916 A1	20001123	US6677386 B1 20040113; MXPA01007503 A 20020621; MX220923 B 20040611; KR20010108128 A 20011207; KR100451527 B1 20041008; JP2002544335 A 20021224; JP3946958 B2 20070718; ES2209813 T3 20040701; EP1159301 A1 20011205; EP1159301 B1 20031015; DE60005932 T2 20040812; CN1337969 A 20020227; CN1293100 C 20070103; CA2361722 A1 20001123; CA2361722 C 20090421; BR0007703 A 20020827; BR0007703 B1 20101019; AU2467300 A 20001205; AU760508 B2 20030515; AT252114 T 20031115	JP19990200203 19990125	GIEZEN FRANCISCUS EGENIUS; JONGBOOM REMIGIUS OENE JULES; FEIL HERMAN; GOTLIEB KORNELIS FESTER; BOERSMA ARJEN	ATO BV	Biopolymer nanoparticles.

WO0076483 A1	20001221	KR20010002589 A 20010115; US6630156 B1 20031007; AU5573400 A 20010102	KR19990022471 19990616	KIM JI HYANG; LEE JAE YONG; SEO MIN HYO	SAMYANG CORP	Process for preparing biodegradable microspheres containing physiologically active agents.
WO0168890 A2	20010920	WO0168890 A3 20020418; AU5080001 A 20010924	US20000188440P 20000310	KURDIKAR DEVDATT L; PASTER MARK D; ZHANG JIANWEI	MONSANTO TECHNOLOGY LLC	Prevention of gelation of polyhydroxyalkanoate solutions using shear
WO2004033700 A1	20040422	US2008118963 A1 20080522, RU2005113285 A 20060120; PL376044 A1 20051212; EP1550724 A1 20050706; CN1694963 A 20051109; CA2499607 A1 20040422; BR0314749 A 20050726; AU2003266709 A1 20040504	JP20020285864 20020930	OGAWA NORIKO; MIYAMOTO KENJI; OSAKADA FUMIO; MATSUMOTO KEIJI	KANEKA CORP	Method of coagulating poly-3-hydroxyalkanoic acid.
WO2005073285 A1	20050811	US2007102836 A1 20070510; KR20060125871 A 20061206; KR100804442 B1 20080220; EP1717263 A1 20061102; EP1717263 A4 20080326; CN1914255 A 20070214; CN100432124 C 20081112; AU2005209541 A1 20050811; AU2005209541 B2 20070712	JP20040019392 20040128	MISHIMA KENJI; MATSUYAMA KIYOSHI	JAPAN SCIENCE & TECH AGENCY	Method for producing fine particles using method of rapid expansion into poor solvent from supercritical fluid.
WO2007034805 A1	20070329	US2009118462 A1 20090507; US7728100 B2 20100601; EP1970399 A1 20080917; EP1970399 A4 20100519; EP1970399 B1 20111109; CN101268123 A 20080917; CN101268123 B 20120118	JP20050273958 20050921	SATO HIROYUKI; KOBAYASHI FUMINORI; AKUTSU FUMIO; MOMOSE KATSUSHI	KUREHA CORP	Process for producing polyglycolic acid resin composition.
WO2008022127 A2	20080221	ZA200901007 A 20100526; WO2008022127 A3 20080424; US2011042841 A1 20110224; RU2009109258 A 20100927; RU2457223 C2 20120727; MX2009001688 A 20090225; KR20090053909 A 20090528; JP2010500937 A 20100114; JP5232985 B2 20130710;	US20060837669P 20060815	WILDI ROBERT H; VAN EGDOM EDWARD; BLOEMBERGEN STEVEN	ECOSYNTHETIX INC	Process for producing biopolyomer nanoparticles.

Continued

—Cont'd

Patent Number	Publication Date	Family Members	Priority Numbers	Inventors	Applicants	Title
		EP2069431 A2 20090617; EP2069431 A4 20130717; CN102862282 A 20130109; CN101535397 A 20090916; CN101535397 B 20121226; CA2660612 A1 20080221; BRPI0716663 A2 20131022; AU2007285951 A1 20080221; AU2007285951 B2 20121213				
WO2010140865 A2	20101209	WO2010140865 A3 20110331; US2011245456 A1 20111006; US8329856 B2 20121211; KR20100131244 A 20101215; KR101105292 B1 20120117; EP2439228 A2 20120411; CN102369234 A 20120307; CN102369234 B 20130724; CA2801706 A1 20101209; AU2010254741 A1 20120202	KR20090050043 20090605	KIM GUN POONG; LEE YONG HOON; LEE KUN PIL	REGEN BIOTECH INC	Biodegradable polymer microparticles and preparation method thereof.
WO2011120155 A1	20111006	US2013101849 A1 20130425; EP2553000 A1 20130206; EP2553000 A4 20130904; CA2794960 A1 20111006; CN102918086 A 20130206	US20100320182P 20100401	TEMELLI FERAL; SEIFRIED BERNHARD	UNIV ALBERTA	Supercritical fluid treatment of high-molecular-weight biopolymers.
WO2012017832 A1	20120209	US2013131209 A1 20130523	JP20100174834 20100803	YAMANE KAZUYUKI; SUZUKI KENSUKE	KUREHA CORP	Polyglycolic acid particles, method for producing polyglycolic acid particles, and uses thereof.
WO2012098340 A1	20120726	FR2970713 A1 20120727	FR20110050438 20110120	LE GUILLAUME; MATHIEU CYRILLE; LOYEN KARINE; PRADEL JEAN-LAURENT; FLAT JEAN-JACQUES	ARKEMA FRANCE	Fine powder of bio-sourced aliphatic polyester and production method thereof.
WO2012121296 A1	20120913		JP20110050795 20110308	YAMAZAKI MASAHIRO; SATO HIROYUKI ABE SHUNSUKE; SAIGUSA KOTAKU; KURUHARA NANAKO	KUREHA CORP	Biodegradable aliphatic polyester resin particulate composition and method for producing same.

WO2012133037 A1	20121004		JP20110068235 20110325	YAMAZAKI MASAHIRO; SAIGUSA KOTAKU ABE SHUNSUKE; KURUHARA NANAKO; SATO HIROYUKI	KUREHA CORP	Biodegradable aliphatic polyester particles, and method for producing same.
WO2012133039 A1	20121004		JP20110068237 20110325	YAMAZAKI MASAHIRO; SATO HIROYUKI; SAIGUSA KOTAK; ABE SHUNSUKE; KURUHARA NANAKO	KUREHA CORP	Biodegradable aliphatic polyester particles, and method for producing same.
WO9402622 A1	19940203	ZA9305179 A 19940419; US5798440 A 19980825; RU2127313 C1 19990310; NZ254186 A 19961126; NO950241 A 19950123; JPH07509131 A 19951012; JP3773526 B2 20060510; FI950284 A 19950123; FI107541 B1 20010831; EP0652969 A1 19950517; EP0652969 B1 19960619; DK0652969 T3 19961021; DE69303282 T2 19961128; CA2137794 A1 19940203; BR9306756 A 19981208; AU677787 B2 19970508; AT139573 T 19960715	GB19920015791 19920724	LIDDELL JOHN MACDONALD; GEORGE NEIL	ZENECA LTD	Process of increasing the particle size of polymers.

REFERENCES

[1] Desgouilles S, Vauthier C, Bazile D, Vacus J, Grossiord J-L, Veillard M, et al. The design of nanoparticles obtained by solvent evaporation: a comprehensive study. Langmuir 2003;19:9504–10.

[2] Bailey N, Niranjan K, Varley J, George N. Thermal agglomeration of polyhydroxybutyric acid granules. UK: ICHEME Research Event; 1996. p. 196–8.

[3] Resch S, Gruber K, Wanner G, Slater S, Dennis D, Lubitz W. Aqueous release and purification of poly(β-hydroxybutyrate) from *Escherichia coli*. J Biotechnol 1998;65:173–82.

[4] Montes A, Gordillo M, Pereyra C, Martínez de la Ossa E. Supercritical CO_2 precipitation of poly(L-lactic acid) in a wide range of miscibility. J Supercrit Fluids 2013;81:236–44.

[5] Sane A, Thies MC. Effect of material properties and processing conditions on RESS of poly(L-lactide). J Supercrit Fluids 2007;40:134–43.

[6] Tom JW, Debenedetti PG, Jerome R. Precipitation of poly(L-lactic acid) and composite poly(L-lactic acid)-pyrene particles by rapid expansion of supercritical solutions. J Supercrit Fluids 1994;7:9–29.

[7] Kim JH, Paxton TE, Tomasko DL. Microencapsulation of naproxen using rapid expansion of supercritical solutions. Biotechnol Prog 1996;12:650–61.

[8] Gadermann M, Kular S, Al-Marzouqi AH, Signorell R. Formation of naproxen–polylactic acid nanoparticles from supercritical solutions and their characterization in the aerosol phase. Phys Chem Chem Phys 2009;11:7861–8.

[9] Imran ul-haq M, Acosta-Ramírez A, Mehrkhodavandi P, Signorell R. Influence of polydispersity of poly(lactic acid) on particle formation by rapid expansion of supercritical CO_2 solutions. J Supercrit Fluids 2010;51:376–83.

[10] Matsuyama K, Donghui Z, Urabe T, Mishima K. Formation of L-poly(lactic acid) microspheres by rapid expansion of CO_2 saturated polymer suspensions. J Supercrit Fluids 2005;33:275–81.

[11] Rantakylä M, Jäntti M, Aaltonen O, Hurme M. The effect of initial drop size on particle size in the supercritical antisolvent precipitation (SAS) technique. J Supercrit Fluids 2002;24:251–63.

[12] Song KH, Lee C-H, Lim JS, Lee Y-W. Preparation of L-PLA submicron particles by a continuous supercritical antisolvent precipitation process. Korean J Chem Eng 2002;19:139–45.

[13] Kluge J, Fusaro F, Casas N, Mazzotti M, Muhrer G. Production of PLGA micro- and nanocomposites by supercritical fluid extraction of emulsions: I. Encapsulation of lysozyme. J Supercrit Fluids 2009;50:327–35.

[14] Kluge J, Fusaro F, Mazzotti M, Muhrer G. Production of PLGA micro- and nanocomposites by supercritical fluid extraction of emulsions: II. Encapsulation of Ketoprofen. J Supercrit Fluids 2009;50:336–43.

Chapter 7

Chemical Treatment (in Bulk)

The terms *chemical treatment* or *chemical modification*, as used herein, mean a process by which at least one feature of the chemical constitution of a polymer is changed either by chemical reaction(s) between the polymer and another chemical or through intramolecular or intermolecular chemical reaction(s) of the polymer.

7.1 INTRODUCTION OF FUNCTIONAL GROUPS

The commonly used biodegradable polymers, and in particular the linear aliphatic polyesters, for example, poly(lactic acid) (PLA), poly(glycolic acid) (PGA), poly(lactic-*co*-glycolic acid) (PLGA), poly(ε-caprolactone) (PCL), etc., do not contain functional groups such as carboxylic acid groups, hydroxyl groups, and amine groups, except at the polymer chain ends. This lack of functional groups greatly limits the applications of these biodegradable polymers. The incorporation of functional groups makes further chemical modification much easier, enabling additional properties to be added to the biodegradable polymer, for example, hydrophilicity and water dispersibility. Functional groups containing reactive sites could also bind to biologically active compounds such as peptides in order to help direct cell behavior in a tissue engineering matrix. As another example, the reactive sites could be used to bind drugs, thus making prodrugs and drug delivery systems.

The known methods for the introduction of functional groups into biodegradable polymers can be summarized as follows:

1. incorporating functional monomers during the polymerization process
2. modification of the terminal functional groups or introduction of side functional groups
3. grafting/block copolymerization

Representative examples of each of the three approaches are:

1. Incorporation of functional monomers during the polymerization process:
   Eguiburu et al. [1] reported the preparation of acrylic macromonomers of poly(L-lactide) (PLLA) by the ring-opening polymerization (ROP) of L-lactide, initiated by acrylic functionalized aluminum alkoxides. Specifically, the initiators were mono- and trihydroxyethyl methacrylate-aluminum alkoxides. The polymerization was carried out in toluene at 60 °C and yielded methacrylate-terminated PLLA macromonomers that were reported to be copolymerizable with other vinyl or acrylic monomers to provide graft copolymers.
   Barakat et al. [2] reported the ROP of L-lactide, initiated by acrylic functionalized aluminum alkoxides, in toluene at 70 °C. The PLLA macromonomer could be synthesized to contain acrylate functionality at either one or both ends of the macromonomer. The acrylate-functionalized macromonomers were then copolymerized with other acrylate comonomers.
   According to **EP0899274** A1 (1999, NAT STARCH CHEM INVEST) these processes suffer from several disadvantages: the acrylate macromonomers are less reactive than the normal acrylate monomers and require more stringent reaction conditions for copolymerization; the higher reaction temperatures needed to prepare the macromonomers can result in uncontrolled polymerization; the aluminum alkoxide initiators give aluminum salt by-products that must be washed from the PLA/acrylate product; and the functionalized PLA polymers are soluble only in relatively noxious solvents.
   PLLA copolymers with pendant carboxyl groups were prepared by copolymerization of L-lactide and 3-(S)-[benzoyloxycarbonyl]-methyl]-1,4-dioxane-2,5-dione (BMD), a cyclic diester monomer consisting of both glycolate and benzyl-α-L-malate units. The copolymerization was carried out in bulk, with stannous 2-ethylhexanoate as catalyst [3,4]. The resulting polymers can only have one pendant carboxyl group for each BMD monomer used, and making them requires a new diester monomer from the beginning of ROP and the removal of the benzoyloxy groups to display the pendant carboxyl group.
   WO9409760 A1 (1994, MASSACHUSETTS INST TECHNOLOGY; CHILDRENS HOSP MEDICAL CENTER) and **US5654381** (1997, MASSACHUSETTS INST TECHNOLOGY), Barrera et al. [5] and Hrkach et al. [6] disclose the making of biodegradable polyesters incorporated with specially designed lysine residue monomers in the ROP. Random incorporation of lysine into the polymer backbone provides sites along the polymer chain that can be chemically modified through reactions of the ε-amine group of the lysine units.

http://dx.doi.org/10.1016/B978-0-323-26698-7.00007-6

Copolymerization has also been used to incorporate pendant functional groups into the polymer chain of PCL. A series of functionalized PCLs described in the literature were synthesized by the radical ROPs of 2-methylene-1,3-dioxepane (MDO), a cyclic ketene acetal, with two vinyl monomers, vinylphosphonic acid and dimethyl vinylphosphonate [7] or *N*-isopropylacrylamide [8].

Another strategy relies on the ROP of ε-caprolactone substituted, mainly in γ-position, by various functional groups [9], e.g., acrylate [10], protected carboxylic acid [11,12], protected alcohol [13], ketal [14], ketone [15], and halogen [16]. The main drawback of this strategy is that the metal-based initiators or catalysts for homogenous ROP, such as aluminum and tin alkoxides, are not tolerant of hydroxyl, carboxylic acid, and epoxy functional groups. In these specific cases, hydroxyl and carboxylic acid groups must be protected before ROP and deprotected after polymerization; whereas after treatment epoxidation has to be considered for grafting epoxides along the chains. Another limitation can be found in the low yield of a multistep process [9,17].

To avoid these problems, a straightforward strategy was proposed for grafting hydroxyl, carboxylic, and epoxide groups along PCL chains [17]. Statistical copolymerization of ε-caprolactone with α-chloro-ε-caprolactone has been initiated by 2,2-dibutyl-2-stanna-1,3-dioxepane (DSDOP), followed by the atom transfer radical addition (ATRA) of but-3-en-1-ol, vinylacetic acid and 1,2-epoxyhex-5-ene, respectively, onto the α-chloro units of the copolymer [9]. Since ATRA is tolerant of the functional groups, there is no need for protection/deprotection reactions [18].

2. Modification of the terminal functional groups (carboxyl acid and hydroxyl groups) or introduction of side functional groups through chemical reactions with reacting compounds:

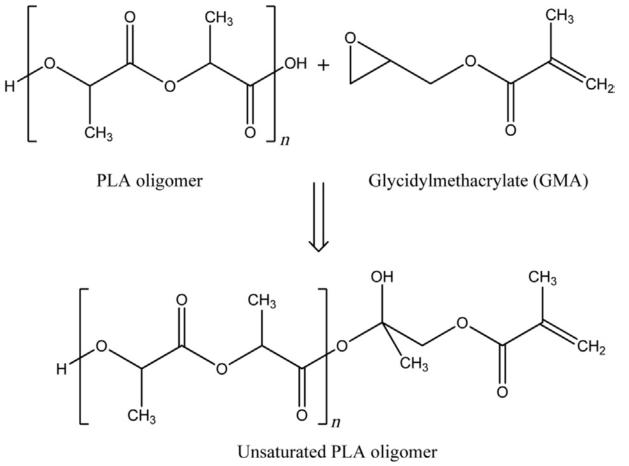
   US5610241 A (1997, CORNELL RES FOUNDATION INC) discloses the modification of biodegradable polyesters such as poly(D-lactic acid-*co*-L-lactic acid) (PDLA) with side chains of amino acid groups such as L-lysine, where the starting biodegradable polymers have repeating units consisting of carbonyl groups and hydrogen atoms on the carbon on the α-position to the carbonyl group. The modification was done first by reacting the starting biodegradable polyesters with a base such as alkali metal alkoxides, to form carbon ions on the α-carbon of the carbonyl groups, and then reacting the carbon-ion-bearing polymers with protected reactive amino acids, followed by the deprotection of side chain groups. The formation of carbon ions in the biodegradable polymers involves low temperature such as −78 °C.

   Lavik et al. [19], disclose the making of a block copolymer of PLGA and polylysine by direct coupling of protected polylysine (poly-ε-carbobenzoic-lysine) with carboxylic-acid-ending PLGA, followed by the removal of the protection groups from the polylysine blocks. **WO0060956** A1 (2000, CORNELL RES FOUNDATION INC) and Zhang et al. [20] disclose the modification of PLGA polymers by first adding vinyl groups at their chain ends and then reacting the modified polymers with vinyl-group-incorporated polysaccharides such as dextran. The resulting network then has both hydrophilic and hydrophobic components (2003, **US2003232929** A1, KIMBERLY CLARK CO).

   Furch [21] describes the synthesis of copolymers of PGA and methyl acrylate (PMA-*g*-PGA), by firstly making vinyl-group-ending PGA macromonomers, which in turn was made by HEMA (2-hydroxylethyl methacrylate)-initiated ROP of glycolide. In the same article, they are mentioned also as copolymers of PLA with vinyl pyrrolidone and *N*,*N*′-dimethyl-acrylamide comonomers. Shinoda and Matyjaszewski [22] describe the making of poly(methyl methacrylate)-*g*-poly(lactic acid) (PMMA-*g*-PLA) by a similar procedure but through ATRA polymerization.

   US2012189860 A (2012, FINA TECHNOLOGY) discloses a method for the modification of PLA by providing a first PLA having a carboxylic acid end group and unsaturating the first PLA to form a second PLA. The modification generally includes unsaturation of the backbone of the PLA. Such unsaturation may be introduced to the PLA through contact with dual functional compounds (i.e., bifunctional compounds). In one or more embodiments, the dual functional compounds may include compounds containing both a first functional group and a second functional group, wherein the first functional group comprises a carbon–carbon double bond on one end of the compound. The second functional group may include any functional group capable of reacting with the carboxylic acid end group of the PLA. In one or more embodiments, the second functional group is selected from epoxies, and isocyanate groups, for example. The dual functional compounds may be formed by known methods or obtained commercially. Examples of suitable dual functional compounds include glycidyl methacrylate (GMA), which is commercially available from Dow Chemicals, and unsaturated aliphatic isocyanate, e.g., TMI® (Cytec Industries, Inc.).

   In one specific example, unsaturated PLA may be formed by reactive extrusion of GMA and PLA. In one or more specific embodiments, PLA may include any PLA including a carboxylic acid end group, as illustrated in Scheme 7.1, wherein *n* is a discrete number (in contrast to a polymer wherein *n* may be unlimited), such as 2, 3, or 4.



SCHEME 7.1 Reaction of PLA oligomer and glycidyl methacrylate (GMA) (2012, **US2012189860** A, FINA TECHNOLOGY).

In another specific example, unsaturated PLA may be formed by reactive extrusion of TMI® (meta) unsaturated aliphatic isocyanate and PLA. The reaction of PLA oligomer and TMI® (meta) unsaturated aliphatic isocyanate is illustrated in Scheme 7.2.

US2012211927 A1 (2012, FINA TECHNOLOGY) discloses a method for forming a polymeric composition by contacting a PLA with a reactive modifier selected from epoxy-functionalized polybutadiene oligomer, ionic monomer such as an organometallic salt having acrylate functional groups, and combinations thereof. The reactive modifier when added to molten PLA may chemically react to form a bond with PLA molecules to impart a plasticizing and toughening effect to PLA. In particular, the reactive modifier may act as a functionalized plasticizer such that a chemical bond is formed between the reactive modifier and the carboxylic acid end groups of the PLA molecules. Modification of PLA with the reactive modifier imparts increased toughness and ductility to the PLA, thereby broadening the utility of PLA in the manufacture of higher impact strength articles while maintaining or improving ease of processing (i.e., processability).

JP2001261797 A (2001, TORAY INDUSTRIES), **JP2002030208** A (2002, TORAY INDUSTRIES), and **JP2007154002** A (2007, TOYODA GOSEI KK) disclose methods for lowering the terminal carboxyl group concentration of an aliphatic polyester such as PLA by adding a terminal blocking agent (e.g., a carbodiimide compound). The treatment improves the hydrolysis resistance and heat resistance of molded articles such as films or fibers. However, these methods have a problem that since the terminal blocking agent is added to and kneaded with polymer chips before extrusion or spinning, the terminal blocking agent causes fuming due to evaporation and decomposition, generating an offensive odor and toxic gas. Another problem is that since the terminal blocking agent is lost due to decomposition, it must be added by an excessive amount. Further, the additional component added to a molten polymer lowers spinnability, affecting productivity. Moreover, it has a further disadvantage that since the production made at a time is large, it is difficult to control the amount of the chemical substance (2009, **WO2009041518** A1, TORAY INDUSTRIES).

Modifying polyhydroxyalkanoates (PHAs) to include reactive terminal groups improves the properties of the materials and expands the range of applications of PHAs. By reacting PHAs with acetic anhydride and capping terminal hydroxyl groups of the PHA, the thermostability of PHAs can be improved (2012, **WO2012012064** A1, ARCHER DANIELS MIDLAND CO). Isocyanate-terminated and/or silane-terminated PHAs are useful as hot melt adhesives that are designed for moisture curing. Hot melt adhesives that are designed for radiation curing, such as ultraviolet (UV) radiation curing or γ-radiation curing, and/or peroxide curing, preferably include PHAs that are vinyl-terminated (2002, **WO0234857** A2, METABOLIX INC).

The known methods to functionalize biodegradable polymers use complicated chemistry and chemical processes. They either use specially designed monomers or multistep reactions, or extreme reaction conditions (2003, **US2003232929** A1, KIMBERLY CLARK CO).

US2003232929 A1 (2003, KIMBERLY CLARK CO) discloses a method to functionalize biodegradable polymers by direct reaction of the biodegradable polymers in the medium of functional monomers, particularly vinyl monomers, in the presence of an initiator. The initiator may be free radical initiators, heat, ionic initiators, UV irradiation, or ionizing irradiation. The vinyl monomer may contain functional groups that may be chosen from carboxylic acid groups, hydroxyl groups, amine groups, chloride groups, sulfonic groups, phosphoric groups, aldehyde groups, oxirane groups, mercaptan groups, isocyanate groups, sulfide groups, activated amide groups, activated ester groups, and combinations thereof. The biodegradable polymers may be chosen from aliphatic (co)polyesters, polyanhydrides, polyorthoesters, poly(ester–ether), polyamines, phosphorus-based polymers, and combinations thereof. An aliphatic polyester may be chosen from PLA, PGA, PLGA, PCL, their copolymers, and combinations thereof. The biodegradable polymer may be dissolved or dispersed in the vinyl monomers. The method may also include a solvent. Particularly preferred combinations of biodegradable polymer and vinyl monomer include PLGA and acrylic acid, PCL and acrylic acid, and PLGA and HEMA.

WO2005078018 A1 (2005, UNIV MICHIGAN STATE) discloses in one of its embodiments a method for the preparation of modified PHAs containing pendant anhydride groups in varying proportions comprising: mixing together an anhydride, a free radical initiator, and a PHA at a temperature where the PHA melts; and using the grafted PHA as compatibilizer with PHA and a dried biodegradable fiber, which reacts with the compatibilizer. Preferred PHAs are poly(3-hydroxybutyrate) (P3HB) poly(3-hydroxyvlerate) (PHV), poly(3-hydroxyoctanoate) (PHO), poly(3-hydroxyprpionate) (PHP), poly(3-hydroxybutyrate-3-valerate) (PHBHV) and the like. The anhydride is selected from maleic anhydride, octadecenyl succinic anhydride, nadic anhydride, and ring-substituted derivatives thereof.

3. Block grafting/copolymerization:

Block and graft copolymerization are well-known and established techniques to modify the chemical and physical properties of polymers.

Block copolymers of PLGA and poly(ethylene glycol) (PEG) have been discussed in the literature [23–26]. These copolymers include PLGA–PEG, PLGA–PEG–PLGA, and PEG–PLGA–PEG types, and are mainly made by PEG-initiated ROP of cyclic esters.

The making of graft copolymers PEG-*g*-PLGA with PEG as the backbone chains and PLGA as the side chains have also been known [27]. The grafting reaction was made possible by first incorporating pendanthydroxyl-group-bearing units in the backbone chains and later using these modified PEG chains to ring-opening polymerize lactide and glycolide monomers.

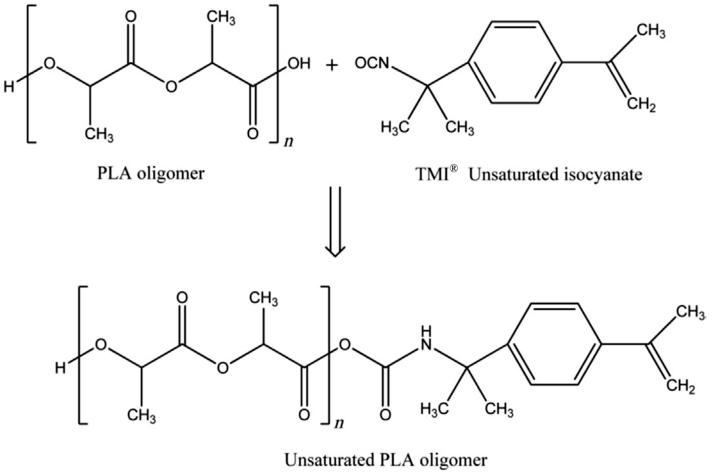
The use of poly(propylene glycol) (PPG) instead of PEG as the initiators for ROP of lactide resulted in PLA–PPG–PLA triblock copolymers [28]. It should be noted that the use of PEG and PPG as polymer initiators, though it may change the hydrophilicity of the final polymers, does not introduce functional groups in the biodegradable polymers.

WO9523175 A1 (1995, SANOL ARZNEI SCHWARZ GMBH); Li et al. [29,30]; and Breitenbach et al. [31] describe the making of graft copolymers with PLGA as side chains and polyols as the backbone chains. The polyols include both neutral polymers such as poly(vinyl alcohol)s (PVOHs) and polyelectrolytes such as dextran sulfate sodium, diethylaminoethyl dextran chloride, and also copolymers of PVOH and poly(methacrylic acid). The copolymers were made by ROP of cyclic ester monomers, with the hydroxyl groups in the polyol backbone chains as the initiators.

Grafting and/or block copolymerization of PHAs, and in particular P3HB with suitable functional polymers/oligomers, is a promising way to overcome the main drawbacks of these polymers such as brittleness, narrow processing window, and thermal instability.

Modification of PHAs via grafting is rarely reported in the literature. Mitomo et al. [32] reported radiation grafting of methyl methacrylate (MMA), HEMA, acrylic acid, and styrene onto P3HB and its copolymers. Lee and Lee [33] studied graft copolymerization of acrylamide onto PHBHV films for its permselectivity. However, these reports are about surface graft copolymerization in the presence of a solvent, restricted to the surface modification of PHA films (see Chapter 8: Surface treatment; Section 8.3: Chemical treatment).

WO02053610 A1 (2002), **WO02053641** A1 (2002), **US2002128384** A1 (2002), **US5952433** A (1999), **WO9906456** A1 (1999), **WO02053610** A1 (2002) of KIMBERLY CLARK CO disclose biodegradable polymers grafted with a polar monomer, oligomer, or polymer, or a combination thereof. The biodegradable



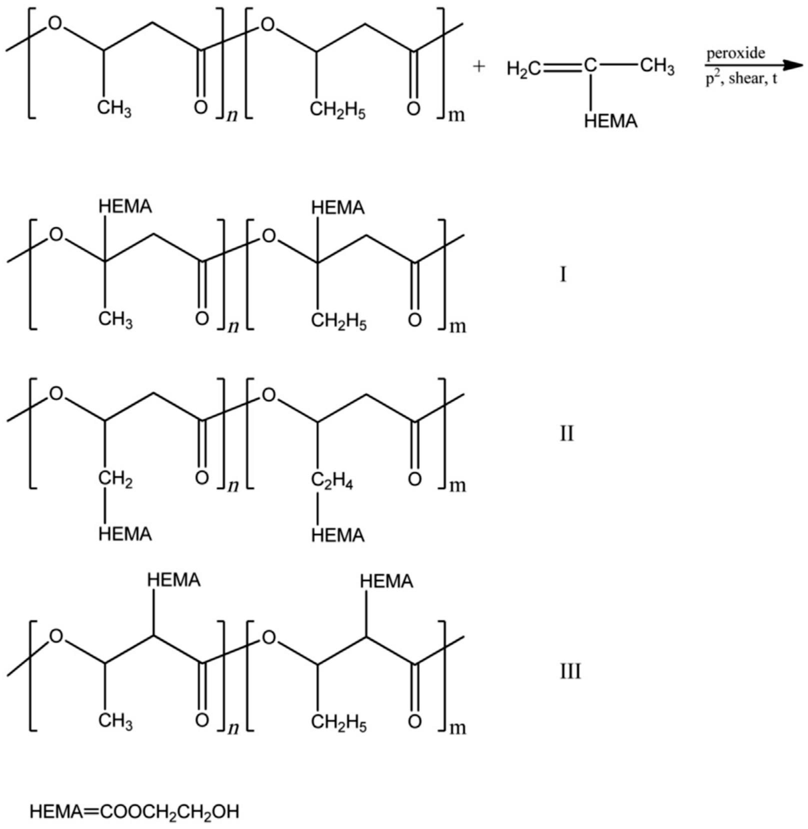
SCHEME 7.2 Reaction of PLA oligomer and TMI® unsaturated aliphatic isocyanate (2012, **US2012189860** A, FINA TECHNOLOGY).

polymers are selected from PLA, P3HB, PHBHV, poly(butylene succinate) (PBS), poly(alkylene succinate) (PES), PCL, or mixtures thereof. The polar monomer is an ethylenically unsaturated monomer containing at least one polar functional group or an oligomer or a polymer polymerized from an ethylenically unsaturated monomer containing at least one polar functional group. Preferred ethylenically unsaturated monomers containing a polar functional group include HEMA and poly(ethylene glycol) methacrylate (PEG-MA). Scheme 7.3 illustrates the grafting of HEMA onto PHBHV. By grafting polar monomers onto one or more of P3HB, PHBHV, PBS, PES, and PCL, the resulting modified polymer is more compatible with polar polymers and other polar substrates. For flushable material development, the modified polymer compositions of this invention have enhanced compatibility with water-soluble polymers, such as PVOH and polyethylene oxide, than with the unmodified biodegradable polymers.

Example: PHBHV (Biopol® P600G, Zeneca Bio-Prodcuts[1]) (9 wt%), HEMA and a liquid, organic peroxide initiator (Lupersol® 101, Arkema) (0.45 wt%) were charged into an extruder and modified. The modified PHBHV strands were cooled by a water bath. Polymer samples were collected in small chunks, allowed to solidify, and chipped into small pieces; two grafted PHBHV were obtained. The grafted PHBHV exhibited elastomeric properties in the melt. After solidification, the grafted PHBV strands were extremely rigid and brittle.

FR2918383 A1 (2009, CT VALORISATION IND AGRO RESSO) discloses a functionalized PLA obtained by reactive extrusion grafting of maleic anhydride on the polymer chain of PLA with decomposition of peroxide. The peroxide is 2,5-dimethyl-2,5-di-(*tert*-butylperoxy) hexane. The functionalization is made by extruding under vacuum at high temperature (100–200 °C, preferably 140–200 °C) and pressure (1–900 mbar, preferably 20–600 mbar). The functionalized PLA is used as compatibilizing agent for charged biodegradable polymer-based formulations in vegetable flour and for improving cohesion energy between polymer phase and flour.

PLA as such has been used in various fields, and when its application to paints, coating materials, inks, etc. is taken into consideration, it is necessary to disperse inorganic pigments, coloring pigments, fillers, etc. into PLA;



SCHEME 7.3 Reactive extrusion process for grafting poly(3-hydroxybutyrate-*co*-hydroxyvalerate) (PHBHV) with 2-hydroxyethyl methacrylate (HEMA) (2002, **WO02053610** A1; 2002, **WO02053641** A1, KIMBERLY CLARK CO).

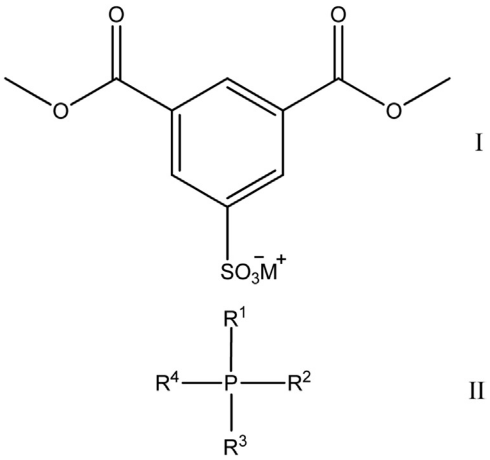
---

[1] Biopol® was sold to Monsanto in 1996, and then, it was bought by Metabolix in 2001.

for example, there have been proposals for a PLA copolymerized with metal sulfonate (2001, **JP2001323052** A, TOYO BOSEKI) and also for PLA where divalent metal salt such as calcium lactate is copolymerized (2002, **JP2002069352**, TOYO BOSEKI; TOPPAN PRINTING CO LTD; TOYO INK MFG CO). Although those polymers exhibit a good dispersibility for pigments, they have a disadvantage that resistance of a coated film to hydrolysis is poor (2008, **WO2008146905** A1, TOYO BOSEKI).

WO2008146905 A1 (2008, TOYO BOSEKI) discloses a copolymerized PLA containing (1) not less than 90 wt% of a lactic acid where the molar ratio (L/D) of L-lactic acid to D-lactic acid is within a range of 1–9 and (2) a phosphonium sulfoisophthalate structure represented by formula of Scheme 7.4 in a concentration of 10–100 eq/10^6 g in the polymer. Incidentally, the unit of eq/10^6 g shows how many (what equivalent) of the phosphonium sulfoisophthalate structures are present per 10^6 g of the polymer. The copolymerized PLA is used to improve hydrolysis resistance of a coating film of PLA, while maintaining dispersibility of PLA.

Although there is no particular limitation for a method of introducing the phosphonium sulfoisophthalate structure into the copolymerized PLA, there may be exemplified a method where lactide is subjected to ROP using a compound having a hydroxyl group and phosphonium sulfoisophthalate structure as an initiator, and a method where phosphonium sulfoisophthalate and lactic acid are directly subjected to a polycondensation. Among the above, a method where ROP is conducted is preferred. The introduction of phosphonium sulfoisophthalate structure into the PLA copolymer is claimed to enhance dispersibility of pigments, fillers, etc., and resistance to hydrolysis, and said modified polymer is useful as paint, coating material, and ink.



SCHEME 7.4 Phosphonium sulfoisophthalate structure (2008, **WO2008146905** A1, TOYO BOSEKI).

In the formula (I), M represents a structure represented by the formula (II). In the formula (II), R^1–R^4 may be the same or different, and each represents a hydrocarbon group having 1–18 carbon atoms.

Chemical modification of starch alters the properties of the material leading to products with a multitude of applications. Chemical modification of starch is the conversion of starch in the presence of starch modifying agents and optionally of substances accelerating the modification reaction that will effect dextrinization, hydrolysis, oxidation, derivatization (etherification or esterification or acetalization), or graft polymerization of the starch. Chemically modified starch includes oxidized starch, etherified starch, esterified starch, starch or a combination of such chemical modifications (e.g., etherified and esterified starch). Typically, a chemically modified starch is prepared by reacting the hydroxyl groups of the starch with one or more reagents. The degree of reaction, often referred to as the degree of substitution (DS), can significantly alter the physicochemical properties of the modified starch compared with the corresponding native starch. The DS for a native starch is designated as 0, and can range up to 3 for a fully substituted modified starch. Where the substituent groups have hydrophobic character, a DS approaching 3 can afford a modified starch that is relatively hydrophobic in character. Such modified starches can be more readily melt blended with biodegradable polyesters, relative to native starch. Suitable etherified starches include those that are substituted with ethyl and/or propyl groups. Suitable esterified starches include, for example, those that are substituted with acetyl, propanoyl, and/or butanoyl groups. Etherified starches may be prepared using techniques well known in the art, such as reacting starch with an appropriate alkylene oxide. Esterified starches may also be prepared using techniques such as reacting starch with appropriate anhydride, carboxylic acid, or acid chloride reagents.

GB1425624 A (1976, SCHOLTEN-HONIG RESEARCH BV) discloses a method for the chemical modification of starch, e.g., esterification or etherification, by subjecting a mixture of starch and one or more modifying agents that effect a chemical transformation of the starch molecule to microwave energy under such conditions that the water content during the radiation treatment is or reduces to less than 10 wt% of the starch. The modifying agent may be monochloroacetic acid or an alkali metal or ammonium salt thereof, a mixture of urea, and a phosphorus-containing acid or the alkali metal or ammonium salt thereof, a mixture of urea and sulfonic acid or ammonium maleate. Starch may also be subjected to graft polymerization with acrylamide in the presence of colloidal silica and benzoyl peroxide under microwave irradiation. Suitable starches for the chemical modification are potato starch, corn starch, wheat starch, tapioca starch, sorghum starch, waxy maize starch, and waxy sorghum starch. Instead of pure starch, protein containing starches such as flours can also be used.

7.2 CONTROLLED DEGRADATION

The processing of biodegradable polymers into commercially attractive products has been hindered by difficulties, such as their poor melt strength during melt processing. One of the proposed techniques for solving these difficulties includes the modification of such polymers by controlled degradation.

WO2008008068 A1 (2008, KIMBERLY CLARK CO) discloses a method for modifying an aliphatic-aromatic copolyester by melt blending the polyester with an alcohol to initiate an alcoholysis reaction that results in a copolyester having one or more hydroxyalkyl or alkyl terminal groups. By selectively controlling the alcoholysis conditions (e.g., alcohol and copolymer concentrations, catalysts, temperature, etc.), a modified aliphatic-aromatic copolyester may be achieved that has a molecular weight lower than the starting aliphatic-aromatic polymer. Such lower-molecular-weight polymers also have the combination of a higher melt flow index (MFI) and lower apparent viscosity, which is useful in a wide variety of fiber-forming applications, such as in the melt blowing of nonwoven webs. The aliphatic-aromatic copolyester is poly(butylene adipate-*co*-terephthalate) (PBAT). The alcohol is monohydric alcohol, polyhydric alcohol, or dihydric alcohol. A catalyst may also be used to facilitate the alcoholysis reaction. A suitable catalyst is a transition metal catalyst based on Group IVA metal and/or Group IVB metal.

Example: PBAT (Ecoflex® F BX 7011, BASF) was modified by melt blending with a reactant solution containing 1,4-butanediol (87.5 wt%), ethanol (7.5), and titanium propoxide (5 wt%). The modified PBAT and the reactant solution were each fed to a barrel of an extruder. The extruded PBAT was cooled on a fan-cooled conveyor belt and formed into pellets. Melt rheology tests were performed at 180 °C and 190 °C with 30 mm/1 mm (L/D) die. The apparent melt viscosity was determined at apparent shear rates of 100, 200, 500, 1000, 2000, and 4000/sec. The modified PBAT had much lower apparent viscosity (61 Pa s) over the entire range of shear rates. The MFI of the sample was 169 g/10 min (measured according to ASTM D1239, at 190 °C and 2.16-kg load). Further, the sample had a $M_w = 68{,}900$ g/mol, and $M_n = 37{,}600$. The results indicated that lower molecular weight, lower apparent viscosity, and increased MFI were due to alcoholysis with butanediol catalyzed. The modified PBAT was suitable for fiber formation.

CA2355206 A1 (2002, UNIV MCGILL) discloses a method for the production of macromers from the thermal degradation of PHAs such as P3HB and PHBHV. The obtained macromers are macromolecules of small size or length, typically of 1000–6000 g/mol, and contain unsaturated end groups as well as a carboxylic acid end groups. The macromers may be polymerized to produce homopolymers and copolymers for different applications in which amphiphilic and biocompatible properties are required, for example, drug delivery systems. Suitably, the thermal degradation is carried out at a temperature of 180–220 °C.

WO2007107808 A1 (2008, ALMA MATER STUDIORIUM UNI DI B; INST OF POLYMERS AND CARBON MA) discloses a method for controlling the thermal degradation of anionically terminated polymers, particularly of PHAs, by protonating or alkylating said anionic moieties, particularly carboxylate groups. Moreover, it described the preparation of polymeric blends having controlled thermal stability by mixing PHAs with polymers having an anionically activated moiety. This invention is mainly based on the finding that PHAs can undergo chain scission, at moderate temperatures, which results in polymer degradation, via an E1cB elimination mechanism.[2] This elimination mechanism involves the anionic moieties of a polymer that abstracts the acidic proton at C2 position of PHA with the generation of a carbanion, which undergoes the elimination reaction, leading to chain scission.

Kawalec et al. [34] have also tried to achieve a controlled degradation of P3HB by reaction with a carboxylate salt, specifically an acetate, at relatively low temperatures (150–170 °C). The results were not satisfactory, since the reaction of P3HB with an acetate yields waxy solids or very viscous liquids, which cannot be easily processed, making them unsuitable for applications on a large scale. Moreover, from the reaction mixture the formed acetic acid is evolved, which, besides being corrosive, can interfere with the degradation reaction, therefore an effective control of the reaction itself is practically unfeasible (2010, **WO2010044112** A1, UNIV BOLOGNA ALMA MATER; INST OF POLYMERS AND CARBON MA).

WO2010044112 A1 (2010, UNIV BOLOGNA ALMA MATER; INST OF POLYMERS AND CARBON MA) discloses a method for producing PHA oligomers and/or polymers of reduced molecular weight, which comprises reacting at least one PHA such as P3HB or PHBHV with at least one carbonate salt at a temperature of 50–300 °C, preferably120–200 °C. The above reaction allows a controlled degradation of the PHA chains, which yields oligomers and/or polymers having a controlled molecular weight, which can be modulated in

---

[2] E1cB or Elimination Unimolecular conjugate Base is an elimination reaction mechanism proceeding under basic conditions by first removing an acidic hydrogen to form a carbanion, followed by slow loss of a leaving group (such as –OH or –OR) to form an additional bond.

view of the specific application for which the oligomers and/or polymers are intended. The carbonate salt is chosen from anhydrous or hydrated carbonate and/or bicarbonate. The carbonate salt has counter-ion chosen from cation of alkali metal chosen from sodium and potassium and alkaline earth metals chosen from magnesium and calcium.

7.3 INCREASING THE MOLECULAR WEIGHT

JPH04189822 A (1992), **JPH04189823** A (1992), and **WO2013061834** A1 (2013) of SHOWA HIGHPOLYMER disclose a method to increase the molecular weight of an aliphatic polyester by adding a diisocyanate to a molten poly(alkylene dicarboxylate) prepolymer having a terminal hydroxyl group and $M_n \geq 5000$, preferably ≥10,000. The objective polyester is obtained by adding a diisocyanate such as 2,4-tolylene diisocyanate having isocyanate groups in an amount corresponding to 0.1–2 equivalent to hydroxyl groups to a poly(alkylene dicarboxylate); the glycol component of the aforementioned polyester is preferably ethylene glycol, or 1,4-butanediol, and the acid component is succinic acid. By this method an aliphatic polyester of $M_w \geq 200{,}000$ is obtained that cannot be achieved by a conventional direct polymerization method. However, by this method, reduction of accuracy in controlling molecular weight and formation of gelation and fish eyes sometimes occurred when adding the isocyanate to a polymerization tank as in the conventional method **WO2012086226** A1 (2012, SHOWA HIGHPOLYMER).

In order to solve the above-mentioned problems, **WO2012086226** A1 (2012, SHOWA HIGHPOLYMER) provides a method for producing an aliphatic polyester having an increased molecular weight comprising the steps of: (1) quantitatively injecting a diisocyanate into the aliphatic polyester prepolymer in a molten state at a temperature not lower than melting temperature (T_m); (2) quantitatively and continuously introducing the diisocyanate-containing aliphatic polyester prepolymer obtained at the step (1) into a mixing tank, discharging same from the mixing tank under stirring and supplying it to a coupling reaction tank; and (3) reacting the aliphatic polyester prepolymer with the diisocyanate in the coupling reaction tank (see Figure 7.1).

7.4 RADIATION (IN BULK)

This type of treatment refers to the radiation of a biopolymer(s) in the bulk and shall be distinguished from the radiation on the surface of a biopolymer(s) (see Chapter 8: Surface treatment; Section 8.2.1: Radiation). As a matter of fact, the radiation in the bulk is stronger and more penetrating (e.g., γ-irradiation and electron beam) than the surface radiation (e.g., UV).

The penetrating power of electron beams is not as great as that of γ-rays, but it has the advantage of allowing for continuous application within a short time. Hence, electron beams are extensively used in modifying high-molecular-weight materials through crosslinking, graft polymerization, or decomposition reaction. The use of electron accelerators is more active than any other types of accelerators since by exposure to accelerated electron beams, a crosslinked structure can be easily introduced into a polymer so as to achieve a marked improvement in its heat resistance (**JPH10287733** A, 1998, JAPAN ATOMIC ENERGY RES INST).

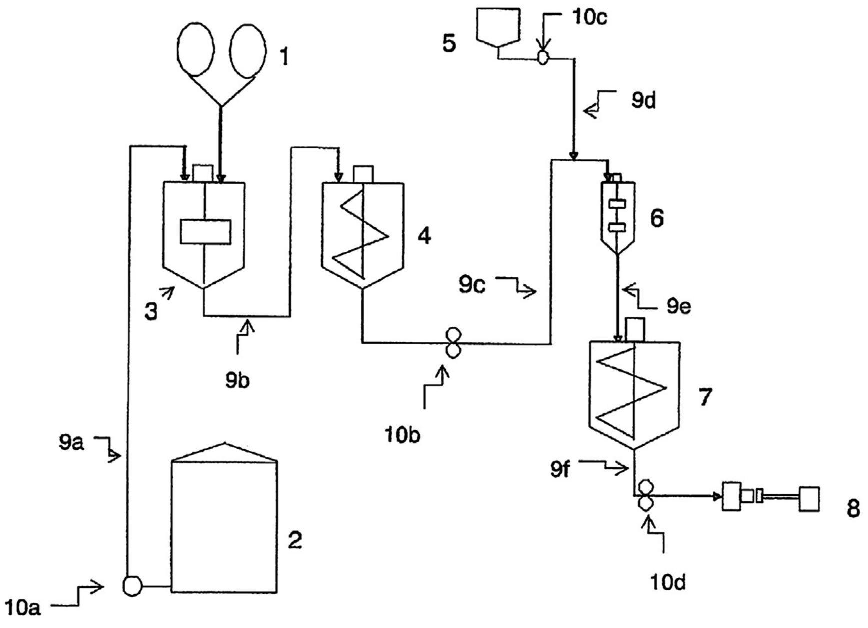


FIGURE 7.1 Schematic drawing of the production method (**WO2012086226** A1, 2012, SHOWA HIGHPOLYMER). 1: weighing hopper; 2: glycol storage tank; 3: transesterification tank; 4: storage tank; 5: diisocyanate storage tank; 6: mixing tank in which the aliphatic polyester prepolymer is mixed with the diisocyanate; 7: coupling reaction in which the mixed aliphatic polyester prepolymer and diisocyanate are reacted; 8: pelletizer; 9a: pipe connecting glycol storage tank 2 and esterification tank 3; 9b: pipe connecting esterification tank 3 and transesterification reaction tank 4; 9c: pipe connecting transesterification reaction tank 4 and mixing tank 6; 9d: pipe connecting diisocyanate storage tank 5 to pipe 9c; 9e: pipe connecting mixing tank 6 and coupling reaction 7; 9f: pipe connecting reaction tank 7 to pelletizer 8; 10a–d: pumps.

WO9946332 A1 (1999, DAICEL CHEM) discloses a PCL composition comprising a PCL that has been treated with a radiation so as to have a gel content of 90% or lower and at least either of other biodegradable polymer such as an aliphatic polyester and a resin additive, and a molding thereof.

In order to crosslink PCL by irradiation at temperatures near room temperature, a dose as high as 200 kGy is required, and yet a maximum gel content (a measure of the degree of crosslinking) that can be achieved is about 25%. Hence, no adequate improvement in the heat resistance of PCL can be accomplished at temperatures near room temperature. On the other hand, crosslinking is more likely to occur in PCL at temperatures near its T_m; however, the crosslinked product formed after the irradiation contains so many voids that a film compression molded from it has only low strength (**JPH10287733** A, 1998, JAPAN ATOMIC ENERGY RES INST).

JPH10287733 A (1998, JAPAN ATOMIC ENERGY RES INST) proposed a method to overcome the above problems according to which PCL is melted at a temperature of 60 °C or higher and subsequently cooled down to a noncrystallizing temperature and then exposed to radiation at that temperature so that it is crosslinked and a product of an extremely high gel content is obtained. Because of the high degree of its crosslinking, heat resistance, and transparency, the PCL product can be used as a heat-resistant tape or a heat-shrinkable film.

JP2002069206 A (2002, DAICEL CHEM) discloses the radiation of an aliphatic polyester composition comprising PCL and diatomaceous earth with γ-rays or electron beams in various doses (up to 160 kGy). With increase of dose, the melt viscosity was increased. The irradiated composition showed improved biodegradation.

Mitomo et al. [32] studied the radiation effects of selected PHAs by irradiation P3HB and PHBHV with γ-rays in air or vacuum. Polymer chain scission occurred and resulted in depression of (T_m), glass transition temperature (T_g), and number-average molecular weight (M_n). Decrease in M_n of the sample irradiated in vacuum was smaller than that irradiated in air, implying introduction of crosslinking. The T_m and T_g of samples irradiated in air were inversely proportional to M_n. Their biodegradability was clearly promoted with decreasing M_n. Radiation grafting of MMA or HEMA was carried out by in-source polymerization. Degree of grafting (X_g) increased as irradiation dose increased and leveled off around 5 kGy. The X_g of P3HB grafted was lower than that of PHBHV because of higher crystallinity of the former. Crosslinking between the grafted PMMA chains was easily formed. Biodegradability of both polymers steeply decreased by introduction of MMA grafting, while that of polymers grafted with HEMA increased at first because of improvement of wettability and then steeply decreased with increasing X_g of HEMA.

7.5 INTERREACTING POLYMERS

Interreacting polymers refer to polymers that interact in the absence of monomers to form branched, bridged, crosslinked, or interpenetrating structures.

7.5.1 Polymer Branching/Bridging

Various techniques are available for providing bridging in PLA and thus converting it into a less linear lactide polymer. For example, free radical–generating peroxides can be used to cleave substituents from the PLA backbones, generating a polymer radical that can bond with another polymer radical. Bridging may also be provided through the reaction of multifunctional chain extenders to link polymer chains together and form a less linear PLA. An advantage of this mechanism for generating interaction among PLA chains is that many radical generators are inexpensive and readily available. In addition, many break down to byproducts that are readily removed, for example, by devolatilization. Also, the extent of bonding is so small that the biodegradability or compostability of the PLA is not significantly lost. **WO9504097** A1 (1995, CARGILL INC) discloses the modification of PLA with linear organic peroxides such as 2,5-dimethyl-2,5-di(*tert*-butylperoxy)hexane and dicumyl peroxide.

WO9518169 A1 (1995, NESTE OY) discloses also the modification of PLA by reactive extrusion of the polymer with linear organic peroxides selected from dilauroyl peroxide, *tert*-butylperoxy-diethylacetate, *tert*-butylperoxy-2-ethylhexanoate, *tert*-butyl-peroxyisobutyrate, *tert*-butylperoxyacetate, *tert*-butylperoxybenzoate, and dibenzoyl peroxide. The modified PLA has good elasticity and melt strength.

The polymers modified according to these prior art processes either result in only a minor degree of branching or suffer from gel formation, due to crosslinking. Gel formation results in the occurrence of "fish eyes" in transparent films or coatings or in particulates in moldings, which is evidently undesired.

WO9914268 A1 (1999, MONSANTO CO) discloses the modification of a PHA using free radical initiators, such as organic peroxides. The peroxides are all linear in nature and include 2,5-dimethyl-2,5-di(*tert*-butylperoxy)hexane and butyl-4,4-di(*tert*-butylperoxy)valerate. The modification of PHA creates branching in the polymer backbone. The branched PHA is produced by melting PHA in the presence of low levels of free radical initiators under conditions that cause their decomposition into free radicals. The free radicals stimulate interchain crosslink formation between linear PHA molecules, giving rise to the branched PHAs. Branched PHAs are claimed to provide significant cost benefits when used for production of PHA-derived articles, particularly coatings and films, by maximizing throughput while minimizing excessive waste of materials. Furthermore, products produced from the disclosed branched PHAs have improved physical, mechanical, and aging characteristics relative to those produced from unmodified, linear PHAs. As the peroxides decompose, they form very high energy radicals that can extract a hydrogen atom from the polymer backbone. These radicals have short half-lives, thereby limiting the population of branched molecules that is produced during the active time period. After reaction with peroxide, the molecular weight remained almost unchanged, due presumably to the simultaneous processes of thermal degradation and branching.

WO2007099056 A1 (2007, AKZO NOBEL NV) discloses a method for the modification of an aliphatic (co) polyester such as P3HB, PHBHV, or PCL, which involves contacting the (co)polyester with a cyclic organic peroxide under conditions whereby at least some of said peroxide is decomposed. Suitable cyclic organic peroxides include cyclic ketone peroxides and 1,2,4-trioxepanes. The modified copolymer combines a high degree of branching with the absence of gel formation. In addition, high-molecular-weight distributions of the (co)polyester can be obtained, thereby improving its melt strength. A further advantage of the disclosed method is that, unlike the peroxides used in the prior art, the cyclic organic peroxides do not release *t*-butanol as decomposition product. This absence of *t*-butanol, which due to its toxicological properties is undesired in (co)polymers for food-related applications, allows the modified (co)polymers to be used in applications involving food contact.

WO2010008447 A1 (2010, METABOLIX INC) discloses a method of branching PHA involving thermolyzing PHA such that the molecular weight is reduced to 25–75% from the original molecular weight, and reacting thermolyzed PHA with a branching agent, for example a free radical initiator, such as a peroxide. The branching agent creates radicals on the backbone of the linear polymer, which then react, either with each other, or under certain conditions, with the reactive groups on the ends of the thermolysed PHA. The branching agent is preferably selected from *t*-amyl-2-ethylhexyl peroxycarbonate (TAEC), *t*-butylperoxybenzoate (TBPB), l,l-bis(*t*-butylperoxy)-3,3,5-trimethylcyclohexane (CPK), dicumyl peroxide (DCP), or *tert*-butylperoxy-2-ethylhexylcarbonate. In certain embodiments, the reacting with a branching agent is done in the presence of a coagent (also referred to herein as a "crosslinking agent"), thereby forming a branched PHA. The thermolysis is performed at 190–250 °C, preferably 190–220 °C for 0.1–1.6 min. The branched polymer has increased melt strength over the melt strength of the starting polymer.

7.5.2 Crosslinking

The term *crosslinking* means chemically or physicochemically making an intramolecular or intermolecular linkage of a polymer material to form a network structure; and the term *crosslinking agent* means a substance having certain reactivity with the above-described polymer material that is added for carrying out the above-described crosslinking reaction. A typical crosslinking procedure involves the irradiation of biodegradable polymers after being molded into the shapes of final products.

JP2003313214 A (2003, JAPAN ATOMIC ENERGY RES INST) discloses a method of crosslinking a biodegradable polymer by using ionizing radiation or a chemical initiator. The method involves melting a biodegradable polymer such as PLA, PCL, PBS, or poly(butylene succinate-*co*-adipate) (PBSA), adding a low concentration of a monomer having an allyl group, kneading the mixture, hot pressing the mixture to a sheet, and irradiating the sheet to crosslink the biodegradable polymer. Another method involves dissolving the biodegradable polymer in a solvent containing a monomer having an allyl group, kneading the mixture, casting the dissolved polymer on a flat plate, and irradiating to crosslink the biodegradable polymer. The crosslinking of the biodegradable polymer improves the dimensional stability and the tensile strength at a temperature, $T \geq T_g$. However, the thus-produced crosslinked biodegradable product is hard and brittle and, therefore, does not exhibit adequate flexibility and elongation.

The crosslinking of the biodegradable biopolymer through irradiation has an advantage that the heat resistance and the shape-maintaining property are improved. Conversely, the above-described crosslinking allows the thermoplasticity of the biopolymer to deteriorate. Therefore, the irradiation is heretofore carried out after the molding into the product is carried out. However, in order to irradiate after the molding into a desired shape is carried out, it is required to introduce an expensive and high administrative cost irradiation facility into a production site or carry the molded part to the place where the irradiation facility is disposed. Therefore, expenses, time and effort, and the like are involved, and the workability and the productivity of the molded part are impaired significantly (2008, **US2008036119** A1, SUMITOMO ELEC FINE POLYMER INC).

US2005242466 A1 (2005, SUMITOMO ELEC FINE POLYMER INC) discloses the production of transparent PLA by (1) kneading PLA with a monomer having at least two double bonds in its molecule; (2) molding the kneaded product a temperature of from the T_m of PLA to 200 °C; (3) quenching the formed molded article after molding; and (4) subjecting the quenched molded article to crosslinking treatment so as to prevent molecules of PLA from undergoing recrystallization (see also Chapter 2: Properties; Section 2.1.6: Transparency).

WO2006098159 A1 (2006, SUMITOMO ELEC FINE POLYMER INC) discloses a method of producing a crosslinked PLA comprising the steps of: (1) mixing PLA with at least a plasticizer containing a rosin derivative or a dicarboxylic acid derivative and/or a glycerol derivative, and a crosslinking monomer, and then kneading the resulting mixture; (2) producing a PLA molded product by molding the PLA composition; and (3) crosslinking the PLA molded product by ionizing radiation (10–100 kGy). Crosslinking monomer preferably used is an allylic-type crosslinking agent, in particular triallylisocyanurate. The content of plasticizer having rosin derivative is 15–30 wt% with respect to 100 wt% of PLA. The content of crosslinkable monomer is 3–8 wt% with respect to 100 wt% of PLA. The content of plasticizer having dicarboxylic acid derivative and/or glycerol derivative is 3–30 wt% with respect to 100 wt% of PLA. The content of allyl-type monomer is 3–15 wt% with respect to 100 wt% of PLA.

US2008036119 A1 (2008, SUMITOMO ELEC FINE POLYMER INC) discloses a method for manufacturing a crosslinked biodegradable polymer powder comprising the steps of: (1) preparing a kneaded product containing a biodegradable polymer and a crosslinking monomer; (2) crosslinking the biodegradable polymer by using ionizing radiation; and (3) pulverizing the kneaded product into a powder; preferably, the method includes a step (4) of swelling the biodegradable polymer powder with an impregnant containing a plasticizer or a polymerizable monomer at a temperature of 60 °C or higher, and lower than or equal of T_m or degradation temperature of the biodegradable polymer. The resulting biodegradable polymer composite powder is heated to a temperature higher than or equal of T_m of the biodegradable polymer and solidified into the shape of pellets. Specific examples of biodegradable polymers include: polysaccharide-based biodegradable polymers including natural polysaccharide, e.g., cellulose, starch, chitin, chitosan, and alginic acid, and derivatives thereof produced by acetylation, esterification, or the like; aliphatic polyesters including PLA, PCL, PBS, poly(ethylene succinate) (PES), and poly(ethylene succinate-*co*-adipate) (PESA); and aliphatic-aromatic polyesters, typified by, for example, PBAT. Examples of crosslinking monomers include acrylic or methacrylic crosslinkable monomers and allyl crosslinking monomers. Types of ionizing radiation include γ-rays, X-rays, β-rays, and α-rays. However, in the industrial production, γ-ray irradiation through the use of ^{60}Co and electron beam irradiation through the use of an electron beam accelerator are preferable.

WO2006103913 A1 (2006), **JP2007092022** A (2007), **JP2007182484** A (2007), **JP2008001837** A (2008), and **CN101146851** A (2008) of SUMITOMO ELEC FINE POLYMER INC disclose a method for producing a PLA complex by crosslinking a PLA in two steps involving a primary and a secondary crosslinking (see Figure 7.2). First, PLA is mixed with a crosslinking monomer (A), and then the mixture is molded into a molded product as shown in (a). The resulting PLA molded product is subjected to primary crosslinking so as to have a gel fraction of approximately 100% as shown in (b). Microscopically, the PLA chains in the crosslinked PLA (1) are bound to each other via the crosslinks (11) as shown in (c). Secondly, the crosslinked PLA (1) is immersed in a liquid crosslinking monomer (B) (2) serving as an impregnant at a temperature that is not lower than the T_g and not higher than the T_m of PLA, and subsequently the crosslinking monomer (B) (2) infiltrates the gaps between the crosslinked PLA chains as shown in (d). Thirdly, in the cooling step, the crosslinked PLA is cooled to room temperature, which is not higher than the T_g of PLA, and as a result, the PLA complex (3) shown in (e) and (D) is obtained. In this state, molecules of the crosslinking monomer (B) (2) simply exist in the gaps between the PLA chains and are not bound to the chains. Then, in the secondary crosslinking step, the molded product is further crosslinked using ionizing radiation or other means. As a result, molecules of the infiltrating crosslinking monomer (B) are bound to each other via crosslinks (12), and at the same time, they are bound also to the PLA chains via graft crosslinking, thus producing the PLA complex (10) having a more complicated crosslinking network as shown in (g) and (h). The combination of two crosslinking steps, primary crosslinking and secondary crosslinking, makes the crosslinking network more complicated and thereby improves the strength of the resulting PLA complex (10). As a result the PLA complex (10) has a sufficient strength for maintaining its shape even at temperatures equal to or higher than 60 °C, the T_g of PLA.

This combination of two crosslinking steps enables the PLA complex to maintain its strength, which has been achieved at temperatures $T \leq 60$ °C, as well as prevents the infiltrating crosslinking monomer from being separated out through binding molecules thereof via crosslinking. The PLA complex can consistently maintain its shape using the PLA crosslinking network even at temperatures at $T \geq 60$ °C. At $T \leq 60$ °C, the PLA complex exhibits an excellent flexibility and elongation because the impregnant infiltrating the PLA crosslinking network inhibits the interactions between the PLA chains.

Examples of the crosslinking monomer (A) mixed with PLA prior to primary crosslinking include acrylic-, methacrylic-, or allylic-type crosslinking monomers. Examples of the crosslinking monomer (B) include acrylic-, methacrylic acid-, styrene-, allylic-, and lactone-type monomers.

US2012053259 A1 (2012, MINIMA TECHNOLOGY CO LTD) discloses a biodegradable polymer composition comprising PBS and a crosslinking agent capable of producing a free radical to allow the polymer component to be subjected to a free radical crosslinking reaction in such a condition that the biodegradable composition has an MFI of 1.5–3.0. The crosslinking agent is used to crosslink PBS, while producing free radicals to function as an initiator for a crosslinking reaction. Specifically, the crosslinking agent can be used to increase grafting and crosslinking of the polymers of the polymer component, thereby resulting in a decrease in MFI to be within 1.5–3.0 and an increase in melting strength of the biodegradable polymer composition. Preferably, the crosslinking agent is a peroxide selected from the group consisting of dicumyl peroxide 2,5-dimethyl-2,5-di(*tert*-butylperoxy)hexane and 3,6,9-triethyl-3,6,9-trimethyl-1,4,7-triperoxonane. In view of environmental considerations, the peroxide used in the preferred embodiments of this invention is 2,5-dimethyl-2,5-di(*tert*-butylperoxy)hexane or 3,6,9-triethyl-3,6,9-trimethyl-1,4,7-triperoxonane. Moreover, the biodegradable composition further includes optionally, a grafting component used to react with the peroxide and the polymer component so as to form a branch group in the polymers of the polymer component, thereby resulting in a decrease in MFI and an increase in the melting viscosity and the melting strength of the biodegradable composition. Preferably, the grafting component is selected from the group consisting of butyl acrylate, vinyl acetate, and the combination thereof. Furthermore, the biodegradable composition comprises a foaming agent. A foam article made from the biodegradable composition of this invention exhibits a relatively high mechanical strength, thermal resistivity, and solvent resistivity.

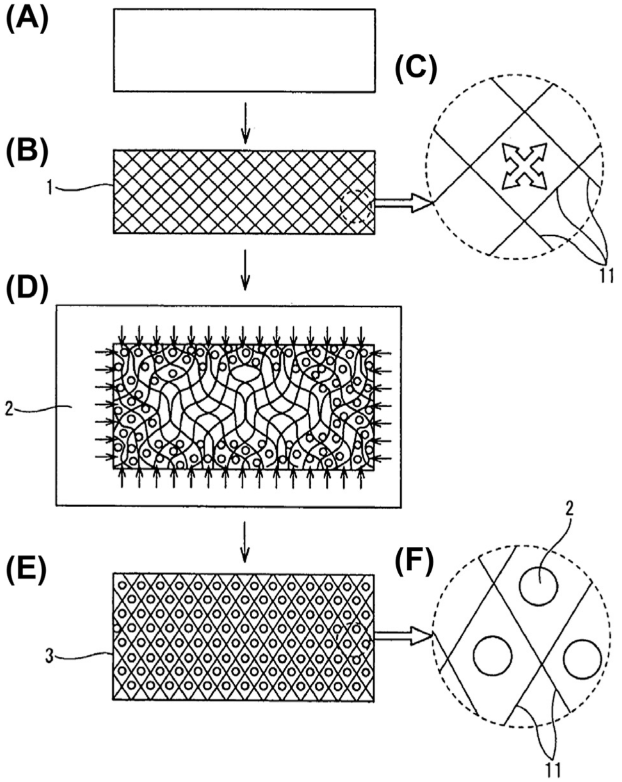


FIGURE 7.2 Schematic diagram showing a production process of the PLA complex (2006, **WO2006103913** A1; 2007, **JP2007092022** A; 2007, **JP2007182484** A; 2008, **CN101146851** A, SUMITOMO ELEC FINE POLYMER INC). 1: Crosslinked PLA; 2: Impregnant (crosslinking monomer (B)); 3, 10: PLA complex; 4: PLA molded product; 5: Crystallization; 11: Crosslinks between PLA chains; 12: Crosslinks between crosslinking monomer molecules.

Crosslinking of starches is well known in the prior art. A description of crosslinking agents and reaction conditions can be found, for example, in Rutenberg and Solarek [35], Wurzburg [36], and Hullinger [37].

JP2001329070 (2001, JAPAN ATOMIC ENERGY RES INST) discloses a method for producing crosslinked starch derivatives by irradiating a pasty mixture of 100 pbw of a starch derivative and 3–1000 pbw of water. The paste of starch derivative is crosslinked by irradiation with γ-rays or electron beams in a dose of 0.1–200 kGy. Two different levels of crosslinking are performed; the first is mild crosslinking by irradiation at a low dose of 0.1–1.0 kGy to such an extent that the viscosity of the overall system increases upon immersion in water, and the second is intensive crosslinking by irradiation at a higher dose than 1.0 kGy to produce a gel that is completely insoluble in water. The crosslinking reaction of conventional carboxy methyl starch that is considered to be difficult is claimed to be performed easily when the starch is mixed to a paste with a small amount of water and subjected to irradiation.

WO0069916 A1 A (2000, ATO BV) proposed a thermomechanical method for the production of crosslinked starch. The thermomechanical process uses an extrusion treatment at raised temperatures, under conditions of high shear and pressure, and in the presence of a crosslinking agent. A plasticizer is preferably present during the thermomechanical treatment. The obtained starch material can readily be dispersed in cold water at increased solids content (up to 40 wt%), and with relatively low viscosity (typically lower than 100 mPa s at 25 °C and 10 wt%) as compared to other cold-water dispersible starches. The size of the dispersed starch particles is in the submicron size range, typically less than 200 nm on the average. An essential step in the disclosed method is the crosslinking during the thermomechanical treatment. The crosslinking is preferably reversible, i.e., the crosslinks are partly or wholly cleaved after the mechanical treatment step. Suitable reversible crosslinkers include those that form chemical bonds at low water concentrations, which dissociate or hydrolyze in the presence of higher water concentrations. This mode of crosslinking results in a temporary high viscosity during processing followed by a lower viscosity after processing. Examples of reversible crosslinkers are dialdehydes and polyaldehydes, which reversibly form hemiacetals, acid anhydrides, and mixed anhydrides (e.g., succinic and acetic anhydride), and the like. Suitable dialdehydes and polyaldehydes are glutaraldehyde, glyoxal, periodate-oxidized carbohydrates, and the like. Glyoxal is a particularly suitable crosslinker.

However, the limited storage stability of these colloidal starch dispersions makes them unsuitable for practical application. Depending on the nature of the starch used, shelf life may be as low as a few hours at 20 wt% before the system turns irreversibly to a gel. Moreover, the sensitivity to humidity of starch is often a restrictive factor for coating application where wet resistance, durability, strength, barrier, etc. are required (2001, **EP1095977** A1, UCB SA).

7.5.3 Interpenetrating Polymeric Networks

The term *interpenetrating network* (IPN) refers to an interpenetrating polymeric network, which is a combination of two or more polymers in which each polymer forms a network. There is entanglement and interaction between the networks. When swollen in a solvent, none of the polymers will dissolve in the solvent.

WO9942147 A1 (1999, MASSACHUSETTS INST TECHNOLOGY) discloses a biodegradable shape memory polymer composition, which can form semi-IPN. Shape memory polymers (SMPs) are generally characterized as phase segregated linear block copolymers having at least one hard segment and at least one soft segment. The hard segment is typically crystalline, with a defined T_m, and the soft segment is typically amorphous, with a defined T_g. In some embodiments, however, the hard segment is amorphous and has a T_g rather than a T_m. The T_g or T_m of the hard segment is preferably between 30 °C and 150 °C, and is at least 10 °C, and preferably 20 °C, higher than the T_g or T_m of the soft segment. At least one of the hard or soft segments can contain a crosslinkable group, and the segments can be linked by formation of an IPN or a semi-IPN, or by physical interactions of the segments. Items can be formed into a given shape at a temperature above the T_g or T_m of the hard segment, and cooled to a temperature below the T_g or T_m of the soft segment. If the item is subsequently formed into a second shape, the item can return to its original shape by heating the item above the T_g or T_m of the soft segment and below the T_g or T_m of the hard segment. Representative biodegradable polymers include polyhydroxy acids, poly(ether ester)s, polyorthoesters, poly(amino acids), polyanhydrides, polycarbonates, PHAs, and PCL. The SMP compositions can be used to prepare numerous articles for use in biomedical and other applications. Examples of biomedical applications include sutures, orthodontic materials, bone screws, nails, plates, catheters, tubes, films, stents, orthopedic braces, splints, tape for preparing casts, and scaffolds for tissue engineering, contact lenses, drug delivery devices, implants, and thermal indicators. Examples of nonmedical-type applications for biodegradable polymers include items for which disposal is an issue, such as disposable diapers and packaging materials.

WO9847445 A1 (1998, CAMBRIDGE SCIENT INC) discloses biodegradable polymeric semi-IPN blends that comprise a first biodegradable polymer such as PLGA capable of producing acidic products upon hydrolytic degradation; and a second biodegradable polymer such as poly(propylene fumarate) (PPF), which, preferably via crosslinking by a vinyl monomer such as vinyl pyrrolidone forms a biopolymeric scaffolding with the requisite dimensional and geometric stability. A beneficial end use of this material is in the form of internal fixation devices (IFDs) such as bone supports, plates, and pins, and/or bone cements for bone repair that are formed from the disclosed semi-IPN blend.

WO2007028258 A2 (2007, OTTAWA HEALTH RESEARCH INST; UNIV OTTAWA) discloses an IPN, wherein at least one of the polymer networks is based on a biopolymer. The biopolymer is denatured gelatin, fibrin-fibrinogen, elastin, glycoprotein, polysaccharide, glycosaminoglycan, proteoglycan, or oxidized polysaccharide or any combination thereof; the polysaccharide is alginate, chitosan, *N*-carboxymethyl chitosan, *O*-carboxymethyl chitosan, *N*,*O*-carboxymethyl chitosan, hyaluronic acid, or chondroitin sulfates. Also disclosed is a hydrogel material comprising the IPN and a method of its production. The hydrogel material is produced by combining a first polymer network with a second polymer network and maintaining the resultant reaction mixture under acidic conditions for formation of an IPN. The first and second polymer networks can be combined with at least one crosslinking agent. The reaction mixture is placed in a mold and allowed to cure. Devices manufactured from the IPN hydrogel material include implants (e.g., corneal implants), corneal onlays, nerve conduit, blood vessels, drug delivery devices and catheters, therapeutic lens, intraocular lens, and methods of manufacture thereof. The IPN hydrogel material is characterized by low cytotoxicity or no cytotoxicity, ability to facilitate cell, and/or nerve growth, and/or moldability. Furthermore, the IPN hydrogel has sufficient mechanical or structural properties to withstand handling, implantation, which may include suturing, and postinstallation wear and tear.

JP2009167225 A (2009, SUMITOMO ELEC FINE POLYMER INC) discloses a method for producing a thermoresponsive material comprising the following steps: (1) forming a PLA crosslinked body having a first network by subjecting a molded body comprising a PLA composition obtained by mixing PLA with a polyfunctional monomer for crosslinking PLA to first irradiation with ionizing radiation; (2) immersing the PLA crosslinked body in a liquid of an ionizing radiation crosslinkable monomer to impregnate the monomer; (3) subjecting the PLA crosslinked body, into which the ionizing radiation–crosslinkable monomer has been impregnated, to second irradiation with ionizing radiation to form an interpenetrating PLA crosslinked body in which a second network comprising an ionizing radiation–crosslinkable polymer penetrates the first network; (4) providing the interpenetrating PLA crosslinked body with water at a temperature $T \geq T_g$ of PLA to incorporate the water; and (5) cooling the interpenetrating PLA crosslinked body to below the T_g of the PLA, while retaining the water. The thermoresponsive material has the property of changing its optical transparency according to the ambient temperature, while using PLA, and which has an adjusted bifurcation temperature at which the optical transparency changes.

PATENTS

Patent Number	Publication Date	Family Members	Priority Numbers	Inventors	Applicants	Title
CA2355206 A1	20020217	US2002042481 A1 20020411; US6534599 B2 20030318	US20000225822P 20000817; US20010929073 20010815	MARCHESSAULT ROBERT H; NGUYEN SOPHIE; YU GA-ER	UNIV MCGILL	Macromers of poly (hydroxyalkanoates).
CN101146851 A	20080319		JP20050090183 20050325	KANAZAWA SHINICHI; KAWANO KIYOSHI	SUMITOMO ELEC FINE POLYMER INC	Polylactic acid complex and production method thereof.
EP0899274 A1	19990303	US5952405 A 19990914	US19970918878 19970826	SCHOENBERG JULES E; HARLAN ROBERT D; HATFIELD STEPHEN F; SAMUEL JOHNSON K	NAT STARCH CHEM INVEST	Lactide graft copolymers and hot melt adhesives prepared from same.
EP1095977 A1	20010502	WO0130905 A1 20010503; US6818686 B1 20041116; MXPA02004230 A 20021216; JP2003513133 A 20030408; CN1391596 A 20030115; CN1211424C 20050720; CA2389245 A1 20010503; AU1854301 A 20010508	EP19990121449 19991028	COLPAERT MARC; BONTINCK DIRK; ROOSE PATRICE	UCB SA	Water based polymer composition comprising a biopolymer and a polymer resin.
FR2918383 A1	20090109	FR2918383 B1 20091016	FR20070056280 20070705	BARBIER JACQUES; DEVER CEDRIC; PICHON THOMAS	CT VALORISATION IND AGRO RESSO	Utilisation d’acide polylactique fonctionnalisé en tant qu’agent compatibilisant. “Use of functionalized polylactic acid as compatibilizing agent.”
GB1425624 A	19760218		GB19730037927 19730810	VERBERNE PETRUS; VLOT TONNY	SCHOLTEN HONIG RESEARCH BFV	Chemical modification of starches.
JP2001261797 A	20010926	JP3440915 B2 20030825	JP20000070098 20000314	MATSUMOTO HIROSHIGE; MASUDA TOYOHIKO; MAEDA YUHEI	TORAY INDUSTRIES	Aliphatic polyester resin and molded product.
JP2001323052 A	20011120	JP3680988 B2 20050810	P20000146633 20000518	SHIBAZAKI SATOKO; MIYAMOTO TAKASHI; ITO TAKESHI; SHINO KATSUYA; HOTTA YASUNARI	TOYO BOSEKI	Metal sulfonate-copolymerized lactic acid-based resin.

JP2002030208 A	20020131	JP4655342 B2 20110323	JP20000213875 20000714	MATSUMOTO HIROSHIGE, MAEDA YUHEI; ARANISHI YOSHITAKA	TORAY INDUSTRIES	Polylactic acid resin composition and molded article.
JP2002069206 A	20020308		JP20000262701 20000831	MITOMO HIROSHI; MURAKAMI TEI	DAICEL CHEM	Aliphatic polyester resin composition.
JP2002069352 A	20020308	JP4795518 B2 20111019	JP20000258829 20000829	MIYAMOTO TAKASHI; ITO TAKESHI; SHINO KATSUYA; SHIBAZAKI SATOKO; HOTTA YASUNARI; WATANABE JIRO; KATO SHUNICHI; ICHIKAWA YOSHITO; WATANABE FUMIO	TOYO BOSEKI; TOPPAN PRINTING CO LTD; TOYO INK MFG CO	Ink composition.
JP2003313214 A	20031106	JP3759067 B2 20060322	JP20020125905 20020426	YOSHII FUMIO; KUME TAMIKAZU; NAGASAWA NAOTANE; MITOMO HIROSHI	JAPAN ATOMIC ENERGY RES INST	Process for manufacturing crosslinked biodegradable material.
JP2007092022 A	20070412		JP20050090183 20050325; JP20050249563 20050830; JP20060085839 20060327	KANAZAWA SHINICHI; KAWANO KIYOSHI	SUMITOMO ELEC FINE POLYMER INC	Polylactic acid complex and production method thereof.
JP2007154002 A	20070621		JP20050349728 20051202	MIZUNO KATSUTOSHI; ANDO YOJI; SHICHIDA HIROAKI	TOYODA GOSEI KK	Lactic acid based resin composition and its molded article.
JP2007182484 A	20070719		P20060000948 20060105	KANAZAWA SHINICHI; KAWANO KIYOSHI	SUMITOMO ELEC FINE POLYMER INC	Polylactic acid complex and production method thereof.
JP2008001837 A	20080110		JP20060174229 20060623	KANAZAWA SHINICHI	SUMITOMO ELEC FINE POLYMER INC	Polylactic acid complex and production method thereof.
JP2009167225 A	20090730	JP5167540 B2 20130321	P20080003380 20080110	KANAZAWA SHINICHI	SUMITOMO ELEC FINE POLYMER INC	
JPH04189822 A	19920708	JP2825969 B2 19981118	JP19900317849 19901126	TAKIYAMA EIICHIRO; NIIKURA ISAMU	SHOWA HIGHPOLYMER	Production of aliphatic polyester.
JPH04189823 A	19920708		JP19900317850 19901126	TAKIYAMA EIICHIRO; NIIKURA ISAMU; HATANO YOSHITAKA	SHOWA HIGHPOLYMER	Production of high-molecular weight polyester.

Continued

—Cont'd

Patent Number	Publication Date	Family Members	Priority Numbers	Inventors	Applicants	Title
JPH10287733 A	19981027	US5977203 A 19991102; JP3570850 B2 20040929	JP19970096844 19970415; US19980028854 19980224	MAKUUCHI KEIZO; YOSHII FUMIO; HASEGAWA SHIN; MITOMO HIROSHI; DARWIS DARMAWAN	JAPAN ATOMIC ENERGY RES INST	Process for producing crosslinked polycaprolactone.
US2002010327 A1	20020124	US6617448 B2 20030909	JP20000152372 20000524	YOSHII FUMIO; KUME TAMIKAZU	JAPAN ATOMIC ENERGY RES INST	Process for producing grosslinked starch derivatives and cross-linked starch derivatives produced by the same.
US2002128384 A1	20020912	US6552124 B2 20030422; MXPA02000573 A 20020917	US20000753223 20001229	WANG JAMES H; SCHERTZ DAVID M	KIMBERLY CLARK CO	Method of making a polymer blend composition by reactive extrusion.
US2003232929 A1	20031218	WO03106521 A1 20031224; US7037983 B2 20060502; MXPA04011846 A 20050331; AU2003241542 A1 20031231	US20020302483 20021122; US20020389026P 20020614	HUANG YANBIN; KIM JAEHO	KIMBERLY CLARK CO	Methods of making functional biodegradable polymers.
US2005242466 A	20051103	KR20060047208 A 20060518; JP2005306943 A 20051104; JP4238174 B2 20090311; DE102005018086 A1 20051208; CN1690105 A 20051102	JP20040123461 20040419	KANAZAWA SHINICHI; KAWANO KIYOSHI; YOSHII FUMIO; YAGI TOSHIAKI; NAGASAWA NAOTSUGU	SUMITOMO ELEC FINE POLYMER INC	Process for producing transparent material made of polylactic acid and transparent material made of polylactic acid.
US2008036119 A1	20080214	US7803298 B2 20100928; TW200817459 A 20080416; KR20080015367 A 20080219; DE102007032746 A1 20080221; CN101125929 A 20080220	JP20060220982 20060814	KANAZAWA SHINICHI	SUMITOMO ELEC FINE POLYMER INC	Molding material, molded part, and method for manufacturing them.
US2012053259 A1	20120301	US8420746 B2 20130416; TW201211152 A 20120316	TW20100129473 20100901	HUANG CHIEN-MING; HUANG YU-KAI	MINIMA TECHNOLOGY CO LTD	Biodegradable composition and foam article made therefrom.
US2012189860 A1	20120726	WO2012102792 A1 20120802; TW201238996 A 20121001	US201113012157 20110124	LI FENGKUI; ASHBAUGH JOHN	FINA TECHNOLOGY	Polymeric compositions comprising polylactic acid oligomers and methods of making the same.

US2012211927 A1	20120823	WO2012112266 A1 20120823; US8628718 B2 20140114; US2014072746 A1 20140313; TW201245326 A 20121116	US201113030194 20110218	LI FENGKUI; ASHBAUGH JOHN; RAUSCHER DAVID; DOTTER ROBERT	FINA TECHNOLOGY	Modified polylactic acid, polymeric blends and methods of making the same.
US5610241 A	19970311	WO9742249 A1 19971113; EP0898590 A1 19990303	US19960646060 19960507	LEE KEUN H; WON CHEE Y; CHU CHIH-CHANG	FINA TECHNOLOGY	Reactive graft polymer with biodegradable polymer backbone and method for preparing reactive biodegradable polymers.
US5654381 A	19970805		US19950491490 19950616	HRKACH JEFFREY S; LANGER ROBERT S; LOTAN NOAH	MASSACHUSETTS INST TECHNOLOGY	Functionalized polyester graft copolymers.
US5952433 A	19990914	US5952433 X6 19990914	US19970903864 19970731	WANG JAMES HONGXUE; SCHERTZ DAVID MICHAEL	KIMBERLY CLARK CO	Modified polylactide compositions and a reactive-extrusion process to make the same.
WO0060956 A1	20001019	US2004122165 A1 20040624; US6916857 B2 20050712; US6388047 B1 20020514; US2003125509 A1 20030703; US6709668 B2 20040323; US2002161169 A1 20021031; US6583219 B2 20030624; JP2002541308 A 20021203; ES2298135 T3 20080516; EP1168934 A1 20020109; EP1168934 A4 20041208; EP1168934 B1 20080213; DK1168934 T3 20080513; DE60038010 T2 20090305; CA2368617 A1 20001019; CA2368617 C 20100316; AU3877200 A 20100316; AT386075 T 20080315	US19990128803P 19990412	WON CHEE-YOUB; ZHANG YELI; CHU CHIH-CHANG	CORNELL RES FOUNDATION INC	Hydrogel-forming system with hydrophobic and hydrophilic components.
WO0069916 A1	20001123	US6677386 B1 20040113; MXPA01007503 A 20020621; MX220923 B 20040611; KR20010108128 A 20011207; KR100451527 B1 20041008; JP2002544335 A 20021224; JP3946958 B2 20070718; ES2209813 T3 20040701; EP1159301 A1 20011205; EP1159301 B1 20031015; DE60005932 T2 20040812;	JP19990200203 19990125	GIEZEN FRANCISCUS EGENIUS; JONGBOOM REMIGIUS OENE JULES; FEIL HERMAN; GOTLIEB KORNELIS FESTER; BOERSMA ARJEN	ATO BV	Biopolymer nanoparticles.

Continued

—Cont'd

Patent Number	Publication Date	Family Members	Priority Numbers	Inventors	Applicants	Title
		CN1337969 A 20020227; CN1293100 C 20070103; CA2361722 A1 20001123; CA2361722 C 20090421; BR0007703 A 20020827; BR0007703 B1 20101019; AU2467300 A 20001205; AU760508 B2 20030515; AT252114 T 20031115				
WO02053610 A1	20020711	US2002128382 A1 20020912; US6500897 B2 20021231; MXPA03005807 A 20050214	US20000752810 20001229	WANG JAMES H; SHERTZ DAVID M	KIMBERLY CLARK CO	Modified biodegradable compositions and a reactive-extrusion process to make the same.
WO02053641 A1	20020711	WO02053641 A9 20030417; US2003018128 A1 20030123; US7053151 B2 20060530; MXPA03005805 A 20030910	US20000753076 20001229	WANG JAMES H; SCHERTZ DAVID M	KIMBERLY CLARK CO	Grafted biodegradable polymer blend compositions.
WO0234857 A2	20020502	WO0234857 A3 20030109; US2006247390 A1 20061102; US7094840 B2 20060822; JP2004512419 A 20040422; ES2362405 T3 20110704; EP1330503 A2 20030730; EP1330503 B1 20110525; AU2582702 A 20020506; AT510898 T 20110615	METABOLIX INC	WHITEHOUSE ROBERT S; ZHONG LUHUA; DAUGHTRY SEAN	METABOLIX INC	Compositions comprising low molecular weight polyhydroxyalkanoates and methods employing same.
WO2005078018 A1	20050825	US2005215672 A1 20050929	US20040543825P 20040211; US20050056622 20050211	MOHANTY AMAR K; DRZAL LAWRENCE T; DESAI SHROJAL M; MISRA MANJUSRI; MULUKUTLA PRASAD	UNIV MICHIGAN STATE	Anhydride functionalized polyhydroxyalkanoates, preparation and use thereof.
WO2006098159 A1	20060921	US2008213209 A1 20080904; KR20070119632 A 20071220; DE112006000594 T5 20080131	JP20050249361 20050830; JP20050071725 20050314	KANAZAWA SHINICHI; KAWANO KIYOSHI	SUMITOMO ELEC FINE POLYMER INC	Process for producing crosslinked material of polylactic acid and crosslinked material of polylactic acid.
WO2006103913 A1	20061005	US2009030160 A1 20090129; KR20070122461 A 20071231; DE112006000699 T5 20080207	JP20050090183 20050325; JP20050249563 20050830; JP20060000948 20060105	KANAZAWA SHINICHI; KAWANO KIYOSHI	SUMITOMO ELEC FINE POLYMER INC	Polylactic acid complex and production method thereof.

WO2007028258 A2	20070315	WO2007028258 A3 20071108; US2008317818 A1 20081225; SG165337 A1 20101028; KR20080065973 A 20080715; JP2009507110 A 20090219; JP2013039425 A 20130228; HK1125395 A1 20130712; EP2535041 A1 20121219; EP1934289 A2 20080625; EP1934289 A4 20110720; CN101305052 A 20081112; CN101305052B B 20121010; CA2621824 A1 20070315; AU2006289625 A1 20070315; AU2006289625 B2 20130829	US20050715411P 20050909	GRIFFITH MAY; LI FENGFU; LIU WENGUANG; RAFAT MEHRDAD	OTTAWA HEALTH RESEARCH INST; UNIV OTTAWA	Interpenetrating networks (IPNs), and related methods and compositions.
WO2007099056 A1	20070907	EP1991601 A1 20081119; EP1991601 B1 20100825; US2009124723 A1 20090514; US8334348 B2 20121218; JP2009528416 A 20090806; MX2008011345 A 20080912; KR20080098048 A 20081106; CA2644444 A1 20070907; RU2008139288 A 20100410; RU2418818 C2 20110520; PT1991601 E 20101129; CN101395199 A 20090325, CN101395199B B 20111214; BRPI0708460 A2 20110531; ES2351526 T3 20110207; AR059725 A1 20080423; AT478909T T 20100915	EP20060110664 20060303; US20060781326P 20060313	HOGT ANDREAS HERMAN; FRIJLINK WILHELM KLAAS	AKZO NOBEL NV	Process for the modification of biodegradable polymers.
WO2007107808 A1	20070927	EP1999189 A1 20081210; EP1999189 B1 20091111; AT448266 T 20091115	WO2006IB00898 20060320	SCANDOLA MARIASTELLA; FOCARETE MARIA; FOLTRAN ISMAELA; KAWALEC MICHAL; KURCOK PIOTR; ADAMUS GRAZYNA; KOWALCZUK MAREK	ALMA MATER STUDIORIUM UNI DI B; INST OF POLYMERS AND CARBON MA	Method of controlling thermal degradation of anionically terminated polymers and materials obtained.
WO2008008068 A1	20080117	EP2041341 A1 20090401; EP2041341 A4 20091216; EP2041341 B1 20101103	WO2006US27337 20060714	WANG JAMES H; HE AIMIN	KIMBERLY CLARK CO	Biodegradable aliphatic-aromatic copolyester for use in nonwoven webs.
WO2008146905 A1	20081204	US2010184915 A1 20100722; EP2151464 A1 20100210; EP2151464 A4 20110323	JP20070143205 20070530	MIYAMOTO TAKASHI	TOYO BOSEKI	Phosphonium sulfoisophthalate structure-copolymerized lactic acid-based resin.

Continued

—Cont'd

Patent Number	Publication Date	Family Members	Priority Numbers	Inventors	Applicants	Title
WO2009041518 A1	20090402	US2011015310 A1 20110120; EP2199456 A1 20100623; EP2199456 A4 20130123; CN101809223 A 2100818; CN101809223 B 20130508	JP20070248766 20070926	SHIMIZU TAKEO; TABEYA TOSHIHIRO; SEKI MASAO; TAKEDA KEIJI	TORAY INDUSTRIES	Polyester fiber, process for producing the same, and textile structure employing the same.
WO2010008447 A1	20100121	WO2010008445 A2 20100121; WO2010008445 A3 20100311; US2011251349 A1 20111013; US2011293865 A1 20111201; TW201022328 A 20100616; TW201012846 A 20100401; KR20110038642 A 20110414; ES2426774 T3 20131025; EP2291430 A1 20110309; EP2291429 A2 20110309; EP2291429 B1 20130605; CN102112519 A 20110629; CA2727016 A1 20100121; AR072205 A1 20100811; AR072203 A1 20100811	US20080133026P 20080625; US20080203542P 20081223; US20090207493P 20090212; US20080199817P 20081120; US20090166950P 20090406; US20080200619P 20081202; US20080133023P 20080625	PADWA ALLEN R; KANN YELENA	METABOLIX INC	Methods for branching PHA using thermolysis.
WO2010044112 A1	20100422	WO2010044112 A8 20100624; US2011275729 A1 20111110; EP2346922 A1 20110727; EP2346922 B1 20140305	WO2008IT00646 20081015	SCANDOLA MARIASTELLA; MAZZOCCHETTI LAURA; FOCARETE MARIA LETIZIA; KAWALEC MICHAL; KURCOK PIOTR; ADAMUS GRAZYNA; KOWALCZUK MAREK	UNIV BOLOGNA ALMA MATER; INST OF POLYMERS AND CARBON MA	Process for controlled degradation of polyhydroxyalkanoates and products obtainable therefrom.
WO2012086226 A1	20120628	US2013289221 A1 20131031; EP2657269 A1 20131030; CN103261259 (A 20130821	JP20100288729 20101224	ICHIKAWA YASUSHI; KIMURA HIDEHARU; ISHII AKIRA	SHOWA DENKO KK	Method for producing aliphatic polyester having increased molecular weight.
WO2013061834 A1	20130502	TW201335209 A 20130901	JP20110232703 20111024	ICHIKAWA YASUSHI; KIMURA HIDEHARU; ISHII AKIRA	SHOWA DENKO KK	Method for producing aliphatic polyester having increased molecular weight.
WO9409760 A1	19940511	US5399665 A 19950321; JPH07506622 A 19950720; ES2156893 T3 20010801; EP0619732 A1 19941019; EP0619732 A4 19950222; EP0619732 B1 20010131; DE69329903 T2 20010719; CA2127463 A1 19940511 CA2127463 C 20050705 AT198980 T 20010215	US19920972156 19921105	BARRERA DENISE; LANGER ROBERT S; LANSBURY PETER T JR; VACANTI JOSEPH P	MASSACHUSETTS INST TECHNOLOGY; CHILDRENS HOSP MEDICAL CENTER	Biodegradable polymers for cell transplantation.

WO9504097 A1	19950209	US5594095 A 19970114; US5359026 A 19941025; US5798435 A 19980825; US6291597 B1 20010918; US5594095 A 19970114; US5998552 A 19991207; NZ271513 A 19970526; JPH09501456 A 19970210; JP3369185 B2 20030120; FI960433 A 19960130; FI112083 B 20031031; ES2186689 T3 20030516; EP0711314 A1 19960515; EP0711314 B1 20021002; EP0711314 B9 20030402; DK0711314 T3 20030210; DK0711314 T5 20030818; DE69431483 T2 20030731; CA2168041 A1 19950209; CA2168041 C 20071009; BR9407212 A 19960917; AU7516294 A 19950228; AU684303 B2 19971211; AT225378 T 20021015	US19930100550 19930730	GRUBER PATRICK RICHARD; KOLSTAD JEFFREY JOHN; WITZKE DAVID ROY; HARTMANN MARK HENRY; BORSCH ANDREA LEE	CARGILL INC	Viscosity-modified lactide polymer composition and process for manufacture thereof.
WO9518169 A1	19950706	US6559244 B1 20030506; NO962751 A 19960826; NO310921 B1 20010917; GR3030372 T3 19990930; FI945264 A 19950701; FI99125 C 19971010; ES2128704 T3 19990516; EP0737219 A1 19961016; EP0737219 B1 19990317; DK737219 T3 19991011; DE69417265 T2 19990805; AT177768 T 19990415	FI19930005964 19931231; FI19940005264 19941109	SOEDERGAARD ANDERS; SELIN JOHAN-FREDRIK; NIEMI MARIA; JOHANSSON CARL-JOHAN; MEINANDER KERSTIN	NESTE OY	Processable poly(hydroxy acid)s.
WO9523175 A1	19950831	US5929196 A 19990727; PT797609 E 20001031; GR3034115 T3 20001130; ES2146751 T3 20000816; EP0797609 A1 19971001; EP0797609 B1 20000510; DK0797609 T3 20000807; DE4406172 A1 19950831; DE4406172 C2 20031002; CA2196698 A1 19950831; CA2196698 C 20000111; AT192765 T 20000515	DE19944406172 19940225	KISSEL THOMAS; LI YOUXIN	SANOL ARZNEI SCHWARZ GMBH	Polyesters.

Continued

—Cont'd

Patent Number	Publication Date	Family Members	Priority Numbers	Inventors	Applicants	Title
WO9847445 A1	19981029	US6153664 A 20001128; US6071982 A 20000606; JP2001523999 A 20011127; EP1003441 A1 20000531; EP1003441 A4 20090513; CA2288661 A1 19981029	US19970844378 19970418	WISE DONALD L; GRESSER JOSEPH D; TRANTOLO DEBRA J; HSU Y Y	CAMBRIDGE SCIENT INC	Bioerodible polymeric semi-interpenetrating network alloys and internal fixation devices made therefrom.
WO9906456 A1	19990211	MXPA02008854 A 20030210; EP1000102 A1 20000517; EP1000102 B1 20051130; DE69832617 T2 20060803; CA2298770 A1 19990211; AU8679198 A 19990222	US19970903862 19970731; US19970903864 19970731; US19970903866 19970731	WANG JAMES H; SOERENS DAVE A; SCHERTZ DAVID M; RHIM HANNONG	KIMBERLY CLARK CO	Modified polylactide compositions, water-responsive, biodegradable films and fibers comprising polylactide and poly(vinyl alcohol) and methods for making the same.
WO9914268 A1	19990325	US6096810 A 20000801; US6201083 B1 20010313; EP1023378 A1 20000802; EP1023378 B1 20020626; DK1023378 T3 20021014; DE69806262 T2 20030313; AU9396898 A 19990405; AT219782 T 20020715	US19970059670P 19970918	ASRAR JAWED; HAENE POL D	MONSANTO CO	Modified polyhydroxyalkanoates for production of coatings and films.
WO9942147 A	19990826	US6160084 A 20001212; TR200002450 T2 20010122; RU2215542 C2 20031110; KR100382568 B1 20030509; JP2007314797 A 20071206; JP2005325336 A 20051124; JP2002503524 A 20020205; JP4034036 B2 20080116; IL137299 A 20070603; HU0100466 A2 20010628; HU0100466 A3 20020328; HU222543 B1 20030828; ES2221363 T3 20041216; EP1056487 A1 20001206; EP1056487 B1 20040512; CZ20003072 A3 20010613; CZ303404 B6 20120829; CA2316190 A1 19990826; CA2316190 C 20050913;	US19980075523P 19980223	LANGER ROBERT S; LENDLEIN ANDREAS; SCHMIDT ANNETTE; GRABLOWITZ HANS	MASSACHUSETTS INST TECHNOLOGY	Biodegradable shape memory polymers.

		BR9907968 A 20001017; BR9907968 B1 20091201; AU2784599 A 19990906; AU751861 B2 20020829; AT266434 T 20040515				
WO9946332 A1	19990916	US2002136848 A1 20020926; EP0984039 A1 20000308; EP0984039 A4 20020102	JP19980080459 19980312; JP19980103385 19980331; JP19980103386 19980331; JP19980103387 1998033; JP19980103388 19980331; JP19980103389 19980331; JP19980103390 19980331; JP19980103391 19980331; JP19980103392 19980331; JP19980103393 19980331; JP19980103394 19980331; JP19980103395 19980331	YOSHII FUMIO; MAKUUCHI KEIZO; MITOMI HIROSHI; DARMAWAN DARWIS; MURAKAMI TADASHI	DAICEL CHEM	Lactone-containing resin composition, molded object thereof, and film.

REFERENCES

[1] Eguiburu JL, Fernandez Berridi MJ, San Román J. Functionalization of poly(l-lactide) macromonomers by ring-opening polymerization of l-lactide initiated with hydroxyethyl methacrylate-aluminium alkoxides. Polymer 1995;36:173–9.

[2] Barakat I, Dubois P, Jérôme R, Teyssié P, Goethals E. Macromolecular engineering of polylactones and polylactides. XV. Poly(D,L)-lactide macromonomers as precursors of biocompatible graft copolymers and bioerodible gels. J Polym Sci Part A Polym Chem 1994;32:2099–110.

[3] Yamaoka T, Kimura Y. Biodegradable copolymers. In: Salamone JC, editor. Concise polymeric materials encyclopedia. Boca Raton: CRC Press; 1998. pp. 109–11.

[4] Yamaoka T, Hotta Y, Kobayashi K, Kimura Y. Synthesis and properties of malic acid-containing functional polymers. Int J Biol Macromol 1999;25:265–71.

[5] Barrera DA, Zylstra E, Lansbury PT, Langer R. Copolymerization and degradation of poly (lactic acid-*co*-lysine). Macromolecules 1995;28:425–32.

[6] Hrkach JS, Ou J, Lotan N, Langer R. Synthesis of poly (L-lactic acid-*co*-L-lysine) graft copolymers. Macromolecules 1995;28:4736–9.

[7] Jin S, Gonsalves KE. Synthesis and characterization of functionalized poly(ε-caprolactone) copolymers by free-radical polymerization. Macromolecules 1998;31:1010–5.

[8] Sun L-F, Zhuo R-X, Liu Z-L. Studies on the synthesis and properties of temperature responsive and biodegradable hydrogels. Macromol Biosci 2003;3:725–8.

[9] Riva R, Lenoir S, Jérôme R, Lecomte P. Functionalization of poly(ε-caprolactone) by pendant hydroxyl, carboxylic acid and epoxide groups by atom transfer radical addition. Polymer 2005;46:8511–8.

[10] Mecerreyes D, Humes J, Miller RD, Hedrick JL, Detrembleur C, Lecomte P, et al. First example of an unsymmetrical difunctional monomer polymerizable by two living/controlled methods. Macromol Rapid Commun 2000;21:779–84.

[11] Lecomte P, D'aloia V, Mazza M, Halleux OG, Detrembleur C. Polym Prepr 2000;4:1534–5.

[12] Trollsås M, Lee VY, Mecerreyes D, Löwenhielm P, Möller M, Miller RD, et al. Hydrophilic aliphatic polyesters: design, synthesis, and ring-opening polymerization of functional cyclic esters. Macromolecules 2000;33:4619–27.

[13] Gautier S, D'Aloia V, Halleux O, Mazza M, Lecomte P, Jérôme R. Amphiphilic copolymers of ε-caprolactone and γ-substituted ε-caprolactone. Synthesis and functionalization of poly(D,L-lactide) nanoparticles. J Biomater Sci Polym Ed 2003;14:63–85.

[14] Tian D, Dubois P, Grandfils C, Jérôme R. Ring-opening polymerization of 1,4,8-Trioxaspiro[4.6]-9-undecanone: a new route to aliphatic polyesters bearing functional pendent groups. Macromolecules 1997;30:406–9.

[15] Latere Dwan'Isa J-P, Lecomte P, Dubois P, Jérôme R. Synthesis and characterization of random copolyesters of ε-caprolactone and 2-Oxepane-1,5-dione. Macromolecules 2003;36:2609–15.

[16] Detrembleur C, Mazza M, Halleux O, Lecomte P, Mecerreyes D, Hedrick JL, et al. Ring-opening polymerization of γ-bromo-ε-caprolactone: a novel route to functionalized aliphatic polyesters. Macromolecules 1999;33:14–8.

[17] Jérôme C, Lecomte P. Recent advances in the synthesis of aliphatic polyesters by ring-opening polymerization. Adv Drug Deliv Rev 2008;60:1056–76.

[18] Mecerreyes D, Moineau G, Dubois P, Jérôme R, Hedrick JL, Hawker CJ, et al. Simultaneous dual living polymerizations: a novel one-step approach to block and graft copolymers. Angew Chem Int Ed 1998;37:1274–6.

[19] Lavik EB, Hrkach JS, Lotan N, Nazarov R, Langer R. A simple synthetic route to the formation of a block copolymer of poly (lactic-*co*-glycolic acid) and polylysine for the fabrication of functionalized, degradable structures for biomedical applications. J Biomed Mater Res 2001;58:291–4.

[20] Zhang Y, Won C-Y, Chu C-C. Synthesis and characterization of biodegradable network hydrogels having both hydrophobic and hydrophilic components with controlled swelling behavior. J Polym Sci Part A Polym Chem 1999;37:4554–69.

[21] Furch M, Eguiburu JL, Fernandez-Berridi MJ, San Roman J. Synthesis and characterisation of copolymers of methyl acrylate and poly (glycolide) macromonomers. Polymer 1998;39:1977–82.

[22] Shinoda H, Matyjaszewski K. Structural control of Poly(Methyl methacrylate)-*g*-poly(lactic acid) graft copolymers by atom transfer radical polymerization (ATRP). Macromolecules 2001;34:6243–8.

[23] Jeong B, Bae YH, Lee DS, Kim SW. Biodegradable block copolymers as injectable drug-delivery systems. Nature 1997; 388:860–2.

[24] Jeong B, Bae YH, Kim SW. Thermoreversible gelation of PEG–PLGA–PEG triblock copolymer aqueous solutions. Macromolecules 1999;32:7064–9.

[25] Riley T, Stolnik S, Heald CR, Xiong CD, Garnett MC, Illum L, et al. Physicochemical evaluation of nanoparticles assembled from poly(lactic acid)–poly(ethylene glycol) (PLA–PEG) block copolymers as drug delivery vehicles. Langmuir 2001;17:3168–74.

[26] Kissel T, Li Y, Unger F. ABA-triblock copolymers from biodegradable polyester A-blocks and hydrophilic poly (ethylene oxide) B-blocks as a candidate for in situ forming hydrogel delivery systems for proteins. Adv Drug Deliv Rev 2002;54:99–134.

[27] Jeong B, Kibbey MR, Birnbaum JC, Won Y-Y, Gutowska A. Thermogelling biodegradable polymers with hydrophilic backbones: PEG-*g*-PLGA. Macromolecules 2000;33:8317–22.

[28] Yamaoka T, Kimura Y. Biodegradable copolymers. In: Salamone JC, editor. Concise polymeric materials encyclopedia. Boca Raton: CRC press; 1998.

[29] Li Y, Nothnagel J, Kissel T. Biodegradable brush-like graft polymers from poly(D,L-lactide) or poly(D,L-lactide-*co*-glycolide) and charge-modified, hydrophilic dextrans as backbone—synthesis, characterization and in vitro degradation properties. Polymer 1997;38:6197–206.

[30] Li Y, Volland C, Kissel T. Biodegradable brush-like graft polymers from poly(D,L-lactide) or poly(D,L-lactide-coglycolide) and charge-modified, hydrophilic dextrans as backbone—in-vitro degradation and controlled releases of hydrophilic macromolecules. Polymer 1998;39:3087–97.

[31] Breitenbach A, Pistel KF, Kissel T. Biodegradable comb polyesters. Part II. Erosion and release properties of poly(vinyl alcohol)-*g*-poly(lactic-*co*-glycolic acid). Polymer 2000;41:4781–92.

[32] Mitomo H, Watanabe Y, Yoshii F, Makuuchi K. Radiation effect on polyesters. Radiat Phys Chem 1995;46:233–8.

[33] Lee HS, Lee TY. Graft polymerization of acrylamide onto poly(hydroxybutyrate-*co*-hydroxy-valerate) films. Polymer 1997; 38:4505–11.

[34] Kawalec M, Adamus G, Kurcok P, Kowalczuk M, Foltran I, Focarete ML, et al. Carboxylate-induced degradation of poly(3-hydroxybutyrate)s. Biomacromolecules 2007;8:1053–8.

[35] Rutenberg MW, Solarek D. Starch derivatives: production and uses. Academic Press Inc.; 1984.

[36] Wurzburg OB. Modified starches-properties and uses. Boca Raton (Florida): CRC Press Inc.; 1986.

[37] Hullinger C. Production and use of crosslinked starch. In: Whistler RL, Paschall E, editors. Starch: chemistry and technology. New York: Academic Press; 1967. pp. 445–50.

Chapter 8

Surface Treatment

8.1 GENERAL

The practical end-use applications of several biopolymers are often dictated by their surface properties. The ability of biopolymers to interact with other materials is controlled by a variety of factors including surface chemistry, topography (on the nano-, micro- and macroscale), and wettability. Adhesion, absorption, coefficient of friction, and compatibility with hydrophilic reagents are examples of surface properties that are negatively affected by the poor surface wetting of hydrophobic biopolymers. The incorporation of functional groups or chemical species in or onto the biopolymer's surface can alter the wettability of the surface. This altered wettability may affect the bonding strength between the biopolymer's surface and material bonded onto it, when this is achieved by adsorption, coating, printing, heat bonding, adhering, or any other processes of material bonding known in the prior art. It is therefore advantageous to change the surface properties of biopolymer articles, such as packaging items, medical devices, automotive parts, or electrical/electronics components in order to widen their applications' range.

The surface nature of biopolymers may be altered by a variety of techniques, which can be grouped into three main categories: (1) physical treatment, (2) chemical treatment, and (3) coating or printing, which can include a pretreatment step by any of the techniques of (1) and (2). The surface treatment is suitably selected in accordance with the type of biopolymer and the intended use.

8.2 PHYSICAL TREATMENT

8.2.1 Physical Treatment with Solvents/Swelling Agents

The surface of biopolymer articles is covered with several contaminants the removal of which is critical for achieving adequate wetting and adhesion properties. Loose surface oligomers, plasticizers, and release agents are some of the most common contaminants found on the surface of biopolymers. Release agents in particular, which are used to prevent other materials from sticking to the surface, add to surface contamination. The hygroscopic nature of these agents will also cause moisture to stick on the surface. The surface tension of these contaminants is typically in the range of 30 mN/m, requiring their removal since most paints and printing inks have surface tensions well above 40 mN/m. These types of contaminations can negatively impact molecular attraction, causing liquids to fail to wet the surface. The surface tension of biopolymers must significantly exceed the surface tension of liquids by a recommended level of 10 mN/m to prevent paint or ink picking/liftoff and delamination [1]. A common technique of surface cleaning is to treat a molded product with a suitable solvent that does not affect (e.g., dissolve) the polymer. Solvent cleaning has limited utility when a distinct change in the chemical nature of the substrate surface is desired. The major drawbacks of this technique are safety hazards (i.e., emissions) and disposal problems [2].

JPH11335475 A (1999, TOKUYAMA CORP) discloses a method for the removal of a lipid (e.g., phospholipid) exuded on the surface of a molded product made of a poly(3-hydroxybutyrate-*co*-3-valerate) (PHBHV) containing 70–95 mol% of 3-hydroxybutyrate by treating the molded product with a solvent (e.g., a neutral organic solvent having a solubility parameter in the range 20.3–18.2 MPa$^{1/2}$, specifically a 1–3C alcohol).

JP2012246421 A (2012, TOYO BOSEKI) discloses a method for reducing the residual monomer content (e.g., lactide) of a poly(lactic acid) (PLA) molded product by contacting the molding with an organic solvent. In particular, a PLA molded product having a specific gravity of 1.252–1.257, and a chromaticity value (L) of 45–64.9 is brought into contact with an organic solvent such as ketone and/or alkyl acetate to obtain a PLA molded product having a specific gravity of 1.263–1.268, an L-value of 65–73 and a residual monomer content of ≤0.8 wt%.

WO03050170 A1 (2003, ASTRAZENECA AB; ASTRAZENECA UK LTD) discloses a method of preparing a polymer film having a plurality of crater-shaped protrusions by contacting a biopolymer film supported on a substrate with a solvent that causes the polymer film to swell, thereby forming blisters, and drying the polymer film so that the blisters collapse to form craters. The biopolymer used is a low molecular weight (12 KDa) PLA. The polymer film is generally an ultra-thin film of 22–300 nm thickness. The polymer film may be applied to the substrate by conventional techniques such as by spin coating the polymer from a solution onto the substrate, followed by annealing. Examples of suitable substrates include inert materials such as glass or silicon. Films having craters have found a number of applications, particularly where the craters are present

Biopolymers: Processing and Products. http://dx.doi.org/10.1016/B978-0-323-26698-7.00008-8

in the form of an array. Examples include the use of these craters to contain chemicals used in high throughput screening to identify properties of the chemical compounds contained in the wells. This application is particularly important in the pharmaceutical industry. They may also be used to grow tissues, such as mammalian tissues.

JP2010144091 A (2010, UNIV OSAKA; OSAKA IND PROMOTION ORG) discloses a method for pretreating the surface of a polymer by bringing the polymer into contact with a swelling agent, then removing the agent from the polymer, thereby processing the surface of the polymer. One of the preferred polymers is PLA.

8.2.2 Roughening

Roughening serves to increase the surface area of the material by increasing the total exposed area prior to coating or adhesive bonding. An example of roughening treatment is mechanical abrasion. Mechanical abrasion can be achieved through dry blasting, wet blasting, or hand/machine sanding. These processes can be very operator sensitive, labor intensive, dirty, and difficult to perform on the high production volumes normally associated with packaging applications. To remove particulates or residues, a solvent wash usually follows mechanical abrasion. In many cases, the abrasive materials consumed fall under the classification of hazardous substances and must be disposed of accordingly [2].

JP2004057134 A (2004, KIMOTO KK) discloses an agricultural film formed by roughening at least one surface of a PLA-based film by sandblast treatment. The treatment is claimed to provide an agricultural film having a high biodegradation rate without lowering its strength, preventing the occurrence of blocking phenomenon, excellent in handling property, and having dripping-proof property and being capable of sufficiently transmitting sunlight, which is necessary for growth of crops, while having an excellent light-scattering property, particularly when the biodegradable film has light transmittance.

Another example of roughening treatment involves the treatment of the surface of a biopolymer with plasma in the presence of an inert gas. The inert gas is used to physically etch the surface of the substrate and create nano-, microscale textures on the polymer's surface. Suitable inert gases include nitrogen, argon, and helium (2012, **US2012156780** A1, ADVANCED TECHNOLOGIES AND REGENERATIVE MEDICINE LLC); see also Section 8.3.2.2: Plasma.

8.2.3 Heat Treatment

JP2001354223 A (2001, TOYO SEIKAN KAISHA LTD) discloses a method for imparting heat resistance and dimension stability to at least a part of a container that comprises a layer made of PLA by applying heat crystallization. The heat crystallization is effected by heating under ultrasonic treatment the mouth and neck portions of the container, which is a blow molded article, having a crystalline nucleus or by heating the mouth and neck portions under the condition of partially forming the crystalline nucleus at a preform stage.

JP2004359763 A (2004, SONY CORP) discloses a method of treating an injection molded article made of a biodegradable polymer such as PLA with infrared rays to carry out heat treatment. The molded product was heat treated at a surface temperature range of 70–85 °C, for 2–15 min with a conveyor-type infrared annealing apparatus. The conveyor-type infrared annealing apparatus is an infrared reactor having an infrared source, and a molded product conveying unit, which conveys the molded product inside the infrared oven continuously. The infrared rays are preferably far infrared rays.

WO2008012981 A1 (2008, YOSHINO KOGYOSHO CO LTD) discloses a method for the heat treatment of a shaped body, namely a preform, formed by extrusion molding, compression molding, or injection molding of poly(L-lactic acid) (PLLA) compounded with a functional filler comprising D-lactic acid. A mouth portion of the shape body is subjected to a heat treatment at a temperature between the glass transition temperature (T_g) and the melting temperature (T_m) of PLLA, in particular between 60 °C and 160 °C. The heat treatment of the shaped body affects the crystallinity of PLLA and improves its heat resistance. The compounded PLLA displays one or more melting peaks in addition to the melting peak of pristine PLLA (145–170 °C) even at a higher temperature of 180–200 °C. The melting peak observed at a temperature higher than that of the pristine PLLA shows that L-lactic acid of PLLA and D-lactic acid of the functional filler form a stereocomplex. The thus formed stereocomplex affects the crystallization behavior of PLLA and contributes to the promotion of the crystallization, and hence the improvement of the heat resistance can be attained.

US2009036639 A (2009, COCA COLA CO) discloses a method of heat treating a biodegradable article comprising the steps of: providing an article made of PLA; supporting the article using a carrier support system; and heat setting or annealing the article at a temperature in the temperature range of 100–140 °C for 5–45 min to cure the PLA. The curing step increases the crystallinity, the thermal stability, dimensional stability, or pressure stability of the article.

8.3 CHEMICAL TREATMENT

The hydrophobic nature of certain biopolymers limits their usefulness, and it is necessary to modify the surface characteristics of the shaped articles made therefrom. Other surface properties of biopolymers like antistatic properties, barrier properties, biodegradation properties, etc. also need to be improved to meet specific application requirements.

The chemical methods used to modify the surface properties of biopolymers can be classified roughly in the following subcategories: (1) hydrolysis/aminolysis/solvolysis; (2) incorporation of functional groups by chemical means, flame treatment, radiation, plasma, corona treatment, or any method that can introduce functional groups to the surface of the biopolymer; and (3) grafting functional monomers or polymers.

8.3.1 Hydrolysis/Aminolysis

A simple technique to chemically functionalize the surface of a biodegradable polyester such as PLA and poly(glycolic acid) (PGA) is via hydrolysis with the use of a strong base such as NaOH [2–5]. The hydroxide anion hydrolyzes the ester groups resulting in chain scission of the polyester chain and formation of two main chains with carboxylic acid (–COOH) and hydroxyl (–OH) end groups. Alternatively, the hydrolysis can be carried out in the presence of an amine (i.e., aminolysis), for example, 1,6-hexanediamine, leading to the formation of free amino groups on the polyester surface [6,7]. The incorporation of carboxylic acid and hydroxyl groups or amino groups increases the hydrophilicity of the surface of the biodegradable polyester.

WO9705193 A1 (1997, SANITARIA SCALIGERA SPA) discloses in one of its embodiments the surface activation of an aliphatic polyester by means of hydrolysis. Hydrolysis is conducted in the presence of an aqueous solution of a base or an acid to accelerate surface reaction, since as excessively long processes of activation can induce a reduction in molecular weight and thus in the mechanical properties of the material. Suitable bases are, for example, strong alkalis, such as LiOH, $Ba(OH)_2$, $Mg(OH)_2$, NaOH, KOH, Na_2CO_3, and $Ca(OH)_2$, and the weak bases, such as NH_4OH and amines such as methylamine, ethylamine, diethylamine, and dimethylamine. Acids suitable for surface hydrolysis treatments can be chosen, for example, from among HCl, $HClO_3$, $HClO_4$, H_2SO_3, H_2SO_4, H_3PO_3, H_3PO_4, HI, HIO_3, HBr, lactic acid, or glycolic acid. Particularly preferred is the use of an aqueous solution of a base, which has demonstrated greater activity. Surface hydrolysis treatment is followed by careful washing to remove all traces of acid or base. The hydrolysis is carried out using homo- or copolymers of lactic acid, preferably poly(L-lactide-*co*-ε-caprolactone) (PLLCL). Hydrolysis is preferably conducted at temperatures between 0 °C and the T_g of the polymer. In the case of PLLCL with a lactic acid/ε-caprolactone weight ratio of 50/50, suitable temperatures are, for example, in the range of 10–60 °C, preferably between 30° and 50 °C.

Surface activation by hydrolysis is claimed to:

- produce a surface change accompanied by a lowering of the wetting angle (measured with water at 23 °C in air), which in the case of PLLCL drops from 82° to 30°;
- modify morphologically the surface of the material with the creation of numerous microporosities, useful in cell seeding processes, for example, endothelialization;
- substantially reduce autoadhesivity of the material, whose shear detachment force drops from an initial 10 kg/cm following colonization, with considerable advantages in manipulation and use of films, medical prostheses, etc.
- the viscosity inherent in the copolymer during the process of activation does not undergo appreciable variation, such as to reduce its mechanical properties.

The hydrolysis/aminolysis chemical treatment has certain side effects such as loss of mechanical properties and faster degradation rates. Strong alkali hydrolysis can cause extended bulk degradation of a biodegradable polyester, and the residual alkali is not easily removed except by rinsing. On the other hand, mild alkali treatment could not break the ester bonds effectively in a short time [4]. Moreover, the degree of surface modification may not be reproducible when comparing polymers of different molecular weight, crystallinity, and tacticity [8]. In addition, the hydrolysis variations generate hazardous chemical waste and can lead to irregular surface etching [9].

8.3.2 Incorporation of Functional Groups

The incorporation of functional groups includes methods such as oxidation (e.g., peroxide oxidation or ozone oxidation), amination, nitration, halogenation (e.g., fluorination), and the like. This subcategory has the disadvantage that the effect gained by the surface treatment (i.e., wettability) is unstable and degenerates over time, leading to a short shelf life of the treated surface and storage instability. Lack of stability of the treated surface is a severe problem, in particular for biopolymers used for (in vivo) medical applications as it may result in undesired features such as alteration of the substrate properties and/or an altered degradation profile and thus possible unpredictable results and/or undesired side effects. On the other hand, the grafting of functional monomers or polymers onto the surfaces is a more stable/permanent alternative (see Section 8.3.3).

Common techniques used to incorporate functional groups to the surface of a biopolymer include flame treatment, radiation, corona treatment, and plasma, which can increase the surface energy of a biopolymer. Flame treatment is a rather obsolete surface treatment technique.

8.3.2.1 Radiation

CN101225221 A (2008, UNIV SICHUAN) discloses a method for the treatment of a PLA molded product by an electron beam irradiation with a radiation dose of 10–180 kGy. The irradiation takes place in a nitrogen or vacuum atmosphere, where the oxygen concentration in the irradiation chamber is 0–2000 mg/L. The electron beam is a low, middle, or high electron beam; energy of low, middle, and high energy electron beam is 0.15–0.5 MeV, 0.5–5 MeV, and 5–10 MeV, respectively. The molded product is composed of PLA, fillers, and a crosslinking agent. Preferred fillers include inorganic particles (e.g., diatomite, silicon oxide, calcium carbonate, and carbon black); organic compounds (e.g., glycerol); polymers (e.g., starch, cellulose, gluten, and PVOH). The crosslinking agents are selected from triallyl cyanurate, triallyl pentaerythritol, tetraalkyl pentaerythritol, triallyl isocyanurate, or trimethylolpropane allyl ether.

8.3.2.2 Plasma

Gas plasma treatment of a biopolymer surface generates high energy reactive species that bond to the surface. Plasma treatment can be carried out in the presence of an inert or reactive gas, for example, air, argon, oxygen, or ammonia, with the formation of surface functional groups, such as –OH, –CHO, –COOH, or $–NH_2$.

Plasma treatment has been used to alter the surface properties of polymers without affecting their bulk properties. Specific surface properties like hydrophobicity, chemical structure, and roughness can be altered to meet target requirements. Some major effects that have been observed in plasma treatment of polymer surfaces are removal of organic contamination, micro and nanoscale etching, crosslinking, and surface chemistry modifications. The main disadvantage of plasma treatment is that the induced surface modification is not permanent and diminishes with time due to surface rearrangement [9,10].

WO9705193 A1 (1997, SANITARIA SCALIGERA SPA) discloses in one of its embodiments the surface activation of an aliphatic (co)polyester such as poly(L-lactide-*co*-ε-caprolactone) (PLLCL) by means of cold plasma (see also Section 8.3.1). The process brings about a substantial increase in surface hydrophilicity and, consequently, a significant lowering of the wetting angle measured with water at 23 °C in air. This can in many cases favor cellular adherence to bioabsorbable medical prostheses made of this (co)polymer, and thus surface activated, such as for endothelialization processes in vascular grafts.

US2007014752 A1 (2007, UNIV TEXAS) discloses a method of functionalizing a polymer surface by exposing the polymer surface to an atmospheric pressure glow plasma discharge (APG). A bioactive agent, such as a small molecule drug, a protein drug, a polypeptide drug, a peptide drug, a DNA drug, an RNA drug, an oligonucleotide drug, an immunomodulatory agent, a vaccine, or a contrast or imaging agent, can be chemically conjugated to the treated surface of a biopolymer particle. A preferred biopolymer is poly(lactide-*co*-glycolide) (PLGA) (e.g., Resomer® RG502H or RG503H, Evonik). Advantages of APG discharge include the (1) highly nonequilibrium chemical and thermal property of the plasma (similar to classical low pressure glow discharges), (2) high degree of uniformity over large areas and volumes (without constriction and the resulting streamer or arc formation), (3) relatively low ion energetics, and (4) 1-atm operation.

US2012156780 A1 (2012, ADVANCED TECHNOLOGIES AND REGENERATIVE MEDICINE LLC) discloses a method of surface modification of a substrate, comprising the steps of: providing a biodegradable polymer substrate, wherein said polymer is semicrystalline; placing the substrate in an inert gas atmosphere; applying an RF plasma treatment at a power of 100–500 W for a length of time of 60–200 min, thereby providing the substrate with a surface crystallinity of 30–50% and a roughness of 20–200 nm. The intensity and quality of the plasma to which a target material is exposed produces a randomized, irregularly etched surface that is characterized by dimensional (i.e., depth and width), morphological (i.e., crystallinity), and functional group (i.e., –OH, $–NH_2$, etc.) variations on the surface. In order to establish this plasma, low background pressures and relatively low power levels are employed. The aliphatic polyester is preferably PLLA. The inert gas is selected from the group consisting of nitrogen, argon, and helium.

8.3.2.3 Corona Treatment

Corona treatment is a surface modification technique that uses a low temperature corona discharge plasma to impart changes in the properties of a surface. Corona treatment has been used to either improve the print fastness of a polymer film or to perforate the film (see Section 8.2.2: Roughening). Corona treatment is used to increase the surface energy of a biopolymer to as much as 50 dyn/cm. Inks that are typically more difficult to apply onto paper coatings, like water-based inks, may be applied directly to corona-treated PLA.

US2004127123 A1 A2 (2004, KIMBERLY CLARK CO) discloses in one of its embodiments a method of subjecting a biodegradable polymeric substrate to a corona glow discharge to impart a durable hydrophilic surface to the biodegradable polymeric substrate. The biodegradable polymeric substrate is preferably a fibrous web made of PLA, PGA, or their copolymers.

Example: PLA (PLA 6200 D grade, Cargill-Dow, LLC) was formed into a spunbond fabric using conventional spunbond apparatus. The spunbond fabric had filaments of an average denier of 1.6 dpf (1.8 dtex) and a basis weight of 0.5 osy (about 17 gsm). A portion of the fabric was left untreated for control purposes, and a portion was exposed to a corona glow discharge under ambient conditions. The field strength was 20 W/ft^2/min (1.33 J/cm^2). Immediately following the corona treatment, the fabric was dipped into one of three aqueous solutions containing 0.1, 0.2, or 0.3 wt%

of ethyl hydroxyethyl cellulose (Bermocol® E481, Akzo Nobel), forming fabrics A, B, and C. After the complete saturation of the fabric, as indicated by a change in color from white to translucent, the fabric was nipped between two rubber rollers at 10 lbs (about 4.5 kg) nip pressure. The coated fabric was then dried in an oven at 60 °C for about 30 min. The fabric was then tested for wettability using the test method in accordance with ISO-903. The treated and the untreated samples (5 g) were placed in 25 °C water and the sink time was measured. The sink times (seconds) for the test/control fabric samples A, B, and C were found to be 3.6/59.3, 3/59.3, and 3.0/59.3, respectively; i.e., the treated fabric has faster sink times as compared to the untreated fabric.

JP2001329082 A (2001, KANAZAWA INST OF TECHNOLOGY) discloses a method of modifying the surface of a PLA molded product with corona discharge treatment. The chemical structure of the surface of the PLA molded product is modified by the introduction of functional oxygen groups that accelerate the biodegradation rate of the polymer. Plasma treatment and flame treatment are also considered as alternatives to corona discharge treatment. The treated PLA molded product is used as film for agriculture, sheet for construction and engineering works, pile, and fiber. **JP2002256088** A (2002, KANAZAWA INST OF TECHNOLOGY) is a modification of the above patent application using poly(butylene succinate) (PBS) or poly(ε-caprolactone) (PCL).

8.3.3 Grafting

8.3.3.1 Polymerizable Compounds

Graft polymerization of hydrophilic monomers onto the surfaces of hydrophobic polymers is a frequently used technique for modifying surface properties. Representative examples of this technique for the treatment of hydrophobic biopolymers to render their surfaces more hydrophilic can be found in the literature.

JP2002121240 A (2002, TOPPAN PRINTING CO LTD) discloses an adhesive biodegradable polymer film produced by graft polymerizing a vinyl compound having a polar group, such as acrylic acid, onto the surface of a PLA film, which has been subjected to irradiation with an electron beam (5–200 Gy). As a result, only the surface layer of the treated film acquires adhesive properties, while the original biodegradability remains intact.

Example: A biaxially oriented PLA film was cut out to sizes of 10 cm × 10 cm, and the film was subjected to irradiation with electron beam (50 KGy) by using a low-energy-type electron beam accelerator, and the treated film was immersed in 40% acrylic acid aqueous solution at 60 °C for 3 min and the acrylic acid was allowed to be grafted thereon. The treated film was washed with ultrasonic waves and dried at room temperature to give an adhesive biodegradable film.

Modification of polyhydroxyalkanoate (PHA) surfaces via grafting is rarely reported in the literature. Mitomo et al. [11] reported radiation-induced graft polymerization of methyl methacrylate (MMA), 2-hydroxyethyl methacrylate (HEMA), acrylic acid, and styrene onto P3HB and its copolymers. Lee et al. [12] studied graft copolymerization of acrylamide onto poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate) (PHBHV) films for its permselectivity, see also Chapter 7: Chemical treatment (in bulk); Section 7.1: Introduction of functional groups and Section 7.4: Radiation (in bulk).

JPH10219012 A (1998, NISSEI KK) discloses the formation of a coating of polymerized oils and fats on the surface of a molding made of starch providing the molding with water resistance. The molding product is obtained by mixing starch with water and pressurizing under heating. Oils and fats mixed with a polymerization initiator and previously irradiated with ultraviolet light (UV) are preferably used.

JPH11147269 A (1999, FUJI XEROX CO) discloses a biodegradable composite material wherein a nonbiodegradable polymer (2) is chemically bonded to the surface of a molded article comprising a biodegradable polymer (1), the fine structure in the surface of the biodegradable composite material is nonuniform, and a domain (4) to which a different kind of the polymeric compound (2) is not bonded is present (see Figure 8.1). This nonbonded domain has a size forming a circle having a diameter of at least 5 nm. The surface treatment is claimed to endow the molded article with excellent functionality while holding high biodegradability. The nonbiodegradable polymer is formed by graft polymerization on the surface of the biodegradable polymer. Suitable monomers are acrylic acid, vinylsulfonic acid, acrylamide-2-methylpropanesulfonic acid, vinylbenzene sulfonic acid, vinyl acetate, vinyl pyrrolidone, etc.

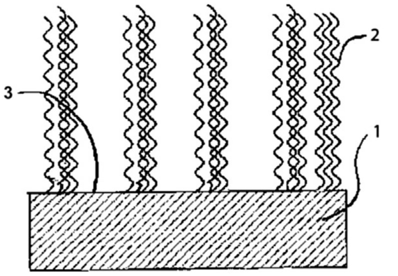


FIGURE 8.1 Surface structure of biodegradable polymer composite (1999, **JPH11147269** A, FUJI XEROX CO). 1, Biodegradable polymer; 2, Grafted nonbiodegradable polymer; 3, Nonbonded domain.

8.3.3.2 Preformed Polymers

Kiss et al. [13] developed a method for the chemical modification of the surface of PLGAs by coupling of either linear or star-like polyethylene glycol (PEG) molecules via chemical bonds to the PLGA surface following amino functionalization as a first step to improve its biocompatibility. It was shown that substantial modification can be achieved by linear PEG, but even higher surface coverage with hydrophilic groups can be obtained when the six-armed PEG is applied with the additional advantage of possible further functionalization via free amino groups available on the surface of the latter. As a final goal, a significant increase of water wettability together with reduced protein adsorption was achieved on PEG-coupled PLGA surfaces.

8.4 COATING

8.4.1 Coating with Inorganic Materials

Surface treatment with inorganic compounds has been traditionally used to reduce blocking. Such a treatment includes dusting the polymer surface with materials that reduce the surface contact between the polymer and the adjacent surface. Examples of materials that may be used in surface treatment of biopolymers include talc, silica, and the like.

PLA has inferior gas barrier properties (see Chapter 2: Properties; Section 2.1.5: Gas barrier properties), and in order to be used in food packaging, attempts have been made to vacuum deposit a metal such as aluminum on the surface of a PLA film or container. A metallized oriented PLA film has good oxygen barrier property due to the polar nature of PLA, which provides good hydrogen bonding of the polymer molecules.

WO9424198 A1 (1994, BASF AG) discloses a PLA film coated on one side with a vapor-deposited layer of metal or silicon oxide. The metallized film has low permeability to oxygen, and it is used as packaging film for food, e.g., coffee, spices, milk, etc.

WO9417220 A1 (1994, DU PONT) discloses a metallized PLA obtained by applying a vapor-deposited coating of a metal such as aluminum on a PLA film. The metallized PLA film is claimed to provide an excellent alternative to polystyrene and other packaging materials, particularly as part of a laminate wherein the metallized film is adhered to a cellulosic substrate with an adhesive. In addition, the metallized PLA film can be quite decorative, thus making such materials the ones of choice for use in packaging.

EP0576993 A2 (1994, MITSUI TOATSU CHEMICALS) discloses in one of its embodiments a metallized PLA-based film having enhanced gas barrier and mechanical properties by vacuum depositing aluminum on a film or a molded product of PLA. However, such metallized PLA-based films are not always suitable in many packaging applications demanding high moisture barrier properties. The polar nature tends to be detrimental for achieving high moisture barrier. It is suggested that water molecules—being polar themselves—may more easily migrate through a polar polymer film than a nonpolar polymer film as compared to typical metallized biaxially oriented polypropylene (BOPP) (2010, **US2010040904** A1; 2010, **US2010330382** A1; 2011, **US2011076511** A1 TORAY PLASTICS AMERICA INC). In addition, a metallized PLA film has reduced transparency, while the transparency of the film is required particularly in food packaging applications, and thus it has a limited variety of applications (2000, **EP0974615** A1, TOYO BOSEKI).

JPH10138433 A (1998, UNITIKA LTD) and **JPH1024518** A (1998, MITSUBISHI PLASTICS IND) provide alternative solutions to the problem of reduced transparency by applying transparent inorganic oxide coatings on a PLA film. In **JPH10138433** A (1998, UNITIKA LTD) a thin layer of silicon oxide is applied on a PLA-based biaxially oriented film. Either vacuum deposition method, sputtering method, or ion plating can be adopted as the method of forming the thin coating layer of silicon oxide. In **JPH1024518** A (1998, MITSUBISHI PLASTICS IND) a nitride oxide layer is applied on a PLA-based film. While such gas barrier films improve the transparency, the running property during the film processing and the gas barrier property after the film has run through a film processing machine while being in contact with a part thereof are not sufficient (2000, **EP0974615** A1, TOYO BOSEKI).

According to **US2010040904** A1 (2010), **US2010330382** A1 (2010) and **US2011076511** A1 (2011) of TORAY PLASTICS AMERICA INC there are several manufacturers of oriented PLA films, in particular biaxially oriented PLA, but none of them provides a satisfactory moisture barrier property when metallized. For example, the data sheet of Envirometᵀᴹ high barrier metallized PLA film of Celplast Metallized Products, Ltd describes a product that exhibits an excellent oxygen barrier of 6.2 cc/m^2/day (23 °C, 50% relative humidity or RH), but a relatively poor moisture barrier of 3.1 g/m/day (38 °C, 90% RH) as compared to typical metallized BOPP; for example, a high barrier metallized BOPP such as Toray Plastics (US), Inc.'s PWX3 product typically demonstrates oxygen barrier of 15.5 cc/m^2/day (23 °C, 0% RH) and moisture barrier of 0.155 g/m^2/day (38 °C, 90% RH). Another quoted example is Ceramis® (Alcan Packaging Inc.), a silicon oxide–coated PLA film. The data sheet of Ceramis® states that this product has an oxygen barrier of 7.75 cc/m^2/day (23 °C, 50% RH) and moisture barrier of 7.75 g/m^2/day (38 °C, 90% RH). Quiceno ALG [14] of Biofilm S.A. presented transparent barrier PLA films demonstrating moisture barrier of 3–10 g/m^2/day (38 °C, 90% RH) using various vacuum chamber deposition processes. For both the latter transparent barrier PLA films, vacuum deposition of a metal such as aluminum on top of the transparent barrier layer (e.g., silicon oxide, aluminum oxide, or other coatings), may be used to improve moisture barrier properties, but such a product is likely to be costly due to the multiple processing steps required.

US2010040904 A1 (2010, TORAY PLASTICS AMERICA INC) discloses a method of making a multilayer biaxially oriented PLA film comprising: extruding a first layer comprising PLA; biaxially orienting the first layer; depositing a second layer comprising metal upon a surface of the first layer; and depositing a third layer comprising metal upon a surface of the second layer. In preferred embodiments, the second layer is deposited by sputtering a thin layer of a metal primer such as copper onto the PLA metal receiving layer, and the third layer is deposited by vacuum vapor deposition of aluminum. The use of a metal primer improves the metal adhesion of the subsequent aluminum layer and also improves the gas barrier of the metallized PLA film when compared to an aluminum metallized PLA film without a primer. Other "primer" metals that are used include titanium and nickel. This metal-primed and metallized PLA film exhibits improved moisture barrier properties versus a nonmetal-primed and metallized PLA film and can be used as part of a lamination structure for food packaging applications. The first PLA-based layer may also include other ingredients such as an amount of ethylene-acrylate copolymer that can act as a processing aid to enable high transverse orientation rates of up to 8–11 times, particularly if this layer includes a majority amount of crystalline PLA. Without such a processing aid, transverse orientation rates of a highly crystalline PLA layer may be on the order of 3–5 times. The first PLA layer may also include an optional amount of amorphous PLA blended with the crystalline PLA as well as the optional ethylene-methacrylate copolymer. The first PLA-based layer can also include various additives such as antiblock particles to allow for easier film handling. Nonmigratory antiblock agents are preferred over migratory slip agents such as fatty amides or silicone oils.

JPH1034807 A (1998, TOYO INK MFG CO) discloses the formation of a thin film layer consisting of silicon oxide and metal fluoride on one face or both faces of a polysaccharide-containing substrate to obtain a biodegradable polymer film with high barrier properties being suitably used as a packaging material for fresh food, pharmaceuticals, cosmetics, electronics, and agricultural materials. A protein is preferably incorporated in the biodegradable polymer. The metal fluoride of the thin film layer is selected from magnesium fluoride, calcium fluoride, strontium fluoride, barium fluoride, sodium fluoride, and aluminum fluoride or their mixtures. In addition, the mol% ratio of the silicon oxide/metal fluoride composition constituting the thin film layer is 99.5–80/0.5–20. The coated biodegradable film is claimed to have high barrier properties and excellent colorless transparency.

JP2000094573 A (2000), **JP2000108202** A (2000), **JP2000103005** A (2000), **JP2000103006** A (2000), **JP2000103879** A (2000), and **EP0974615** A1 (2000) of TOYO BOSEKI disclose in one of its embodiments a vapor-deposited transparent coating of an inorganic oxide selected from aluminum oxide/silicon oxide, aluminum oxide, and silicon oxide on an aliphatic polyester film such as PLA. The deposited layer is characterized by the following features:

1. the content of aluminum oxide in the aluminum oxide/silicon oxide-based vapor-deposited layer is in the range of 20–99 wt%;
2. the "b" value, which is calculated according to the following Eqn (8.1) based on the specific gravity (d) of the vapor-deposited layer and the aluminum oxide content (a) in wt% in the vapor-deposited layer, satisfies the following Eqn (8.2):

$$b = d - 0.01a \tag{8.1}$$

$$1.6 \le b \le 2.2 \tag{8.2}$$

3. the specific gravity of the aluminum oxide-based vapor-deposited layer is about 2.70–3.30; and
4. the specific gravity of the silicon oxide-based vapor-deposited layer is about 1.80–2.20.

The disclosed gas barrier film is claimed to provide satisfactory transparency, flexibility, running property during the film processing and gas barrier property after the film has run through a film processing machine while being in contact with a part thereof. These are important properties required in a packaging film for use with, e.g., fresh food, processed food, drugs, medical devices, or electronics.

JP2003311876 A (2003, TOYO METALIZING; ISHIDA SEISAKUSHO; JAPAN PULP & PAPER CO LTD; NAKAMOTO PAKKUSU KK) discloses a biodegradable film having a vapor-deposited layer. The vapor-deposition metal is aluminum, tin, copper, titanium, nickel, and/or chromium, or oxide of metals such as aluminum, magnesium, tin, and/or silicon. The biodegradable vapor-deposited film is claimed to have excellent gas barrier property and stability.

JP2008260205 A (2008, TOHCELLO CO LTD) discloses a method for depositing an inorganic thin film on one surface or both surfaces of an aliphatic polyester-based nonstretched film. The film is made of a composition comprising (A) an aliphatic polyester copolymer component made of (a1) an aliphatic or alicyclic dicarboxylic acid component having a melting temperature (T_m) of 80–120 °C and a crystallization temperature (T_c) of 35–75 °C with (T_m)−(T_c) in the range of 35–55 °C, (a2) an aliphatic or alicyclic dihydroxy compound component, and (a3) a difunctional aliphatic hydroxycarboxylic acid component; and (B) an aliphatic/aromatic polyester component having a crystallinity of 10%

or less with a content of 10 wt% or less. The inorganic film is selected from aluminum oxide, aluminum, silicon oxide, and indium tin oxide (ITO). The aliphatic polyester-based nonstretched film is suitable for packaging applications.

While silicon oxide exhibits excellent gas-barrier property, especially when it is vacuum deposited onto PET bottles, it presents problems when it is vacuum deposited onto containers made from a biodegradable polymer having a low T_g and a low heat resistance, such as PLA (T_g about 60 °C). That is, in order to exhibit barrier property, the silicon oxide must be vacuum deposited under a high-output condition (usually, vacuum deposited with a microwave output of not less than 600 W for not shorter than 4 s) while using an oxygen gas and an organometal gas. When vacuum deposited under such a high-output condition, the wall of PLA bottle is thermally deformed and thermally deteriorated due to the heat of oxygen plasma and other plasma occurring in the step of vacuum deposition, and offensive odor generates in the bottle. Further, the vacuum-deposited film of silicon oxide is hard, brittle, and lacks flexibility, and forms a hydrophilic group such as silanol group. Therefore, the vacuum-deposited film of silicon oxide poorly follows deformation of the PLA-base material, not so closely adheres thereto, and, besides, exhibits low barrier property against water (2008, **WO2008149918** A1, TOYO SEIKAN KAISHA LTD).

CN102504311 A (2012, UNIV HENAN NORMAL) discloses a method for coating a modified hydroxyapatite on a PLA surface, by soaking the PLA material in an activation solution containing activated surface covalently introduced hydroxyl anion, carboxyl anion, or amide ion active groups; soaking the activated PLA surface in a solid waste solution containing calcium Ca^{2+} ions, and subsequently in solid waste solution containing a phosphate PO_4^{3-} alkali immersed in the solvents; repeating the process 3–50 times; and growing a layer of uniform and dense hydroxyl apatite coating on the surface of the material, where the PLA has a molecular weight of 10,000–200,000. The activating solution comprises dopamine, β-alanine, ethylene diamine, sodium hydroxide, ammonia water, and hydrochloric acid, where the concentration of the solution is 0.01–1 mol/l. The solid waste solution containing Ca^{2+} ion comprises calcium chloride, water solution of nitric acid, and calcium hydroxide, where the concentration of the solution is 0.01–1 mol/l. The solid waste containing $(PO_4)^{3-}$ ion water solution comprises diammonium phosphate, monoammonium phosphate, sodium (potassium) dihydrogen phosphate, and buffered aqueous solution (potassium), where the $(PO_4)^{3-}$ solution has concentration of 0.006–0.6 mol/l and pH of 8–12 in alkaline solution.

8.4.2 Coating with Low-Molecular-Weight Organic Materials

EP0802219 A2 (1997, MITSUI TOATSU CHEMICALS) discloses a biodegradable membrane formed by applying an aqueous coating composition comprising an antistatic agent or anticlouding agent on one or both surfaces of an aliphatic polyester film. The membrane is claimed to have good blocking and anticlouding resistance and improved adhesion to the aliphatic polyester film, and thus the antistatic effect or anticlouding effect can be continuously exhibited for a long period.

JPH11116709 A (1999, MITSUI CHEMICALS INC) discloses the production of an antistatic aliphatic polyester film by applying a coating liquid containing an antistatic agent having a perfluoroalkyl and a perfluroalkenyl group in the molecule to at least one surface of the film. The aliphatic polyester is preferably PLA and comprises 0.1–2 pbw of at least one of a lubricant and an antiblocking agent per 100 pbw aliphatic polyester. The film has a low surface resistivity, sufficient antistatic effect, and a good sliding property, and it can be used as packaging material, magnetic recording material, optical material, electrically insulating material, agricultural film, and so on.

JP2008285610 A (2008, RISU PACK CO LTD) discloses a PLA-based sheet obtained by coating a sucrose fatty acid ester on the surface of a sheet base material formed from a polymer composition comprising monoglyceride (3–5 pbw) and PLA (100 pbw). The monoglyceride is composed of an ester of an 8–22C aliphatic monocarboxylic acid and glycerol. The sucrose fatty acid ester, which is preferably a sucrose oleic acid ester or sucrose laurate, has an hydrophilic–lipophilic balance (HLB) value of not less than 13 and is coated on the sheet base material in an amount of 20–50 mg/m^2. The PLA sheet exhibits a suitable antifogging effect even in packaging foods and a molded article formed of the sheet.

JP2001018290 A (2001, TOYO SEIKAN KAISHA LTD) and **JP2005014966** A 20050120 (2005, SHISEIDO CO LTD) disclose a method of vacuum depositing a hydrocarbon film (also called diamond-like carbon film, DLC film), on a biodegradable polymer molded product such as a biaxially stretched film or bottle. The biodegradable polymer is an aliphatic polyester such as PLA. The hydrocarbon vapor-deposited film has the problem of getting colored but can be formed with a low output and in a short period of time as compared to the silicon oxide film and can, therefore, be formed on the surface of a PLA-based sheet without causing the polymer to be thermally deformed or thermally deteriorated. However, the known hydrocarbon-type vacuum deposited-films proposed in those two patents are still not satisfactory concerning the barrier property against oxygen and the like. For example, if a PLA bottle having a hydrocarbon film vacuum evaporated on the inner surface thereof is used for containing an oily content as represented by an edible oil such as frying oil, a problem occurs in that the oily content undergoes deterioration by oxidation (2008, **WO2008149918** A1, TOYO SEIKAN KAISHA LTD). Furthermore, the hydrocarbon vapor-deposited film is mainly constituted by carbon element and hydrogen element, is inert, has poor chemical affinity to PLA-based material, and involves a problem concerning the closely adhering property. As means for improving the closely adhering property between the PLA-base material and the hydrocarbon vapor-deposited film, there is generally employed a method of introducing impurity elements other than carbon element and hydrogen element into the hydrocarbon film. In this case, however, the water- and oxygen-barrier property decreases though the closely adhering property is improved relative to the PLA-base material (2010, **WO2008129688** A1, TOYO SEIKAN KAISHA LTD).

WO2008149918 (2010, TOYO SEIKAN KAISHA LTD) discloses a method of producing a PLA bottle having a vapor-deposited film on the inner surface of the bottle comprising the following steps: (1) feeding, as a reaction gas, a mixed gas of a gas of at least one kind of hydrocarbon compound selected from an aliphatic unsaturated hydrocarbon and an aromatic hydrocarbon, and a gas of a polar group–containing organic compound selected from ethanol, acetone, or carbonic acid; and (2) forming a hydrocarbon vacuum-deposited film on an inner surface of the biodegradable biopolymer bottle by a plasma-enhanced chemical vapor deposition (CVD) using microwaves or high frequency waves. The PLA bottle is effectively prevented from thermally deforming during film deposition and functions as an excellent barrier to oxygen and water.

WO2008129688 A1 (2008, TOYO SEIKAN KAISHA) discloses a PLA-based molded product having a vapor-deposited film formed on the surface of the product by a plasma-enhanced CVD method, wherein the vapor-deposited film includes an organometal vapor-deposited layer having an element ratio C/Si of 2.5–13 and an element ratio O/M of not larger than 0.5, and a hydrocarbon vapor-deposited layer. The hydrocarbon vapor-deposited layer has a thickness in a range of 40–180 nm, and contains CH, CH_2, and CH_3 groups, wherein the CH_2 ratio is not larger than 35% and the CH_3 ratio is not less than 40%.

WO2013140868 A1 (2013, TOYO SEIKAN GROUP HOLDINGS LTD) discloses a PLA molding product, e.g., a bottle, comprising a PLA base (1) and a hydrocarbon-based deposited film (3) formed on the surface of the base material by plasma-enhanced CVD, wherein the hydrocarbon-based deposited film (3) includes two layers: namely, a high-CH_2 layer (3a) formed on the surface of the PLA base (1) and designed so that the CH_2 ratio relative to the total of CH, CH_2, and CH_3 is 40% or higher (preferably 44–60%), and a low-CH_2 layer (3b) formed on the high-CH_2 layer (3a) and designed so that the CH_2 ratio relative to the total of CH, CH_2, and CH_3 is 35% or lower (see Figure 8.2). The high-CH_2 layer and the low-CH_2 layer have thickness of 5–15 nm and 15–100 nm, respectively. In initial stage of formation of the hydrocarbon-type vapor deposition film, low-output plasma process (350–600 W for 0.9–3 s) is performed, such that a high-CH_2 layer is formed, and then, high-output plasma process (1000–1400 W for 0.4–2.7) is performed to form a low-CH_2 layer. The hydrocarbon-based deposited film is formed without producing thermal deformation or thermal degradation of the PLA-base material by a continuous series of plasma-enhanced CVD steps in which there is no switching of the reaction gas and exhibits high adhesiveness to the PLA base material.

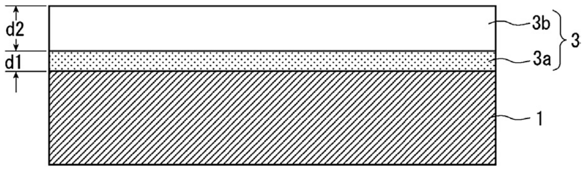


FIGURE 8.2 Cross-sectional view of a PLA-molded product provided with a hydrocarbon-deposited film (2013, **WO2013140868** A1, TOYO SEIKAN GROUP HOLDINGS LTD). 1, PLA base; 3, Hydrocarbon-type vapor-deposited film; 3a, High-methylene (CH_2) group layer; 3b, Low-methylene (CH_2) group layer.

JP2002161155 A (2002, KANAZAWA INST OF TECHNOLOGY) discloses a method of introducing fluorine functional groups in a surface layer of a biodegradable molded product made of PCL. The fluorine-type surface modifying agent is a compound having fluorinated alkyl groups such as C_6F_{13}, $C_6F_{13}H$, C_7F_{15}, C_8F_{17}, or $C_4F_9C_2H_5$. The treated molded product has a controlled biodegradation and can be used for producing wrapping materials and magnetic cards, agricultural films, piles, construction sheets, etc.

8.4.3 Single Polymer Coating

WO9515260 A1 (1995, ZENECA LIMITED) discloses a method for making a coated biodegradable film of at least one layer comprising water swellable, water insoluble, biodegradable cellulose, or cellulose acetate and at least one layer comprising crystalline or crystallizable PHA; the PHA is applied as an aqueous suspension of at least partly amorphous particles of PHA to preformed cellulose such as regenerated cellulose (e.g., “cellophane”) and/or cellulose acetate film and heated to cause the applied layer to adhere thereto. The step of heating is sufficient to crystallize the PHA to the extent of 40–60%. The PHA is preferably P3HB or PHBHV containing 3–20 mol% 3-hydroxybutyrate, balance 3-hydroxyvalerate. A composite film may be made by laying the PHA sides of two films together and heat sealing them together. In addition to providing a water vapor barrier, the PHA layer in general also enables the film to be heat sealed to similar sheets and to various other materials if it is a surface layer.

JPH0797545 A (1995, KANEGAFUCHI CHEMICAL IND) discloses the coating of a food container made of a starch-based material having poor water resistance with a biodegradable coating composition having good water resistance. The biodegradable coating composition is produced by dissolving an aliphatic polyester (preferably PLA) in a halogenated hydrocarbon (preferably CFC 123). The concentration of the aliphatic polyester in the coating composition is preferably 1–2 wt%. The coating of the food container is preferably carried out by dip-coating the container in the coating composition from the viewpoint of uniform and efficient application of the coating composition to the whole surface of the container.

JPH08244781 A (1996, TOPPAN PRINTING CO LTD) discloses the formation of a coating film of a poly(vinyl alcohol) (PVOH) on the surface of a container made of PLA. The surface of the container is subjected to activation treatment so as to chemically adsorb the PVOH. Although the container has enhanced gas barrier property, its heat resistance is lacking.

DE19615348 A1 (1997, BAYER AG; BIOTEC BIOLOG NATURVERPACK) discloses a method of coating a biodegradable material with a solution of a biodegradable polymer selected from (a) aliphatic or partly aromatic polyesters, (b) thermoplastic aliphatic polyurethanes, (c) aliphatic-aromatic polyester-carbonates, and (d) aliphatic polyester-amides. The biodegradable coating is for waterproofing biodegradable materials, e.g., wood, paper, textiles, starch foam, leather, chitin-based products, etc.

EP1225196 A1 (2002, TORAY INDUSTRIES) discloses a biodegradable-oriented film of a plasticizer-containing biodegradable polymer such as PLA, of which both surfaces are coated with at least one thin layer and of which the loop stiffness (or flexural strength index) change after heat treatment at 130 °C for 30 min is at most 20%. The thin layer prevents the plasticizer in the biodegradable film from bleeding out. The thin layer is made of at least one resin selected from polyesters, acrylics, polyurethanes, vinyl resin, epoxy resins, and polyamides. Plasticizers include ether-ester derivatives, glycerol derivatives, phthalic acid derivatives, glycolic acid derivatives, citric acid derivatives, adipic acid derivatives, and epoxy plasticizers. Preferred plasticizers are biodegradable ones such as glycerol triacetate (triacetin), butyl esters of epoxidated linseed oil fatty acids, acetyl tributyl citrate, epoxidated soybean oil, and polyester of adipic acid and 1,3-butylene glycolic acid.

Example: PLLA was melted at 200 °C in an extruder. Acetyl tributyl citrate (15 wt%) was added to form a polymer melt flow, which was then extruded at 200 °C to give a film. The film was cast at 25 °C to prepare a nonstretched film. This was directly passed between heat rolls at 70 °C, and both surfaces of the film were exposed to corona discharge. Both surfaces were then coated separately with an acrylic resin composition comprising acrylic resin emulsion having a mean particle size of 0.05 μm diluted with water to have a solid content of 3 wt%. The produced thin layer-coated oriented PLA film having a thickness of 10 μm was flexible (3% loop stiffness change) and favorable for wrapping films.

WO2010040707 A1 (2010, BASF SE) discloses a method for enhancing the gas barrier properties of polymer substrates used in packaging by applying a composition comprising (a) a vinyl alcohol-vinyl amide copolymer, (b) a crosslinker, and, optionally, (c) a multifunctional acrylate and a photoinitiator to the polymer surface and curing the composition by irradiation with UV light, visible light, IR irradiation, and/or electron beam or by exposure to heat. The method includes the optional step of subjecting the polymer surface to a low temperature plasma discharge or a corona discharge prior to applying the composition. In a preferred embodiment, the substrate is made of PLA. Currently, PLA is used as a food packaging polymer for short shelf life products such as fruit and vegetables. One major drawback for expanding the use of PLA is its high oxygen permeability. The gas barrier properties, in particular the oxygen barrier properties, of PLA packaging material are enhanced by application and crosslinking of the present vinyl alcohol-vinyl amide copolymer composition.

In a particular example, the following coating composition was used: component (a) Glascol® R910 (available as 10% aqueous solution) a commercially available vinyl alcohol-vinyl amide copolymer; component (b) Gosefimer® Z-410 (available as 10% aqueous solution) a commercially available acetoacetylated PVOH as a crosslinker; component (c) a mixture of 34.2% polyethylene glycol 400 diacrylate as multifunctional acrylate, 61.0% polymeric phenylglyoxylate as photoinitiator, and 4.8% of a surfactant (a dodecylbenzene sulfonic acid derivative). Parts (of solids) are by weight, and each formulation is diluted to 100 total parts with water. The formulation was coated onto a corona-treated PLA film (Earthfirst™ PLA) of 12 μm thickness after drying and then cured using a 200 W/cm m.p. mercury lamp, at curing speed 35 m/min.

JP2006124439 A (2006, UNITIKA LTD) discloses a biodegradable aqueous dispersion containing PLA (100 pbw) and tin oxide group ultrafine particles (30–2000 pbw), dispersed in an aqueous medium, which is used to coat a biodegradable film. The biodegradable aqueous dispersion gives a coating film having biodegradability, transparency, water resistance, adhesiveness to a substrate film, and antiblocking property as well as antistatic property.

US2007172663 A1 (2007, FUJITSU LTD) discloses a method of making an article, such as a mobile phone, comprising: preparing a base or body made of a biodegradable polymer such as PLA and applying a coating resin composition containing a conductive material to a surface of the base. The coating film functions as a shield for electromagnetic waves, a ground, and the like. Sandblast may be employed to remove the coating film off the surface of the base after the end of its service life. The base can eventually be decomposed in the ground.

JP2005194383 A (2005, UNITIKA LTD) discloses an antifogging PLA-based biaxially oriented film that has at least on one surface a coating layer comprising a nonionic surfactant (a) and a water-based polyurethane resin (b); the weight ratio (a/b) of components (a,b) in the application layer is 90/10–10/90. The nonionic surfactant is preferably polyoxyethylene sorbitan fatty acid ester, polyglycerol fatty acid ester, and/or sucrose fatty acid ester. The PLA film is used for packaging of hydrate food containing vegetables and fruits. The antifogging PLA-based biaxially stretched film is claimed to have excellent low temperature fog-prevention property, blocking resistance, mechanical strength, economical efficiency, printability, lamination property, and coating ability. The coating layer is firmly adhered to the base film, and the back transfer of the nonionic surfactant is suppressed. Generation of cracks and splits on the film during rolling up and fracture by film tension, are prevented.

JP2007331154 A (2007, MITSUBISHI PLASTICS IND) discloses a biaxially stretched PLA film coated with a resin composition comprising at least one nonionic surfactant (a) selected from a polyoxyethylene sorbitan fatty acid ester and a polyglycerol fatty acid ester and an aqueous acrylic resin (b), wherein the weight ratio (a/b) of the nonionic surfactant (a) and the aqueous acrylic resin (b) is 70/30–30/70. The biaxially stretched PLA film has low temperature antifogging properties and blocking resistance.

JP2008063697 A (2008, KUREHA GOSEN KK) discloses the treatment of a PLA fibrous substrate with a neutral or alkaline coating liquid containing silicone resin to provide the substrate with antibacterial property. The alkaline coating liquid contains a water-soluble alkali. The PLA fibrous substrate is used for clothing such as disposable undergarments, socks, insoles of slippers, shirts, bath mats, and diapers.

JP2008043905 A (2008, TOHO CHEM IND CO LTD) discloses a method for applying a moisture-proof coating on a PLA film wherein a primer processing is preliminarily carried out with an aqueous dispersion of (un)substituted styrene or its derivative and α-, β-unsaturated carboxylic acid copolymer, and then an aqueous dispersion of an olefin, α-, β-unsaturated carboxylic acid copolymer, and optionally a wax resin is applied on the PLA film. The moistureproof PLA film is endowed with water vapor barrier property, adhesiveness, and transparency.

BRPI0520831 A2 (2010, COMISSAO NAC ENERGIA NUCLEAR; CBPAK EMBALAGENS ECO SUBSTANTA) discloses a method for sealing a biodegradable polymer substrate by immersing the substrate in a solution of an aliphatic-aromatic copolyester at a temperature of 30–50 °C. The obtained substrate is dried in an oven by cold air, hot air, or UV light. The solvent is xylene, toluene, methyl ethyl ketone, methanol, cyclohexane, ethyl acetate, chloroform, alcohol, ketone, ether, or ester.

8.4.4 Multiple Coatings

The multiple coatings as used herein comprise at least one coating based on a biodegradable polymer.

EP2141191 A1 (2010, AMCOR FLEXIBLES TRANSPAC N V) discloses a modified gas atmosphere food packaging comprising a multilayer structure including a regenerated cellulose film, an additional gas or water vapor barrier layer applied to the cellulose film, and an extrusion coating of biodegradable copolyester on the additional barrier layer on the inside of the packaging relative to the cellulose film, the packaging further comprising one or more microperforations formed therein to maintain the modified gas atmosphere within the packaging. At least one surface of the cellulose film is precoated with a solvent or water-based coating of copolyester before being coated with copolyester polymer extrusion. The extruded copolyester comprises an aliphatic-aromatic copolyester such as poly(butylene adipate-*co*-terephthalate) (PBAT), mixture of aliphatic-aromatic copolyester with starch or PBS, or mixture of PBS with PLA or starch. A preferred regenerated cellulose film is NatureFlex® (Innovia Films).

The layer of biodegradable copolyester that is extrusion coated onto the surface of the cellulose film is claimed to overcome the limitations of cellulose film as a packaging film for fresh food and still retain the biodegradability, compostability, and stiffness of the overall structure. Additionally, good bond strength between the cellulose film and the extruded copolyester is achieved by applying a thin coating of copolyester to the surface of the cellulose film by means of a solvent or water-based coating process. A biodegradable copolyester is extrusion coated onto an additional barrier layer to provide a significant barrier enhancement in high humidity environments beyond levels that would be reasonably predicted.

WO2012002707 A2 (2012, KOLON INC) discloses a shrinkable film comprising a biodegradable film containing 10–99 wt% of PLA and 1–90 wt% of another aliphatic (e.g., PCL or PBS) or aliphatic-aromatic polyester; a coating layer formed by applying a water-dispersed polyurethane coating composition on one surface of the biodegradable film; and a metal deposition layer formed on the polyurethane coating layer. The coating composition contains preferably 0.5–1.0 wt% of polyurethane binder, 0.01–0.5 wt% of silicon wetting agent, and the remaining water. The metal-deposited layer is preferably an aluminum layer. The polyurethane-coating layer enhances the adhesion of the film with the metal layer. The shrinkable film is claimed to retain excellent moisture barrier properties while having superior flexibility, transparency, and biodegradability. The shrinkable film is suitable for food packaging, capable of having no occurrence of delamination of a metal deposition layer due to printing, and lamination after forming the metal deposition layer.

8.5 PRINTING

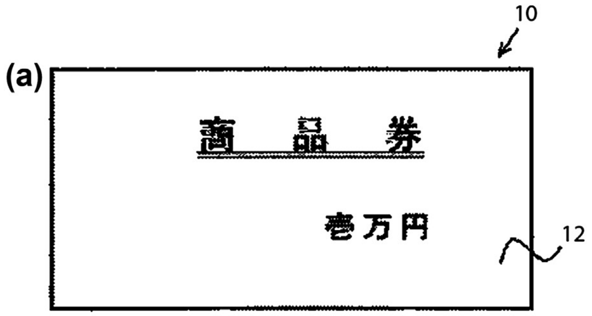
Printing as used herein includes bonding of inks onto biopolymer surfaces, e.g., surfaces for consumer product packaging.

Biopolymer films, which are suited for printing applications, have high surface tension. For instance, the relatively high surface tension (38–44 dyn/cm) of PLA films makes them receptive to (printed) ink often without any additional treatment to the surface. This leads to a surface with satisfactory printing characteristics without surface modification. Thus, inks that are typically more difficult to apply onto films, like water-based inks, may be applied directly to PLA films.

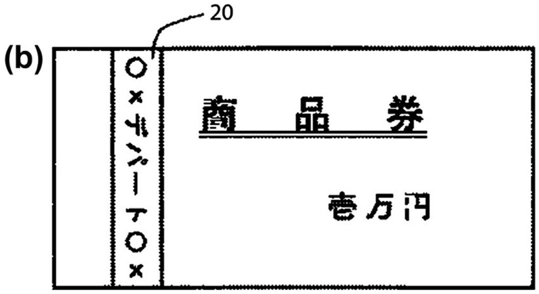
A smoother surface aids also in the printing process that is performed in many end applications, for example, labels. Another important factor to consider is the response of a film when subjected to heat, particularly as the film will need to withstand the often-elevated temperatures experienced during printing, through drying ovens or heat emitted by UV curing lamps. The presence of plasticizers in several biopolymers above a recommended maximum concentration results in exudation of the excess material and can jeopardize the operations of printing and surface finishing on the product.

JPH07195814 A (1995, TOPPAN PRINTING CO LTD; SHOWA HIGHPOLYMER) discloses a biodegradable film printed with an ink containing nitrocellulose or polyurethane. The printing ink is applied to a uniaxially or biaxially stretched film based on an aliphatic polyester, which may contain polyurethane, with a number-average molecular weight (M_n) of 10,000–100,000. The type of ink can be adapted to various biodegradable films, and the printed material does not display any printing inferiority such as the peeling of ink after printing.

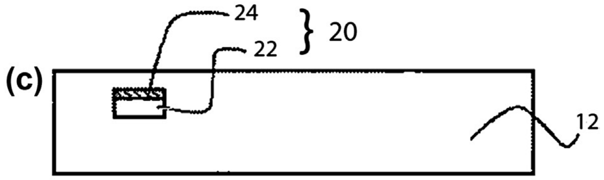
JP2000096491 A (2000, TOPPAN PRINTING CO LTD) discloses a paper sheet (10) containing strips (20) having 1–5 mm width in which a design (24) such as character or logo is printed with a white ink having high opacifying properties on a biodegradable transparent support film (22) comprising PLA and having 10–35 μm thickness are made into a pulp base paper (12) (see Figure 8.3). The paper sheet is claimed to have a high forgery-preventing effect and even amateurs are capable of readily judging whether the paper is genuine or false by making strips in which a prescribed design is printed on a transparent support into pulp-based paper.



Antiforgery paper sheet



Antiforgery paper sheet with strip



Detail of a strip in an antiforgery paper sheet

FIGURE 8.3 Antiforgery paper sheet (2000, **JP2000096491** A, TOPPAN PRINTING CO LTD). 10, Antiforgery paper sheet; 12, Pulp-base paper; 20, Strips; 22, Biodegradable transparent support film; 24, Design.

In a printed biodegradable polymer film, the layer of printing ink may hinder the biodegradation so that degradation of the film may be impeded or retarded. **WO03082963** A1 (2003, UNI CHARM CORP) addresses this problem by disclosing a package for a disposable bodily discharge absorbent article (1), comprising a biodegradable polymer film (2) having at least one surface formed with a printed region (5) and a nonprinted region (6) around the printed region (5), said polymer film (2) further comprising nonprinted subregions (7) distributed substantially evenly within said printed region (5) formed on said polymer film (2), said nonprinting subregions (7) comprising a plurality of individual nonprinted subregions (7) each enclosed with printing ink defining said printed region (5); characterized in that said individual nonprinted subregions (7) totally occupy 10–20% of said printed region (5); each of said individual nonprinted subregions (7) is dimensioned to be in a range of 15–30 μm in two directions orthogonal to each other; and each of said individual nonprinted subregions (7) is separated from at least one adjacent individual nonprinted subregion (7) by a distance (*p*) shorter than twice as long as thickness (*t*) of said polymer film (see Figure 8.4). The film (2) is made of, for example, poly(ethylene succinate) (PES), PBS, or PLA. The disclosed printed biodegradable polymer film in which the nonprinted subregions are evenly distributed within the printed region, and the biodegradation of the film in the region covered with the printing ink is not hindered or retarded due to the presence of the printing ink.

JP2004223786 A (2004, TOYO BOSEKI) discloses an anchor agent for improving the adhesion of a biodegradable film and biodegradable printing ink, in particular a PLA film and ink containing PCL and/or esterified starch as a binder

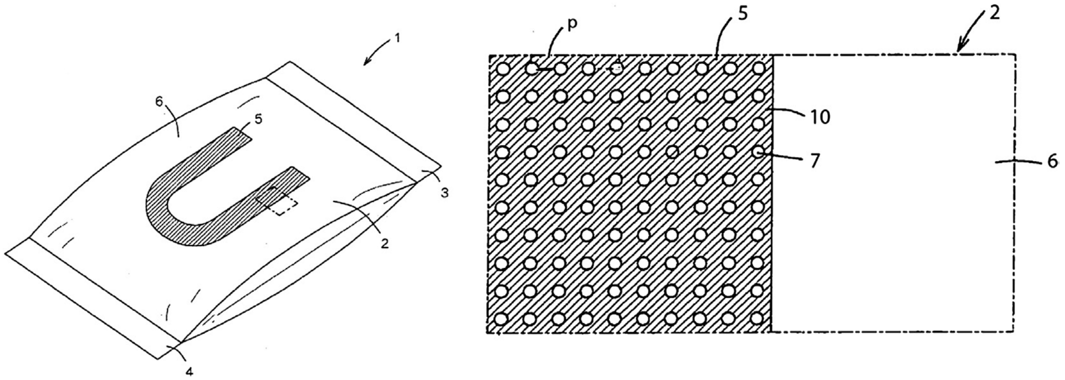


FIGURE 8.4 Perspective view showing an individual package for disposable bodily discharge absorbent article such as a disposable diaper, disposable training pants, or a sanitary napkin (2003, **WO03082963** A1, UNI CHARM CORP). 1, individual package; 2, biodegradable polymer film; 3,4, sealed upper and lower ends; 5, U-shaped printed region; 6, nonprinted region; 7, nonprinted subregions; 10, printing ink; *p*, distance between two nonprinted subregions.

(e.g., the commercial products Biotech Color HGP Series and Biotech Color HGC Series of Dainichi Seika Co., Ltd.), and a biodegradable laminate using the anchor agent. The anchor agent for the biodegradable printing ink is composed mainly of PLA characterized by a molar ratio of L-lactic acid to D-lactic acid (L/D) of 0.05–19 and a reduced viscosity is 0.3–1.0 dl/g.

Example: A PLA (10 pbw) with a molar ratio L/D = 1 was dissolved in a mixed solvent of toluene (200 pbw) and methyl ethyl ketone (2000 pbw). The obtained solution was coated on a PLLA film of 50 µm thickness and dried to a film thickness of 0.1 µ. A biodegradable ink was applied on the formed film and dried. A printed film was obtained, which has a favorable adhesivity and biodegradabilitry.

JP2003182266 A (2003, TOPPAN PRINTING CO LTD; TOYO BOSEKI; TOYO INK MFG CO) discloses the formation of a printed layer (16) on a PLA film (10) using an ink that comprises a binder predominantly composed of an aliphatic polyester comprising a PLA segment and a polyglycerol segment (see Figure 8.5). The printed structure (4) includes an overcoat layer (14) composed of a mixture of a PLA-based resin containing a PLA segment and a polyglycerol segment, and an organic solvent-soluble polysaccharide to prevent adhesion due to heat.

JP2003165570 A (2003, TOPPAN PRINTING CO LTD; TOYO BOSEKI; TOYO INK MFG CO) is a modification of the **JP2003182266** A patent application describing the formation of a printed heat-shrinkable packaging (4′) (see Figure 8.5). The heat-shrinkable packaging (4′) is made by fusion sealing ends of the film to each other into a bag form for packaging a product with the bag-formed film. A printed layer (16′) is formed on the film (16′) using the same ink as before, and an overcoat layer (14′) composed of the same composition as the overcoat layer (14) is applied on the top.

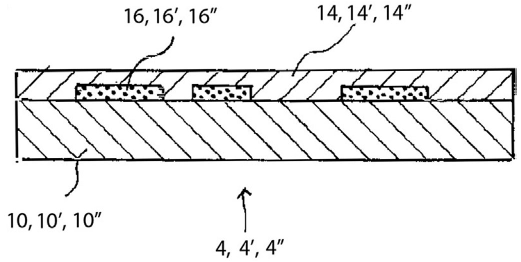


FIGURE 8.5 Printing of a biodegradable film (2003, **JP2003182266** A; 2003, **JP2003165570** A; 2003, **JP2003175569** A, TOPPAN PRINTING CO LTD; TOYO BOSEKI; TOYO INK MFG CO). 4, printed structure; 10, biodegradable film; 14, overcoat layer; 16, printing layer; 4′, packaging; 10′, biodegradable film; 14′, overcoat layer; 16′, printing layer; 4″, releasable sheet; 10″, biodegradable film or paper; 14″, releasing agent layer; 16″, printing layer.

JP2003175569 A (2003, TOPPAN PRINTING CO LTD; TOYO BOSEKI; TOYO INK MFG CO) is another modification of the **JP2003165570** A patent application describing the formation of a printed biodegradable releasable sheet (4″) (see Figure 8.5). A printed layer (16″) is formed on the film (10″) using the same ink as before, and a releasing agent layer (14″) of the same composition as the overcoat layer (14″) is applied on the top.

8.5.1 3D Printing

3D printing is an additive process of making three-dimensional objects from a computer-aided design (CAD) model. 3D printing is achieved by laying down successive layers of material to form shapes. To print, the machine reads the design from an .stl file (stereolithography format) and lays down successive layers of material to build a series of cross-sections. These layers are joined or automatically fuse to create the final shape.

This technique allows the ability to create almost any shape or geometric feature. Among other uses, 3D printing has found applications in the biomedical field as a means to generate tissue scaffolds out of biodegradable polymers as well as potentially tissues by printing cells and matrix into a defined area. Compared to a conventional 2D scaffold, a 3D-bioresorbable scaffold system is preferred for the generation and maintenance of highly differentiated, tissues. Although conventional 2D scaffolds are satisfactory for multiplying cells, they are less satisfactory when it comes to generating functional tissues.

Among the different 3D-printing processes available, fused deposition modeling (FDM) is particularly used for the 3D printing of biodegradable polymers such as PLA, PCL, PLGA, and the like. The FDM method involves the melt extrusion of a thermoplastic filament through a heated nozzle and deposition as thin solid layers on a platform. The material solidifies, laminating to the preceding layer. Parts are fabricated in layers, where each layer is built by extruding a small bead of material, or road, in a particular lay-down pattern, such that the layer is covered with the adjacent roads. After a layer is completed, the height of the extrusion head is increased and the subsequent layers are built to construct the part (2004, **US6730252** B1, TEOH SWEE HIN; HUTMACHER DIETMAR WERNER; TAN KIM CHENG; TAM KOCK FYE; ZEIN IWAN).

US6730252 B1 (2004, TEOH SWEE HIN; HUTMACHER DIETMAR WERNER; TAN KIM CHENG; TAM KOCK FYE; ZEIN IWAN) uses FDM to process a bioresorbable polymer, such as PCL, as well as a bioresorbable composite of two biomaterials, namely PCL and ceramic.

WO2009045176 A1 (2009, BIO SCAFFOLD INTERNAT PTE LTD) uses 3D printing for making a scaffold consisting of a biodegradable polymer and a binder or alternatively using FDM consisting of a biodegradable polymer. The biodegradable polymer is selected from PLA, PLLA, PGA, PGLA, PCL, P3HB, and combinations thereof.

Saito et al. [15] investigated the use of 3D printing for generating scaffolds of PLLA and PLGA (molar ratio of lactic acid to glycolic acid 50/50). In this research, biodegradable porous scaffolds were generated as potential bone graft materials.

PATENTS

Patent Number	Publication Date	Family Members	Priority Numbers	Inventors	Applicants	Title
BRPI0520831 A2	20100727		BR2005PI20831 20050728	ARR LAURA GONCALVES; PONCE PATRICIA; LUGAO ADEMAR BENEVOLO; PARRA DUCLERC FERNANDES; BASTOS CLAUDIO ROCHA		Processo de impermeabilização de substratos biodegradáveis. "Process for impermeabilizing biodegradable substrates."
CN101225221 A	20080723	CN101225221 B 20110511	CN2007151000 20071227	GANG YANG; PEIKAI MIU; WENRUI TANG; KE ZENG; YAN TANG; KE ZHOU; YIPENG WANG; HONGFEI ZHOU; TAO LIU; CHUNE ZHAO; GUOLIANG XU; SHAOHONG ZHOU; HAIBING HONG	UNIV SICHUAN	Polylactic acid and electron beam radiation modifying method for copolymer composite material thereof.
CN102504311 A	20120620		CN20111327654 20111026	LIN YANG; ZHIKAI TAO; KUI WANG; XIAOMING MA; YUMING GUO; TAO LIU; PEIPEI ZHANG	UNIV HENAN NORMAL	Method for polylactic acid high polymer material surface modified hydroxyapatite coating.
DE19615348 A1	19971023	WO9740111 A1 19971030; JP2000508700 A 20000711; EP0894118 A1 19990203; CN1216568 A 19990512; CA2251829 A1 19971030; AU2509397 A 19971112	DE1996115348 19960418	GRIGAT ERNST; IDEL KARSTEN; WESTEPPE UWE; SCHULZ-SCHLITTE WOLFGANG; POMMERANZ WINFRIED; LOERCKS JUERGEN; SCHMIDT HARALD	BAYER AG; BIOTEC BIOLOG NATURVERPACK	Kompostierbarer wasserfester Überzug. "Compostable waterproof coating."
EP0576993 A2	19940105	US5556711 A 19960917; JPH068370 A 19940118; EP0576993 A3 19940309; EP0576993 B1 19980318; EP0576993 B2 20020130; DE69317474 T2 19981119; DE69317474 T3 20021002	US19930078847 19930621; JP19920170806 19920629; US19950380311 19950130	AJIOKA MASANOBU; ENOMOTO KATASHI; YAMAGUCHI AKIHIRO; SUZUKI KAZUHIKO	MITSUI TOATSU CHEMICALS	Decomposable composite material.

Continued

—Cont'd

Patent Number	Publication Date	Family Members	Priority Numbers	Inventors	Applicants	Title
EP0802219 A2	19971022	US6139948 A 20001031; US5914188 A 19990622; EP0802219 A3 19980513; EP0802219 B1 20011024; DE69707547 T2 20020627	JP19960096616 19960418; JP19960105125 19960425	KOBAYASHI NAOKI; IKADO SHUHEI; KAWANO AKIRA; KUROKI TAKAYUKI; WANIBE HIROTAKA	MITSUI TOATSU CHEMICALS	Coated aliphatic polyester film.
EP0974615 A1	20000126	US2003135020 A1 20030717; US6600008 B1 20030729; US6649732 B2 20031118; EP1785449 A2 20070516; EP1785449 A3 20070829; EP0974615 B1 20100721; EP2236548 A2 20101006; EP2236548 A3 20070516; EP2236548 B1 20130116; EP1967603 A2 20080910; EP1967603 A3 20081210	JP19980206297 19980722; JP19980211089 19980727; JP19980211090 19980727; JP19980211091 19980727; JP19980223180 19980806; JP19990045075 19990223	KOBAYASHI HISATO; MORI KEIJI; ODA NAONOBU; OKUDAIRA TADASHI	TOYO BOSEKI	Aliphatic polyester film and gas barrier film.
EP1225196 A1	20020724	US2002160201 A1 20021031; JP2002210886 A 20020731; DE60218764 T2 20070705; AT356847 T 20070415		OHKURA MASATOSHI; SASAMOTO TAI; SHINNUMADATE HIROSHI	TORAY INDUSTRIES	Biodegradable oriented film.
EP2141191 A1	20100106	US2010003457 A1 20100107; CA2670850 A1 20100101; AU2009202657 A1 20100121	EP20080159463 20080701	ETTRIDGE PETER; WHITE CHRISTOPHER R	AMCOR FLEXIBLES TRANSPAC N V	Emballage composite.
JP2000094573 A	20000404	JP3085459 B2 20000911	JP19980206297 19980722; JP19990207828 19990722	KOBAYASHI HISATO; MORI KEIJI; ODA NAONOBU; OKUDAIRA TADASHI	TOYO BOSEKI	Gas barrier aliphatic polyester film.
JP2000096491 A	20000404	JP3473441 B2 20031202	JP19980269530 19980924	ARAI HIROSHI; KOGA TAKANORI	TOPPAN PRINTING CO LTD	Paper for preventing forgery.
JP2000103005 A	20000411	JP3085460 B2 20000911	JP19990212322 19990727; P19980211090 19980727	KOBAYASHI HISATO; MORI KEIJI; ODA NAONOBU; OKUDAIRA TADASHI	TOYO BOSEKI	Aliphatic polyester film having gas barrier property.
JP2000103006 A	20000411	JP3085461 B2 20000911	JP19990212323 19990727; JP19980211091 19980727	KOBAYASHI HISATO; MORI KEIJI; ODA NAONOBU; OKUDAIRA TADASHI	TOYO BOSEKI	Aliphatic polyester film having gas barrier property.
JP2000103879 A	20000411	JP3196895 B2 20010806	JP19990212321 19990727; JP19980211089 19980727	KOBAYASHI HISATO; MORI KEIJI; ODA NAONOBU; OKUDAIRA TADASHI	TOYO BOSEKI	Aliphatic polyester biaxially oriented film.

JP2000108202 A	20000418	JP3206747 B2 20010910	JP19990222350 19990805; JP19980223180 19980806	KOBAYASHI HISATO; MORI KEIJI; ODA NAONOBU; OKUDAIRA TADASHI	TOYO BOSEKI	Aliphatic polyester film.
JP2001018290 A	20010123		JP19990193585 19990707	ITO TAKURO; YAMAGUCHI YUJI; WATANABE SUKETAKA; ARITA TSUNEO	TOYO SEIKAN KAISHA LTD	Aliphatic polyester stretch-molded object and production thereof.
JP2001329082 A	20011127	JP3783199 B2 20060607	JP20000155174 20000525	OSAWA SATOSHI; OGAWA TOSHIO	KANAZAWA INST OF TECHNOLOGY	Polylactic acid resin molded product having controlled biodegradation period and its manufacturing method.
JP2001354223 A	20011225		JP20000173978 20000609	ITO TAKURO; MARUYAMA YUZURU; KANEKO TOMOAKI; SAKAGUCHI TOSHIKI; MATSUHASHI SETSU; WATANABE SUKETAKA	TOYO SEIKAN KAISHA LTD	Container made of aliphatic polyester.
JP2002121240 A	20020423	JP4872149 B2 20120208	JP20000310194 20001011	FURUTA TATSUHIKO; KAWAMOTO KENJI	TOPPAN PRINTING CO LTD	Biodegradable resin composition having adhesion and method for producing the same.
JP2002161155 A	20020604	JP3477642 B2 20031210	JP20000361718 20001128	OGAWA TOSHIO; OSAWA SATOSHI	KANAZAWA INST OF TECHNOLOGY	Molded material whose biodegradation period is controlled and its manufacturing method.
JP2002256088 A	20020911		JP20010059359 20010305	OGAWA TOSHIO; OSAWA SATOSHI	KANAZAWA INST OF TECHNOLOGY	Molded product of aliphatic polyester-based resin, improved in biodegradation rate, and production method thereof.
JP2003165570 A	20030610		JP20010366514 20011130	MIYAMOTO TAKASHI; HOTTA YASUNARI; KAKU TOSHIYUKI; KUYAMA KAZUNORI; SUZUKI AKIRA	TOPPAN PRINTING CO LTD; TOYO BOSEKI; TOYO INK MFG CO	Packaging material.

Continued

—Cont'd

Patent Number	Publication Date	Family Members	Priority Numbers	Inventors	Applicants	Title
JP2003175569 A	20030624	JP3942883 B2 20070711	JP20010378547 20011212	MIYAMOTO TAKASHI; HOTTA YASUNARI; KAKU TOSHIYUKI; OKUYAMA KAZUNORI; SUZUKI AKIRA	TOPPAN PRINTING CO LTD TOYO BOSEKI; TOYO INK MFG CO	Biodegradable releasable sheet.
JP2003182266 A	20030703		JP20010381159 20011214	IYAMOTO TAKASHI; HOTTA YASUNARI; KAKU TOSHIYUKI; OKUYAMA KAZUNORI; SUZUKI AKIRA	TOPPAN PRINTING CO LTD; TOYO BOSEKI; TOYO INK MFG CO	Printed matter.
JP2003311876 A	20031106		JP20020120485 20020423	YAMAMOTO MASAKAZU; IWASAKI YOSHIO; ABE SHINGO; KIDO HIROSHI	TOYO METALIZING; ISHIDA SEISAKUSHO; JAPAN PULP & PAPER CO LTD; NAKAMOTO PAKKUSU KK	Biodegradable vapor-deposited film.
JP2004057134 A	20040226		JP20020222680 20020731	SUGIYAMA YASUNORI	KIMOTO KK	Agricultural film.
JP2004223786 A	20040812	JP4273391 B2 20090603	JP20030011997 20030121	MIYAMOTO TAKASHI; MORIMOTO OSAMU	TOYO BOSEKI	Anchor agent for biodegradable printing ink and biodegradable laminate.
JP2004359763 A	20041224		jP20030158251 20030603	FUJIHIRA HIROKO; NOGUCHI TSUTOMU; MORI HIROYUKI	SONY CORP	Method of improving elastic modulus of biodegradable resin composition.
JP2005014966 A	20050120	JP4105600 B2 20080625	JP20030181518 20030625	SHISEIDO CO LTD	SATO TATSUO	Resin container and manufacturing method for the same.
JP2005194383 A	20050721	JP4530670 B2 20100825	JP20040002001 20040107	TSURUSAKI YOSHIYUKI	UNITIKA LTD	Antifogging polylactic acid-based biaxially oriented film and its production process.
JP2006124439 A	20060518		JP20040311629 20041027	KOBUNE MOMOO; OKAMOTO MASASHI; YAMADA AKIFUMI	UNITIKA LTD	Biodegradable aqueous dispersion and biodegradable laminated film.

JP2007331154 A	20071227		JP20060163454 20060613	NISHIHARA SHUNICHI	MITSUBISHI PLASTICS IND	Polylactic acid-based biaxially stretched film and its manufacturing method.
JP2008043905 A	20080228		JP20060223643 20060818	ENDO TERUYA; AKIMOTO MIKIO	TOHO CHEM IND CO LTD	Moisture-proof coating method for poly(lactic acid)-based resin.
JP2008063697 A	20080321		JP20060242871 20060907	SUGISAWA TOYOO; SEKIGUCHI KUNITAKA; MASUMURA NOBUYUKI	KUREHA GOSEN KK	Polylactic acid resin base material, fiber and clothing having high antibacterial property, and method for producing the same.
JP2008260205 A	20081030		JP20070104496 20070412	NARITA JUNICHI; TOYAMA TATSUYA	TOHCELLO CO LTD	Non-stretched film having deposit of inorganic thin film.
JP2008285610 A	20081127		JP20070133221 20070518	HAYAKAWA MAKOTO; GOTO TAKESHI	RISU PACK CO LTD	Polylactic acid-based resin sheet and molded article formed of its sheet.
JP2010144091 A	20100701			UYAMA HIROSHI; TSUJIMOTO KEI; KITAGAWA SATORU; KITAGAWA IYUKI; OKA TATSUYA	UNIV OSAKA; OSAKA IND PROMOTION ORG	Method for processing surface of polymer.
JP2012246421 A	20121213		JP20110120411 20110530	AWATA T	TOYO BOSEKI	Method for producing polylactic acid resin molded body.
JPH07195814 A	19950801		JP19940000241 19940106	NAKAGAWA YOSHIHIRO; TANIGUCHI MASAYUKI; FUJIMAKI TAKASHI	TOPPAN PRINTING CO LTD; SHOWA HIGHPOLYMER	Biodegradable plastic film printed matter.
JPH0797545 A	19950411		JP19930244295 19930930	NAGOSHI TOSHIHARU; HAYASHI HISATAKA; YAMADA NAOAKI	KANEGAFUCHI CHEMICAL IND	Biodegradable coating agent having water resistance and biodegradable container for food.
JPH08244781 A	19960924		JP19950044465 19950303	UMEYAMA HIROSHI; YOSHIHARA TOSHIAKI; TANIGUCHI MASAYUKI; HACHIFUSA KAZUYA	TOPPAN PRINTING CO LTD	Container, production thereof and preform.

Continued

—Cont'd

Patent Number	Publication Date	Family Members	Priority Numbers	Inventors	Applicants	Title
JPH10138433 A	19980526		JP19960304454 19961115	KAWAKITA SHUNICHI; KOYANAGI KENJI	UNITIKA LTD	Gas barrier biaxially oriented poly-lactic acid film.
JPH10219012 A	19980818	JP3476325 B2 20031210	JP19970023582 19970206	ANDO SADAMASA; KARASAWA TAIZO; OZASA TERUO; KURISAKA TAKAYUKI; SHINOHARA RUMI	NISSEI KK	Biodegradable molding product having water resistance and its production.
JPH1024518 A	19980127		JP19960180457 19960710	TAKAGI JUN; ARITAKE TOSHIYUKI; TERADA SHIGENORI	MITSUBISHI PLASTICS IND	Polylactic biodegradable gas barrier film.
JPH1034807 A	19980210		JP19960198599 19960729	YAGINUMA MASAKI; MACHIDA TOSHINORI	TOYO INK MFG CO	Biodegradable plastic with barrier property.
JPH11116709 A	19990427	JP3638416 B2 20050413	JP19970283560 19971016	KOBAYASHI NAOKI; IMON SHUHEI; KOUNO AKIRA; KUROKI TAKAYUKI; IWATA MASATAKA; WANIBE HIROTAKA	MITSUI CHEMICALS INC	Aliphatic polyester coated film.
JPH11147269 A	19990602		JP19970317854 19971119	AKASHI KAZUSHIROU; KOMURA AKIMASA; UEMATSU TAKASHI	FUJI XEROX CO LTD	Biodegradable resin composition.
JPH11335475 A	19991207		JP19980146081 19980527	INOUE YOSHIO; YOSHIE NAOKO	TOKUYAMA CORP	Production of biodegradable resin molded product.
US2004127123 A1	20040701	WO2004058314 A2 20040715; US7700500 B2 20100420; MXPA05006144 A 20050826; KR20050085432 A 20050829; JP006521412 A 20060921; EP1575842 A2 20050921; BR0317157 A 20051101; AU2003297236 A1 20040722	US20020436086P 20021223; US20030734004 20031210	JORDAN JOY FRANCINE; YAHIAOUI ALI; WALLAJAPET PALANI RAJ RAMASWAM	KIMBERLY CLARK CO	Durable hydrophilic treatment for a biodegradable polymeric substrate.
US2007014752 A1	20070118	WO2007008755 A2 20070118; WO2007008755 A3 20070419	US20050697480P 20050708	ROY KRISHNENDU; RAJA LAZMINARIYAN L	UNIV TEXAS	Surface functionalization of polymeric materials.

US2007172663 A1	20070726	TWI331621 B 20101011; KR20070078053 A 20070730; KR20080087774 A 20081001; KR100865097 B1 20081024; KR100898359 B1 20090520; JP2007197523 A 20070809; JP5007504 B2 20120822; EP1813652 A1 20070801; EP1813652 B1 20090902; CN101009979 A 20070801	JP20060015890 20060125	YUI YASUSHI	FUJITSU LTD	Article made of biodegradable resin and method of making the same.
US2009036639 A1	20090205	WO2009018380 A2 20090205; MX2010001049 A 20100301; JP2010535120 A 20101118; EP2178423 A2 20100428; CN101815454 A 20100825; CA2694935 A1 20090205; AU2008282212 A1 20090205	US20080181415 20080729; US20070952925P 20070731	ZHANG QIUCHEN PETER; OKOROAFOR MICHAEL O; HUANG XIAOYAN; JONES STUART MICHAEL RUAN; DENT PHILIP ANDREW; GOULD CLAIRE LOUISE	COCA COLA CO	Post-processing of polylactic acid article.
US2010040904 A1	20100218;	WO2010019944 A 20100218; MX2011001623 A 20110524; EP2323788 A1 20110525; EP2323788 A4 20121219; CA2733581 A1 20100218	US20090542428 20090817; US20080089128P 20080815	CLOUTIER JOSHUA R; MIZUMURA TAKESHI; CHANG KEUNSUK P	TORAY PLASTICS AMERICA INC	Biaxially oriented polylactic acid film with high barrier.
US2010330382 A1	20101230	WO2010151872 A1 20101229	US20100824759 20100628; US20090220840P 20090626	DOU SHICHEN; CHANG KEUNSUK P	TORAY PLASTICS AMERICA INC	Biaxially oriented polylactic acid film with improved moisture barrier.
US2011076511 A1	20110331	WO2011038248 A1 20110331; US2013143064 A1 20130606; US2013143057 A1 20130606; EP2480710 A1 20120801	US20100890349 20100924; US20090246048P 20090925	PAOLILLI TRACY A; FITCH JOHN J	TORAY PLASTICS AMERICA INC	Multi-layer high moisture barrier polylactic acid film.
US2012156780 A1	20120621	WO2012087616 A2 20120628; WO2012087616 A3 20120823; EP2655487 A2 20131030	US20100974216 20101221	COOPER KEVIN L; MARTIN ALISHA; NATARAJAN SRIRAM; VETRECIN ROBERT; LIU CHANGDENG	ADVANCED TECHNOLOGIES and REGENERATIVE MEDICINE LLC	Polymer substrates having improved biological response from HKDCS.
US6730252 B1	20040504	US7968026 B1 20110628; US8071007 B1 20111206	US20000233874P 20000920; US20010957407 20010920	TEOH SWEE HIN; HUTMACHER DIETMAR WERNER; TAN KIM CHENG; TAM KOCK FYE; ZEIN IWAN	TEOH SWEE HIN; HUTMACHER DIETMAR WERNER; TAN KIM CHENG; TAM KOCK FYE; ZEIN IWAN	Methods for fabricating a filament for use in tissue engineering.
WO03050170 A1	20030619	US2005124786 A1 20050609; JP2005511840 A 20050428; EP1456285 A1 20040915; AU2002350935 A1 20030623	GB20010029547 20011211	JONES RICHARD ANTHONY LEWIS; SHARP JAMES SINCLAIR	ASTRAZENECA AB; ASTRAZENECA UK LTD	Films with crater-shaped protrusions.

Continued

—Cont'd

Patent Number	Publication Date	Family Members	Priority Numbers	Inventors	Applicants	Title
WO03082963 A1	20031009	US2006204727 A1 20060914; US8182901 B2 20120522; TWI225012 B 20041211; JP2003292640 A 20031015; JP4179585 B2 20081112; EP1491575 A1 20041229; EP1491575 A4 20080423; EP1491575 B1 20131106; CN1522273 A 20040818; CN1237096 C 20060118; AU2003220893 A1 20031013	JP20020096126 20020329	UNI CHARM CORP; HINO TOMOHARU; OHARA TORU	UNI CHARM CORP	Printed biodegradable plastic film.
WO2008012981 A1	20080131	US2009226655 A1 20090910; KR20090023737 A 20090305; KR101039649 B1 20110609; JP2008030306 A 20080214; EP2047967 A1 20090415; CN101495290 A 20090729; CN101495290 B 20120725; CA2658794 A1 20080131; AU2007277961 A1 20080131; AU2007277961 B2 20100527	JP20060206473 20060728	SUGAI MASAHIRO; SUZUKI MASATO; SHIMURA HIROMI; CHIBA JUNICHI	YOSHINO KOGYOSHO CO LTD	Heat-resistant poly(L-lactic acid) preform
WO2008129688 A1	20081030	US2010112252 A1 20100506; US8133562 B2 20120313; TW200840879 A 20081016; KR20100014717 A 20100210; JP2008254794 A 20081023; JP4420052 B2 20100224; EP2135734 A1 20091223; EP2135734 A4 20130123; EP2135734 B1 20140108; CN101678642 A 20100324; CN101678642 B 20130717	JP20070100755 20070406	ITO TAKURO; MORI TAKUMI; NAKAO HIROSHI; YAMAZAKI KAZUHIKO	TOYO SEIKAN KAISHA	Plastic molded product with vapor deposition film and its manufacturing method.
WO2008149918 A1	20100210	US2010140205 A1 20100610; US8470421 B2 20130625; KR20100007869 A 20100122; JP5136551 B2 20130206; EP2151395 A1 20100210; EP2151395 A4 20120808; CN101678920 A 20100324; CN101678920 B 20110511	JP20070150408 20070606	ITO TAKURO; MORI HIROKI; NAKAO HIROSHI; YAMAZAKI KAZUHIKO	TOYO SEIKAN KAISHA LTD	Biodegradable resin bottle and process for producing the same.
WO2009045176 A1	20090409		US20070960558P 20071003	MARGAM CHANDRASEKARAN; LEE WAN KHENG VICTOR; LEE YONG CHIAH VINCENT; YEO BOON HON; HASSAN RAMANATH SATHYANARAYANA	BIO SCAFFOLD INTERNAT PTE LTD	

WO2010040707 A1	20100415	US2010255326 A1 20101007; EP2344577 A1 20110720; CA2739669 A1 20100415	US20080195414P 20081007	CHIAPPINI EMANUELA; GARDI STEFANO; NAISBY ANDREW J; TELESCA ROSANNA; TAPLIN WALTER; FORSYTHE NEIL	BASF SE	Printable gas barriers.
WO2012002707 A2	20120105	WO2012002707 A3 20120503; US2013136922 A1 20130530 KR20120001539 A 20120104; JP2013535353 A 20130912; EP2589489 A2 20130508; EP2589489 A4 20131211; CN103097128 A 20130508	KR20100062374 20100629	KIM DONG JIN; KIM SI MIN; KIM YUN JO; SONG GI SANG	KOLON INC	Shrinkable film and method for manufacturing same.
WO2013140868 A1	20130926	JP2013193336 A 20130930	JP20120063241 20120321	ITO TAKURO; OZAWA SATOMI; KITOU SATOSHI; YAMAZAKI KAZUHIKO	TOYO SEIKAN GROUP HOLDINGS LTD	Polylactic acid molding provided with deposited film and method for producing same.
WO9417220 A1	19940804	JPH08505825 A 19960625; JP2635218 B2 19970730; EP0680522 A1 19951108; EP0680522 B1 19961002; DE69400638 T2 19970227; CA2153998 A1 19940804	US19930008899 19930121 US19930171080 19931221	O'BRIEN WILLIAM GEORGE	DU PONT	Metallized poly(lactic acid) films.
WO9424198 A1	19941027	DE4313136 A1 19941027	DE19934313136 19930422	STERZEL HANS-JOSEF	BASF AG	Mit Metallen oder Siliziumoxiden beschichtetes Polylactid als Verpackungsmaterial. "Polylactide coated with metal or silicon oxide for use as packaging material."
WO9515260 A1	19950608	JPH09506303 A 19970624; FI962251 A 19960529; EP0731754 A1 19960918; EP0731754 B1 19990303; DE69416857 T2 19991007; CA2177065 A1 19950608; AU1112995 A 19950608; AT177054 T 19990315	GB19930024512 19931130	KEMMISH JOHN DAVID; MONTADOR JAMES HENRY	ZENECA LTD	Biodegradable film.
WO9705193 A1	19970213	ITVR950068 A1 19970128; IT1277799 B1 19971112; EP0842217 A1 19980520; DE6962569 T2 20031023; AU6667696 A 19970226; AT230772 T 20030115	IT1995VR00068 19950728	ZUCCATO ALESSANDRO; PEREGO GABRIELE; CELLA GIAN DOMENICO	SANITARIA SCALIGERA SPA	A Process of surface activation of biocompatible and bioabsorbable aliphatic polyesters and polyesters thus activated.

REFERENCES

[1] Enercon Industries Corporation. Green plastics. Can they be decorated? http://www.enerconind.com/mediaLib/stml/techPaper/Enercon-green-plastics-can-they-be-decorated.pdf?ext=.pdf. [retrieved 01.10.2013].

[2] Finson E, Kaplan SL. Surface treatment. In: Brody A, Marsh K, editors. The Wiley Encyclopedia of packaging technology, 1997. New York: John Wiley & Sons, Inc; 1997.

[3] Park GE, Pattison MA, Park K, Webster TJ. Accelerated chondrocyte functions on NaOH-treated PLGA scaffolds. Biomaterials 2005;26:3075–82.

[4] Wang S, Cui W, Bei J. Bulk and surface modifications of polylactide. Anal Bioanal Chem 2005;381:547–56.

[5] Gao J, Niklason L, Langer R. Surface hydrolysis of poly(glycolic acid) meshes increases the seeding density of vascular smooth muscle cells. J Biomed Mater Res 1998;42:417–24.

[6] Zhu Y, Gao C, Liu X, Shen J. Surface modification of polycaprolactone membrane via aminolysis and biomacromolecule immobilization for promoting cytocompatibility of human endothelial cells. Biomacromolecules 2002;3:1312–9.

[7] Zhu Y, Gao C, Liu Y, Shen J. Endothelial cell functions in vitro cultured on poly (L-lactic acid) membranes modified with different methods. J Biomed Mater Res Part A 2004;69:436–43.

[8] Goddard JM, Hotchkiss JH. Polymer surface modification for the attachment of bioactive compounds. Prog Polym Sci 2007;32:698–725.

[9] Morent R, De Geyter N, Desmet T, Dubruel P, Leys C. Plasma surface modification of biodegradable polymers: a review. Plasma Process Polym 2011;8:171–90.

[10] Rasal RM, Janorkar AV, Hirt DE. Poly(lactic acid) modifications. Prog Polym Sci 2010;35:338–56.

[11] Mitomo H, Watanabe Y, Yoshii F, Makuuchi K. Radiation effect on polyesters. Radiat Phys Chem 1995;46:233–8.

[12] Lee HS, Lee TY. Graft polymerization of acrylamide onto poly(hydroxybutyrate-*co*-hydroxy-valerate) films. Polymer 1997;38:4505–11.

[13] Kiss E, Kutnyánszky E, Bertóti I. Modification of poly(lactic/glycolic acid) surface by chemical attachment of poly(ethylene glycol). Langmuir 2010;26:1440–4.

[14] Quiceno ALG, Biofilm SA. Prospects on PLA applications – clear barrier technology. Innovation takes root. Las Vegas (Nevada): NatureWorks LLC; 2008.

[15] Saito E, Liao EE, Hu W-W, Krebsbach PH, Hollister SJ. Effects of designed PLLA and 50:50 PLGA scaffold architectures on bone formation in vivo. J Tissue Eng Regen Med 2013;7:99–111.

Chapter 9

Foaming and Foamed Products

9.1 BIOPOLYMER FOAMS

Polymer foams include a plurality of cells (alias voids) in a polymer matrix. A foam can have an open, partially open, or closed cell structure. A polymer foam uses less material than a solid polymer for a given volume, and material costs can be reduced in many applications. Polymer foams have been used in packaging containers, shock absorbers, and cushioning materials in large quantities. Although polymer foams are light weight, they are difficult to recycle because of their bulky size. In addition, most foams used as packaging, protective, insulating, and cushioning material are made of nonbiodegradable fossil fuel–based polymers. To address and alleviate these problems, numerous efforts have been made for the development of biodegradable polymer foams. By using biodegradable polymers, the environmental impact of waste accumulation can be reduced or, in some cases, eliminated. Part of these efforts is directed to the development of bio-based foams, which may or may not be biodegradable, in which part or the whole of the raw materials is derived from renewable resources. Soy-based polyols have been developed for this purpose as an alternative to fossil fuel–based polyols for the production of polyurethane because the soy-based material can offer cost advantages and alleviate the environmental concerns associated with fossil fuel–based polyols. Examples of the use of soy-based polyols to formulate soy-based polyurethane foams can be found in **US2002192456** A1 (2002, MASHBURN LARRY E; HARRISON WILLIAM H; PATTERSON THOMAS E); **EP1264850** A1 (2002, CLATTY JAN L); **US5710190** A (1998, a UNIV IOWA STATE RES FOUND INC); and **WO0015684** A1 (2000, URETHANE SOY SYSTEMS CO).

9.2 TYPES OF BIOPOLYMERS

Most of the commercial biodegradable polymer foams produced are made of polyesters and starch and their derivatives alone or in combination with other (bio) degradable polymers. There are also efforts to develop bio-based polystyrene, polyolefins, aromatic polyesters, and polyurethane, which, on a direct cost basis of the raw material, can be used in the future as substitutes of the fossil fuel–based counterparts in the manufacture of foams (see Chapter 1: Introduction; Section 1.3: Types and Chemistry of Biopolymers).

9.2.1 Polyesters

The main types of biodegradable polyesters are aliphatic homopolyesters, copolyesters, and aliphatic-aromatic copolyesters. There are, also, nonbiodegradable aromatic polyesters derived from renewable resources.

9.2.1.1 Aliphatic Polyesters

Aliphatic polyesters include poly(hydroxy acid)s, such as poly(lactic acid) (PLA) and poly(glycolic acid) (PGA); polyhydroxyalkanoates (PHAs), derived mainly from microorganisms; and poly(alkylene dicarboxylate)s, derived from both fossil fuel and renewable resources, such as poly(butylene succinate) (PBS) and poly(butylene adipate-*co*-terephthalate) (PBAT).

Aliphatic polyesters have been used mainly because of their biodegradability. The feature of biodegradability has effectively been used in outdoor applications where the aliphatic polyesters are used and disposed. On the other hand, the feature of early biodegradability can be problematic in applications such as cushioning materials or heat-insulating materials, if they are going to be used in high-temperature and high humidity environments or require long-term resistance.

PLA and PBS have been proposed as replacement of polystyrene for the manufacture of foamed products because of their relatively mild environmental impact. However, PLA foams have several disadvantages that have limited their use in packaging and other applications. The glass transition temperature (T_g) of the various types of PLA is usually in the range of 50–60 °C, which is too low, and thereby results in poor heat resistance. A foam product made of PLA may deform when used at temperatures in the vicinity of T_g. This low dimensional stability at elevated temperatures can be particularly problematic during summer months when packaging articles comprising PLA may be exposed to relatively high temperatures during storage or transportation.

One way to improve the heat resistance of PLA is by increasing the degree of crystallinity. However, the crystallization rate of PLA is generally exceedingly slow, and high-temperature curing for a long time is required for increasing the degree of crystallinity (see Chapter 2: Properties; Sections 2.2.1: Poly(lactic acid) and 2.3.2: Heat Resistance. Furthermore, the increase of the degree of crystallinity

Biopolymers: Processing and Products. http://dx.doi.org/10.1016/B978-0-323-26698-7.00009-X

occurs at the expense of foamability. **JP2002317066** A (2002, SEKISUI PLASTICS) discloses that the use of an amorphous PLA having a particular melt viscosity can enhance foamability. However, the amorphous PLA used has a low heat resistance (2007, **WO2007083705** A1, ASAHI KASEI LIFE & LIVING CORP).

Moreover, each of PLA and PBS has a relatively high melt flow index (i.e., 4–4.5 and 4.5, respectively), which results in lower melt strength and inferior gas barrier properties. The low melt strength causes a decrease in the closed cell content because of the burst of air cells generated in the foaming process. When air cells burst, foaming agents within the air cells dissipate outside the air cells. As a result, the air cells stop growing and, therefore, the expansion ratio is decreased. In **JPH04304244** A (1992, MITSUI TOATSU CHEMICALS), a PLA foam having a density of 0.26–0.48 g/cm^3 provides only a thin foam sheet (1.1–2.8 mm). A foam having a low expansion ratio (i.e., a high density) does not acquire light weight, cushioning properties, and heat insulating properties (2007, **WO2007083705** A1, ASAHI KASEI LIFE & LIVING CORP).

Furthermore, PLA lacks flexibility when used in applications, such as cushioning materials where the foam is compressed. Therefore, there arises a problem that the extent to which the foam that has been compressed and crushed recovers a thickness is small. To solve this problem, a method is used wherein a polyolefin or polystyrene having high foamability and high heat resistance is blended with PLA. The problem in this case is the incompatibility between the highly polar PLA and the nonpolar polyolefin or polystyrene, which results in a nonuniform mixture that does not foam, or if the mixture foams, the closed cell content is decreased because of exfoliation occurring in the interface between them. In **WO2006103969** A1 (2006, TORAY INDUSTRIES), a polyolefin copolymer containing glycidyl (meth)acrylate units, which are capable of reacting with the terminal group of PLA, is used as a compatibilizer component for blending PLA and a polyolefin. However, only a foam in a thin sheet form having a low expansion ratio and a small section is obtained (2007, **WO2007083705** A1, ASAHI KASEI LIFE & LIVING CORP).

JP2003020355 A (2003, SEKISUI PLASTICS) discloses a PLA foam obtained by extruding an amorphous PLA having a melt viscosity at 75 °C ranging from 1.0×10^8 to 3.0×10^6 Pa s and a melt viscosity at 100 °C ranging from 1.0×16^8 to 3.0×10^5 Pa s. Dimethyl ether is used as foaming agent.

JP2003261704 A (2003) and **JP2003301066** A (2003) of SEKISUI PLASTICS) disclose PLA foams obtained by extruding a mixture of a PLA made by copolymerization of 2–10 wt% D-lactic acid and 98–90 wt% L-lactic acid and a foaming agent comprising dimethyl ether.

JP2004307662 A (2004, SEKISUI PLASTICS) discloses a method for producing a crystalline PLA foam that comprises performing an extruding expansion of a mixture of a crystalline PLA made by copolymerization of 2–13 wt% D-lactic acid and 98–87 wt% L-lactic acid and a foaming agent comprising dimethyl ether and a hydrocarbon (e.g., isobutane) in the weight ratio of 95/5–5/95.

JP2003327737 A (2003, KANEGAFUCHI CHEMICAL IND) discloses the production of an extruded foam using a PHA and a non–halogen-based foaming agent at a certain melt viscosity. A foam having an expansion ratio of eight times or less can be obtained using poly(3-hydroxybutyrate-*co*-3-hydroxyhexanoate) (P3HBHHx) as the PHA, and carbon dioxide gas, dimethyl ether, or hydrocarbon as a foaming agent. However, in some cases, it is difficult to produce the PHA foam continuously for a long period by the disclosed method. Furthermore, the extruded foam has a high closed-cell rate (e.g., 51%), with the lowest closed-cell rate being 29%. Depending on the application of the foam, extruded foams having a high open-cell rate could be obtained such as loose shock absorbers (2006, **WO2006103926** A1; 2006, **WO2006103928**, KANEKA CORP).

WO2006103926 A1 (2006, KANEKA CORP) discloses a method of producing a PHA extruded foam comprising the following: melt-kneading PHA and a foaming agent to form a mixture; and extruding the mixture through a molding die in a low pressure region, wherein the PHA temperature, T_o (temperature of PHA measured at the extruder discharge outlet), satisfies the equation: $T_g < T_o < T_m$ of PHA. A preferred PHA copolymer is P3HBHHx. The extruded PHA foam has a high foaming ratio (>8×) and many open cells (≥80%) (see also **WO2006103928**, KANEKA CORP) in Section 9.4.2: Organic Compounds.

9.2.1.2 Aliphatic-Aromatic Polyesters

JP2003039524 A (2003) and **JP2004058352** A (2004) of SEKISUI PLASTICS disclose a method for producing an aliphatic-aromatic copolyester foam comprising the steps of press injecting a foaming agent comprising a dimethyl ether and/or a hydrocarbon in the aliphatic-aromatic copolyester melt in an extruder, extruding and foaming the copolyester. A preferred aliphatic-aromatic copolyesters is PBAT, and in particular the commercial product Ecoflex® (BASF AG), Eastar® Bio (Eastman Chemical).[1]

9.2.2 Starch

Starch-based foams are well known in the prior art. A variety of foamed products made of starch beads are discussed in **WO0214043** A1 (2002, BLUE MARBLE POLYMERS LTD).

---

[1] The Eastman Chemical's Eastar Biotechnology was bought in 2004 by Novamont.

Foamed starch is suitable as an economic packaging material for the protection of vulnerable goods. It is used also in many other purposes, such as thermal and sound insulation. Unlike polystyrene foam, the starch foam is insoluble in organic solvents and does not melt under the influence of heat. Its combustibility is negligible in comparison with polystyrene or polyethylene, but it can be further affected by adding known flame-inhibiting agents. The resistance of starch to water can be improved at high porosity (e.g., by the simultaneous use of an aldehyde (e.g., glyoxal) to insolubilize the starch or by the addition of insolubilizing resins (e.g., by adding urea or melamine resin (1983, **WO8302955** A1, BIJENKORF ZETMEEL).

WO8302955 A1 (1983, BIJENKORF ZETMEEL) discloses a method for preparing foamed gelatinized products made of starch, by heating granular or pulverized starch in an extruder at a temperature of 60–220 °C in the presence of 10–30 wt% of water and a physical or chemical foaming agent. The obtained foamed material has open pores and high water solubility, which makes it suitable for use only as packaging material for the protection of fragile articles, as a sound-adsorbing or thermal-insulating material, or as a foodstuff.

US4863655 A (1989, NAT STARCH CHEM CORP) discloses a method for preparing a biodegradable packaging material by supplying starch or modified starch, and water as a foaming agent to an extruder, followed by foam molding. The foamed starch product may be formed in different shapes by varying the size and configuration of the die opening. However, it is difficult to prepare starch foams having various shapes and sizes by foam molding using an extruder. There is a method of preparing foams, in which starch is foamed by using an extruder, and then the foamed starch extrudate is subjected to a complex working process, such as a compression, junction, and cutting to give a specific shape. However, equipment of foaming expandable polystyrene beads cannot be used, and also there are limitations on the use and economic feasibility of such a multistep process (2012, **WO2012008784** A2, DAESANG CORP).

US2007021515 A1 (2007, KHASHOGGI E IND) discloses a method for preparing starch foams by extruding a starch composition, including starch, and a foaming agent, such as water or alcohol, by an extruder to prepare beads, and then foam molding the prepared beads to a specific shape. However, there are limitations regarding the selection of suitable foaming agents because of properties of starch, so that special foaming equipment is required instead of equipment for foaming expandable polystyrene beads, which uses various molds and steam when preparing foams, and there are limitations on a rate of foaming (2012, **WO2012008784** A2, DAESANG CORP).

EP0812877 A2 (1997, MAFO SYSTEMTECH GMBH & CO KG) discloses a method and device for making a starch-based foam molding, in which a dough made of starch, water, and foaming agent is expanded by microwave heating in a mold made of material that is transparent to microwaves.

9.3 FOAMING AGENTS

Foaming agents (alias blowing or expanding agents) are substances that are introduced into a polymer, and under proper conditions, they expand the polymer and create polymer foam. There are two major types of foaming agents: physical and chemical foaming agents. Physical foaming agents tend to be volatile liquids or compressed gases that change state during melt processing to form a cellular structure. Chemical foaming agents are low-molecular-weight organic compounds that decompose at a particular temperature and release a gas, such as nitrogen, carbon dioxide, or carbon monoxide.

Foaming agents can be divided also into two major classifications: organic and inorganic. Organic foaming agents are available in a wide range of different chemistries, physical forms, and modification, such as, for example, azodicarbonamide. Inorganic foaming agents tend to be more limited, such as, for example, sodium carbonate.

Polymer foams are commonly made using a continuous process where a foaming agent laden molten resin is extruded under pressure through an appropriate die into a lower-pressure atmosphere. Alternatively, a batch or staged process can be used, where small polymer beads (alias particles or pellets) are impregnated with foaming agent and then expanded by heating rapidly to a temperature near or above the T_g or melting temperature (T_m) of the polymer-foaming agent system, or subjected to an external compressive stress at a temperature up to the T_g or T_m of the polymer-foaming agent system. Stable thermoplastic foams are achieved using foaming agents that are environmentally benign.

The effectiveness of a foaming agent depends on its solubility in the polymer and its ability to expand the polymer-foaming agent solution when such a solution is subjected to thermodynamic instability, such as, for example, when the solution exits a die attached to an extruder (to provide the extrudate) or when the foaming agent laden polymer is rapidly heated. The expansion of the polymer-foaming agent solution depends on the difference between the T_g and the boiling point of the foaming agent (T_b). In general, the solubility of the foaming agent in the polymer depends on the difference between T_g and T_b (T_g–T_b): the smaller the difference, the higher the solubility. In the case of semicrystalline polymers, such as certain biodegradable polymers, the characteristic temperature controlling expandability is the T_m, and that controlling foaming agent solubility is T_m–T_b. Because volatility follows an inverse relationship with T_b, it is understood that at the same conditions of temperature and pressure, a higher volatility foaming agent will have lower solubility compared with a lower volatility foaming agent (2008, **WO2008076755** A1, PACTIV CORP).

Care should be exercised in selecting the foaming agent. The foaming agent of choice should be environmentally friendly. In the past, chlorofluorocarbons, such as Freon, were extensively used in the making of foams. Nowadays, these foaming agents have been banned throughout much of the world because of growing evidence that contributes to ozone depletion in the upper atmosphere. The foaming agent should be also safe in its handling and use. Lower alkanes ($C_{2\text{-}4}$), such as butane, pentane, or even hexane, would vaporize at melting temperatures. The biggest disadvantage of these foaming agents is their flammability. The solubility of the foaming agent in the biopolymer will affect the quality of foam. If the foaming agent is soluble in the biopolymer, it may act as a plasticizer, reducing the viscosity of the polymer melt, making it difficult to maintain a good cell structure in the foam. If the foaming agent is not sufficiently soluble in the polymer, it is dispersed evenly throughout the polymer melt and tends to “pop” out of the melt when it exits the extruder.

9.3.1 Physical Foaming Agents

Physical foaming agents or evaporation type foaming agents are inorganic or organic gaseous agents that are dissolved in a polymer matrix and generate foam cells by vaporization. According to a commonly applied technique, the physical foaming agent is injected into a molten polymer to form a mixture. The mixture is subjected to a pressure decrease, causing the foaming agent to expand and form cells in the polymer.

Examples of inorganic physical foaming agents include carbon dioxide, nitrogen, argon, and air.

Examples of organic physical foaming agents include aliphatic hydrocarbons and halogenated hydrocarbons. Representative hydrocarbons are propane, butane, isobutane, cyclobutane, pentane, neopentane, isopentane, cyclopentane, hexane, isohexane, and butadiene.

Types of halogenated hydrocarbons are chlorinated hydrocarbons, hydrochlorofluorocarbons (HFCs), and hydrofluorocarbons. Examples of chlorinated hydrocarbons are trichloromethane (chloroform) and methylene chloride. Examples of hydrochlorofluorocarbons include the following: trichlorofluoromethane, dichlorodifluoromethane, chlorofluoromethane, 1-chloro-1,1-difluoroethane, and 1-chloro-1,2,2,2-tetrafluoroethane. Examples of hydrofluorocarbons include the following: trifluoromethane, 1,1-difluoroethane, and 1,1,1,2-tetrafluoroethane.

Hydrocarbons with three or more carbon atoms are considered volatile organic compounds (VOCs) that can lead to formation of smog. Other hydrocarbons, such as pentane, present a fire hazard. Furthermore, some halogenated hydrocarbons are VOCs, may have high ozone depletion potential (ODP) or global warming potential (GWP), or may be hazardous air pollutants (HAPs); at times, they may fall into more than one of these categories. Therefore, the use of hydrocarbon and halogenated hydrocarbon foaming agents for preparing polymer foams is not preferred environmentally and imposes many limitations on the manufacturing process, thus complicating and significantly increasing the cost of manufacturing. In efforts to make biodegradable polymer foams, the conventionally used foaming agents, such as VOCs, have been the obvious choice, although such uses are associated with the same environmental concerns as noted above. It is, therefore, desirable to minimize or eliminate altogether the use of such compounds as foaming agents for preparing biodegradable polymer foams.

Carbon dioxide (CO_2) is a common foaming agent for production of foamed polymer foams. In particular, carbon dioxide is recognized as an environmentally acceptable foaming agent because of its inert nature and low GWP. There are, however, limits on carbon dioxide and other commonly used foaming agents, particularly in producing low-density foams. Low-density foams often have an unacceptable post-production collapse. In other words, the structure of the foam (e.g., closed cell) fails and the volume of the foam is reduced. This may be due, in part, to the fast diffusion of the carbon dioxide or other foaming agent out of the foamed product. Thus, carbon dioxide and other common foaming agents are often limited to foaming high-density foams with sufficient mechanical strength to minimize or prevent collapse of the foam.

Other foaming agents to replace HFCs are methyl formate and dimethyl ether. Dimethyl ether is highly flammable, and new equipment is needed to handle flammable gases. Methyl formate[2] has good foaming efficiency and is classified as a non-VOC, is non-HAP, has 0 ODP, and has negligible GWP. A list of physical blowing agents used in foaming compositions of biodegradable polymers is given in Table 9.1.

Certain thermoplastic polymers behave differently with respect to the structural collapse of the foam. For example, polystyrene has not shown the same degree of collapse as PLA. One difference between the various classes of thermoplastic polymers may be due, in part, to the amount of foaming agent that can be added to the polymer composition and how quickly the foaming agent diffuses from the foam. For example, the solubility and diffusivity of carbon dioxide in polystyrene are believed to be less than that for PLA. The carbon dioxide diffuses out of the PLA foam faster than air is able to diffuse into the foam, resulting in the collapse of the foam structure (2011, **WO2011038081** A1, ARKEMA INC).

---

[2] Federal Register, volume 69, number 228, November. 29, 2004.

TABLE 9.1 Physical Foaming Agents Used in Biodegradable Foaming Compositions of Representative Patents

Biopolymer	Foaming Agent(s)	Patents
PLA	Chloroform, methyl formate, methyl acetate, propyl acetate, dioxane, methyl ethyl ketone	**EP0592911** A1 (1994, BASF AG)
PLA	Dimethyl ether	**JP2003301066** A (2003); **JP2003020355** A (2003); **JP2003261704** A (2003, SEKISUI PLASTICS)
PLA	Dimethyl ether and hydrocarbon (e.g., isobutane)	**JP2004307662** A (2004, SEKISUI PLASTICS)
PLA	Ethane, butane, methyl chloride, carbonic acid gas, water	**JP2000007815** A (2000); **JP2000007816** A (2000, MITSUI CHEMICALS INC)
PLA	Isobutane, mixture. of n-pentane (70–90 wt%), and isobutane (10–30 wt%)	**WO2012121960** A1 (2012, CRYOVAC INC)
PLA, PLGA	Ethane, butane, pentane, hexane, heptane, ethylene, propylene, petroleum ether; halogenated hydrocarbon (e.g., methyl chloride, monochlorodifluoromethane, dichlorodifluoro methane, monochlorotrifluoromethane, dichlorotetrafluoro ethane), carbonic acid gas, nitrogen	**JPH05170966** A (1993, MITSUI TOATSU CHEMICALS)
PLGA	Ethane, butane, methyl chloride, monochlorotrifluoromethane, dichlorodifluoromethane, carbon dioxide	**JPH05170965** A (1993, MITSUI TOATSU CHEMICALS)
Epoxide-modified PLA	Inorganic-type physical foaming agents: carbon dioxide, nitrogen, air, and mixture	**WO2013058056** A1 (2012, JSP CORP)
PLA	Carbon dioxide	**WO2012138282** A1 (2012, SIOX MACHINES AB)
PLA	Carbon dioxide in its super critical state	**US2012009420** A1 (2012, LIFOAM IND LLC)
PLA, PGA, PLGA, PCL, PHA, PBAT (Exoflex®), PLA/Exoflex® (Ecovio®), starch, cellulose	Methyl formate and cofoaming agent (1,1,1,2-tetrafluoroethane)	**WO2008076755** A1 (2008, PACTIV CORP)
PHA blend (P3HB and P3HB4HB)	1,1,1,2-Tetrafluoroethane, butane, carbon dioxide, nitrogen, pentane, isopentane, isobutane	**WO2010065053** A1 (2010, METABOLIX INC)
P3HBHHx	Carbon dioxide gas, dimethyl ether, or hydrocarbon	**JP2003327737** A (2003, KANEGAFUCHI CHEMICAL IND)
P3HBHHx	Dimethyl ether, diethyl ether, and/or methyl ethyl ether	**WO2006103970** A1 (2006); **WO2006103926** A1 (2006, KANEKA CORP)
PAA	Isobutane, n-butane	**JPH10152572** A (1998, JSP CORP)
PAA	Propane, butane, pentane	**JPH08253617** A (1996, DAINIPPON INK & CHEMICALS)
PBAT	Dimethyl ether and/or hydrocarbon (e.g., isobutane)	**JP2003039524** A (2003); **JP2004058352** A (2004, SEKISUI PLASTICS)
Starch	Water	**US4863655** A (2007, NAT STARCH CHEM CORP)
Starch	Acetone, methanol, ethanol, isopropanol; plasticizer (polyol, glycerol, sorbitol); nucleating agent; water-resistant polymer (e.g., PBS, PBSA, PHBHV)	**US2007021515** A1 (2007, KHASHOGGI E IND)
Starch (≥amylose)	Water	**EP0376201** A1 (1990, NAT STARCH CHEM CORP)

P3HB, poly(3-hxdroxybutyrate); P3HB4HB, poly(3-hydroxybutyrate-*co*-4-hydroxybutyrate); P3HBHHx, poly(3-hydroxybutyrate-*co*-3-hydroxyhexanoate); PAA, poly(alkylene alkanoate); PBAT, poly(butylene adipate-*co*-terephthalate); PBSA: poly(butylene succinate-*co*-adipate) PCL, poly(ε-caprolactone); PGA: poly(glycolic acid); PHA, polyhydroxyalkanoate; PLA, poly(lactic acid); PLGA, poly(lactide-*co*-glycolide).

Occasionally, the foaming agent composition includes a cofoaming agent. Typical cofoaming agents include the following:

HFC-134a: 1,1,1,2-tetrafluoroethane,
HFO-1243zf: 3,3,3-trifluoropropen,
HFO-1234yf: 2,3,3,3-tetrafluoropropene,
trans-HFO-1234ze: trans-1,3,3,3-tetrafluoropropene, and
trans-HCFO-1233zd: trans-1-chloro-3,3,3-trifluoropropene.

Particularly suitable cofoaming agents have low GWPs. For example, hydrofluoroolefins are known to generally exhibit low GWPs. Thus, it is preferable to select a cofoaming agent with a GWP of less than 150, preferably less than 50, or more preferably, less than 20. In particular, 3,3,3-trifluoropropene (HFO-1243zf), 2,3,3,3-tetrafluoropropene (HFO-1234yf), trans-1,3,3,3-tetrafluoropropene (trans-HFO-1234ze), and mixtures thereof have beneficially low GWP values. In addition, it is contemplated that a cofoaming agent is VOC free (i.e., free of volatile organic compounds) or has minimal VOC emissions (2011, **WO2011038081** A1, ARKEMA INC).

WO2011038081 A1 (2011, ARKEMA INC) discloses a method of making a low-density biodegradable foam by mixing the biodegradable polymer, such as PLA, and the foaming agent system comprising carbon dioxide and a cofoaming agent, cooling and then extruding the expandable polymer composition from the die where the decrease in pressure initiates foaming. The cofoaming agent is selected from the group consisting of HFC-134a, HFO-1243zf, HFO-1234YF, E-HFO-1234ze, and mixtures thereof.

9.3.2 Chemical Foaming Agents

Chemical foaming agents (alias thermal decomposable foaming agents) are a class of foaming agents that are solids or liquids at room temperature and, on heating, decompose at a particular temperature, releasing a gas such as nitrogen, carbon dioxide, or carbon monoxide. Typically, they are used by mixing a chemical foaming agent with a solid polymer and heating the mixture while maintaining the mix under pressure. Heating fluidizes the polymer and causes the foaming agent to release a gas through a chemical reaction. The gas forms bubbles or cells in the fluid polymer. The mixture is maintained under pressure until it is placed into a mold where the gas expands, and in turn causes the fluid polymer to expand. On solidifying, the cell structure remains. Different foaming agents release gas at different temperatures, and the choice of foaming agent depends on the processing conditions, type of polymer, and the size of the desired gas cells. Chemical foaming agents have the advantages over physical (gaseous) foaming agents in that they can be added to a solid polymer before heating. Physical foaming agents, such as nitrogen and some fluorocarbons, must be injected into the already fluidized polymer.

Chemical foaming agents generally are low-molecular-weight inorganic or organic compounds and are usually supplied in powder or pellet form. Examples of inorganic chemical foaming agents include sodium bicarbonate, ammonium carbonate, ammonium bicarbonate, and calcium azide. Examples of organic foaming agents include azodicarbonamide, hydrazocarbonamide, benzenesulfonyl hydrazide, dinitrosopentamethylene tetramine, toluenesulfonyl hydrazide, p,p'-oxybis(benzenesulfonylhydrazide), azobisisobutyronitrile, and barium azodicarboxylate. A list of chemical blowing agents used in foaming compositions of biodegradable polymers is given in Table 9.2.

9.4 COMPOUNDING INGREDIENTS

A biodegradable polymer foam may contain several additives (see Chapter 5: Compounding; Section 5.5: Additives and Modifiers). Nonlimiting examples of additives are selected from the group consisting of plasticizers, nucleating agents, antioxidants, flame retardants, light stabilizers, viscosity modifiers, melt strength improvers/modifiers, colorants (dyes or pigments), fibers, antiblocking agents, heat stabilizers, impact modifiers, biocides, compatibilizers, tackifiers, colorants, IR attenuating agents, coupling agents, antistatic agents, electrically conductive fillers, pigments, additional polymers, thermally insulating additives, and mixtures thereof. The additives may be incorporated into the polymer composition in different forms (e.g., powders, pellets, and granules) and compositions (e.g., masterbatches). The amount and type of additives in the biodegradable foam composition may vary depending on the polymer matrix and the desired physical properties of the finished foam (2012, **US2012009420** A1, LIFOAM IND LLC). The choice of each additive shall be environmentally acceptable, and its incorporation into the biodegradable polymer composition will not affect negatively the other properties of the resulting foam product (e.g., the use of a high amount of a halogenated additive as a flame retardant additive such as hexabromocyclododecane) in a polymer foam to meet the fire retardancy requirements of the stringent European fire retardancy tests can have a detrimental impact on the strength of the foam).

9.4.1 Inorganic Compounds

Many inorganic compounds can be added to a biodegradable foaming composition with the purpose of improving several desired properties, such as cell nucleation, compression strength, and heat resistance. A list of inorganic compounds used in foaming compositions of biodegradable polymers is given in Table 9.3.

Foaming processes, in some cases, incorporate nucleating agents, some of which are inorganic solid particles, into the polymer melt during processing. These agents can be of a variety of compositions, such as talc and calcium carbonate, and are dispersed into the polymer melt, typically

TABLE 9.2 Chemical Foaming Agents Used in Biodegradable Foaming Compositions of Representative Patents

Biopolymer	Foaming Agent(s)	Other Components	Patents
PLA	Azodicarbonamide	Plasticizer (lactic acid, lactic acid oligomer or lactide)	**US5238968** A (1993, MITSUI TOATSU CHEMICALS)
PLA	Azodicarbonamide	Paper dust	**JP2005060689** A 20050310 (2005, TORAY INDUSTRIES)
PLA and 2nd polymer (PBS, PBSA, PBAT)	Azodicarbonamide, benzenesulfonyl hydrazide, dinitrosopentamethylene tetramine, toluenesulfonyl hydrazide, azobisisobutyronitrile, barium azodicarboxylate, sodium bicarbonate; preferably azodicarboxylamide	Citrate or sugar alcohol-based plasticizer	**WO2012091366** A2 (LG HAUSYS LTD)
Starch	Powdered sodium bicarbonate (0.1–2 wt%)	Malic acid (0.2–7 wt%)	**WO9308014** A1 (1993, BIO PROD INT)
Starch	Sodium bicarbonate (0.01–10 wt%)	Pulverized acid (citric acid, adipic acid)	(1983, **DE3206751** A1BIJENKORF ZETMEEL)
Polysaccharide (sodium hyaluronate, sodium alginate, carrageenans, chitosan)	Sodium dodecyl sulfate and physical foaming agent (lower alkane [propane, butane, pentane, nitrogen, carbon dioxide])	Plasticizer (glycerol, glucose, polyhydric alcohols, triethanolamine, stearates)	**US5840777** A (1998, ALBANY INT CORP)
Crosslinked poly-α (1→4)glucopyranose	Potassium bicarbonate	Citric acid	**WO2009038783** A1 (2009, SURMODICS INC)
Proteinaceous biopolymer (e.g., albumin)	Inorganic bicarbonates (sodium, potassium, aluminum, iron bicarbonates)	Dialdehyde or polyaldehyde and acidic titrant (phosphoric acid, sulfuric acid, hydrochloric acid, acetic acid, or citric acid)	**US2002059001** A (2002, CRYOLIFE, INC)

PBAT, poly(butylene adipate-*co*-terephthalate); PBS: poly(butylene succinate); PBSA poly(butylene succinate-*co*-adipate); PLA, poly(lactic acid); PLGA, poly(lactide-*co*-glycolide).

to promote cell nucleation. The dispersion of nucleating agents within the polymer mixture is often critical in forming a uniform cell structure (2000, **JP2000007816** A, MITSUI CHEMICALS INC; 2010, **WO2010065053** A1, (METABOLIX INC). Nanoclays are added to improve the compressive strength of the foam (1996, **DE19504899** A1 NAT INST RES INORGANIC MAT) and stabilize the foam structure (2004, **EP1484357** A, UNIV LIEGE).

US2011217430 A1 (2011, MULTISORB TECH INC) discloses in one of its embodiments a PLA-based foam sheet containing an oxygen scavenger having a particle size of less than 25 μm. The oxygen scavenger comprises iron or iron particles, sodium chloride, and sodium bisulfate. A most preferred oxygen scavenger is reduced iron powder coated with activating and acidifying materials. The foam sheets can be thermoformed into containers by using the conventional thermoforming processes. The advantages of incorporating active oxygen scavengers in foam containers include extending freshness of meat/food packages, providing additional freshness for case ready meat, activating the scavengers with liquids leaking from the meat/foods, and no or less need of scavenging sachets.

9.4.2 Organic Compounds

A range of organic compounds can be added to a biodegradable foaming composition with the purpose of improving several desired properties, such as foam stability, heat resistance, and flexibility. A list of organic compounds used in the foaming compositions of biopolymers is given in Table 9.4.

JP2000007815 A (2000, MITSUI CHEMICALS INC) discloses a composition for producing a biodegradable foam comprising the following: (1) 100 pbw PLA; (2) 0.01–20 pbw thickener (e.g., a multivalent isocyanate or a polybasic acid anhydride); and (3) 0.1–20 pbw volatile foaming agent (e.g., a hydrocarbon, such as ethane or

TABLE 9.3 Inorganic Compounds Used in Biodegradable Foaming Compositions of Representative Patents

Biopolymer	Inorganic Component	Function	Patents
PLA, P3HB, PHBHV, PCL	Organomodified clay nanofiller	Stabilization of the foamed structure	**EP1484357** A1 (2004, UNIV LIEGE)
PLA	Iron particles coated with an inorganic salt, sodium chloride, sodium bisulfate	Oxygen scavenger	**US2011217430** A1 (2011, MULTISORB TECH INC)
PLA	Talc	Foam cell nucleating agent	**JP2000007816** A (2000, MITSUI CHEMICALS INC)
PLA	Active carbon	Thermal insulation	**WO2010041936** A2 (2010, SYNBRA TECH B.V.)
PHA blend (P3HB and P3HB4HB)	Talc (e.g., Flextalc 610D; clay, SCPX3016)	Foam cell nucleating agent	**WO2010065053** A1 (2010, METABOLIX INC)
Starch	Natural clay (montmorillonite, saponite, beidellite, kaolinite, allophane, or bentonite); synthetic clay	Improves compressive strength	**DE19504899** A1 (1996, NAT INST RES INORGANIC MAT)

P3HB, poly(3-hydroxybutyrate); P3HB4HB, poly(3-hydroxybutyrate-*co*-4-hydroxybutyrate); PCL, poly(ε-caprolactone); PHA, polyhydroxyalkanoate; PHBHV, poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate); PLA, poly(lactic acid).

TABLE 9.4 Organic Compounds Used in Biodegradable Foaming Compositions of Representative Patents

Biopolymer	Organic Component	Function/Properties	Patents
PLA	Benzoic acid amide or cyclic hydrazide (decane dicarboxylic acid bisbenzoyl hydrazide, phthalic acid hydrazide) (0.1–10 wt%)	Improve heat resistance	**JP2007262319** A (2007, ADEKA CORP)
PLA	Polyolefin or wax (natural candelilla wax and paraffin wax) (0.2–10 wt%)	Improve moisture barrier property, heat resistance, resistance to oxygen permeation, and heat resistance	**WO2007052543** (2007, UNITIKA LTD)
PLA	Polyolefin wax (0.0001–1 pbw)	Control of average cell diameter of PLA expandable particles	**US2006167122** A1 (2006); **JP2006233192** A (2006, JSP CORP)
PLA	Glycerol derivative, ether ester derivative, glycolic acid derivative, citric acid derivative, adipic acid derivative, rosin derivative, and/or tetrahydro furfuryl alcohol derivative	Improve fusibility	**JP2006282750** A (2006, JSP CORP)
PHA blend (P3HB and P3HB4HB)	Epoxy functional cpd. (epoxy- functional styrene-acrylic polymer, epoxy-functional acrylic copolymer, epoxy-functional polyolefin copolymer, oligomer comprising a glycidyl group with an epoxy functional side chain, epoxy-functionalized poly(ethylene-glycidyl methacrylate-*co*-methacrylate), or an epoxidized oil)	Increase melt strength of PHA by branching	**WO2010065053** A1 (2010, METABOLIX INC)
P3HBHHx	Fatty acid amide compound and/or a liquid paraffin	Suppression of crystallization	**WO2006103928** A1 (2006, KANEKA CORP)
PBAT	Fatty acid amide or a fatty acid ester	Increasing expansion ratio (>10×) and compression recovery	**JP2003103595** A (2003, SEKISUI PLASTICS)
Mater-bi® NF01U (70–90 wt%) (≥85 wt% starch and PBAT)	Plasticizer (5–15 wt% tributyl citrate or 5–12.5 wt% acetyl tributyl citrate)	Flexibility, reduced bleeding	**WO2011153653** A1 (2011, BIOAPPLY SARL)

P3HB, poly(3-hxdroxybutyrate); P3HB4HB, poly(3-hydroxybutyrate-*co*-4-hydroxybutyrate); P3HBHHx, poly(3-hydroxybutyrate-*co*-3-hydroxyhexanoate); PBAT, poly(butylene adipate-*co*-butylene terephthalate); PHA, polyhydroxyalkanoate; PLA, poly(lactic acid).

butane, a halogenated hydrocarbon, such as methyl chloride, carbonic acid gas, or water). The composition is melt foamed, and a PLA foam or sheet both improved in foaming property is obtained. Melt tension in melt foaming is sufficient, and it is possible to produce molded foam in a high expansion ratio. The addition of the thickener is claimed to improve the melt viscosity of the foam composition.

WO2006103928 A1 (2006, KANEKA CORP) discloses a method for producing an extruded foam of PHA by melt kneading a PHA copolymer, a volatile foaming agent, a fatty acid amide compound, and/or a liquid paraffin to thereby obtain a mixture and extruding the mixture through a molding die into a low-pressure zone. The temperature, T_o, of the mixture measured at the extruder discharge outlet satisfies the equation: $T_g < T_o < T_m$ of PHA. A preferred PHA copolymer is P3HBHHx. The addition of a fatty acid amide-based compound and/or liquid paraffin to PHA can suppress crystallization of PHA in an extruder, whereby the PHA extruded foam can be stably produced for a long period. Moreover, the problem of slow crystallization in PHA foam can be improved to achieve an increase in expansion ratio, preferably when a volatile foaming agent with high plasticizing ability (e.g., dimethyl ether) is used, and the resin temperature at the extruder outlet is cooled near to the crystallization temperature of PHA, particularly to approximately the maximum crystallization temperature.

JP2003103595 A (2003, SEKISUI PLASTICS) discloses an aliphatic-aromatic copolyester foam obtained as follows: (1) melt mixing an aliphatic-aromatic copolyester and a fatty acid compound in an extruder, (2) cooling the mixture at a temperature lower than the T_m of the copolyester and injecting the foaming agent, and (3) extruding and expanding the mixture. The fatty acid compound contributes to the stability of the foam. A preferred fatty acid compound is fatty acid amide or a fatty acid ester compound. A preferred aliphatic-aromatic copolyester is PBAT and, in particular, the commercial products Ecoflex® (BASF AG) and Eastar® Bio (Eastman Chemical).

9.4.3 Polymer Components

A biodegradable polymer can be blended with various polymers for improving desired properties of the foam (see also Chapter 3: Blending). A list of polymer components used in the foaming compositions of biodegradable polymers is given in Table 9.5.

In **WO2006103969** A1 (2006) and **WO2008126660** A1 2008) of TORAY INDUSTRIES), PLA is blended with a polyolefin using a vinyl-carboxylate–modified polyolefin as compatibilizer to improve the heat resistance of the foam.

In **WO2007083705** A1 (2008, ASAHI KASEI LIFE & LIVING CORP), PLA is mixed with polyolefin or polystyrene in combination with a styrene-butadiene block copolymer to improve the heat resistance and compression recovery of the foam. The biodegradable polymer foam is suitable as a cushioning material.

WO2010065053 A1 (2010, METABOLIX INC) discloses a method for producing a PHA foam comprising the following steps: (1) mixing a PHA with an epoxy functional compound and a foam cell nucleating agent under conditions that cause reaction of the polymer with the epoxy functional compound, thereby forming a molten foam composition; (2) combining the molten foam composition with a physical foaming agent under conditions that cause foaming of the molten foam composition; and (3) cooling the foamed polymer composition, thereby forming a PHA polymer foam. The epoxy functional compound is an epoxy-functional styrene-acrylic polymer, an epoxy-functional acrylic copolymer, an epoxy-functional polyolefin copolymer, an oligomer comprising a glycidyl group with an epoxy functional side chain, an epoxy-functionalized poly(ethylene-glycidyl methacrylate-co-methacrylate), or an epoxidized oil or combinations thereof. The foam cell nucleating agent is talc (e.g., SCPX3016) or clay (Flextalc 610D).

WO2012099357 A2 (2012, KOREA INST OF FOOTWEAR & LEATHER TECHNOLOGY; COMTECH CHEMICAL CO LTD) mixes PLA with ethylene-vinyl acetate copolymer, styrene-butadiene-styrene copolymer, and ethylene-methacrylic acid copolymer, and several additives, including plasticizer, silane coupling agent, crosslinking agent, foaming agent, metal oxide, and calcium carbon, to prepare a shoe insole claiming to have excellent durability and hardness.

WO2013030300 A1 (2013) and **US2013059141** A1 (2013, BASF SE) disclose a foam layer comprising the following: (1) PLA (51–95 wt%); (2) poly(propylene carbonate) (5–49 wt%); (3) an aliphatic-aromatic polyester (0–25 wt%); (4) an epoxide group, containing copolymer based on styrene, acrylic acid ether, and/or methacrylic acid ether; and (5) additives (0–15 wt%). The obtained foam layer is claiming to have high stability, improved density, and excellent haptic properties. The foam layer is useful for thermal insulation and sound deadening or as a packaging material for food or drink.

9.4.4 Mixtures of Compounding Ingredients

JP2000007816 A (2000, MITSUI CHEMICALS INC) discloses a polymer composition for producing a biodegradable foam comprising the following: (1) PLA (100 pbw); (2) inorganic foaming nucleating agent, (0.1–5.0 pbw), preferably talc, having 1–10 μm average particle diameter; (3) foaming aid (0.01–0.5 pbw), preferably a stearic acid–based compound or montanoic acid; and (4) 0.1–20 pbw volatile foaming agent (e.g., a hydrocarbon, such as ethane and butane, a chlorinated hydrocarbon, such as methyl chloride,

TABLE 9.5 Polymer Components Used in Biodegradable Foaming Compositions of Representative Patents

Biopolymer	Polymer Component	Patents
PLA (20–28 wt%)	Polyolefin (5–75 wt%) and glycidyl (meth)acrylate-modified polyolefin (3–30 wt%)	**WO2006103969** A1 (2006, TORAY INDUSTRIES
PLA (1–80) pbw)	Polyolefin containing PP (100 pbw) and vinyl-carboxylate–modified polyolefin (<30 pbw)	**WO2008126660** A1 2008, TORAY INDUSTRIES)
(A): PLA (80–20 wt of A + B)	(B): Polyolefin or polystyrene (20–80 wt%); and styrene-butadiene block copolymer (e.g., SBS, SEBS, SBBS) (1–10 pbw)	**WO2007083705** A1 (2008, ASAHI KASEI LIFE & LIVING CORP)
PLA	EVA, SBS, and EVMA	**WO2012099357** A2 (2012, KOREA INST OF FOOTWEAR & LEATHER TECHNOLOGY; COMTECH CHEMICAL CO LTD)
PLA (51–95 wt%)	PPC (5–49 wt%)	**US2013059141** A1 (2013, BASF SE)
PHA	Epoxy-functional styrene-acrylic polymer, epoxy-functional acrylic copolymer, epoxy- functional polyolefin copolymer, oligomer comprising a glycidyl group with an epoxyfunctional side chain, epoxy-functionalized poly(ethylene-glycidyl methacrylate-co-methacrylate)	**WO2010065053** A1 (2010, METABOLIX INC)
Starch (80–10 wt%)	EVA, EAA (10–80 wt%)	**WO9102023** A1 (1991, BUTTERFLY SRL)

EAA, ethylene-acrylic acid copolymer; EVOH, ethylene-vinyl alcohol copolymer; EVA, ethylene-vinyl acetate copolymer; EVMA, ethylene-methacrylic acid copolymer; PHA, polyhydroxyalkanoate; PLA, poly(lactic acid); PP, polypropylene; PPC, poly(propylene carbonate); SBBS, styrene-butadiene-butylene-styrene copolymer; SBS, styrene-butadiene-styrene copolymer; SEBS, styrene-ethylene-butylene-styrene copolymer.

carbonic acid gas, or water). The composition is melt kneaded, and a PLA foam or sheet, both improved in foaming property, is obtained. The addition of a specific foaming nucleating agent and a foaming aid to PLA in a specific ratio is claimed to provide a molded foam having uniform cell diameter and improved in foaming property.

EP1624024 A1 (2006, UNITIKA LTD) discloses a biodegradable foam obtained by foam molding a biodegradable polyester composition comprising the following: (1) a biodegradable polyester (100 pbw); (2) a (meth)acrylic acid ester compound (0.01–10 pbw); and (3) a layered silicate (0.05–20 pbw). The layered silicate and the (meth) acrylic acid ester compound have a synergistic effect on the crystallization rate and the extrusion moldability of the biodegradable polyester, and provide a molded foam having favorable mechanical strength, heat resistance, rheological characteristics, and gas barrier properties. The biodegradable polyester is selected from PLA, PBS, and PBAT. The (meth)acrylic acid ester compound is selected from polyethylene glycol dimethacrylate, trimethylpropane trimethacrylate, polyethylene glycol diacrylate, and glycidylmethacrylate.

WO2013017895 A1 (20,130, FLAHERTY MICHAEL JOHN) provides a material comprising a biopolymer blend, including a crosslinked mixture of PLA and a polysaccharide, blended with particles of calcium carbonate that have been coated with a fatty acid compound, particles of mica, and a cellulose filler.

9.5 EXPANDABLE PARTICLES

Foams are commonly manufactured as expanded beads or extruded sheets. The difference between the expanded and extruded foams is that the extruded foams, in the form of continuous sheets, are made in a single-step process, whereas expanded foams, in the form of discrete, small pieces, are made in a multistep process. Thus, the dimensions of expanded foam are much smaller than those of extruded foam. Furthermore, the expanded foams do not necessarily have to be in the form of beads or granules, but can also be made from pellets, rods, platelets, thin sheet, or film (2008, **WO2008076755** A1, PACTIV CORP).

EP0592911 A1 (1994, BASF AG) discloses a method for the preparation of a PLA injection-molding composition by melt extruding and then pelletizing a mixture of PLA and 10–30 wt% of a solvent, such as methyl formate, followed by drying the pellets at room temperature and allowing the PLA to crystallize. Alternatively, the crystalline PLA pellets are obtained by mixing the pellets with the solvent at room temperature and allowing sufficient time for the solvent to diffuse into the pellets.

Methods for producing expandable particles that comprise PLA have been described in general terms in **DE19938008** A1 (20010, BASF AG), but there is no mention of the specific PLA mixture (2011, **WO2011086030**, BASF SE). There are wider ranges where this process does not give reproducible moldable foams and, in particular, it does not prevent the premature foaming of the expanded particles.

WO2011086030 A2 (2011, BASF SE) discloses a method for producing expandable PLA-containing granules, comprising the following: (1) melting and mixing PLA, one additional polymer, a diepoxide, or a polyepoxide and at least one nucleating agent; (2) mixing an organic foaming agent and a cofoaming agent, including nitrogen, carbon dioxide, argon, and/or helium, into the polymer melt via a static or dynamic mixer; (3) discharging the mixture via a nozzle plate with holes; and (4) granulating the foaming agent–containing melt directly behind the nozzle plate under water. The additional polymer is an aliphatic or aliphatic-aromatic polyester. The aliphatic polyester is selected from poly(alkylene alkanoate)s (PAAs), such as PBS, poly(butylene adipate), poly(butylene succinate-*co*-adipate), poly(butylene succinate-*co*-sebacate), poly(butylene sebacate-*co*-adipate), poly(butylene-*co*-sebacate), or corresponding polyesteramides. Suitable commercial aliphatic polyesters are Bionolle (Showa Highpolymers Co. Ltd.) and GS Pla® (Mitsubishi Chemical). A preferred aliphatic-aromatic polyester is PBAT. A suitable commercial PBAT is Ecoflex (BAF AG). Epoxides are, in particular, a copolymer that is based on styrene, or (meth)acrylate, and that contains epoxy groups. A suitable commercial copolymer containing epoxy groups is Joncryl® ADR (BASF resins B.V.).

Example: Isopentane (5.7 parts) was mixed in a melt of PLA (79.6 parts), PBAT (Ecoflex® F BX 7011, BASF AG) (20 parts), an epoxide group–containing copolymer (Joncryl® ADR 4368 CS, BASF SE) (0.4 parts), and talc (HP 325) (0.3 parts) in an extruder at a melt temperature of 220 °C. The melt was conveyed with a flow rate of 3.5 kg/h through the nozzle plate with holes, and the compact granules were produced via pressurized underwater granulation at a pressure of 12 bar, where the temperature of water was 40 °C.

JP2009242728 A (2009, UNIV RYUKOKU) discloses a method of manufacturing PLA porous particles comprising the following steps: (1) mixing PLA with a first solvent, which is a good solvent of PLA, and heat and melt the mixture; (2) cooling the melted liquid at the crystallization temperature of PLA. The method further involves separating the PLA particles from the mixture, contacting the particles with a second solvent exhibiting high solubility in the first solvent compared with solubility in PLA, washing the PLA particles, and drying the washed crystals. The PLA porous particles are spherical, have an average particle size of 99–700 μm, and have a degree of crystallinity of at least 50%. The porous structure has an average pore diameter of 0.27–1.4 μm. The PLA porous particles can be used as medical base material, preferably as scaffold for sustained release of drugs and biological tissue regeneration.

WO2010041936 A2 (2010, SYNBRA TECH B.V.) discloses a particulate, expandable polymer (e.g., PLA), polystyrene, or a combination thereof, which can be processed to form a foam having a fine cell structure and a low density, and which contains active carbon having a particle size of at most 12 μm for increasing the thermal insulation value of the material.

WO2008076755 A1 (2008, PACTIV CORP) discloses, in one of its embodiments, a method for producing biodegradable polymer expandable beads comprising the following steps: (1) melting a biodegradable polymer; (2) mixing an effective amount of a foaming agent comprising methyl formate in the biodegradable polymer; and (3) extruding the mixture into a low-temperature zone to form the expandable bead. Preferred biodegradable polymers include PLA, PGA, poly(lactide-*co*-glycolde) (PLGA), poly(ε-caprolactone) (PCL), PHA, PBAT (e.g., Exoflex®, BASF AG), PLA/Exoflex® (Ecovio®, BASF AG), starch, cellulose, or a combination thereof.

JP2000017038 A (2000, KANEBO LTD; RES INST INNOVATIVE TECH EARTH; KANEBO SYNTHETIC FIBERS LTD) discloses a PLA composition obtained by: (1) blending PLA (a) with at least one amorphous polymer (b) of polycarbonate, polystyrene, or poly(ethylene-terephthalate), wherein the weight ratio of (a)/(b) = 99/1 to 80/20 and the PLA has a molar ratio of L-lactic acid to D-lactic acid of 95/5–60/40 or 40/60–5/95; and (2) incorporating in the mixture a polyisocyanate compound having an isocyanate group of ≥2 eq/mol in an amount of 0.5–5 wt% based on PLA, and causing them to react. The particles produced from the previously mentioned PLA compositions are impregnated with a foaming agent and a foaming aid, the resulting foamable particles are preliminarily foamed to produce preliminarily foamed particles, and the preliminarily foamed particles are filled into a mold and then are foamed to form a molded article with a desired shape. However, because PLA has a molar ratio of the stereoisomer component of the L-lactic acid or the D-lactic acid, whichever is less, of 5 mol% or more, the PLA is low in crystallinity or amorphous and is poor in heat resistance. Therefore, a molded article obtained from the PLA composition has insufficient heat resistance (i.e., approximately 50 °C) at most, which has caused problems in practical use (2008, **WO2008123367** A1, SEKISUI PLASTICS CO., LTD).

JP2002302567 A (2002, ACHILLES CORP) discloses a method for continuously producing preliminarily expanded PLA particles for in-mold molding, wherein PLA and a foaming agent are kneaded in an extruder and extruded in the form of a foamed strand; and the foamed strand is cut to obtain preliminarily foamed particles. A method for cutting the foamed strand, a so-called hot cutting system, in which a strand under foaming is cut while being cooled is preferred. In the previously mentioned continuous production method, however, because a strand is cut at its portion, which has already expanded, there is a possibility that a cut section of the strand may fall into a condition that cut sections of cells are exposed. As a result, the resulting preliminarily expanded particles have had a problem that foaming gas is apt to escape from the cut sections of cells exposed on their surfaces and, therefore, they are low in foaming property. Furthermore, preliminarily foamed particles obtained by cutting a strand have another problem that the crystallinity degree of the polyester-based resin constituting the preliminarily expanded particles has increased because they have not been cooled forcibly, and, as a result, the thermal fusion bonding property will be deteriorated (2008, **WO2008123367** A1, SEKISUI PLASTICS CO., LTD).

JP2003073495 A (2003, JSP CORP) discloses a method for producing expandable PLA particles comprising impregnating PLA particles having a calorific value of 15 J/g or more (measured in differential scanning calorimetry) with carbon dioxide under particular conditions. It has been reported by **WO2008123367** A1 (2008, SEKISUI PLASTICS CO., LTD) that, because the calorific value is 15 J/g or more, PLA is low in crystallinity and is insufficient in heat resistance (i.e., having a heat resisting temperature of about 80 °C). Moreover, because the gas pressure applied when PLA particles are impregnated with carbon dioxide is 0.5–10 MPa, there has arisen a problem that crystallization of the PLA proceeds during the impregnation of the PLA particles with carbon dioxide, so that the thermal fusion bonding property of the resulting expandable PLA particles is deteriorated and that expandable PLA particles become flat, so that the foaming property thereof will be deteriorated.

WO2008123367 A1 (2009, SEKISUI PLASTICS CO., LTD) discloses a method for producing expanded PLA particles by extruding PLA in a nozzle metal mold, and foaming using a foaming agent to obtain expanded PLA particles. The PLA contains stereoisomers, a D-lactic acid, and an L-lactic acid, as constituent monomer components, the content of one of the optical isomers, the D-form or the L-form, whichever is less, being less than 5 mol%, or contains only one of optical isomers, a D-form or an L-form, as a constituent monomer component. The nozzle metal mold is attached to the front end of an extruder. The foaming process is performed by contacting the front-end surface of the nozzle metal mold. The rotary blade rotates at a speed of 2000–10,000 rpm. The surfaces of the expanded PLA particles are preferably coated with optical isomers. The inert gas is carbon dioxide.

WO9854244 A1 (1998, JSP CORP) discloses expanded particles of a crosslinked aliphatic polyester obtained by crosslinking aliphatic polyester particles with a crosslinking agent containing an organic peroxide and foaming the crosslinked aliphatic polyester particles. A preferred aliphatic polyester is PBS. The crosslinked particles have a gel fraction of at least 5 wt%. Biodegradable foamed moldings are obtained by thermally foaming the foamed crosslinked aliphatic polyester resin particles in a mold.

EP1378538 A1 (2004, JSP CORP) discloses expandable PLA beads comprising crystalline PLA (45–85 wt%) and non-crystalline PLA, and being impregnated with a foaming agent. The PLA beads require re-impregnation with foaming agent before molding. A preferred foaming agent is carbon dioxide, because carbon dioxide is impregnated efficiently in the PLA particles, and expanded beads having a small apparent density can be obtained even with a small amount of the foaming agent.

US2006167122 A1 (2006) and **JP2006233192** A (2006) of JSP CORP disclose expandable PLA particles comprising the following: (1) PLA, (2) a polyolefin wax in an amount of 0.0001–1 pbw per 100 pbw of PLA, and (3) a foaming agent in an amount of 1–30 wt% based on the weight of the PLA particles. The expandable resin particles can give expanded beads having an average cell diameter of 10–500 μm. For reasons of low costs and environmental concerns, the use of inorganic physical foaming agent, especially air, nitrogen, or carbon dioxide, is preferred. Above all, the use of carbon dioxide as the foaming agent is particularly preferred, because expanded beads having a small apparent density may be obtained even with a small amount of the foaming agent. The above foaming agents may be used singly or in combination of two or more thereof (e.g., in combination of carbon dioxide with isobutane).

JP2006282750 A (2006, JSP CORP) discloses expandable PLA particles comprising the following: (1) PLA; and (2) a fusibility improving agent selected from glycerol derivative, ether ester derivative, glycolic acid derivative, citric acid derivative, adipic acid derivative, rosin derivative, and/or tetrahydro furfuryl alcohol derivative; and the same foaming agent as in previous patent(s).

WO2008093284 A1 (2008, BIOPOLYMER NETWORK LTD) discloses a method of producing expandable PLA beads by impregnating PLA beads with carbon dioxide and holding the impregnated beads at a temperature and pressure that prevents the beads from expanding while allowing the level of impregnated carbon dioxide to reduce to 5–18 wt% with respect to total weight of the bead and carbon dioxide. The beads are pre-expanded at a pre-expansion temperature, to form a composition of expanded PLA beads.

US2012007267 A1 (2012) and **US2012009420** A1 (2012) of LIFOAM IND disclose expandable PLA beads prepared by a method outlined in Figure 9.1 and comprising the following steps: (1) melt processing PLA in an extruder; (2) injecting a foaming agent into the melt; and (3) extruding the mixture into expandable beads. The foaming agent is carbon dioxide in its super critical state. The expandable beads have a substantially closed cell structure after pelletization of the extrudate at the face of an extrusion die. The expandable beads have an average diameter of <10 mm (preferably <3 mm) and a spherical or nearly spherical shape. The beads are capable of holding an internal pressure

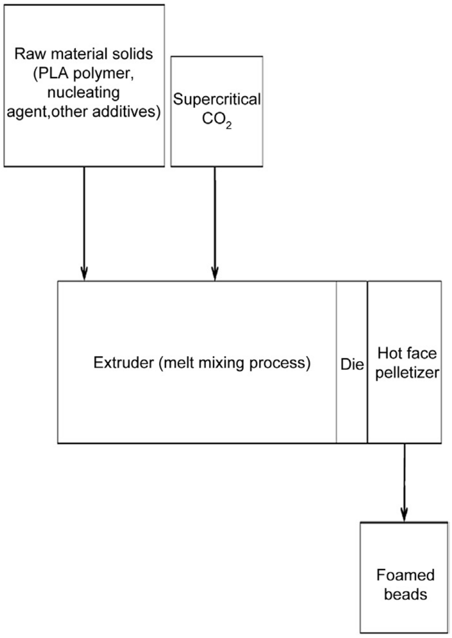


FIGURE 9.1 Drawing of a general process for production of expanded beads by extrusion foaming process (2012, **US2012007267** A1; 2012, **US2012009420** A1, LIFOAM IND).

of gas in excess of ambient conditions within the closed cell structure of the foam.

JP2001098104 A (2001, KANEBO LTD; RES INST INNOVATIVE TECH EARTH; KANEBO SYNTHETIC FIBERS LTD) discloses expanded PLA beads obtained by: (1) mixing 1–20 wt% talc as a foam-nucleating agent in an amorphous PLA; (2) impregnating the composition with a low boiling point organic foaming agent (e.g., isobutene and dimethyl ether) to form an expanded bead particle; and (3) compounding 0.01–1 wt% one or more higher fatty acids or metal salts, esters, or amides thereof onto the surface of the expandable particles.

JP2005068306 A (2005, KANEBO LTD; KANEBO SYNTHETIC FIBERS LTD) discloses expandable PLA beads obtained by adding a polyoxyethylene derivative during impregnation of foaming agent. The polyoxyethylene derivative is polyoxyethylene fatty acid ester, polyoxyethylene alkyl ether, or polyoxyethylene sorbitan fatty acid ester. The foaming agent is isobutane, butane, isopentane, and/or pentane.

WO2006103970 A1 (2006, KANEKA CORP) discloses a method of producing expanded PHA particles comprising the step of feeding particles of a PHA copolymer, such as P3HBHHx, and a foaming agent into an airtight container, and the step of heating the mixture until the resin particles become soft, then releasing one end of the airtight container and discharging the resin particles into an atmosphere with a pressure lower than the pressure in the airtight container to thereby expand the PHA particles. The foaming agent is dimethyl ether, diethyl ether, and/or methyl ethyl ether. The molar ratio of poly(3-hydroxy butyrate) (P3HB) to poly(3-hydroxy hexanoate) in the copolymer is 99/1–80/20.

WO2011141573 A1 (2011, NOVAMONT SPA) discloses starch pellets expandable by irradiation, which are particularly suitable for the manufacture of foam articles; said pellets have a porous internal structure with a low porous external skin. The starch pellets are prepared as follows:

1. Feeding a composition comprising starch and water to an extruder;
2. Extruding said composition to form a melt and at an extrusion rate, residence time, and shear rate at the outlet suitable to destroy the native crystallinity of the starch and to produce a swelling followed by collapsing of the extrudate on leaving the nozzle;
3. Cutting the collapsed extrudate into the form of pellets soon after the exit from the die to seal possible open pores and reconstitute a skin at the cut surface;
4. Conditioning the pellets to adjust the moisture content at level between 10 and 45 wt%, with respect to the total dry weight of a pellet by exposure to air at room temperature or higher.

9.5.1 Sintering Expandable Particles

Expandable PLA particles have the drawback that insufficient fusion between the individual particles of the PLA occurs during the formation of foamed molded products based on said expandable PLA. To obtain a good fusion, a high pressure and a high temperature are required. However, because PLA has a limited thermal stability, it is not possible to use such a high temperature and pressure without this resulting in degradation of PLA or collapse of the foam. Consequently, this leads to foamed molded products not having the required mechanical properties, which is undesirable in those cases in which the foamed molded product is used for constructional purposes (2008, **WO2008130226** A2, SYNBRA TECH B.V.).

DE4239781 A1 (1994, BASF AG) discloses a method for producing foamed PLA moldings obtained by fusing foamed amorphous PLA granules with finely divided, unfoamed, semicrystalline PLA particles. The unfoamed PLA particles are devoid of any foaming agent. The foamed amorphous PLA granules are formed by impregnating the PLA granules with foaming agent, preferably a mixture of methyl formate and pentane.

JP2002020525 A (2002, ASAHI CHEMICAL CORP) discloses expanded PLA beads useful for producing in-mold foam moldings. Melt kneading of PLA was performed using a twin-screw extruder. The mixture was extruded in the shape of a strand, followed by water cooling. The strand was disconnected to a diameter of 0.7 mm and length of 1.3 mm; 100 pbw of the obtained PLA particles and 300 pbw of water were mixed, and heated to 80 °C. Carbon dioxide was introduced, to obtain expandable beads. The beads were introduced into a foam apparatus and heated to 80 °C, to obtain a primary expandable bead. Dry aging of the primary expandable particles was performed for 24 h at 60 °C. The expandable beads filled a mold and were heated with water steam to give an in-mold foam molding. With the expanded beads, however, steam having a temperature of 141–161 °C must be used to produce a molding in a mold because of a high degree of crystallization of PLA. Therefore, it is necessary to use a specific molding apparatus that can withstand the high pressure steam. Furthermore, much steam should be consumed. In addition, part of PLA, which has not yet been crystallized, is susceptible to thermal decomposition during the molding step, and thereby can cause shrinkage and surface undulations of the resulting foam molding (2006, **US2006167122**, JSP CORP).

JP2001131433 A (2001, MIYOSHI YUSHI KK) discloses that an aqueous dispersion of an expandable biodegradable polymer is obtained by dispersing particles of a biodegradable polymer containing a chemical foaming agent in water in the presence of a dispersion stabilizer in the form of fine particles. The fine particles of an expandable biodegradable polymer are obtained by filtering the aqueous dispersion of the expandable biodegradable polymer containing the chemical foaming agent and drying it.

WO0214043 A1 (2002, BLUE MARBLE POLYMERS LTD) discloses a method of producing a biodegradable bio-based foamed product, as outlined in Figure 9.2, comprising the following steps: (i) mixing a bio-based biodegradable polymer with additive(s); (ii) extruding resulting mixture in presence of water (acting as foaming agent); (3) transferring extrudate (in the form of pellets or long rods) to mold; and (iv) heating extrudate using dielectric heating in a microwave equipment that consists of (a) preheating extrudate below flash point of foaming agent for uniform temperature distribution and then (b) rapid heating of extrudate above flash point of the foaming agent. The biodegradable bio-based polymer is selected from proteins, starches, including cereal, root, and tuber starches, modified starches, food residues, biodegradable polymers, and their mixtures. The microwave treatment of the extrudate is performed in microwave transparent mold containers by an irradiating microwave frequency of 915 MHz to 25 GHz, preferably 2.40–2.50 GHz.

JPH05271458 A (1993, TOPPAN PRINTING CO LTD) discloses biodegradable pulp foamed beads comprising regenerated pulp, a biodegradable thickener (e.g., sodium alginate or poly[vinyl alcohol] (PVOH)), and a foaming agent (e.g., azodicarbonamide or sodium bicarbonate).

Example: Cotton-like pulp (100 pbw), 10 wt% PVOH aqueous solution (800 pbw), and $NaHCO_3$ (20 pbw) were kneaded and formed into beads with a particle diameter of 7–8 mm, heated, and foamed at 180 °C to give pulp-foamed beads with an apparent density of 0.1 g/cm^3.

9.6 COMPOSITE FOAMS

EP1484357 A1 (2004, UNIV LIEGE) discloses a biodegradable composite foam obtained by mixing a molten biodegradable polyester with an organomodified clay nanofiller, and a silicone surfactant and foaming the mixture in the presence of a foaming agent. A preferred clay is montmorillonite (Claytone HY). The silicone surfactant reduces the surface tension of the polyester and the nanofiller stabilizes the foamed structure. A preferred polyester is PCL, PLA, PBS, and PHBHV.

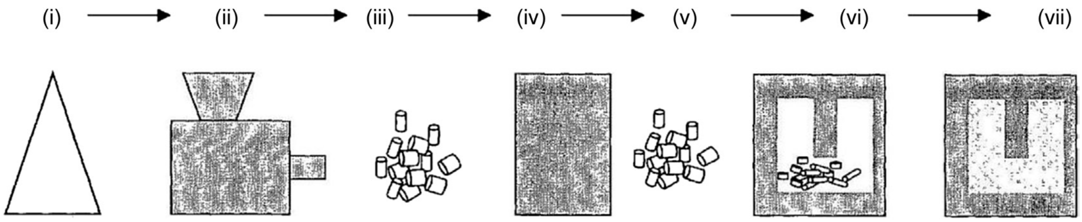


FIGURE 9.2 Flow chart for biodegradable foamed product manufacture (2002, **WO0214043** A1, BLUE MARBLE POLYMERS LTD).

The blend (i) is extruded in an extruder (ii) of known type at a moisture content of 15–30 wt% to achieve an extrudate (iii). The extrudate (iii) is cut into pellets or long rods or rolled into final mold ready shapes. The extrudate is conditioned (iv) to a moisture content in the range of 12–16 wt% at a temperature of 15–40 °C. This occurs in 25–80% relative humidity in a controlled climate container (iv) to minimize case hardening of the extrudate (iii). This gives a shelf stable and easily transported product, which can be stored for later use (v). The conditioned extrudate (v) is loaded into a microwave-transparent mold in the shape required (vi). For this example, 70 g of extrudate (v) is loaded into an 18 cm × 8 cm × 4 cm container (vi). The mold is placed into a microwave field (vi) using 2.45 GHz frequency microwave energy with a variable power output of 10 W–5 kW, for the example set to a 2 kW source to produce a uniform, resilient, molded foam block (vii).

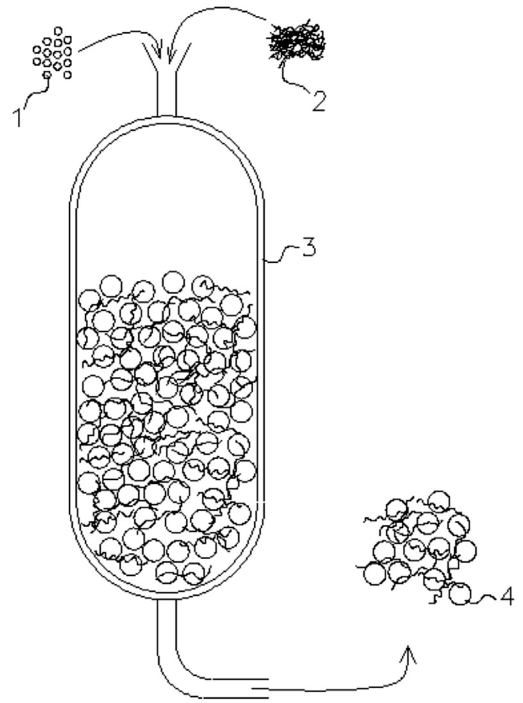


FIGURE 9.3 Explanatory drawing of the state of supplying biodegradable polymer beads and biodegradable staples into the primary foaming tank, in the manufacturing method of a biodegradable composite foam (2005, JP2005002289 A, OFAA SEKKEI JIMUSHO KK).
1, biodegradable foam bead; 2, biodegradable staple; 3, primary foaming tank; 4, biodegradable foam bead after primary foaming.

JP2005002289 A (2005, OFAA SEKKEI JIMUSHO KK) discloses a biodegradable polymer composite obtained by mixing biodegradable polymer expandable beads and biodegradable fibers, as shown in Figure 9.3, molding mixture in metallic mold, increasing fracture strength of foam by bonding foam and fiber in molded product, and producing gaps in foam by performing corrosion decomposition of fiber. The gaps increase surface area, and surface area in turn increases decomposition rate of foam. The expandable beads are preferably made of PLA and the biodegradable fibers are cellulose. The biodegradable composite foam is claimed to have high resistance to rupture and partial breakage of the molded foam, because the foam is produced by mixing biodegradable fiber materials having different levels of biodegradation rate, when the biodegradable foam is produced. The biodegradable composite foam is used as shock absorbing material and packing material of marine products.

WO2011145461 A1 (2011, SHOWA DENKO KK) discloses a foamable polymer composition comprising the following: (1) modified starch or mixture of modified starch and non-processed starch; (2) a biodegradable polymer and/or a polyolefin (≤10 pbw); (3) water (10–30 pbw); (4) inorganic filler (0.01–5 pbw); and (5) plasticizer (0.01–5 pbw). Further disclosed is a foam that is formed by foaming the foamable polymer composition.

US2012053256 A1 (2012, CHEN JONG-WU; HSIAO HSIANG-JEN; LI Chapter IA-HUNG; CHEN CHIN-FU) discloses a biodegradable composite foam comprising the following: (1) a polyester blend containing a biodegradable polyester (40–50 wt%) and a fossil fuel–based polymer (50–60 wt%); (2) a reinforcing agent (15–20 pbw); (3) foaming agent (0.1–5 pbw); (4) compatibilizer (1–3 pbw); (5) lubricant (1–3 pbw); (6) impact modifier (1–3 pbw); and (7) optionally a polyolefin elastomer-graft maleic anhydride (1–10 pbw). The reinforcing agent is selected from talc powder, clay, mica, calcium carbonate, silicon dioxide, plant fiber, artificial fiber, wood flour, and sawdust. The compatibilizer is fluoropolymer grafted with acrylic acid. The lubricant is at least one of stearic acid and its derivative (preferably calcium stearate, zinc stearate, magnesium stearate, or stearamide). Preferably, the foaming agent is core–shell Expancel® (AkzoNobel) or core–shell Expancel® masterbatch. Expancel® is an expanding microsphere consisting of a thermoplastic polymer shell, such as poly(vinylidene chloride-*co*-acrylonitrile), PVOH, poly(vinyl butyral), poly(methyl methacrylate), polyacrylonitrile, poly(vinylidene chloride), and polystyrene, encapsulating a hydrocarbon gas, such as isobutane, propane, and pentane. When the gas inside the shell is heated, it increases in pressure and the thermoplastic polymer shell softens, resulting in a dramatic increase in the volume of the microsphere.

Example: A biodegradable composite composition was prepared comprising a polyester blend containing PLA (50 wt%) and polycarbonate (50 wt%); talc powder (15 pbw); polyolefin Expancel (3 pbw); fluoropolymer grafted with acrylic acid (5 pbw); stearic acid (3 pbw); and methacrylate-butadiene-styrene (3 pbw).

9.7 CROSSLINKING

Biodegradable foams made of aliphatic polyesters have several inherent deficiencies, such as low dimensional stability and low melt strength, which have retarded their expansion in several applications areas. In general, it is considered difficult to form high-molecular-weight aliphatic polyesters because of undesirable adverse reactions, such as hydrolysis caused by water generated during polycondensation. As a result, the melt viscosity during extrusion foaming is not sufficient to maintain optimal or even adequate cell structure. As such, foams having good cell structure and surface appearance cannot be obtained (2003, **WO03046060** A1, TORAY INDUSTRIES).

Several approaches have been developed to address the problems of low-dimensional stability of foams made of aliphatic polyesters. One approach includes the use of a crosslinking agent, such as peroxide, in the foam. For example, crosslinking the foam matrix can increase the melt strength of the polymer and minimize cell wall collapse. However, the addition of crosslinking in the foam reduces the ability of the foam to decompose. Furthermore, inducing crosslinking in the foam generally requires an additional step that can add to the complexity and cost of producing the foam.

JPH06248104 A (1994, SHOWA HIGHPOLYMER; SHOWA DENKO KK) discloses a method of crosslinking a foam made of a PAA using an ionized radiation. A PAA having a melt viscosity of 1.0×10^2–1.0×10^5 Pa s (1.0×10^3–1.01×10^6 P) at 190 °C under a shear rate of 100/s, and a T_m of 70–190 °C is thermally foamed using a foaming agent. However, the method has some drawbacks and deficiencies in that radiation cannot reach the inner portion of the foam to be radiated because it is over 1 mm thick and the cells in the inner portion of the subject on foaming are coarse and uneven. Also, crosslinking by radiation should be performed under a nitrogen atmosphere to prevent deterioration of PAA. Thus, it is considered to be difficult to prepare foams having various thickness and sufficient mechanical properties through the implementation of this method (2003, **WO03046060** A1, TORAY INDUSTRIES).

WO9854244 A1 (1998, JSP CORP) discloses a method for crosslinking expandable particles of an aliphatic polyester essentially comprising the following steps: (1) dispersing the particles into a dispersing medium, such as water, ethylene glycol, and methanol; and (2) heating the dispersion after adding an organic peroxide and, if necessary, a crosslinking promoter (see also section 9.5). However, expandable particles prepared by this method may be hydrolyzed, which may result in undesirable and nonoptimal foam particles. Furthermore, when these particles are subjected to a secondary process of forming them into a desired shape, a problem typically arises in that such particles may break out at their laminated sides. Thus, formulation of a complicated and/or sophisticated shape is rarely possible when using this method (2003, **WO03046060** A1, TORAY INDUSTRIES).

JPH11279311 A (1999, JAPAN ATOMIC ENERGY RES INST; DAICEL CHEM) discloses foams comprising PCL or a composition thereof with another biodegradable polymer that have been treated with ionizing radiation at a time (e.g., before, during, or after the molding). Because degradation of PCL also takes place simultaneously with crosslinking when it is subjected to treatment by radiation, the melt viscosity during foaming is not sufficient to maintain adequate cell structure. Thus, it is difficult to obtain foams with good surface appearance. In other words, irradiation at approximately room temperature typically requires the exposure of as high as 200 kGy. To address this problem, it is described that after melting PCL, irradiation is preferably performed in its melt phase before crystallization. Thus, at low exposure, foams having high crosslinking degree cannot be readily prepared (2003, **WO03046060** A1, TORAY INDUSTRIES).

JP2000053792 A (2000, SANWA KAKO CO) discloses a method for the preparation of a biodegradable foam generally comprising the following steps: (1) mixing starch (e.g., corn starch) (A), polyethylene (e.g., high-pressure, low-density polyethylene) (B), a chemical foaming agent (e.g., azodicarbonamide) (C), and a crosslinking agent (e.g., dicumyl peroxide) (D); (2) filling the mixture in a closed-type mold; (3) heating the mixture heated under pressure, preferably at 140–160 °C for 10–50 min to effect decomposition of the foaming agent and the crosslinking agent; and (4) depressurizing the mold. The weight ratio A/B is preferable (30–85)/(10–25). The produced biodegradable polymer foam is claimed to have fine cells, even if highly expanded, and sufficiently high durability and mechanical strength. However, because the decomposition temperature of an organic peroxide is similar to that of a foaming agent, the cell size of the obtained foams is uneven (2003, **WO03046060** A1, TORAY INDUSTRIES).

WO03046060 A1 (2003, TORAY INDUSTRIES) discloses a method for producing a crosslinked biodegradable polymer continuous foam sheet comprising the following steps: (1) preparing a sheet from a biodegradable polymer composition comprising a biodegradable polymer, a chemical foaming agent, and a crosslinking promoter; (2) irradiating the sheet with an ionizing radiation (e.g., electron beam) to crosslink the biodegradable polymer composition; and (3) subjecting the crosslinked sheet to heat treatment to continuously prepare a crosslinked foam sheet having an expansion rate of approximately 1.5 to approximately 50 and a gel fraction of at least approximately 3%.

US2002059001 A1 (2002, CRYOLIFE, INC) discloses a method of making a bio-based polymer foam by introducing an inorganic foaming agent (e.g., ammonium bicarbonate) into a proteinaceous crosslinkable prepolymer liquid material, and allowing the liquid material to crosslink simultaneously with evolution of gas from said foaming agent to thereby form a bio-based polymer having a cellular foam structure.

WO2009038783 A1 (2009, SURMODICS INC) discloses a system for forming a biocompatible biodegradable foam comprising the following: a covalently crosslinkable polymer comprising poly-α (1→4)glucopyranose and pendant polymerizable groups; a polymerization initiator (e.g., peroxide-based initiator); and a gas-producing component. The biocompatible polymer foams can be used in association with a target tissue for its treatment.

9.8 AFTER TREATMENT OF FOAMS

9.8.1 Heat Treatment

Common traditional methods of preparing thermoformed PLA foamed articles require a two-step molding process in which a heated PLA foam sheet is first subjected to a hot mold step, followed by a cold mold step. In the hot mold step, the heated PLA foam sheet is introduced into a hot mold that is heated to at least 100 °C. While being in the hot mold, the foam sheet is molded to a desired shape and configuration. In addition to shaping the article, the hot mold step also induces crystallization into the PLA foam. In a second step, the thus molded foam is transferred to a cold mold that "freezes" the foam into the desired shape. The temperature of the cold mold is typically less than 30 °C. Generally, to improve the dimensional stability of the thermoformed article, the PLA foam is exposed to the hot mold for a period to induce a sufficient amount of crystallization in the PLA foam so as to improve heat resistance of the molded article. For example, in some cases, it may be necessary to expose the PLA foam to the hot mold for at least 15 s. As a result, longer production times are generally needed to prepare heat-resistant PLA foamed articles (2012, **WO2012121296** A1 CRYOVAC INC).

In particular, **WO2012121960** A1 (2012, CRYOVAC INC) discloses a method of preparing a thermoformed article composed of PLA comprising the following steps: (1) providing a foam sheet comprising PLA having a D-lactic acid stereoisomer content of about 3 mol% or less; (2) exposing the sheet to a temperature of at least 190 °C; and (3) forming the heated sheet in a mold at a mold temperature of at least 50 °C, and for a length of time of less than 10 s to form a thermoformed article having a PLA crystalline content of at least approximately 10%. An example of a suitable PLA is Ingeo™ 4032D grade (NatureWorks LLC), which has a D-lactic acid stereo-isomer content of approximately 2 mol%. PLA foam can be prepared by melt processing the PLA with a nucleating agent, foaming agent, and chain extender agent (when present) in an extruder to form a pressurized molten mixture. In the extrusion process, the PLA may be heated to a temperature at or above its T_g or T_m. Suitable temperatures are at least 160 °C, and preferably at least 170 °C. The foaming agent may be introduced under pressure and mixed into the heated PLA. The foaming agent comprises isobutane. The foaming agent may comprise 70–90 wt% of a relatively heavier weight hydrocarbon foaming agent (e.g., n-pentane) and 10–30 wt% (e.g., isobutane) of a relatively lighter weight hydrocarbon foaming agent, based on the total weight of hydrocarbon foaming agent. Pressures during the mixing step may be maintained high enough so that foam expansion does not begin until the molten mixture passes through the extrusion die.

9.8.2 Coating

JPH10330527 A (1998, TOYO PURASUTO KK) discloses a method of making a biodegradable polymer cushioning material comprising the following steps: (1) a starch-containing biodegradable composition is pre-expanded in a specific shape; (2) PCL is dissolved in a solvent, and the solution is sprayed over the surface of the biodegradable polymer foam. Next, this foam is packed into a mold and heated with hot air to melt the surface heat-bondable PCL. The entire material is compressed to bond to each other to produce a biodegradable polymer cushioning material having a specific shape. If required, the surface of the obtained material is sprayed with another biodegradable resin, is adhesively coated with a biodegradable polymer film, or is adhesively coated with a biodegradable polymer film. The cushioning material is used for packing electric machinery products, pottery, and fruits.

WO2008130226 A2 (2008, SYNBRA TECH B.V.) discloses a complicated multistage method for producing expandable PLA beads provided with a coating in an amount of 0.5–15 wt%, preferably between 2–10 wt% based on the weight of PLA. The coating is selected from polyvinyl acetate, polyvinyl acetate-based polymer, casein, ethyl cellulose, PCL, amorphous PLA and one or more combinations thereof. The PLA beads are coated and then postimpregnated with a foaming agent, such as carbon dioxide, or the beads are postimpregnated with carbon dioxide and then coated. The coating improves the fusion properties of the PLA beads. The postimpregnation with carbon dioxide leads to preexpanded beads, and this completely changes the technology for further processing of the moldable foams (2011, **WO2011086030** A2, BASF SE).

9.8.3 Elimination of a Liquid or Solid Phase from a Biopolymer Composition or Article (e.g., Leaching Out)

This technique is mainly used for the production of sponges, especially for medical applications. A sponge of starch has been known for more than a century. The sponge is produced by cooling a starch paste, which has first been boiled, to temperatures lower than the freezing point, which results in retrogradation (i.e., a reversal of the starch to a cold water–insoluble state, after which the frozen mass is defrosted and the water is removed from the spongy mass). Such spongy starch materials could be used in the medical field (e.g., as resorbable aids for absorbing secretions). This preparation, however, is cumbersome and leads to products that are relatively unstable and have hardly been used (1983, **WO8302955** A1, BIJENKORF ZETMEEL).

JPH01104635 A (1989, TAKI CHEMICAL) discloses a biodegradable porous material obtained as follows: (1) dissolving a PLGA in an organic solvent (e.g., 1,4-dioxane); (2) adding a specific filling substance substantially inert to organic solvent and soluble in water; (3) solidifying the solution; (4) removing the organic solvent; and (5) adding water and removing the filling substance. Sucrose is preferably used as the filling substance.

Example: 1 g of PGLA (L-lactic acid is 49 mol%, molecular weight = 15,000) was dissolved in 49 g of 1,4-dioxane. The polymer solution was added to 117 g of granular sugar (size, approximately 0.5 mm) laid in pan (20×20 cm), homogenized, and then frozen at 0 °C. The solidified mass was dried under 1 mmHg and then immersed in water at 27 °C for extracting sugar. Porous material was obtained by air drying.

EP0223708 A2 (1987, RES TRIANGLE INST) discloses a method of forming a porous bioabsorbable polyester medical device by shaping a blend of PCL with a polyether, followed by selectively eluting the polyether component with an aqueous solution of an organic solvent (e.g., methanol, ethanol, or acetone) to form interconnected pores within the shaped PCL. Suitable pore forming additives are low-molecular-weight aliphatic polyethers, which are commercially available (e.g., Pluronic F-68, BASF). The shaped article is suitable for use as a reservoir for the controlled release of high-molecular-weight drugs.

DE19504899 A1 (1996, NAT INST RES INORGANIC MAT) discloses a microporous polysaccharide or polysaccharide/clay composite obtained by mixing an aqueous solution of a polysaccharide or its derivative, such as starch with a clay sol, quickly freezing the mixture, and vacuum drying the frozen product. This quick freezing is performed at an average rate of freezing of at least 1×10^{-2} ml/s. It is also possible to add a natural fiber, a colorant, a perfume, or the like to the composite foam. The polysaccharide or its derivative is selected from among starch, sodium alginate, and carboxymethylcellulose. As the clay, a natural clay, such as montmorillonite, saponite, beidellite, kaolinite, allophane, or bentonite, or a synthetic clay prepared by chemically modifying or changing such a natural clay, may be used. The polysaccharide/clay composite can be used as a shock-absorbing, heat insulator, or sound-absorbing material. The presence of clay provides high compression strength when compared with other commercially available foamed polymers.

PATENTS

Patent Number	Publication Date	Family Members	Priority Numbers	Inventors	Applicants	Title
DE19504899 A1	19960328	US6228501 B1 20010508; DE19504899 B4 20060420; JPH0892417 A 19960409; JP2636186 B2 19970730	JP19940256186 19940926	NAKAZAWA HIROMOTO; OHTA SHUN-ICHI	NAT INST RES INORGANIC MAT	Poröser Körper aus polysaccharid oder Polysaccharid-Ton-Komposit und Verfahren für dessen Herstellung. "Porous products of polysaccharide or polysaccharide-clay composite."
DE19938008 A1	20010215	WO0112706 A1 20010222; US6573308 B1 20030603; ES2203500 T3 20040416; EP1204700 A1 20020515; EP1204700 B1 20030723; AU6439800 A 20010313; AT245671 T 20030815	DE1999138008 19990811	BRAUN FRANK; GLUECK GUISCARD	BASF AG	Biologisch abbaubare Schaumstoffpartikel. "Biologically degradable foamed material particles."
DE4239781 A1	19940601	US5348983 A 19940920; US5378792 A 19950103; NO934265 A 19940527; JPH06293841 A 19941021; FI935282 A 19940527; EP0601390 A1 19940615	DE19924239781 19921126	STERZEL HANS-JOSEF	BASF AG	Formkörper aus geschäumten Polylactiden und Verfahren zu ihrer Herstellung. "Foamed polylactide moldings and production thereof."
EP0223708 A2	19870527	US4702917 A 19871027; NO864507 A 19870519; EP0223708 A3 19880113; EP0223708 B1 19910807; JPS62164743 A 19870721; DK549486 A 19870519; CA1283051 C 19910416; AU6515986 A 19870521; AU599612 B2 19900726	US19850798883 19851118	SCHINDLER ANTON	RES TRIANGLE INST	Porous bioabsorbable polyesters.
EP0592911 A1	19940420	US5422053 A 19950606; DE4234620 A1 19940421; JPH06190853 A 19940712; CA2107018 A1 19940415	DE19924234620 19921014	STERZEL HANS-JOSEF	BASF AG	Verfahren zur Herstellung von geschäumten Polylactid-Spritzgiessteilen hoher Festigkeit und Steifigkeit. "Method for manufacturing injection moulded foamed polylactide objects of high strength and stiffness."

Continued

—Cont'd

Patent Number	Publication Date	Family Members	Priority Numbers	Inventors	Applicants	Title
EP0812877 A2	19971217	DE19623464 A1 19971218; EP0812877 A3 19980422; EP0812877 B1 20020508; AT217331 T 20020515	DE1996123464 19960612		MAFO SYSTEMTECH GMBH & CO KG	Verfahren und Vorrichtung zur Herstellung geschäumter Formteile auf der Basis von Stärke und Verwendung der Formteile. "Process and apparatus for making foamed forms based on starch, and use of the forms."
EP1264850 A1	20021211	US2003083394 A1 20030501; US2003166735 A1 20030904; RU2002114915 A 20031220; NZ519353 A 20031128 JP2003026757 A 20030129; HU0201931 A2 20030328; ES2294064 T3 20080401; EP1264850 B1 20070919; DK1264850 T3 20071210; DE60222496 T2 20080619; CN1390869 A 20030115; CA2388585 A1 20021207; CA2388585 C 20100803; BR0202107 A 20030422; AU4583302 A 20021212; AT373684 T 20071015	US20010876778 20010607	CLATTY JAN L	CLATTY JAN L	Polyurethane foams having improved heat sag and a process for their production.
EP1378538 A1	20040107	JP2009084581 A 20090423; JP5004247 B2 20120822; CN1495223 A 20040512; CN100344680 C 20071024, CN1931902 A 20070321; CN100523064 C 20090805	JP20020192434 20020701	SHINOHARA MITSURU; TOKIWA TOMOO; SASAKI HIDEHIRO	JSP CORP	Expanded polylactic acid resin beads and foamed molding obtained therefrom.
EP1484357 A1	20041208	WO2004108806 A1 20041216; WO2004108805 A1 20041216; US2006140842 A1 20060629; EP1636299 A1 20060322; EP1636299 B1 20110921; EP1636298 A1 20060322; AT525423 T 20111015	EP20030076761 20030606	STASSIN FABRICE	UNIV LIEGE	Process to prepare biodegradable polyester foams, polyester foams obtained thereby, their use, and process to modify nanofillers.
EP1624024 A1	20060208	EP1624024 A4 20060621; EP1624024 B1 20070704	WO2003JP05914 20030512	UEDA KAZUE; MATSUOKA FUMIO; OGAMI AKINOBU; MATSUMOTO TATSUYA; YANO TAKUMA; YOSHIMURA KAZUKO; YAMADA KAZUNOBU; OKAMOTO MASAM	UNITIKA LTD	Biodegradable polyester resin composition, process for producing the same and foamed article and molded article using the same.

JP2000007815 A	20000111		JP19980173554 19980619	YOSHIDA IKUNORI; OBUCHI SEIJI; KITAHARA YASUHIRO; WATANABE TAKAYUKI; AIHARA HISASHI; NAKADA TOMOYUKI	MITSUI CHEMICALS INC	Composition for producing foam, production of foam and foam.
JP2000007816 A	20000111		JP19980173556 19980619	YOSHIDA IKUNORI; OBUCHI SEIJI; KITAHARA YASUHIRO; WATANABE TAKAYUKI; AIHARA HISASHI; NAKADA TOMOYUKI	MITSUI CHEMICALS INC	Composition for producing foam, production of foam and foam.
JP2000017038 A	20000118	JP3802680 B2 20060726	JP19980183906 19980630	KUBO TAKAYOSHI; YAMA SHINKO; NAITO HIROSHI; NAKAE TSUNAHIRO	KANEBO LTD; RES INST INNOVATIVE TECH EARTH; KANEBO SYNTHETIC FIBERS LTD	Expandable resin composition having biodegadability.
JP2000053792 A	20000222		JP19980254511 19980805	SAWARA MASAAKI; NAKAMURA SHINYA; OBARA CHOJI	SANWA KAKO CO	Biodegradable resin foam and its production.
JP2000136261 A	20000516		JP19980243799 19980828; JP19990241144 19990827	OBUCHI SEIJI; AIHARA HISASHI; WATANABE TAKAYUKI; KITAHARA YASUHIRO; YOSHIDA IKUNORI; NAKADA TOMOYUKI	MITSUI CHEMICALS INC	Foaming particle and production of the same.
JP2001098104 A	20010410		JP19990277790 19990930	kUBO TAKAYOSHI; YOSHIMOTO SEI; YAMA SHINKO; NAKAE TSUNAHIRO	KANEBO LTD; RES INST INNOVATIVE TECH EARTH; KANEBO SYNTHETIC FIBERS LTD	Expanded particle having biodegradability and mold thereof.
JP2001131433 A	20010515	JP4697821 B2 20110608	JP19990318279 19991109	KAMATA YUKIRO; HOSODA KAZUO; YOKOMIZO OSAMU; KAMIO KATSUHISA	MIYOSHI YUSHI KK	Aqueous dispersion of expandable biodegradable resin, its manufacturing method and fine particle of expandable biodegradable resin.
JP2002020525 A	20020123	JP4582871 B2 20101117	JP20000206745 20000707	SUKIGARA MASAYUKI	ASAHI KASEI CORP	Noncrosslinked expandable resin beads.

Continued

—Cont'd

Patent Number	Publication Date	Family Members	Priority Numbers	Inventors	Applicants	Title
JP2002302567 A	20021018		JP20010106876 20010405	NAKAYAMA NAOKI	ACHILLES CORP	Method for continuous production of pre-expanded bead of biodegradable polyester-based resin.
JP2002317066 A	20021031		JP20010122137 20010420	FUTAMURA NAOYUKI; DOI TSUNEO	SEKISUI PLASTICS	Polylactic acid-based resin foam and method for producing the same.
JP2003020355 A	20030124		JP20010207152 20010709	FUTAMURA NAOYUKI; DOI TSUNEO	SEKISUI PLASTICS	Poly(lactic acid)-based resin foam and preparation process thereof.
JP2003039524 A	20030213	JP3732125 B2 20060105	JP20010231255 20010731	HIRAI TAKAAKI; TARUMOTO HIROYUKI; ANAMI SHINICHI	SEKISUI PLASTICS	Foamed aliphatic-aromatic copolyester resin and its production method.
JP2003073495 A	20030312	JP4748698 B2 20110817	JP20010262255 20010830	SHINOHARA MITSURU; TOKIWA TOMOO; SAKAGUCHI MASAKAZU; TOKORO TOSHIO	JSP CORP	Method for producing expandable particle of polylactic acid.
JP2003103595 A	20030409	JP3732135 B2 20060105	JP20010300122 20010928	HIRAI TAKAAKI; TARUMOTO HIROYUKI; ANAMI SHINICHI	SEKISUI PLASTICS	Aliphatic/aromatic copolyester resin foam and manufacturing method thereof.
JP2003261704 A	20030919	JP3892745 B2 20070314	JP20020064668 20020311	HIRAI TAKAAKI; TARUMOTO HIROYUKI; ANAMI SHINICHI	SEKISUI PLASTICS	
JP2003301066 A	20031021	JP4299490 B2 20090722	JP20020108950 20020411	HIRAI TAKAAKI; TARUMOTO HIROYUKI; ANAMI SHINICHI	SEKISUI PLASTICS	Lightweight structural material and thermal insulation with good degradability when scrapped and manufacturing method thereof.
JP2003327737 A	20031119	JP3808400 B2 20060809	JP20020133678 20020509	HIROSE FUMINOBU; MIYAGAWA TOSHIO; SENDA KENICHI	KANEGAFUCHI CHEMICAL IND	Biodegradable polyhydroxy alkanoate extruded foam and its production method.
JP2004058352 A	20040226	JP3810354 B2 20060816	JP20020217673 20020726	HIRAI TAKAAKI; ANAMI SHINICHI; TARUMOTOHIROYUKI	SEKISUI PLASTICS	Method for manufacturing aliphatic-aromatic copolyester resin foam, and foamed sheet.
JP2004083890 A	20040318	JP2004083890 A 20040318	JP20030185453 20030627; JP20020192434 20020701	SHINOHARA MITSURU; TOKIWA TOMOO; SASAKI HIDEHIRO	JSP CORP	Polylactic acid foamed particle and molded product of the polylactic acid foamed particle.
JP2004307662 A	20041104	JP4011512 B2 20071121	JP20030103757 20030408	HIRAI TAKAAKI; TARUMOTO HIROYUKI; ANAMI SHINICHI	SEKISUI PLASTICS	Method for producing crystalline polylactic acid-based resin foam.
JP2005002289 A	20050106		JP20030169894 20030613	NISHIDA TOSHIO; SHIBUYA MASAHIRO; UEDA MASANORI; YAMAGISHI MASANAO	OFAA SEKKEI JIMUSHO KK	Biodegradable foam.
JP2005060689 A			JP20040221739 20040729; JP20030204417 20030731	KUMAZAWA SADANORI; OOME HIROKAZU	TORAY INDUSTRIES	Foam and its producing method.

JP2005068306 A	20050317		JP20030300863 20030826	KISHI ATSUSHI; FUKUNAGA SHINICHI	KANEBO LTD; KANEBO SYNTHETIC FIBERS LTD	Expandable polylactic acid-based resin composition and method for producing the same resin composition.
JP2006233192 A	20060907	JP4807834 B2 20111102	JP20050017050 20050125; JP20060008962 20060117	HARAGUCHI KENJI; OTA HAJIME	JSP CORP	Foamable polylactic acid resin particle, polylactic acid foamed particle, and polylactic acid foamed particle molded article.
JP2006282750 A	20061019	JP4664106 B2 20110406	JP20050101958 20050331	TOKIWA TOMOO; OTA HAJIME; SASAKI HIDEHIRO	JSP CORP	Polylactic acid-based resin foamed particle and polylactic acid-based resin in-mold foamed particle, and method for producing polylactic acid-based resin foamed particle.
JP2006282753 A	20061019	JP4697861 B2 20110608	JP20050102030 20050331	TOKIWA TOMOO; OTA HAJIME; SASAKI HIDEHIRO	JSP CORP	Polylactic acid-based resin foamed particle and polylactic acid-based resin in-mold foamed particle.
JP2007262319 A	20071011		JP20060091971 20060329	HIDA ETSU; KAWAMOTO HISAFUMI; SAKAI ATSUSHI	ADEKA CORP	Foamable polylactic acid-based resin composition and molded article using the same.
JP2009062502 A	20090326	JP5044337 B2 20121010	P20070234066 20070910	SHINOZAKI HIROKI; SASAKI HIDEHIRO	JSP CORP	Polylactic acid-based resin foam particle and foam particle molded product.
JP2009242728 A	20091022		JP20080093877 20080331	NAKAOKI TAKAHIKO; NAKASUGI HISAHIKO	UNIV RYUKOKU	Polylactic acid porous particle and method of manufacturing the same.
JP2012040787 A	20120301	CN102407633 A 20120411	JP20100184436 20100819	MASAHARU FUTAKAWA; ITSURU SASAHARA SASAK HIDEHIRO	JSP CORP	Composite laminated body.
JPH01104635 A	19890421	JPH0564982 B2 19930916	JP19870262310 19871016	OKADA TAKAO; FUKUZAKI HIRONOBU	TAKI CHEMICAL	Production of cellular substance.
JPH04304244 A	19921027		JP19910068232 19910401	AJIOKA MASANOBU; ENOMOTO TSUYOSHI; YAMAGUCHI TERUHIRO; SUZUKI KAZUHIKO	MITSUI TOATSU CHEMICALS	Degradable foam.
JPH05170965 A	19930709	JP3270087 B2 20020402	JP19910340788 19911224	SUZUKI KAZUHIKO; WATANABE TAKAYUKI; KITAHARA YASUHIRO; AJIOKA MASANOBU	MITSUI TOATSU CHEMICALS	Foamed granule of decomposable polymer.
JPH05170966 A	19930709	JP3270088 B2 20020402	JP19910340789 19911224	SUZUKI KAZUHIKO; WATANABE TAKAYUKI; KITAHARA YASUHIRO; AJIOKA MASANOBU	MITSUI TOATSU CHEMICALS	Foamed granule of decomposable polymer.

Continued

—Cont'd

Patent Number	Publication Date	Family Members	Priority Numbers	Inventors	Applicants	Title
JPH05271458 A	19931019	JP3240676 B2 20011217	JP19920068837 19920326	SAKAIRI K	TOPPAN PRINTING CO LTD	Pulp foaming beads.
JPH06248104 A	19940906	JP2655796 B2 19970924	JP19930090165 19930416; JP19920122201 19920514; JP19920122202 19920514; JP19920120786 19920513	KIMURA HIDEJI; IMAIZUMI MITSUHIRO; KAMEI RYOSUKE; TAKIYAMA EIICHIRO	SHOWA HIGHPOLYMER; SHOWA DENKO KK	Production of polyester foam.
JPH06271694 A	19940927	JP3344759 B2 20021118	JP19930085803 19930319	AKAMATSU YOSHIMI; TOMORI MASAHIKO	NIPPON SYNTHETIC CHEM IND	Biodegradable resin foam.
JPH08253617 A	19961001	JP3550782 B2 20040804	JP19950054189 19950314	EBATO HIROSHI; FUKUKITA TAKESHI	DAINIPPON INK & CHEMICALS	Foamable particle of lactic acid-based polyester.
JPH10152572 A	19980609		JP19970278187 19970925; JP19960274030 19960925	IWAMOTO AKIRA; MOMOSE YOSHIAKI; KINO TORU; ISHIKAWA KOICHI; HASHIZUME YUICHIRO	JSP CORP	Production of biodegradable aliphatic polyester-based resin foamed sheet and the same.
JPH10330527 A	19981215		JP19970177530 19970529	HAYASHIBARA HITOSHI; HAYASHIBARA KAZUNORI	TOYO PURASUTO KK	Heat-bondable biodegradable resin foam and biodegradable resin cushioning material.
JPH11279311 A	19991012		JP19980103390 19980331	YOSHII FUMIO; MAKUUCHI KEIZO; MITOMO HIROSHI; DALMAWAN DALWISS; MURAKAMI TEI	JAPAN ATOMIC ENERGY RES INST; DAICEL CHEM	Degradable-resin foam body.
US2002059001 A1	20020516	WO02085284 A2 20021031; WO02085284 A3 20040226; CA2425935 A1 20021031; EP1416946 A2 20040512; JP2004537136 A 20041209; US2005158364 A1 20050721; US2005163819 A1 20050728; AU2001297782 B2 20060302; US7226615 B2 20070605; EP1416946 A4 20091028; US8057818 B2 20111115; US8071124 B2 20111206; CA2425935 C 20110329	US20010986124 20011107; US20000246063P 20001107	YUKSEL K UMIT; BIRD ANA T; BLACK KIRBY S	CRYOLIFE, INC	Expandable foam-like biomaterials and methods.

US2002192456 A1	20021219	WO03078493 A2 20030925; WO03078493 A3 20040122; US2008132134 A1 20080605; US2009325444 A1 20091231; AU2003225805 A1 20030929; AU2003225805 A8 20030929	US20010275631P 20010315; US20020097439 20020315	MASHBURN LARRY E; HARRISON WILLIAM H; PATTERSON THOMAS E	MASHBURN LARRY E; HARRISON WILLIAM H; PATTERSON THOMAS E	Carpet backings prepared from vegetable oil-based polyurethanes.
US2006167122 A1	20060727	US7863343 B2 20110104; SG144167 A1 20080729; KR20060086288 A 20060731; EP1683828 A2 20060726; EP1683828 A3 20090916; EP1683828 B1 20111116; SG124395 A1 20060830; CN1810877 A 20060802; CN1810877 B 20101201; AT533811 T 20111215	JP20050017050 20050125	HARAGUCHI KENJI; OHTA HAJIME	JSP CORP	Expandable polylactic acid resin particles, expanded polylactic acid resin beads and molded article obtained from expanded polylactic acid resin beads.
US2007021515 A1	20070125		US20050184614 20050719	GLENN GREGORY M; HODSON SIMON K	KHASHOGGI E IND	Expandable starch-based beads and method of manufacturing molded articles therefrom.
US2012007267 A	20120112		US201113178300 20110707; US20100362009P 20100707	PAWLOSKI ADAM R; CERNOHOUS JEFFREY J; KASKE KENT	LIFOAM IND	Method of producing compostable or biobased foams.
US2012009420 A1	20120112	WO2013006781 A2 20130110; WO2013006781 A3 20130404; WO2013006781 A9 20130523; CA2778582 A1 20130107	US201113178293 20110707; US20100362009P 20100707	PAWLOSKI ADAM R; CERNOHOUS JEFFREY J; KASKE KENT	LIFOAM IND	Compostable or biobased foams.
US2012053256 A1	20120301	US8420707 B2 20130416	TW20100128445 20100825	CHEN JONG-WU; HSIAO HSIANG-JEN; LI CHIA-HUNG CHEN CHIN-FU	CHEN JONG-WU; HSIAO HSIANG-JEN; LI CHIA-HUNG CHEN CHIN-FU	Biomass composite composition and foaming method thereof.
US2013059141 A	20130307		US201213602870 20120904; US201161530421P 20110902	FUESL ANDREAS; SANDLER JAN KURT WALTER; NALAWADE SAMEER; STEINKE TOBIAS HEINZ; WARZELHAN VOLKER; KUENKEL ANDREAS; HAHN KLAUS; LOHMANN JEROME; BRYM ANNA KATHARINA	BASF SE	Foams comprising polypropylene carbonate.

Continued

—Cont'd

Patent Number	Publication Date	Family Members	Priority Numbers	Inventors	Applicants	Title
US4863655 A	19890905	ZA8909905 A 19910424	US19880292089 19881230	LACOURSE NORMAN L; ALTIERI PAUL A	NAT STARCH CHEM CORP	Biodegradable packaging material and the method of preparation thereof.
US5238968 A	19930824		US19930005375 19930115; JP19910094351 19910424; US19920870336 19920417	MORITA KENJI; UCHIKI KOHICHI; SHINODA HOSEI	MITSUI TOATSU CHEMICALS	Process for preparing a degradable high polymer network.
US5710190 A	19980120		US19950487047 19950607	JANE JAY-LIN; ZHANG SU SHE	UNIV IOWA STATE RES FOUND INC	Soy protein-based thermoplastic composition for foamed articles.
US5840777 A	19981124		US19940196079 19940215; GB19920012976 19920619; WO1993US05993 19930618; GB19920024255 19921119	EAGLES DANA BURTON; BAKIS GEORGE; JEFFERY ANDREW BRUCE; MERMINGIS CONSTANTINOS; HAGOORT THOMAS HENR	ALBANY INT CORP	Method of producing polysaccharide foams.
WO0015684 A1	20000323	US2008051506 A1 20080228; US6465569 B1 20021015; US2004102596 A1 20040527; US6867239 B2 20050315; US2004034163 A1 20040219; US6881763 B2 20050419; US2004029988 A1 20040212; US6864296 B2 20050308; US2003105178 A1 20030605; US6624244 B2 20030923; US6180686 B1 20010130; US2005182228 A1 20050818; TWI257399 B 20060701; PT1127086 E 20050429; MXPA01002680 A 20020408; JP2002524627 A 20020806; GT200000029 A 20010907; ES2235516 T3 20050701; ES2235516 T5 20080601; EP1127086 A1 20010829; EP1127086 A4 20010919; EP1127086 B1 20050112; EP1127086 B2 20080109; DK1127086 T3 20050523; DK1127086 T4 20080513; DE69923210 T2 20060105;	US19980154340 19980917	KURTH THOMAS M	URETHANE SOY SYSTEMS CO	Improved cellular plastic material.

		DE69923210 T3 20080724; CN1323326 A 20011121; CN1245428 C 20060315; CA2344378 A1 20000323; CA2344378 C 20120904; BR9913784 A 20010529; BR9913784 B1 20100713; AU5926899 A 20000403; AU766760 B2 20031023; AT286929 T 20050115				
WO0214043 A1	20020221	US2004092613 A1 20040513; US7563830 B2 20090721; NZ506328 A 20020927; ES2401990 T3 20130426; EP1332030 A1 20030806; EP1332030 A4 20090211; EP1332030 B1 20121226; CA2419180 A1 20020221; CA2419180 C 20100831; CN1446144 A 20031001; CN1236901 C 20060118; AU5278601 A 20020225	NZ20000506328 20000814	HASTINGS MARIA LOUISE; ERRINGTON JOHN GOUGH; HORNSEY ANYA JANE; CHAPMAN TIMOTHY JAMES; QUINN PHILIP JAMES	BLUE MARBLE POLYMERS LTD	Method for the production of biodegradable foamed products.
WO03046060 A1	20030605	US2005032923 A1 20050210; US7265160 B2 20070904; KR20090014382 A 20090210; KR20040066148 A 20040723; KR100923833 B1 20091027; JP2009091588 A 20090430; JP4311204 B2 20090812; EP1449869 A1 20040825; EP1449869 A4 20050119; CN1596279 A 20050316; CN100344679 C 20071024; AU2002349540 A1 20030610; AU2002349540 B2 20071101	JP20010364399 20011129; JP20020007111 20020116	OKA YOSHIYUKI; GOTO JUN; AKIMARU FUSAYOSHI; TSUKADA NORIAKI; TAINAKA JUNICHI	TORAY INDUSTRIES	Crosslinked biodegradable resin continuous foamed sheet and method for production thereof.
WO2006103926 A1	20061005	US2009082484 A1 20090326; EP1870222 A1 20071226; JP4653162 B2 20110316; CN101146663 A 20080319; CN101146663 B 20110406	JP20050090862 20050328	HIROSE FUMINOBU; SENDA KENICHI; MIYAGAWA TOSHIO	KANEKA CORP	Process for producing extruded polyhydroxyalkanoate resin foam.
WO2006103928 A1	20061005	US2009131545 A1 20090521; JP4733694 B2 20110727; EP1870220 A1 20071226; CN101184597 A 20080521; CN101184597 B 20110615	JP20050090864 20050328	HIROSE FUMINOBU; SENDA KENICHI; MIYAGAWA TOSHIO	KANEKA CORP	Process for producing extruded foam of polyhydroxyalkanoate resin and extruded foam obtained by the process.

Continued

—Cont'd

Patent Number	Publication Date	Family Members	Priority Numbers	Inventors	Applicants	Title
WO2006103969 A1	20061005	US2009270524 A1 20091029; KR20080000572 A 20080102; JP5076499 B2 20121121; EP1865021 A1 20071212; EP1865021 A4 20090819; CN101151310 A 20080326; CN101151310 B 20110330; AU2006229153 A1 20061005	JP20050092482 20050328; JP20050268023 20050915	OKA YOSHIYUKI; YOSHIOKA TAKAHIDE; OYAMA MASAHIKO	TORAY INDUSTRIES	Polylactic acid foam.
WO2006103970 A1	20061005	EP1870431 A1 20071226; EP1870431 A4 20090812; EP1870431 B1 20110601	JP20050087574 20050325	HIROSE FUMINOBU; MIYAGAWA TOSHIO; SENDA KENICHI	KANEKA CORP	Foamed polyhydroxyalkanoate resin particles and method of producing the foamed particles.
WO2007052543 A1	20070510	US2009258175 A1 20091015; US7972669 B2 20110705; KR20080072815 A 20080807; JP5264176 B2 20130814; EP1944333 A1 20080716; EP1944333 A4 20091202; CN101268125 A 20080917; CN101268125 B 20130327	MATSUOKA FUMIO; UEDA KAZUE; MATSUMOTO TATSUYA; OOGI YUTAKA	MATSUOKA FUMIO; UEDA KAZUE; MA TATSUYA; OOGI YUTAKA	UNITIKA LTD	Biodegradable resin foam sheet, biodegradable resin foam article and biodegradable resin molded container.
WO2007083705 A1	20070726	US2009012194 A1 20090108; US7947754 B2 20110524; US2009012194 A1 20090108; US7947754 B2 20110524; JP5274845 B2 20130828; EP1975195 A1 20081001; EP1975195 A4 20090408; CN101370860 A 20090218; CN101370860 B 20111109	JP20060011437 20060119	OKUDA TOHR; HARADA SHOICHIRO; FUKASAWA YOSHIHITO	ASAHI KASEI LIFE & LIVING CORP	Foam.
WO2008076755 A1	20080626	US2008146686 A120080619; US7846987 B2 20101207; US2009123728 A1 20090514; US7872056 B2 20110118; PL2089460 T3 20120229 MX2009006045 A 20090617 JP2010513604 A 20100430; ES2372988 T3 20120130; EP2089460 A1 20090819; EP2089460 B1 20110907; CA2672476 A1 20080626; CA2672476 C 20131022; AT523552 T 20110915	US20060869932P 20061214	HANDA Y PAUL	PACTIV CORP	Expanded and extruded biodegradable and reduced emission foams made with methyl formate-based blowing agents.

WO2008093284 A1	20080807	US2010029793 A1 20100204; US8283389 B2 20121009; NZ552936 A 20090925; JP2010516884 A 20100520; JP5357056 B2 20131204; EP2115053 A1 20091111; EP2115053 A4 20110316; CN101675101 A 20100317; CN101675101 B 20130130; CA2675473 A1 20080807; AU2008211581 A1 20080807; AU2008211581 B2 20130718	NZ20070552936 20070130	WITT MICHAEL RALPH JUERGEN; SHAH SAMIR	BIOPOLYMER NETWORK LTD	Methods of manufacture of polylactic acid foams.
WO2008123367 A1	20081016	US2010136338 A1 20100603; US8372512 B2 20130212; KR20090125139 A 20091203; KR101050338 B1 20110719; JP4213200 B2 20090121; EP2135724 A1 20091223; CN102617999 A 20120801; CN101646539 A 20100210; CN101646539 B 20120815	JP20070088074 20070329; JP20080036852 20080219	HIRAI TAKAAKI; NISHIJIMA KATSUNORI; OCHIAI TETSUYA	SEKISUI PLASTICS	Polylactic acid resin foam particle for in-mold foam forming, process for producing the same, and process for producing polylactic acid resin foam molding.
WO2008126660 A1	20081023	US2010120932 A1 20100513; EP2133386 A1 20091216; EP2133386 A4 20100407; EP2133386 B1 20111207; AT536386 T 20111215	JP20070099206 20070405	YOSHIOKA TAKAHIDE; OHYAMA MASAHIKO; OKA YOSHIYUKI	TORAY INDUSTRIES	Polylactic acid foam.
WO2008130226 A2	20081030	WO2008130225 A2 20081030; WO2008130225 A3 20100429; WO2008130226 A3 20090226; US2010098928 A1 20100422; US2010087556 A1 20100408; US8268901 B2 20120918; US2010087556 A1 20100408; US8268901 B2 20120918; NL1033719 C2 20081021; JP2010525099 A 20100722; JP2010526163 A 20100729; EP2137250 A2 20091230; EP2137249 A2 20091230; AU2008241682 A1 20081030; AU2008241682 B2 20121004	NL20071033719 20070419	BRITTON ROBIN NICHOLAS; NOORDEGRAAF JAN; DOORMALEN FRANCISCUS ADRIANUS HENDRIKUS CORNELIS VAN; MOLENVELD KARIN; SCHENNINK GERALDUS GERARDUS JOHANNES	SYNBRA TECH B.V.	A polymer mixture, a method for producing an extruded product, methods for producing a starting material for a foamed moulded product and methods for producing a foamed moulded product, the products obtained with said methods and applications thereof.
WO2009038783 A1	20090326	US2009093550 A1 20090409; JP2010538791 A 20101216; EP2185637 A1 20100519; EP2185637 B1 20130403; CA2699868 A1 20090326	US20070994596P 20070919	ROLFES EMILY R	SURMODICS INC	Biocompatible foams, systems, and methods.

Continued

—Cont'd

Patent Number	Publication Date	Family Members	Priority Numbers	Inventors	Applicants	Title
WO2010041936 A2	20100415	WO2010041936 A3 20100930; US2011218257 A1 20110908; MX2011003767 A 20110929; NL1036039 C 20100412; KR20110079715 A 20110707; JP2012505288 A 20120301; EP2334719 A2 20110622; CN102177195 A 20110907; CA2740142 A1 20100415	NL20081036039 20081009	NOORDEGRAAF JAN; KUIJSTERMANS FRANCISCUS PETRUS; DE JONG JOSEPHUS PETRUS MARIA	SYNBRA TECH B.V.	Particulate, expandable polymer, method for producing particulate expandable polymer, as well as a special use of the obtained foam material.
WO2010065053 A1	20100610	US2011306693 A1 20111215; TW201022341 A 20100616; EP2370508 A1 20111005; CA2745223 A1 20100610; AU2009322983 A1 20110630; AR072204 A1 20100811	US20080200619P 20081202; US20080203542P 20081223; US20090166950P 20090406	BOSNYAK CLIVE P; PITZI THOMAS J; CHRIS SCHWIER	METABOLIX INC	Production of polyhydroxyalkanoate foam.
WO2011038081 A1	20110331	US2012225961 A1 20120906; JP2013506032 A 20130221; EP2690129 A2 20140129; EP2690129 A3 20140226; EP2480222 A1 20120801; EP2480222 A4 20130508; CN102573818 A 20120711; CA2775121 A1 20110331	US20090245743P 20090925	VAN HORN BRETT L; YACKABONIS WILLIAM E	ARKEMA INC	Biodegradable foams with improved dimensional stability.
WO2011086030 A2	20110721	WO2011086030 A3 20110909; US2013150468 A1 20130613; KR20120125628 A 20121116; EP2617771 A2 20130724; EP2617771 A3 20130821; EP2524004 A2 20121121; CN102712801 A 20121003; CA2787222 A1 20110721; AU2011206716 A1 20120816	EP20100150730 20100114; EP20100193484 20101202	FUESL ANDREAS; SAMPATH BANGARU; HOFMANN MAXIMILIAN; BELLIN INGO; NALAWADE SAMEER; HAHN KLAUS; KUENKEL ANDREAS; LOOS ROBERT	BASF SE	Verfahren zur Herstellung von expandierbaren Polymilchsäurehaltigen Granulaten. "Method for producing expandable granulates containing polylactic acid."
WO2011141573 A1	20111117	US2013065055 A1 20130314; KR20130109002 A 20131007; ITMI20100865 A1 20111115; EP2569363 A1 20130320; CN102892826 A 20130123; CA2797285 A1 20111117; AU2011251907 A1 20121122	IT2010MI00865 20100514	BASTIOLI CATIA; LOMBI ROBERTO; NICOLINI MATTEO; TURATI DANIELE	NOVAMONT SPA	Biodegradable pellets foamed by irradiation

WO2011145391 A1	20111124	US2013059154 A1 20130307; TW201209089 A 20120301; KR20130092405 A 20130820; EP2573133 A1 20130327 CN102884115 A 20130116	JP20100113951 20100518; JP20100164749 20100722	SHINOHARA MITSURU; OIKAWA MASAHARU	JSP CORP	Expanded particles of polylactic acid-based resin, and moldings of the expanded particles.
WO2011145461 A1	20111124		JP20100256600 20101117; JP20100114536 20100518	AKAHASHI KEI; KOTANI TERUMITSU	SHOWA DENKO KK	Foamable resin composition and foam.
WO2011153653 A1	20111215	EP2580277 A1 20130417	CH20100000910 20100608; WO2011CH00137 20110607	MAUCH FREDERIC; WAMPFLER-VON ROTZ BRUNO KARL; KEHL KARL; THOENY-MEYER LINDA CHRISTIANE	BIOAPPLY SARL	Bio-degradable foamable material suitable for the production of slippers.
WO2012008784 A2	20120119	WO2012008784 A3 20120518; US2013116352 A1 20130509; KR20120007733 A 20120125; KR110010638 B1 20120215; JP2013530301 A 20130725	KR20100068412 20100715	JO YOUNG MO; KIM SSANG OK; LEE GUN KYU; YOON JEE YOUNG; JEON YOUNG SEUNG WO	DAESANG CORP	Expandable starch bead and method for preparing same.
WO2012086305 A1	20120628	US2013288056 A1 20131031; TW201233718 A 20120816; EP2657279 A1 20131030; CN103261299 A 20130821	JP20100285159 20101221	SHINOHARA MITSURU; OIKAWA MASAHARU	JSP CORP	Polylactic acid resin foam particle and polylactic acid resin foam particle molding.
WO2012091366 A2	20120705	WO2012091366 A3 20121018; US2013266767 A1 20131010; R20120076718 A 20120710; EP2658906 A2 20131106; CN102582173 A 20120718	KR20100138391 20101230	CHUNG GUN SOO; NAM YOUN WOO; LEE SI YOUNG	LG HAUSYS LTD	Eco-friendly foaming sheet.
WO2012099357 A2	20120726	WO2012099357 A3 20121018; KR20120084447 A 20120730	KR20110005813 20110120	CHOI KYUNG MAN; PAIK IN KYU; KIM YOUNG MIN; PARK JAE HYUNG; LEE JI EUN; HAN DONG HUN; LIM DAE HWI; CHOE IN CHEOL	KOREA INST OF FOOTWEAR & LEATHER TECHNOLOGY; COMTECH CHEMICAL CO LTD	Biodegradable foam compounds using poly lactic acid for shoe.
WO2012121960 A1	20120913	US2012223459 A1 20120906	US201113040632 20110304	NAWABY A VICTORIA; KRAGNESS ERIC; BABROWICZ ROBERT; RAMESH NATARAJAN S; AMRUTIYA NILESH; LONGO EUGENIO	CRYOVAC INC	Process for preparing a heat resistant polylactic acid foamed article.

Continued

—Cont'd

Patent Number	Publication Date	Family Members	Priority Numbers	Inventors	Applicants	Title
WO2012138282 A1	20121011		SE20110050293 20110404	MARCUSSON ANDERS; KARTHAEUSER JOACHIM; HAMREFORS JAN	SIOX MACHINES AB	Method of impregnating and purifying polylactic acid resin.
WO2013017895 A1	20130207		GB20110013415 20110804	FLAHERTY MICHAEL JOHN	FLAHERTY MICHAEL JOHN	Compostable and biodegradable materials and articles formed from them.
WO2013030300 A1	20130307		EP20110179871 20110902	FUESL ANDREAS; SANDLER JAN KURT WALTER; NALAWADE SAMEER; STEINKE TOBIAS HEINZ; WARZELHAN VOLKER; KUENKEL ANDREAS; HAHN KLAUS; LOHMANN JEROME; BRYM ANNA KATHARINA	BASF SE	Polypropylene carbonate-containing foams.
WO2013058056 A1	20130425		JP20110228625 20111018	HINOHARA MITSURU; OIKAWA MASAHARU	JSP CORP	Method for producing expanded polylactic acid resin particle.
WO8302955 A1	19830901	JPS59500251 A 19840223; EP0087847 A1 19830907; DE3206751 A1 19830901; DE3206751 C2 19860821	DE19823206751 19820225	GRAEFE JUERGEN ERNST	BIJENKORF ZETMEEL	Vefahren zur Herstellung von aufgeschäumter, gelatinierter Stärke-produkte. "A process for preparing foamed gelatinized starch products."
WO9308014 A1	19930429	US5252271 A 19931012; AU2798492 A 19930521	US19910781509 19911022	JEFFS HYRUM J	BIO PROD INT	Biodegradable packaging foam and method of preparation.
WO9600746 A1	19960111	US5523372 A 19960604; MX9700046 A 19971231; EP0767810 A1 19970416; EP0767810 A4 19980204; EP0767810 B1 19970416; DE69530203 T2 20040212; CN1156465 A 19970806; CN1088723 C 20020807; CA2194001 A1 19960111; AU2913495 A 19960125; AU690304 B2 19980423	US19940267193 19940629	FISK DONALD	UNI STAR IND LTD	Starch graft copolymer from prime starch.

WO9854244 A1	19981203	US6110983 A 20000829; TW512158 B 20021201; SG101495 A1 20040130; JPH10324766 A 19981208; JP3229978 B2 20011119; ES2260835 T3 20061101; EP0989159 A1 20000329; EP0989159 A4 20020116; EP0989159 B1 20060419; DE69834248 T2 20061102; AT323736 T 20060515	JP19970151627 19970526	TOKORO HISAO; SHIOYA SATORU; SHINOHARA MITSURU	JSP CORP	Aliphatic polyester-based resin foamed particles having biodegradability and crosslinked structure, formed product and production of the same particles.

Chapter 10

Manufacture of Films/Laminates

The present chapter relates to films and laminates composed of biodegradable polymers and/or polymers derived from renewable resources.

10.1 FILMS

Environmental problems arise with packaging films in that the environment is increasingly contaminated with plastic bags and plastic sheets that do not degrade, or degrade only slowly. The tendency is, therefore, to replace nonbiodegradable polymers derived from fossil fuel resources with biodegradable polymers for the formulation of packaging films.

It is often required that a biodegradable film exhibits certain physical and thermomechanical properties, such as stiffness, flexibility, water resistance, tensile strength, elongation, temperature stability, or gas permeability. The intended application of a particular biodegradable polymer will often dictate which properties are necessary for a particular film manufactured there to exhibit the desired performance criteria. In the case of sheets and films suitable for use as packaging materials, desired performance criteria may include elongation, dead fold, strength, printability, imperviousness to liquids, breathability, temperature stability, and the like.

It is often difficult, or even impossible, to identify one single biodegradable polymer or copolymer that meets all, or even most, of the desired performance criteria for a given application. This is particularly true in the area of packaging materials. Polymers that have a high glass transition temperature (T_g) are either difficult to blow into films on a mass scale or, at the least, tend to be too brittle for use as a packaging material, such as a wrap. On the other hand, polymers that have a low T_g also usually have relatively low softening and/or melting temperature (T_m) which makes them difficult to mass produce into sheets and films without the tendency of blocking, or self-adhesion. Moreover, such sheets and films may lack adequate strength, water vapor barrier, and/or modulus to be suitable for certain applications, such as in the manufacture of wraps or laminate coatings. For these reasons, biodegradable polymers have found little use in the area of packaging materials, particularly in the field of wraps.

Any known technique may be used to form a film from biodegradable polymers, including blowing, casting, and flat die extruding. Blown film is created by extruding melted polymer through an annular die, usually vertically, to form a thin walled tube, and forcing air via a hole in the center of the die to blow up the tube into a bubble. An air ring, mounted on top of the die, blows air onto the hot film to cool it down. The film then passes into a set of nip rolls, which collapse the bubble and flatten it into two flat film layers. Cast film is created by feeding a sheet of heated resin along a rolling path with chilled rollers. The cooling solidifies the film, and it is made into large rolls. Both techniques have advantages and disadvantages.

Among the conventional biodegradable polymer films, films based on cellulose, starch, and aliphatic polyesters produced by microorganisms are unsatisfactory in barrier properties, mechanical properties (strength), and heat resistance and are difficult to melt process, so that their processing costs become high. The same applies *mutatis mutandis* to biodegradable polymer films based on synthetic type polyesters, such as poly(ethylene succinate) or poly(butylene succinate) (PBS) (1995, **JPH07173271** A, MITSUI TOATSU CHEM INC), whereas the raw materials, succinic acid and butanediol, for making for example PBS, are considerably expensive (1997, **EP0805175** A1, KUREHA CHEMICAL IND CO LTD).

10.1.1 Films by Chemical Type

10.1.1.1 Starch

The use of starch to form film products is well known in the art. In the past, films have been prepared from amylosic materials by casting a solution of the amylosic material in a solvent on a suitable surface and then peeling the resulting film from the surface. In other instances, there have been suggestions of extruding amylosic materials, but invariably these extrusion processes also involved the use of a complete solution of the amylose in the carrier. Many of these techniques consisted of a chemical modification, followed by a regeneration of the amylose or starch, similar to the viscose process for cellulose. In any case, the films that resulted from such extrusion processes were frequently deficient in tensile strength, pliability, and transparency.

GB965349 A (1964, DEPT OF AGRICULTURAL AND INSPECTION OF THE STATE OF NEBRASKA, USA) discloses the extrusion of amylose material without using solvents to form films claimed to have excellent tensile strength. Another film-forming operation using starch is shown in **US3116351** A (1963, US AGRICULTURE), where an unsupported amylose film is made by extruding

Biopolymers: Processing and Products. http://dx.doi.org/10.1016/B978-0-323-26698-7.00010-6

an aqueous alkali-amylose solution into a coagulation mixture of ammonium sulfate and sodium sulfate.

EP0032802 A1 (1982, US AGRICULTURE) discloses a method of producing a flexible, self-supporting, and biodegradable film, wherein a mixture comprising a partially or completely gelatinized starchy material in an amount up to 60 wt% and an ethylene-acrylic acid copolymer is converted into a plasticized matrix and then shaped into a film comprising the following steps: (1) incorporating into said matrix a neutralizing agent selected from the group of aqueous ammonia and anhydrous ammonia; (2) adjusting the moisture content of said matrix to within the range of approximately 2–10 wt% based on the weight of the matrix; and (3) extrusion blowing said ammoniated and moisture-adjusted matrix into a film.

US2008147034 A1 (2008, KIMBERLY CLARK CO) discloses a film that is biodegradable and water sensitive (e.g., water soluble and water dispersible) in that it loses its integrity over time in the presence of water. The film comprises 1–50 wt% of at least one biodegradable polyester, and 50–99 wt% of at least one water-sensitive thermoplastic starch (TPS), wherein the TPS includes 40–95 wt% of at least one starch and 5–60 wt% of at least one plasticizer. The biodegradable polyester has a T_m of 50–180 °C and a T_g of approximately 25 °C or less, and is preferably an aliphatic-aromatic copolyester. The plasticizer is a polyhydric alcohol, such as sugar alcohol. The film has a thickness of approximately 50 μm or less, and is used for release liner, absorbent article, pouch, wrap, bag, diapers, training pants, absorbent underpants, incontinence articles, feminine hygiene products, swim wear, baby wipes, medical absorbent articles, food service wipers, and clothing articles. Figure 10.1 shows an embodiment of a method for forming a uniaxially oriented film by casting.

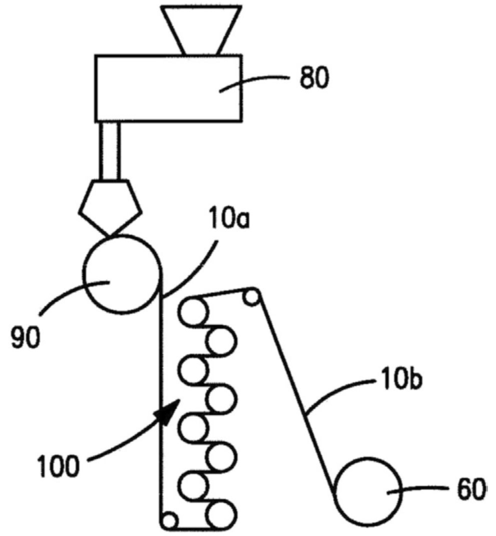


FIGURE 10.1 Schematic diagram of an embodiment of the method for forming a water-sensitive biodegradable film (2008, **US2008147034** A1, KIMBERLY CLARK CO). 10a, single-layered precursor film; 10b, resulting film; 60, take-up roll; 80, extrusion apparatus; 90, casting roll; 100, film-orientation unit or machine direction orienter (eight rolls).

KR20090008110 A (2009, YOU YOUNG SUN; KIM MAN SOO) and **KR20090008111** A (2009, ENFORECO CO LTD; YOU YOUNG SUN) disclose a biodegradable film that contains starch (5–80 wt%) plasticizer (5–20 wt%), biodegradable material (5–50 wt%) and co-additive (3–55 wt%).

The manufacture of the biodegradable film comprises the following steps: (1) mixing starch, inorganic filler, plasticizer, lubricant, and, optionally, an aliphatic polyester, in a high-speed mixer and removing moisture; (2) adding antioxidant, biodegradable material, and compatibilizer to the moisture-free mixture, and mixing the mixture at high speed; (3) manufacturing the mixture into the raw material pellet by using a twin extruder, wherein the twin extruder comprises a kneading part, at least one reverse direction screw, and at least one vent hole for ejecting volatile materials; and (4) processing the raw material pellet and, optionally, additive into a film.

10.1.1.2 Poly(Lactic Acid)

A film made of poly(lactic acid) (PLA) is stiff and has little flexibility and adhesive properties at temperatures $T \leq 60\,°C$ (i.e., its glass transition temperature) but is too flexible to maintain its shape at temperatures $T \geq 60\,°C$, thus being difficult to use in practice. Although the temperature of air and water in nature do not often increase to 60 °C, for example, the interior space and windows of closed automobiles may be heated to such a temperature in midsummer. This significant change in the characteristics is attributable to the crystalline structure of PLA. More specifically, when cooled at a usual cooling rate after the melt-forming process, PLA is negligibly crystallized and a large portion thereof becomes solidified in an amorphous state. The crystallized portions of PLA, whose melting temperature (T_m) is as high as 160 °C, cannot easily melt, but the amorphous portions accounting for the major portion of the entire product start to move without restriction at temperatures close to 60 °C.

Some early PLA films have been made by casting from solutions or by pressing, as disclosed already in some old patent publications (see **US2703316** A (1955, DU PONT) and **US4045418** A (1977, GULF OIL CORP)).

PLA films are mostly manufactured by either blown film or casting method. The main drawback of thin PLA films obtained under normal conditions, by either the blown or cast method, is their low tear resistance. Blown films comprising PLA have proved difficult to manufacture. Indeed, currently available PLA blown films require the addition of additives, such as plasticizers, to enable their production. However, plasticizers are often undesirable for films with food-related applications; they are costly, and they seldom, if at all, are as environmentally friendly as PLA itself. To circumvent these issues, some manufacturers have resorted to manufacturing PLA film with casting method (e.g., cast and tenter). The cast film is generally better suited for certain end-user applications, such as those requiring film "sleeves" rather than "wrap-around" film. Furthermore, cast film generally has much better optical properties than a blown film and can be produced at higher line speeds. However, PLA films that are manufactured by current casting methods exhibit excessive shrinkage in the machine direction, which substantially contributes to curling and limits their range of application. In addition, casting technology produces films with limited applications and can be 5–10 times more costly than blown film processing (2006, **US2006045940** A1, PLASTIC SUPPLIERS INC).

US5443780 A (1995, SHIMADZU CORP) discloses the production of oriented films made from PLA. The process starts from a PLA melt, which is extruded and rapidly cooled. This prefilm can subsequently be subjected to a uniaxial stretching process or subjected to sequential or simultaneous biaxial stretching. The stretching temperature is between the T_g and the crystallization temperature (T_{c1}) of the PLA. The stretching results in increased strength and a higher Young's modulus in the final film. If desired, the stretching is followed by heat setting.

WO02087851 A1 (2002, TRESPAPHAN GMBH) discloses a film comprising at least one base layer containing PLA and a minority component of a polyolefin, such as polyethylene or polypropylene, in an amount of 0.2–1 wt% of the base layer. Such a formulation is particularly suitable for thermoforming or biaxial stretching by means of pneumatic drawing or other mechanical forming.

JP2003103628 A (2003, TOYO BOSEKI) discloses a method for the manufacture of a biaxially stretched PLA film in which the difference between the heat of fusion ΔH_m of the crystal of the film during a period from the point of time when biaxial stretching is completed to the start of thermal fixing treatment and the heat of crystallization ΔH_c based on crystallization during a temperature increase is $(\Delta H_m - \Delta H_c) \geq 30$ J/g. The disclosed PLA film is claimed to be excellent in stretchability and reduced in thickness irregularity, and to have an excellent winding state generating no winding shift or wrinkles.

JP2004277682 A (2004, TOHO CHEM IND CO LTD) discloses a biodegradable film obtained by mixing 100 pbw of a PLA with 3–80 pbw of a rosin compound. The disclosed film is claimed to have improved flexibility and adhesive properties. However, the patent application does not discuss whether the shape of the film can be maintained at temperatures equal to or higher than the T_g of PLA. Furthermore, the flexibility of the film is also insufficient because the percentage elongation after fracture of the film is in the range of approximately 1.7–3.4% (2006, **WO2006098159** A1, SUMITOMO ELEC FINE POLYMER INC).

US2006045940 A1 (2006, PLASTIC SUPPLIERS INC) discloses PLA films substantially free of plasticizers and methods of manufacturing same by blown film process. In an embodiment, a method of making a PLA blown film is provided comprising the following steps: (1) providing dry pellets of PLA; (2) melting the pellets to form a molten mass at a first desired viscosity value or range of values; (3) increasing the viscosity of the molten mass to a second desired viscosity value or range of values; (4) forming a heated bubble from the resulting molten mass; (5) collapsing the bubble to form a film, in which the PLA film is substantially free of plasticizer; and, optionally (6) annealing the film at a temperature range of approximately 120 °F (49 °C) to approximately 285 °F (141 °C). The first viscosity value is 1000–5000 P (100–500 Pa s) at 480 °F (249 °C) at an apparent shear rate of 55/s. The second viscosity value is 14,000–16,000 (1400–1600 Pa s) at approximately 375 °F (191 °C) at an apparent shear rate of 55/s. The viscosity increasing step may be performed most conveniently, but not exclusively, in a polymer cooling unit, and the step of forming a heated bubble may include a stretching step, which orients the film. Alternatively, the viscosity increasing step may be performed by internal cooling of the die mandrel (by air or liquid fluid), controlling the temperature of the die (by heated or cooled liquid fluid), and/or the addition of chemical viscosity enhancers, the latter being preferably added during or before the melting step. Preferred commercial PLA products are NatureWorks polymers grades, and especially 4060D, 4042D, and 4032D. The PLA blown films find applications in food packaging and labeling (e.g., envelopes and signage).

WO2011082052 A1 (2011, 3M INNOVATIVE PROPERTIES CO) discloses a method for providing a semicrystalline PLA film, including the steps of providing a PLA composition that includes PLA, nucleating agent, and a plasticizer. Preferred plasticizers are as follows: acetyl tris-3-methylbutyl citrate, acetyl tris-2-methylbutyl citrate, acetyl tris-2-ethylhexyl citrate, and acetyl tris-2-octyl citrate. The composition is extruded as a molten sheet, which is then cooled to crystallize PLA and provide the film (see also Chapter 5: Compounding; Section 5.4: Plasticizing).

US2013004760 A1 (2013, AMPAC HOLDINGS LLC) discloses a PLA-based film composition comprising 90–99 wt% of one or more PLA and 1–10 wt% of one or more polyterpene resin additives (e.g., polymerized D-limonene and polymerized β-pinene) based on the total film composition. The film exhibits a low water vapor transmission rate (≤35 g/100 in^2/day/mil). In one embodiment, the PLA-based film includes one or more coating layers chosen from PVDC, poly(vinyl alcohol) (PVOH), acrylic, or low-temperature sealable coating. In another embodiment, the PLA-based film includes one or more vacuum-deposited aluminum layers. In a further embodiment, the PLA-based film includes a skin layer chosen from ethylene-propylene random copolymer, ethylene-propylene-butene-1 terpolymer, high-density polyethylene, medium-density polyethylene, low-density polyethylene (LDPE), linear LDPE, propylene-butene-1 copolymer, ethylene vinyl alcohol copolymer, amorphous polyester, and ionomer. The PLA-based film is useful in frozen food packaging, snack food packaging, beverage packaging, labeling applications, and pet food packaging applications.

JP2002146170 A (2002, UNITIKA LTD) discloses a film comprising a crystalline PLA, a plasticizer, and a nucleating agent as essential components having prescribed thermal properties. In addition, **JP2006063308** A (2006, KASEI CO C I) discloses a method for performing a crystallization treatment on a film comprising a PLA composed of a weak crystalline or amorphous PLA and a crystalline PLA, a plasticizer, and an anti-clouding agent. According to **WO2011162046** A1 (2011, TORAY INDUSTRIES), in the last two patent applications, the anti-blocking property and the anti-bleeding property are not sufficiently attained, and there is no disclosure at all with regard to a method for improving the tear resistance and impact resistance of the film.

JP2009138085 A (2009, TORAY INDUSTRIES) discloses a film that is composed of a composition comprising a PLA and a plasticizer and has prescribed film elongation at break, thickness, and thermal contraction rate. The disclosed film is claimed to have excellent flexibility, impact resistance, and dimensional stability, as well as blocking resistance and bleeding resistance, especially of a good quality when produced by an inflation method. However, there is no disclosure at all with regard to a method for improving the tear resistance of the film (2013, **WO2011162046** A1, TORAY INDUSTRIES).

WO2013021772 A1 (2013, TORAY INDUSTRIES) discloses a biodegradable film comprising a lactic acid–based polymer (a) dispersed in a continuous phase comprising a biodegradable polyester (b). The dispersed phase is in the form of ellipse or layer, which is elongated in the length direction of the film, and has a thickness of 5–100 nm. The lactic acid–based polymer (a) comprises a block copolymer having a polyester-type segment and a PLA segment and/or a block copolymer having a polyether-type segment and a PLA segment. The biodegradable polyester (b) is chosen from PBS, poly(butylene succinate adipate) (PBSA), and poly(butylene adipate terephthalate) (PBAT). The film has tearing strength of 5 N/mm or more (measured using trouser tear method based on JIS K7128-1, 1998) along length direction and width direction. The ratio of melt viscosity of PLA (a) and melt viscosity of biodegradable polyester (b), at 200 °C with shear rate of 100/s is 0.3–1. The biodegradable film further contains a compatibilizing agent. The weight ratio of lactic acid–type block copolymer and biodegradable polyester is 5/95–60/40. The disclosed biodegradable film is used for packaging material for food, garment, and industrial commodity, hand-carried bag for shopping, vegetable and fruit, agricultural mulch film, and sheet for pine beetle fumigation, manure bag, and garbage bag.

US2009326130 A (2009, FINA TECHNOLOGY) discloses a method of producing an oriented film comprising blending PLA (1–40 wt%) and polypropylene (51–99 wt%) and forming the polymer blend into a film, and orienting the film. The dispersed PLA phase in the blend functions as a cavitating agent. Herein, a cavitating agent refers to a compound(s) capable of generating voids in the structure of film during the film-making process. In an embodiment, the polypropylene/PLA blend further comprises a cavitating booster. The polypropylene/PLA blend displays desirable characteristics such as an increased strength and/or improved optical properties when compared to either polypropylene or PLA alone. In particular, the disclosed film has a haze of 10–95% and a gloss 45° from approximately 50 to approximately 125.

10.1.1.3 Poly(glycolic acid)

US2676945 A (1954, DU PONT) discloses a biodegradable amorphous film based on polyglycolic acid (PGA), which is a synthetic aliphatic polyester. The film has a thickness of 3 mils (76.2 μm) and is biaxially stretched. The PGA polymer is obtained by directly polycondensing glycolic acid, and not by ring-opening polymerization of glycolide. However, the polycondensation process of glycolic acid includes heating and polycondensing glycolic acid for a long period (approximately 40 h) at a high temperature of at least 200 °C, and hence tends to involve side reactions such as decomposition reactions. This patent application describes, in its example, the melt viscosity of PGA as being approximately 2000 P (200 Pa s) at 245 °C measured at a shear rate of approximately 0/s. This melt viscosity value corresponds to a value extremely as low as approximately 20 P (2 Pa s) at 245 °C when converted into a value measured at a shear rate of 100/s. In addition, there is high possibility that this PGA may have an unstable structure because of adverse reactions. Therefore, oriented films formed from PGA obtained by such a direct polycondensation process have low mechanical strength and, hence, they are insufficient from the view point of practical use (1997, **EP0805175** A1; 1997, **EP0805176** A1, KUREHA CHEMICAL IND CO LTD).

A biaxially oriented film of PGA obtained by ring-opening polymerization of glycolide is expected to enhance the gas barrier properties and mechanical properties thereof by the stretch processing. Therefore, there have been proposed various processes for producing a biaxially oriented film of PGA.

In general, PGA is melt processed into the form of a film, and the resultant film is then subjected to stretch processing within the temperature range $T_g < T < T_{c1}$. If the stretching temperature is lower than the T_g, this makes it impossible to conduct stretching or tends to cause breaking during stretch processing because the film is hard. A stretching temperature higher than the crystallization temperature T_{c1} makes it impossible to conduct stretching or tends to cause breaking during stretch processing because the crystallization is caused to proceed (2009, **WO2009107425** A1, KUREHA CORP).

PGA has a relatively small temperature difference $T_{c1}-T_{g.}$ In general, a thermoplastic polymer small in this temperature difference $T_{c1}-T_g$ involves a problem that the stretchable temperature range is narrow on stretch processing of the film formed from such a polymer, or stretch blow molding of the polymer. On the other hand, PGA has a high crystallization temperature T_{c2} detected in the course of its cooling from a molten state and a relatively small temperature difference T_m-T_{c2}. A thermoplastic polymer small in this temperature difference T_m-T_{c2} tends to crystallize on cooling of a sheet or fiber extruded from such a polymer from its molten state and is difficult to provide a transparent formed product. Therefore, the forming processing of PGA has involved a problem that forming conditions, such as forming temperature and stretching temperature, are limited to narrow ranges (2009, **WO2009107425** A1, KUREHA CORP).

JPH06256480 A (1994) and **JPH06256481** A (1994) of TOYO BOSEKI disclose the use of PGA having a viscosity-average molecular weight (M_v) of 280,000 or 250,000 as a raw material for the preparation of a biaxially stretched film. The polymer was melt extruded and cast at 280 °C into an unoriented sheet, and the unoriented sheet was then stretched three times in a machine direction and three or four times in a transverse direction at 160 °C to obtain a biaxially oriented film. It is known that PGA tends to undergo thermal decomposition at a temperature exceeding approximately 255 °C and actually substantially undergoes thermal decomposition at a temperature as high as 280 °C, so that any satisfactory unoriented sheet cannot be obtained. It is a matter of course that if such an unoriented sheet is biaxially stretched, it is scarcely possible to obtain a biaxially oriented film having sufficient strength. An amorphous sheet of PGA is crystallized at a temperature exceeding its crystallization temperature T_{c1} (approximately 80 °C) and highly crystallized at a temperature as high as 160 °C, so that the biaxial stretching of the amorphous sheet (e.g., three times in a machine direction and three or four times in a transverse direction) is extremely difficult or actually impossible under such stretching conditions. Accordingly, any oriented film having sufficient strength cannot be obtained under the conditions disclosed in these patents (1997, **EP0805175** A1; 1997, **EP0805176** A1 1997, KUREHA CHEMICAL IND CO LTD).

EP0805175 A1 (1997) and **EP0805176** A1 (1997 of KUREHA CHEMICAL IND CO LTD) disclose a process for producing an oriented film, in which PGA is melt extruded into a film from a T-die or a tube at the temperature range of $T_m < T < 255\,°C$; immediately quenching the film or tube at a temperature $T \leq T_{c1}$ of the polymer; stretching the quenched sheet or tube at a temperature $T_g < T < T_{c1}$ in a machine direction through stretching rolls at a draw ratio higher than one time but not higher than 20 times; and optionally heat setting the stretched sheet for 1 s–3 h in a temperature range of $T_{c1} < T < (T_m + 10\,°C)$ while maintaining its length constant, or under tension.

JP2006182017 A (2006, UNITIKA LTD; KUREHA CORP) discloses a process for producing a biaxially oriented PGA film in which the PGA is formed into an unstretched sheet, and sequentially biaxially stretch the unstretched film in machine and transverse directions, wherein the temperature of the film on stretching is within a temperature range defined by the equation: $(T_g + 2)\,°C < T(T_g + 20)\,°C$.

However, it has been difficult to stably and continuously produce a sequentially biaxially oriented PGA film having satisfactory properties (e.g., gas barrier properties, mechanical properties, transparency, and resistance to heat shrinkage) on an industrial scale by applying the sequentially biaxially stretching process. More specifically, by simply controlling the stretching temperature, a waviness phenomenon or whitening phenomenon of a film is easy to occur on stretch processing. According to a sequentially biaxially stretching process by a roll/tenter system with stretching rolls and a tenter stretching machine combined, a uniaxially oriented film formed by roll stretching tends to shrink, and so it is difficult to surely grasp both edges of the film by chucks of the tenter stretching machine to biaxially stretch the film (2009, **WO2009107425** A1, KUREHA CORP).

WO2009107425 A1 (2009, KUREHA CORP) discloses a production process of a sequentially biaxially oriented PGA film, comprising the following steps:

1. Stretching an amorphous PGA sheet in one direction at a stretching temperature within a range of 40–70 °C in such a manner that a primary draw ratio falls within a range of 2.5–7.0 times, thereby forming a uniaxially oriented film.
2. Causing the uniaxially oriented film to pass through within a temperature environment controlled to a temperature within a range of 5–40 °C and lower by at least 5 °C than the stretching temperature in step.
3. Stretching the uniaxially oriented film passed through step 2 in a direction perpendicular to the stretching direction in step 1 at a stretching temperature within a range of 35–60 °C and higher by at least 3 °C than the temperature in step 2 in such a manner that a secondary draw ratio falls within a range of 2.5–6.0 times, thereby forming a biaxially oriented film, the area stretch ratio represented by a product of the primary draw ratio and the secondary draw ratio, which falls within a range of 11–30 times.

4. Subjecting the biaxially oriented film to a heat treatment at a temperature within a range of 70–200 °C.

The cooling step 2 cannot only inhibit the crystallization of the uniaxially oriented film from proceeding, but also inhibit the film from shrinking in both machine (or longitudinal) and transverse directions. When the uniaxially oriented film is inhibited from shrinking in both machine and transverse directions by arranging the cooling step, both edges of the uniaxially oriented film can be surely grasped by chucks of a tenter stretching machine even when a tenter stretching machine is used in the secondarily stretching step. In the secondarily stretching step, the uniaxially oriented film can be stretched at a temperature within a range from a relatively low temperature somewhat lower than T_g to 60 °C because the crystallization of the uniaxially oriented film is inhibited from proceeding.

The produced sequentially biaxially oriented PGA film is claimed to be excellent in gas barrier properties and mechanical properties, such as falling ball impact strength and puncture strength, small in haze value, free of occurrence of white stripe-like marks and thickness unevenness, and good in resistance to heat shrinkage.

JP2007326290 A (2007, KUREHA CORP) discloses a PGA film with improved gas barrier property obtained by extruding PGA through an annular die at a temperature *T*, which satisfies the equation:

$$212\exp(0.0004\times \mathrm{V}) < \mathrm{T} < 220\exp(0.0001\times \mathrm{V}) \quad (10.1)$$

and inflation molding while being cooled with air. The PGA has a melting viscosity (V) of 300–2000 Pa s at a temperature of 270 °C and a shearing speed of 122/s.

10.1.1.4 Polyhydroxyalkanoates (PHA)s

US3275610 A (1966, MOBIL OIL CORP) discloses a film made by poly(3-hydroxybutyrate) (P3HB) prepared by the solvent-cast method and described as a "milky white pliable" film. There have been many other references in the literature to films made of P3HB. Their production has always involved solvent casting, as above, and/or calendering a coarse sheet or article. For instance, in **EP0058480** A (1982, ICI PLC), a P3HB polymer gel is oriented uniaxially or biaxially by cold rolling or drawing at temperatures preferably lower than 160 °C to give tough films, or other shaped articles. The properties of solvent cast and/or cold-calendered thin films are not commercially satisfactory in that the films are too brittle for packaging or many other uses.

Some of the patents on P3HB describes the production of films by a multistage process that includes, at an early stage, a melt extrusion step. However, the melt extrusion step does not itself form the desired film but instead merely reduces the P3HB polymer composition to a form that can then be processed into a film (e.g., by cold calendering). For instance, in **EP0078609** A2 (1983, ICI PLC), a relatively coarse article was reduced in thickness by cold processing. Thus, in example 1, plaques were made by compression molding and were then rolled at room temperature to thicknesses ranging from 1.3 mm down to 400 μm. In example 4, a ribbon was made by melt extrusion through a 1.5-mm slot die and was then cold calendered down to 450 μm. In example 11, a sheet 1 mm thick was made by solution casting and was then compressed and cold calendered to give an oriented film 25 μm thick.

For this and other reasons, it has so far proved impossible to produce thin films of P3HB polymers. In particular, it has been impossible to use P3HB polymers as a partial or complete replacement for the non-biodegradable polymers (e.g., polypropylene and PVC) from which most common films are produced (1987, **EP0226439** A1, GRACE W R & CO).

EP0226439 A1 (1987, GRACE W R & CO) discloses a means of achieving a free-standing PHBHV film of a thickness less than approximately 200 μm by co-extruding the PHBHV between two layers of sacrificial polymer (e.g., polyolefin or ethylene–vinyl acetate (EVA)), stretching and orienting the multilayer film, and then stripping away the polyolefin or EVA layers after the PHBHV has had time to crystallize. The PHBHV film is then laminated to either water-soluble films or water-insoluble films, such as PVDC or other polyolefins. The PHBHV films were used for diaper backsheet applications.

WO9416000 A1 (1994, ZENECA LTD) discloses a supported or cast film of a PHA polymer, such as PHBHV, prepared by applying a layer of molten polymer to a cool (typically 4–20 °C) surface not substantially higher than the T_g of the polymer, so as to form a solid, glassy film with a high density of nucleation sites; subsequently, the temperature of the film so formed is increased (e.g., to 40 °C or more, preferably 60–80 °C) towards the optimum temperature for growth of the polymer's spherulites, effectively separating the film formation/nucleation step from the crystallization step (growth of spherulites around the nucleation sites). Reference is made by way of example to Figure 10.2, which shows an apparatus suitable for PHA film coating a web. The developed process was based on the finding that the optimum temperature for creating nucleating sites is considerably lower than the optimum temperature for growth of the crystallites. The film so produced has smaller crystallites than that produced if the chill-roll is at higher temperatures. This can have two advantages: first, it may lead to improved mechanical properties; and second, smaller crystallites can lead to reduced voiding/pinholing at the boundaries between crystallites. This improves the coatings barrier properties, and is an important feature of films whether free standing or supported (e.g., on paper or board). If the

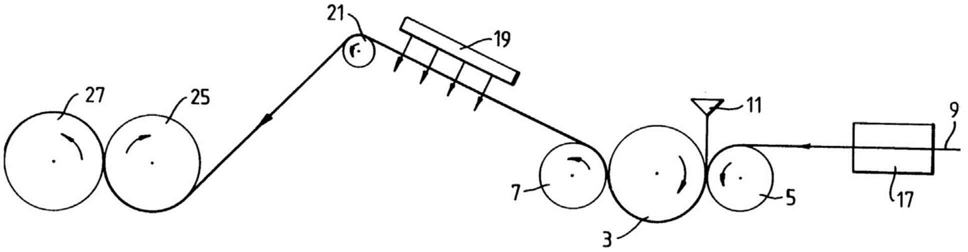


FIGURE 10.2 Schematic diagram of an apparatus for film coating a web (1994, **WO9416000** A1, ZENECA LTD). 3, chill-roll; 5, nip-roll; 7, nip-roll; 9, coated web; 11, extruder; 17, corona treater; 19, infrared heater; 21, free-moving roller; 25, wind-up roll; 27, wind-up roll.

coating tends to pinhole or crack, its efficiency is reduced as a barrier medium.

GB2243327 A (1991, PROCTER & GAMBLE) teaches that biodegradable PHA polymers, such as poly(3-hydroxybutyrate-*co*-3-valerate) (PHBHV) cannot be formed into thin films while maintaining the required strength and tear resistance for applications, such as a diaper backsheet. This problem was addressed by combining a thin biodegradable thermoplastic polymer film into a sheet laminate with at least one layer of a fiber substrate composed of biodegradable fibers. However, a cast film of PHBHV (6.5% HV) 20–24 μm thick when laminated with a rayon nonwoven showed elongation at break of less than 10% in the machine direction, which was less than that for the rayon portion alone.

WO9400293 A (1994, PROCTER & GAMBLE) discloses multilayer films wherein the PHBHV component may be co-extruded as an internal layer surrounded by outer layers of films (e.g., biodegradable films) to be used in the application (e.g., diaper films) so that the external layers are not stripped away from the PHBHV layer. They remain as an integral part of a biodegradable multilayer film.

CA2076038 A1 (1995, PULP PAPER RES INST) discloses a method of forming a self-supporting film comprising the following: (1) casting a dilute solution of 15–25% w/w solids of a latex consisting of colloidal suspension in water of essentially non-crystalline particles of a PHA polymer or copolymer, such as P3HB or PHBHV on a impervious support surface to form a wet film; (2) drying the wet film; and (3) heating the dry film at a temperature, $T < T_m - 30\,°C$ to produce moderate fusion within the film, and removing the resulting film from said support surface. The film is white and opaque and has a microporous structure.

EP736563 A1 (1996, SAFTA SPA) discloses a process for producing cast and blown films from PHBHV copolymers that have been compounded with plasticizers, nucleating agents, and/or other additives. No specifications of the copolymer were disclosed other than an HV content of 4–16%. The molecular weights of the PHBHV powder used in the examples ranged up to 520,000 before compounding and extrusion into pellets. In their disclosed process, films of the compounded PHBHV were extruded on a preformed supportive bubble of EVA-resin or LDPE with a melt flow index (MFI) of less than 2.5 g/10 min.

10.1.1.5 Poly(ε-Caprolactone)

Poly(ε-caprolactone) (PCL) is a biodegradable synthetic aliphatic polyester, which is problematic in film formation because of its relatively low T_m (60 °C), insufficient heat resistance, and tensile strength. Accordingly, because it includes a limitation in a practical use as a film (e.g., mulch film for agriculture or wrapping film) under natural circumstances at high temperatures, it cannot be used without any modifications.

JPH08188706 A (1996, GUNZE KK) discloses a biodegradable film obtained by molding 100 pbw of a composition composed of 80–100 wt% of PCL and 20–0 wt% of an aliphatic polyester produced by microorganisms, and 0.3–0.8 pbw of a lubricant. However, it includes a problem in the mechanical strength during film formation. Accordingly, it is difficult to produce films on a large scale, and even a bag for garbage prepared from such a film, when thrown into a compost apparatus together with foods wastes, takes at least 100 days for its decomposition.

JPH0811206 A (1996, OKURA INDUSTRIAL CO LTD) discloses the manufacture of a PCL film by making use of an inflation extrusion molding device, which is fitted with a downward die.

JPH08150658 A (1996, NIPPON SYNTHETIC CHEM IND) discloses an inflation film composed of starch, EVA, PCL, and a plasticizer. The film is produced by extruding the resin composition in a tubular shape from an annular die and inflating the formed tube by compressed air blown in the tube, subsequently folding the tube by a nip roll to produce an inflation film. In this inflation film forming method, the temperature of the resin composition at the time of extrusion is set to 135–150 °C and the temperature of the tube at the time of the passage through the nip roll is set to 30 °C and a blow ratio (tube diameter/die diameter) is set to two or more and a taking-over ratio (die gap/film thickness)/blow ratio (tube diameter/die diameter) is set to 20 or less. The inflation film is claimed to have an excellent heat-sealing property, mechanical strength, and moisture resistance. However, there is a problem that EVA does not have a complete biodegradability.

10.1.1.6 Poly(alkylene Alkanoate)s

Films made from poly(alkylene alkanoate)s (PAA)s have a T_g lower than room temperature, have high crystallizability, and are crystalline at room temperature. An aliphatic polyester tends to become opaque because it is difficult to suppress growth of spherulites even if it is quickly cooled after melt extrusion. A film made from PAA is thus non-transparent even compared with polyethylene or polypropylene film of the same thickness. If an article is put in a bag made from PAA, the article and its color cannot be seen clearly through the bag. This impairs display effects. Although trials are being made to improve transparency, even slightly by adjusting the dicarboxylic component and the diol component so as to lower crystallizability, if the crystallizability is too low, the material is less likely to solidify when cooled after extrusion, and thus more likely to stick to the cast rolls. This makes it difficult to pull it in the form of a film (2002, **US20020052445** A1, TERADA SHIGENORI; TAKAGI JUN).

US20020052445 A1 (2002, TERADA SHIGENORI; TAKAGI JUN) attempted to address the above problems by disclosing a biodegradable film comprising PLA and an aliphatic polyester other than PLA in a weight ratio of 70/30–20/80, the film having a tensile modulus of at least 250 kg/mm^2 and a light transmittance of at least 65%. The aliphatic polyester other than PLA (e.g., Lacty®, Shimadzu Corp) preferably comprises a PAA, such as PBS (e.g., Bionolle® 1001, Showa High Polymer, Ltd.) and PBSA (e.g., Bionolle® 3001).

10.1.1.7 Aliphatic-Aromatic Copolyesters

US2011237750 A1 (2011, BASF SE) discloses a method of producing films from aliphatic-aromatic copolyesters. The aliphatic-aromatic copolyesters are obtained by polycondensation of: (1) at least one of dicarboxylic acids, including succinic acid, adipic acid, sebacic acid, azelaic acid, or brassylic acid or its derivatives (65–80 mol% based on (1)–(2)); (2) terephthalic acid derivative (35–20 mol% based on (1)–(2)); (3) 2-8C-alkylenediol or 2-6C-oxyalkylenediol (98–102 mol% based on (1)–(2)); and (4) at least trifunctional crosslinking agent or difunctional chain extender (0.05–2 wt% based on (1)–(3)).

The method is useful for producing blown films and stretch films, which are useful in basal-fold bags, lateral-seam bags, carrier bags with hole grip, shrink labels, vest-style carrier bags, inliners, heavy-duty bags, freezer bags, composting bags, agricultural films (mulch films), film bags for food packaging, salad film, freshness-retention film (stretch film) for fruit and vegetables, meat, and fish, stretch film for pallet-wrapping, net film, packaging films for snacks, chocolate bars, and muesli bars, and peelable lid films for dairy packaging (yoghurt or cream). The method provides films that are claimed to be resistant to tear propagation; use biodegradable polyesters and polyester mixtures with good adhesion properties, thus enabling their use in paper coating (e.g., for paper cups and plates); exhibit excellent mechanical properties; and have a thickness ≥240 µm.

EP2551301 A1 (2013) and **US2013029124** A1 (2013) of BASF SE disclose a biodegradable polyester film comprising: (1) a biodegradable polyester based on aliphatic and aromatic dicarboxylic acids and an aliphatic dihydroxy compound (80–95 wt%, based on the total wt% of components (1)–(2)); (2) a PHA (5–20 wt%, based on the total wt% of components (1)–(2)); (3) calcium carbonate (0–25 wt%, based on the total weight of components (1)–(4)); (4) talc (0–15 wt%, based on the total wt% of components (1)–(4)); and (5) PLA and/or starch (0–30 wt%, based on the total wt% of components (1)–(4)). The polyester film can be produced by a blown film process, where a blow-up ratio is of 2/1/1–6. The disclosed biodegradable polyester film is useful for manufacturing (e.g., shopping bags).

WO2013038770 A1 (2013, TORAY IND INC) discloses a biodegradable film comprising the following: (1) PLA, (2) an aliphatic polyester and/or aliphatic-aromatic polyester, and (3) a transesterification catalyst and/or compound derived from a transesterification catalyst. The disclosed film is claimed to have improved flexibility and tear propagation resistance.

WO2010013483 A1 (2010, KANEKA CORP) discloses in one of its embodiments a polyester film made of a biodegradable polyester composition comprising a biodegradable polyester having a $T_g \leq 10\,°C$ derived from fossil fuel resources (25–75 wt%) and a biodegradable polyester having a $T_g \leq 10\,°C$ derived from renewable resources (75–25 wt%). The biodegradable polyester derived from fossil fuel resources is selected from the group consisting of PBAT, PBSA, PBS, and PCL; and is preferably PBAT. The biodegradable polyester derived from renewable resources is an aliphatic polyester copolymer, preferably poly(3-hydroxybutyrate-*co*-3-hydroxyhexanoate). The polyester film is 250 µm thick and is produced by casting on chilled rollers.

10.1.1.8 Aliphatic Carbonates

EP0803532 A1 (1997, PAC POLYMERS INC) discloses a monolayer or multilayer structure consisting essentially of poly(ethylene carbonate) (PEC) in which the concentration of ether linkages is 8 mol.% or less. The fewer the number of ether linkages in the PEC, the greater is the oxygen barrier property. The monolayer or multilayer structure is useful for packaging, storing, or transporting oxygen-sensitive substances.

10.1.2 Shrinkable Films

Heat-shrinkable films have been widely used for various industrial applications, such as, for example, with shrink-wrap films, shrinkable labels, and cap seals, by making use of their property of heat-dependent shrinkage. The films have been applied to a variety of surfaces, including plastic and glass surfaces. Shrinkable films have been traditionally manufactured from polypropylene, poly(vinyl chloride) (PVC), polystyrene, or aromatic polyester. Because these shrinkable films are chemically and biologically stable, they need a significantly long time to decompose, which causes serious environmental problems. In many instances, film shrinkage is concomitant with an undesirable draw-back of the outer edges of the film, which has limited the application of shrinkable films.

Commonly used biodegradable shrinkable films are mainly made of PLA, but because they have low shrinkage ratios and exhibit brittle behavior due to crystallization in the film manufacturing process, their uses thereof are limited. Various techniques used to improve the crystallization behavior of a biodegradable polymer are described in Chapter 2: Properties; Section 2.3.2: Heat Resistance. However, the usability of most of these techniques is questioned as they increase film opacity and reduce productivity, whereas the shrinkage ratios of final products are difficult to control.

Attempts have been made to improve the toughness of PLA heat-shrinkable films. These efforts may be classified into three categories: (1) mixing different kinds of biodegradable polymers with PLA; (2) adding certain additives, such as plasticizers; and (3) making the film in multilayer with different material having better toughness than PLA, such as polyolefins.

1. Mixing different kinds of biodegradable polymers with PLA.

   JPH09169896 A (1997, SHINETSU CHEMICAL CO) discloses a het shrinkable film, which is made of a composition comprising PLA, PAA, and PCL. The PAA is an aliphatic polyester synthesized by the condensation polymerization of a glycol and an aliphatic dicarboxylic acid and has a glycol content of 20–70 wt%.

   JP2002234117 A (2002, MITSUBISHI PLASTICS IND) discloses a heat-shrinkable film in the form of a laminate having a layer, which comprises a resin composition based on PLA and an aliphatic-aromatic copolyester, and a layer based on a PLA.

   JP2003103632 A (2003, KASEI CO C I) discloses a heat-shrinkable film, which is made of a composition comprising 82–97 wt% of a mixture of 60–80 wt% of PLA (1) in which the composition ratio of an L-lactic acid unit to a D-lactic acid unit is 85/15–90/10 and 82–97 wt% of PLA (2) in which the composition ratio of the L-lactic acid unit to the D-lactic acid unit is 95/15–100/0 and 3–18 wt% of PCL is molded into a sheet, and the sheet is stretched four to seven times in one direction to obtain the heat-shrinkable film. In the film, shrinkage rates in the main shrinkage direction at 80 and 100 °C are at least 40% and at least 60%, respectively, a shrinkage rate in the direction perpendicular to the main shrinkage direction is 15% or lower, haze is 10 or lower, and elongation in the direction perpendicular to the main shrinkage direction is at least 200%.

   JP2004002776 A (2004, MITSUBISHI PLASTICS IND) discloses a heat-shrinkable PLA film having at least one layer comprising PLA and an aliphatic polyester having a T_m of 100–170 °C and a $T_g \leq 0$ °C, such as PBS, and the film is at least uniaxially oriented.

2. Adding certain additives

   JPH0995605 A (1997, SHINETSU CHEMICAL CO) discloses a biodegradable shrinkable film, which is made from a composition comprising the following: (a) PLA, (b) a plasticizer, and (c) a lubricant. The plasticizer (c) is preferably an aliphatic dibasic acid ester, a phthalic ester, a hydroxypolycarboxylic ester, polyester plasticizer, a fatty acid ester, an epoxy plasticizer or their mixture (e.g., di-2-ethylhexyl azelate). The lubricant (c) is preferably a fatty acid ester, a hydrocarbon resin, paraffin, a higher fatty acid, a hydroxyl fatty acid, a fatty acid amide, an alkylene bis(fatty acid amide), an aliphatic ketone, a fatty acid lower alcohol ester, a fatty acid polyhydric alcohol ester, a fatty acid polyglycol ester, a fatty alcohol, a polyhydric alcohol; optionally, a heat stabilizer is used, suitably a lactic acid inorganic salt (e.g., sodium lactate). The disclosed heat shrinkable PLA film is claimed to have excellent elongation at break, Izod impact strength, heat shrink age, and printability and is useful for labels.

   JPH09151310 A (1997, SHINETSU CHEMICAL CO) discloses a heat shrinkable film, which is made of a composition comprising the following: (a) PLA and (b) an EVA copolymer. The composition comprises optionally (c) a lubricant, (d) a plasticizer, (e) a heat-stabilizing agent, and (f) a releasing agent. It is preferable that the component (b) contains 10–70 wt% ethylene and 30–90 wt% vinyl acetate. The component (c) is preferably a fatty acid ester, a hydrocarbon resin, or a paraffin. The component (c) is preferably an aliphatic dibasic acid ester, a phthalic acid ester, or a hydroxy polyvalent carboxylic acid ester. The component (e) is preferably an inorganic salt of lactic acid in an amount of 0.5 five pbw based on 100 pbw of component (a). The component (f) is preferably a silicone oil having a viscosity 100–10,000 cS in amount of 0.05–5 pbw based on 100 pbw of component (a). The heat-shrinkable film is claimed to have improved breaking elongation and impact strength while keeping its transparency, excellent in releasing property in its processing, and useful as a shrink film.

JP2001226571 A (2001, C I KASEI CO LTD) discloses a biodegradable heat-shrinkable film, which is made from a composition comprising 100 pbw PLA and 0.05–5 pbw nucleating agent. The disclosed heat shrinkable PLA film has high transparency, compatibility with printing inks and exhibits sufficient heat shrinkability at low temperatures. Furthermore, the film exhibits constant heat-shrinkable properties and, at the same time, a low shrinkage stress, and thus the finish becomes of high quality when shrink packaging is effected. The film can be used in high-quality shrink labels.

WO2006121118 A1 (2006, MITSUBISHI PLASTICS INC) discloses a heat-shrinkable film, which is made from a composition comprising: PLA (a) and a (meth) acrylic resin (b), where the weight ratio (a)/(b) is 95/5–50/50; or PLA (a) and a silicone/acrylic composite rubber (c), where the weight ratio (a)/(c) is 95/5–50/5; or has at least one layer made from the mixed resins and which exhibits a heat shrinkage percentage of at least 20% in the main shrinkage direction when dipped in water at 80 °C for 10 s. The heat-shrinkable film is claimed to be excellent in mechanical characteristics, such as heat-shrinkage characteristics, impact resistance, and transparency, and in the finish of shrinkage and which is suitable for shrink packaging, shrink bundling, and shrinkable labels.

3. Making the film in multilayer with different material having better toughness than PLA

   JP2008044363 A (2008, MITSUBISHI PLASTICS IND) discloses a heat-shrinkable laminated film having at least two layers, wherein the first layer contains, as a main component, a PLA composed of a copolymer of a D-lactic acid and an L-lactic acid, and the second layer contains, as main components, an EVA copolymer and a polyolefin, preferably a polypropylene. The film is stretched at least in one direction. The film has a heat-shrinkage ratio of at least 20% in a main shrinkage direction when the film is immersed in warm water of 80 °C for 10 s. The disclosed laminated film has heat-shrinkable characteristics, transparency, and shrink finish characteristics and can be attached as a heat-shrinkable label on a plastic container.

   Furthermore, **US2007116909** A1 (2007, PLASTIC SUPPLIERS INC) discloses in one of its embodiments a heat-shrinkable PLA film exhibiting heat-induced shrinkage in the transverse direction with little to no concomitant shrinkage in the machine direction. The film may comprise any grade of PLA, optionally including additives, such as antiblock, slip, plasticizers, viscosity enhancers, and combinations thereof. The PLA film is manufactured by the cast and tenter method, which includes four essential steps: extrusion, casting, temperature conditioning, and stretching.

   Cast and tenter processing involves the extrusion of PLA melted through a slot or flat die to form a thin, molten sheet or film. This film is first "polished" by the surface of a chill roll (typically temperature-regulated and chrome-plated). The film is then rolled through a machine direction orienting ("MDO") machine for temperature conditioning and stretched through a tenter frame either simultaneously or sequentially. Finally, the film edges are slit before winding. Figure 10.3 is a schematic diagram of the movement of polymer film from a die through casting and MDO machines and then to a tenter machine in accordance with one embodiment of the present invention. The pathway through the casting machine and tenter machine is illustrated with arrows. A general outline of the respective machines is provided by dashed lines. Circles represent rollers.

   US2012142854 A (2012, BONSET AMERICA CORP) discloses a biodegradable heat-shrinkable film comprising PLA (70–90 wt%) and a dual-purpose plasticizer and toughness enhancer additive (30–10 wt%). The disclosed heat-shrinkable PLA film is suitable for use as sleeve labels.

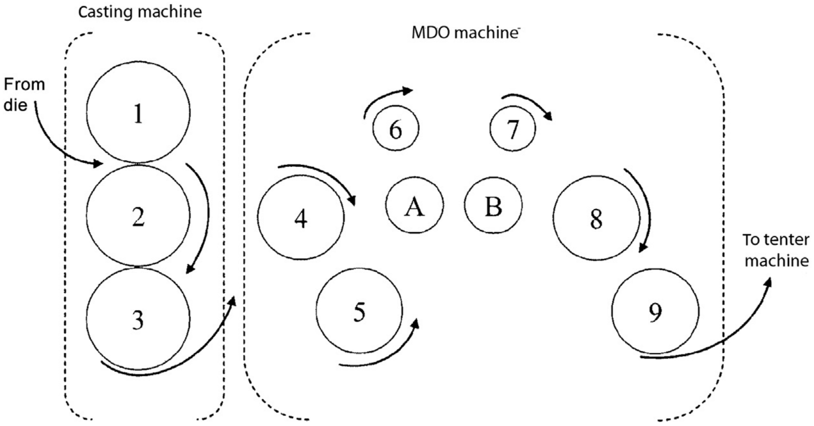


FIGURE 10.3 Schematic diagram of the movement of the PLA film from a die through casting and machine direction orienting (MDO) machines and then to a tenter machine (2007, **US2007116909** A1, PLASTIC SUPPLIERS INC). 1,2, casting rollers at 30–40 °C; 3, casting roller at 55–60 °C; 4, roller at approximately 72 °C; 5,8, rollers at approximately 85 °C; 6,7, idle rollers; no temperature controlled; 9, roller at approximately 60 °C; A, B, central rollers.

CN102993653 A (2013, ZHANGJIAGANG CHAINENG BIOLOG TECHNOLOGY CO LTD) discloses a heat-shrinkable film obtained by melt extrusion a composition comprising 95–99.5 wt% of a PLA-based component and 0.5–5 wt% of a plasticizer. The PLA-based component is prepared through mixing of PLA having a weight-average molecular weight (M_w) of 20,000–250,000, polybutylene adipate glycol having a M_w of 6000–100,000 and PCL having a M_w of 30,000–200,000, according to a weight ratio of 1/0.05-1/0.05-1, and the plasticizer is a polyethylene glycol *m*-phthalate copolymer having a number-average molecular weight (M_n) of 8000–10,000 and a T_m of 110–150 °C.

10.1.3 Porous Films

Porous films are typically formed by compounding a specific proportion of an organic or inorganic incompatible particle with a polymer that is extruded and then subjected to unidirectional or bidirectional stretching. Commonly used fillers include talc or calcium carbonate. Films prepared from these fillers appear white or silvery as the voids around the talc or calcium carbonate affect transmission of light through the film. These porous films are mainly used for leakproof films for sanitary materials, such as disposable paper diapers and packaging materials (e.g., as wrappers for candy bars, bags for salty snacks like potato chips, packages for medicines), and are generally applied to so-called throw away uses where the films are abandoned immediately after use.

EP0510998 A2 (1992) and **JPH0827296** A (1996) of MITSUI TOATSU CHEMICALS discloses a porous film formed by melt-extruding into a film a mixture consisting of 100 pbw of a PLA-based composition containing 80–95 wt% of PLA or its copolymer and 20–5 wt% of a plasticizer selected from triethyl acetylcitrate and tributyl acetylcitrate; and 40–250 pbw of a fine powder filler having an average particle size of 0.3–4 μm; then stretching the film by 1.1–10 times in at least an axial direction. The porous film is useful for packaging or filter material.

JP2003082140 A (2003) and **JP2004149679** A (2004) of UNITIKA LTD disclose porous films produced by biaxially stretching a melt-extruded film comprising PLA, an aliphatic aromatic copolyester, a fine powder filler, and a common plasticizer. A suitable filler is barium sulfate, calcium carbonate, and/or magnesium oxide. The plasticizer is selected from aliphatic multivalent carboxylates, aliphatic polyhydric alcohol esters, aliphatic polyhydric alcohol ethers, and oxyacid esters. The porous films have a porosity of ≥10%.

JP2007112867 A (2007, KAO CORP) discloses a porous film that is produced by stretching at least uniaxially a film comprising PLA, a filler, and a common polyester-based plasticizer.

According to **WO2012023465** A1 (2012, TORAY INDUSTRIES), the techniques described in **JP2007112867** A and **JP2004149679** A are not sufficiently effective in improving moisture permeability, although able to a certain extent, and resultant films are poor in heat resistance and bleed-out resistance.

JP2007254509 A (2007, ASAHI KASEI CHEMICALS CORP) discloses a PLA porous film having a water vapor transmission rate at 38 °C in 90% RH of at least 10,000 g μm/(m^2 day), an apparent density of at most 1.10 g/cm^3, and an absolute value of an orientation degree of at most 0.15, and is obtained by treating PLA molded item having a crystallinity of at most 30% with a mixed solvent of at least two solvents having a different penetration degree into the amorphous part of the PLA.

KR101030231 B1 (2011, FOLLRI SCIEN TEC CO LTD) discloses a PLA-based porous film prepared by melt extruding a composition comprising 100 pbw of PLLA, 5–500 pbw of PDLA and 0.1–10 pbw of nano inorganic particles having an average particle diameter of 10–500 nm to form a film; and forming pores on the film by laser or mechanical punching so that oxygen permeability is 5000–50,000 cc/m^2 day atm.

WO2012023465 A1 (2012, TORAY INDUSTRIES) discloses a porous film comprising 100 pbw of a blend consisting of (1) PLA (10–95 wt%) and (2) a thermoplastic polymer (5–90 wt%) that is not PLA, and 1–400 pbw of a filler. The porous film has a porosity of 1–80%. The presence of polymer (2) ensures improved flexibility and moisture permeability. Exemplary polymers (2) include PBAT (Ecoflex® FBX7011, BASF), PBS (GSPla® AZ91T, Mitsubishi Chemical Corporation), and PBSA (Bionolle® 3001, Showa Highpolymer Co Ltd). The PLA-based porous film is claimed to have high flexibility, moisture permeability (>1000 g/m^2 day), heat resistance, and bleed-out resistance (mass loss ratio after hot-water treatment ≤10%). The PLA porous film can be used preferably in applications that require flexibility, moisture permeability, and heat resistance. Specific applications include medical and sanitary supplies, clothing materials, and packaging materials.

10.2 LAMINATES

Laminates is another means, alternative to blends, to improve properties of individual polymers, such as gas barrier properties, water resistance, abrasion resistance, and printing. Polymer laminates are manufactured particularly for the needs of the packaging industry. Food packaging containers, in particular, require laminates with two or more polymer layers, one of which can have good gas and/or vapor barrier properties against substance migration, whereas another layer is acting as a layer improving adherence of different layers to each other, and the third has suitable surface properties for heat sealing or is compatible to the food stuff to be in contact with it. Furthermore, the superimposed polymer layers can be placed on top of a cellulose-based basic layer providing the required strength to the material, and this layer can be paper or board (e.g., paper with suitable outer surface properties for printing, greaseproof paper, or liquid packaging board, folding boxboard, or sack paper).

Films and laminates used for packaging create huge amounts of waste, which are difficult to handle and dispose properly. With the growing environmental awareness, there is a tendency to replace the conventional film-forming polymeric materials, such as polyethylene or poly(ethylene terephthalate) with biodegradable polymers. The problem with biodegradable polymers is, however, that, as such, they are often unsuitable for use as packaging materials, which require strength and specific properties. Therefore, biodegradable polymer layers are combined with other polymer layers, which may be biodegradable or non-biodegradable, in multilayered structures, which have a combination of properties, including enhanced biodegradability.

Most biodegradable laminates are produced by either co-extrusion or adhesive lamination. The second type of biodegradable laminates is described in Chapter 12: Composites; Section 12.5: Bonding. Preformed Biopolymers to the Same or Other Solid Material. Heat shrinkable laminated films are discussed in section: 10.1.2, subsection: 3.

Laminate structures containing biodegradable polymers, and their industrial manufacture, are often impaired by the poor strength and difficult processability of biodegradable polymers (**WO9901278**, 1999, UPM KYMMENE OYJ).

Various multilayer structures have been developed based on PHAs. For example, **EP0603876** A1 (1994, BUCK CHEM TECH WERK) discloses a biodegradable packaging material with a core layer of PVOH acting as an oxygen barrier, and on both sides of the core layer P3HB and/or poly(3-hydroxyvalerate) (PHV) or PHBHV acting as a water vapor barrier. This three-layer structure is further coated on both sides with a layer of cellulose derivative or paper (e.g., with a cellulose derivative on the side in contact with aqueous food stuff), and with paper on the outmost outer surface. The purpose of the layers of PHAs, P3HB, PHV, or PHBHV on both sides of the layer of PVOH with poor water resistance is to protect this oxygen barrier layer from the damaging effect of water.

WO9901278 A1 (1999, UPM KYMMENE OYJ) discloses a biodegradable laminate with a cellulose-based basic layer (1), which provides the product its strength; and on top of the basic layer (1) two or more polymer layers at least one of which is PHA, such as P3HB or PHBHV. Next to the PHA layer (2) and attached to it there is a layer (3) of biodegradable poly(ester amide) (e.g., BAK® 1095, Bayer AG) or biodegradable starch derivative. All the layers that are brought together to form the laminate are compatible and have good runnability in co-extrusion. They combine to provide a structure having adequate strength and barrier properties but remain biodegradable (Figure 10.4).

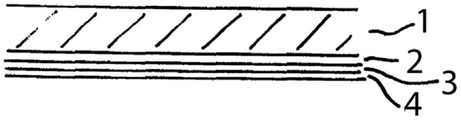


FIGURE 10.4 Schematic perspective view of the biodegradable laminate (1999, **WO9901278** A1, (UPM KYMMENE OYJ). 1: cellulose-based basic layer, 2: PHA layer, 3: polyester amide, 4: PHA layer.

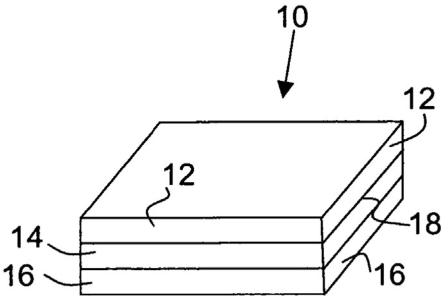


FIGURE 10.5 Schematic perspective view of the inventive laminate (2006, **US2006051603** A1, INT PAPER CO). 10, biodegradable laminate; 12, substrate; 14, 16, first and second copolyester layers; 18, substrate surface.

US2006051603 A1 (2006, INT PAPER CO) discloses a biodegradable laminate (10), as shown in Figure 10.5, comprising a paper-based substrate (12) laminated with first copolyester layer(s) (14) and second copolyester layer(s) (16) on at least one surface (18). The first layer is an inner layer providing adhesion to the paper-based substrate, and the second layer is an outer layer preventing chill roll sticking and blocking in the roll and providing greater thermal stability compared with the first layer. The first copolyester is preferably an aliphatic-aromatic copolyester, such as poly(butylene adipate-*co*-terephthalate) (PBAT); commercially available products are Ecoflex® (BASF AG) or Eastar Bio (Eastman Chemical Co). The second copolyester is preferably poly(trimethylene terephthalate) partly derived from renewable resources; a commercially available product is Biomax (DuPont).

EP0514137 A2 (1992, MITSUI TOATSU CHEMICALS) discloses a laminate comprising a regenerated cellulose film (cellophane) as a substrate coated with an aqueous gelatin acting as an adhesive, and on top a PLA layer. Other suitable biodegradable substrates are leather, cloth, or fibers. Alternative biodegradable adhesives are glue, gelatin, casein, and starch.

DE10104829 A1 (2002, BASF AG) discloses a multilayer polymer film comprising a first layer consisting of biodegradable polyester with a T_m of 80–200 °C, small amounts of beeswax and/or Montana wax and lubricant, and optionally mineral anti-blocking agent, and a second layer consisting of biodegradable polyester with a T_m of 40–80 °C and optionally polyester, wax, and/or lubricant, as above. Preferably, the first layer is made of aliphatic-aromatic polyester(s) and the second layer is made of PCL.

WO02088230 A1 (2002, TRESPAPHAN GMBH) discloses a multilayer film design using a PLA base layer formulated with a cyclic polyolefin copolymer (COC) (0.5–30 wt%) as a cavitating agent to produce an opaque biaxially oriented PLA film.

Example: An opaque film having characteristic mother-of-pearl-like gloss and thickness 30 μm was obtained by extrusion and subsequent stepwise orientation in the machine and transverse directions. This layer was built up from approximately 95 wt% PLA having a $T_m = 135$ °C and an MFI = 3 g/10 min and a $T_g = 60$ °C and approximately 5 wt% of COC (Topas 6013, Ticona & Topas Advanced Polymers, Inc.) having a $T_g = 140$ °C. The layer additionally comprised stabilizers and neutralizers in conventional amounts.

JP2008265117 A (2012, DAINIPPON PRINTING CO LTD) discloses a multilayered laminate product comprising a light barrier film of PBS layer containing a black pigment. Alternatively, the multilayered laminated film has at least a light barrier PBS layer consisting of a PBS-based composition containing black pigment and white pigment and characterized in that the content of the black pigment is 0.1–5.0 wt% of PBS and the content of the white pigment is 1–30 times of that of the black pigment. The black pigment consists of iron black, graphite, or black type pigment that contains carbon black. The white pigment consists of basic lead carbonate, basic lead sulfate, basic silicic acid lead, zinc white, zinc sulfide, lithopone, antimony trioxide, anatase type titanium oxide, or rutile type titanium oxide. Such a layer would only be suitable for providing a fat and aroma barrier, but the barrier properties with regard to oxygen and water vapor are not sufficient for many high-barrier applications. The disclosed multilayer laminated film is claimed to be suitable for storage of food.

US2009155611 A1 (2009, INTERNATIONAL PAPER COMPANY) discloses a film including a core layer of PLA, PHA, or another renewable polymer, with a layer composed of a heat-resistant polymer, such as polypropylene, substantially surrounding this core layer. Such a formulation is particularly suitable for the transport or storage of PLA through or in hot areas where a high temperature may cause PLA without such an outer layer to deform due to heat. However, the patent does not contemplate such a formulation with an outer PHA skin layer, nor does it contemplate metallization of such a film with superior gas and moisture barrier properties, nor such a film with a biodegradable, metal receiving layer.

WO02088230 A1 (2002, TRESPAPHAN GMBH) discloses a multi-layer film design using a PLA base layer formulated with a COC as a cavitating agent to produce an opaque, biaxially oriented PLA film. However, this patent does not contemplate metallization of such a film with superior gas and moisture barrier properties, nor such a film with a degradable, non-PLA metal receiving layer.

JP2006130848 A (2006, TOHCELLO CO LTD) discloses a biaxially stretched polyester laminate constituted of a biaxially stretched sulfonate group-containing aromatic polyester film and a biaxially stretched PGA film. As an example of a stretching process, both PGA and sulfonate group-containing aromatic polyester are co-extruded, the resultant laminated sheet is stretched in a machine direction by stretching rolls at a stretching temperature of 55–70 °C, and the resultant uniaxially oriented film is then stretched in a transverse direction by a tenter at a temperature of 60–90 °C. The disclosed biaxially stretched polyester film is claimed to be excellent in heat resistance and gas barrier properties and has transparency and biodegradability.

JP2006130847 A (2006, TOHCELLO CO LTD) discloses a biaxially stretched polyester multilayered polyester manufactured by co-extruding PGA and PLA and stretching the formed laminated film under the specific stretching conditions.

WO2013080788 A1 (2013, TORAY INDUSTRIES) discloses a laminate sheet having a layer (A) that is formed of a composition (A1) containing a PLA and a layer (B) that is formed of a composition (B1) containing poly(meth) acrylate, an ionic surfactant and a nonionic surfactant. The laminate sheet is characterized in that at least one outermost layer of the sheet is composed of the layer (B); the content of the acrylic resin is 50–99.5 wt% (inclusive) in 100 wt% of the whole composition (B); and the weight ratio of the ionic surfactant to the nonionic surfactant 2–25. The laminate sheet is claimed to have excellent heat resistance, antistatic properties, transparency, and blocking resistance and be particularly suitable for uses in molded articles that are subjected to printing.

JP2008155385 A (2008, YAMATO ESURON KK) discloses a laminated film, as shown in Figure 10.6, produced by laminating a PLA film on each of the surfaces of a polyamide film obtained by the polycondensing *m*-xylylenediamine and adipic acid (MX nylon 6007, Mitsubishi Gas Chemical Co), or an ethylene-vinyl alcohol copolymer

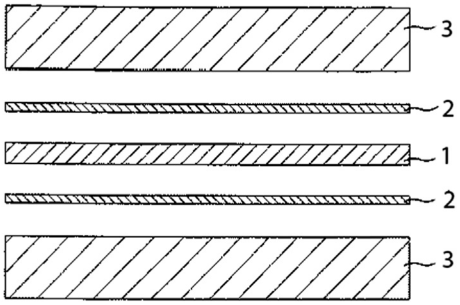


FIGURE 10.6 Laminated film (2008, **JP2008155385** A, YAMATO ESURON KK). 1: intermediate film, 2: adhesive film (EVOH, polyamide), 3: surface film (PLA).

(EVOH) film by means of an unsaturated carboxylic acid-α-olefin or cyclic olefin copolymer adhesive film. The laminated film is vacuum or pressure formed to obtain a food storage container.

Example: An adhesive film of thickness 10 μm, formed from an acid-modified polyolefin (Modic F534, Mitsubishi Chemical Corp), was interposed on both surfaces of an intermediate film made of EVOH (Eval F101A, Kuraray Co., Ltd.). The intermediate film had a thickness of 50 μm. Then, a surface film was bonded to the adhesive film. The surface film was formed using PLA (Lacea H440, Mitsui Chemicals, Inc.) and had a thickness of 215 μm. Thus, a laminated film was formed. The obtained laminated film was molded to form a container. The obtained container had an excellent appearance and was transparent. Jam was filled in the container and was sealed using an aluminum lid. The jam was left at 40 °C for 120 h, and discoloration of jam was investigated. The jam was not discolored, and the container had excellent weather resistance.

JPH08290526 A (1996, NIPPON FOIL MFG) discloses an aluminum-coated biodegradable polymer laminate. As the aluminum material, aluminum foil, aluminum-deposited layer, or the like is used. The biodegradable polymer is in the form of a film, an adhesive, or an ink. As the biodegradable polymer, PHBHV or PLA is used. The disclosed laminate is easily decomposed when disposed in the ground. The biodegradable polymer generates an acid during decomposition. The acid acts on the aluminum material to convert it into aluminum oxide, whereupon the aluminum material is decomposed and disappeared.

US2005287358 A1 (2005, INGLIS THOMAS L) discloses biaxially oriented multilayer co-extruded PLA films with a PLA skin layer containing 0.05–0.6% of crosslinked polymer antiblock spherical particles. The spherical particles are preferably crosslinked polymethylsilsesquioxane or crosslinked acrylic resin. In a preferred method, the film surface opposite the skin layer containing the spherical particles is vacuum metalized with a deposited aluminum. Surfaces of the film are subjected to corona, flame, or plasma treatment. The disclosed PLA film is claimed to exhibit improved coefficient of friction, blocking resistance, reduced static generation, improved winding, and improved package formation on packaging machines.

US2009148713 A (2009, TORAY PLASTICS AMERICA INC) discloses a laminate film, including a core layer of PLA and a skin layer comprising a polyolefin metal receiving layer. The metal receiving layer, the core layer, or both may be blended with an amount of polar-modified tie-resin to improve bonding. Alternatively, a discrete tie-resin layer may be interposed between the polyolefin metal receiving layer and the crystalline PLA core layer. The polyolefin metal receiving layer may be discharge treated on the side opposite the core layer and metalized. This polyolefin metal receiving layer can improve moisture barrier properties after metallization. However, such a hybrid structure is not 100% biodegradable.

WO2010151872 (2010, TORAY PLASTICS AMERICA INC) discloses a biaxially oriented multilayer film comprising a skin layer of P3HB, a core layer of PLA, and a sealant layer with a metal deposited on one surface of the skin layer of P3HB. This metalized co-extruded film exhibits improved moisture barrier property versus a metalized, non-P3HB-*co*-extruded PLA film.

WO2013047285 A1 (2013, NEC CORP) discloses a case for electronic devices, which comprises the following: a base that is mainly formed of PLA, a close adhesion layer that is coated over the base and is mainly formed of PLA, a resin layer that exhibits good adhesion to the close adhesion layer and can be plated with a metal, and a metal plating that is provided on the resin layer. The disclosed molded body is claimed to have sufficient electromagnetic shielding performance and exhibit good adhesion to the metal plating.

JPH60287347 A (1994, MITSUI TOATSU Chapters EMICALS) and **JPH9263651** A (1997, DAINIPPON INK & CHEMICALS) disclose biodegradable laminates in each, of which a biodegradable non-foam layer made of PLLA is laminated on the surface layer of a biodegradable foam article made also of PLLA.

JP2000109045 A (2000, JUJO CENTRAL KK) discloses a heat-insulating paper cup in which a biodegradable foam article, a sheet of paper, and a sheet of biodegradable film are laminated in this order.

WO2011032727 A1 (2011, HUHTAMAKI FORCHHEIM) discloses a predominantly biodegradable double-separating film comprising at least one carrier layer (1) that is based on at least one biodegradable polymer, and at least one release layer (2) that is based on at least one cured polysiloxane. The curing of said release layer is based, at least partially, on at least one crosslinked monomer or oligomer additive. Said additive also promotes adhesion between the carrier layer (1) and the release layer (2), and has no siloxane groups but does have at least two functional groups, of which at least one is a functional group with at least one carbon double bond.

PATENTS

Patent Number	Publication Date	Family Members	Priority Numbers	Inventors	Applicants	Title
CA2076038 A1	19910822	WO9113207 A1 19910905; US5451456 A 19950919; CA2076038 C 20010327	CA19902076038 19900221; WO1990CA00058 19900221	MARCHESSAULT ROBERT HENRY; LEPOUTRE PIERRE F; WRIST PETER E	PULP PAPER RES INST; UNIV MCGILL	Poly-β-hydroxyalkanoates for use in fiber constructs and films.
CN102993653 A	20130327		CN20111270631 20110914	BIAN ZHONGHUA	ZHANGJIAGANG CHAINENG BIOLOG TECHNOLOGY CO LTD	Biodegradable heat-shrinkable material, biodegradable heat-shrinkable film and preparation method of biodegradable heat-shrinkable film.
DE10104829 A1	20020808		DE2001104829 20010201		BASF AG	Mehrschichtige Polymerfolie. "Multilayer polymer film."
EP0032802 A1	19810729	US4337181 A 19820629; JPS56149444 A 19811119; EP0032802 B1 19850424; CA1171579 A1 19840724	US19800112980 19800117	OTEY FELIX HAROLD; WESTHOFF RICHARD	US AGRICULTURE	Flexible, self-supporting and biodegradable films and their production.
EP0058480 A1	19820825	JPS57152893 A 19820921; EP0058480 B1 19850626	GB19810004312 19810212	BARHAM PETER JOHN; SELWOOD ALAN	ICI PLC	Extraction of poly(beta-hydroxybutyric acid).
EP0078609 A2	19830511	US4427614 A 19840124; EP0078609 A3 19850807; EP0078609 B1 19870506	GB19800014256 19800430; GB19810000326 19810107; GB19820008577 19820324	BARHAM PETER J; HOLMES PAUL A	ICI PLC	3-Hydroxybutyric acid polymers.
EP0226439 A1	19870624	US4880592 A 19891114; US4826493 A 19890502; MX169228 B 19930625; JPS62209144 A 19870914; JPH0674340 B2 19940921; GR3002778 T3 19930125; EP0226439 B1 19910828; CA1288922 C 19910917; BR8605989 A 19870915; AU6601286 A 19870611; AU603076 B2 19901108; AT66685 T 19910915; AR245159 A1 19931230	GB19850030324 19851209; GB19850030325 19851209; GB19850030326 19851209; GB19850030327 19851209; GB19850030328 19851209; GB19850030329 19851209	MARTINI FRANCESCO; PERAZZO LUIGI; VIETTO PAOLO	GRACE W R & CO	Polymeric products and their manufacture.
EP0510998 A2	19921028	US5340646 A 19940823; EP0510998 A3 19930203; EP0510998 B1 19960904; DE69213304 T2 19970306	JP19910096538 19910426	MORITA KENJI; UCHIKI KOHICHI; SHINODA HOSEI	MITSUI TOATSU CHEMICALS	Porous film.

Continued

—Cont'd

Patent Number	Publication Date	Family Members	Priority Numbers	Inventors	Applicants	Title
EP0514137 A2	19921119	US5434004 A 19950718; EP0514137 A3 19930407; EP0514137 B1 19980318; EP0514137 B2 20070725; DE69224772 T2 19980910; DE69224772 T3 20080228; CA2068368 A1 19921114	JP19910107052 19910513; JP19910199164 19910808	AJIOKA MASANOBU; YAMAGUCHI AKIHIRO; ENOMOTO KATASHI; SHINODA HOSEI	MITSUI CHEMICALS INC	Degradable laminate composition.
EP0603876 A1	19940629	SK146393 A3 19940907; PL301609 A1 19940627; DE4244000 A1 19940630	DE19924244000 19921223	SCHROETER JOHANNE; KAMMERSTETTER HERIBERT	BUCK CHEM TECH WERKE	Biologisch abbaubarer Verpackungswerkstoff. "Biodegradable packaging material."
EP0736563 A1	19961009		EP19950105261 19950407	DE MICHELI CLAUDIO; NAVARINI FRANCO; RONCORONI VITTORIO	SAFTA SPA	Process for the manufacture of totally bio-decomposable films with high mechanical characteristics and relevant products and applications.
EP0803532 A1	19971029		EP19960106387 19960423	MOTIKA STEPHEN ANDREW; ROKICKI ANDRZEJ	PAC POLYMERS INC	Oxygen-barrier articles.
EP0805175 A1	19971105	US5853639 A 19981229; KR100233184 B1 19991201; JPH1060136 A 19980303; JP3731838 B2 20060105; EP0805175 B1 20040922; DE69730771 T2 20050929	JP19960134217 19960430; JP19970105160 19970408	KAWAKAMI YUKICHIKA; SATO NOBUO; HOSHINO MITSURU; KOUYAMA TOSHITAKA; SHIIKI ZENYA	KUREHA CHEMICAL IND CO LTD	Oriented polyglycolic acid film and production process thereof.
EP0805176 A1	19971105	US5908917 A 19990601; KR100244057 B1 20000201; JPH1060137 A 19980303; JP4073052 B2 20080409; EP0805176 B1 20040929; DE69730897 T2 20051006	JP19960134218 19960430; JP19970105161 19970408	KAWAKAMI YUKICHIKA; SATO NOBUO; HOSHINO MITSURU; KOUYAMA TOSHITAKA; SHIIKI ZENYA	KUREHA CHEMICAL IND CO LTD	Polyglycolic acid sheet and production process thereof.
EP2551301 A1	20130130	WO2013017431 A1 20130207; CN103703077 A 20140402; CA2840783 A1 20130207	EP20110175967 20110729	LOOS ROBERT; YANG XIN; AUFFERMANN JORG; FREESE FRANZISKA	BASF SE	Biologisch abbaubare Polyesterfolie. "Biodegradable polyester film."
GB2243327 A	19911030		GB19900003537 19900216	CRACCO FRANCIS JEAN; HALE PETER		Biodegradable, liquid-impervious sheet laminate.
GB965349 A	19640729		US19610159752 19611216		DEPARTMENT OF AGRICULTURE AND INSPECTION	Improvements in the extrusion of amylosic material.
JP2000109045 A	20000418		JP19980293068 19980930	OMORI KEIICHI	JUJO CENTRAL KK	Heat insulation paper cup.

JP2001226571 A	20010821	JP4583537 B2 20101117	JP20000035811 20000214	TAYA NAOKI; SATANI SHOICHI; TAYAUCHI MASATO	C I KASEI CO LTD	Polylactic acid based resin material and heat-shrinkable film.
JP2002146170 A	20020522	JP3410075 B2 20030526	JP20000351238 20001117	MIYAKE MUNEHIRO	UNITIKA LTD	Crystalline polylactic acid resin composition and film and sheet using the same.
JP2002234117 A	20020820	JP3718636 B2 20051124	JP20010032589 20010208	HIRUMA TAKASHI; TERADA SHIGENORI	MITSUBISHI PLASTICS IND	Heat-shrinkable film-like article.
JP2003082160 A	20030319		JP20010273348 20010910	OSAKI MISA; HONDA KEISUKE ARANISHI YOSHITAKA	TORAY INDUSTRIES	Thermally plasticized cellulose ester composition and fiber composed of the same.
JP2003103628 A	20030409		JP20010302929 20010928	YOSHIDA SHIGETO; ODA NAONOBU; KOBAYASHI HISATO	TOYO BOSEKI	Method for manufacturing lactic acid type polyester biaxially stretched film.
JP2003103632 A	20030409		JP20010304820 20011001	AYAUCHI MASATO; SHIRAISHI AKIHIKO; SATANI SHOICHI	KASEI CO C I	Heat-shrinkable polylactic acid film.
JP2004002776 A	20040108	JP3655619 B2 20050602	JP20030093526 20030331; JP20020099541 20020402	HIRUMA TAKASHI	MITSUBISHI PLASTICS IND	Thermally shrinkable polylactic acid film.
JP2004149679 A	20040527		JP20020316913 20021031	HIOKI MASANOBU; NISHIMURA HIROSHI	UNITIKA LTD	Biodegradable porous film and manufacturing method therefor.
JP2004277682 A	20041007	JP4316285 B2 20090819	JP20030113445 20030314	AKIMOTO MIKIO; ICHIKAWA KENGO; NAGASAWA KAZUYUKI	TOHO CHEM IND CO LTD	Modified biodegradable resin.
JP2006063308 A	20060309		JP20040031569 20040209; JP20040031570 20040209; JP20040213951 20040722; JP20040219512 20040728; JP20050031700 20050208	MIYOSHI MASANAO; WATANABE TAKAKO; ARIME MORITATSU	KASEI CO C I	Polylactic acid film for agriculture and method for producing the same.
JP2006130847 A	20060525	JP4530809 B2 20100825	JP20040324270 20041108	SAWAI TORU	TOHCELLO CO LTD	Biaxially stretched polyester multilayered film and its manufacturing method.
JP2006130848 A	20060525	JP4916105 B2 20120411	JP20040324272 20041108	SAWAI TORU	TOHCELLO CO LTD	Biaxially stretched polyester laminated film.

Continued

—Cont'd

Patent Number	Publication Date	Family Members	Priority Numbers	Inventors	Applicants	Title
JP2006182017 A	20060713	JP5093872 B2 20121212	JP20040348564 20041201; JP20050330201 20051115	NANJO KAZUNARI	UNITIKA LTD; KUREHA CORP	Biaxially oriented film made of resin composed mainly of polyglycolic acid and its manufacturing method.
JP2007112867 A	20070510	JP4863684 B2 20120125	JP20050304353 20051019	NODA AKIRA; MIMURA KOJI; NAKANO YUKIHIRO; KASAHARA RUMIKO	KAO CORP	Porous sheet.
JP2007254509 A	20071004	JP4850550 B2 20120111	JP20060077669 20060320	KOIKE YUTAKA	ASAHI KASEI CHEMICALS CORP	Polylactic acid-based porous item.
JP2007326290 A	20071220	JP4794365 B2 20111019	JP20060159356 20060608	HIDA KAZUNORI; SATO TAKU	KUREHA CORP	Manufacturing method for polyglycolic acid resin inflation film.
JP2008044363 A	20080228	JP5037249 B2 20120926	JP20060197397 20060719; JP20070187688 20070718	TOZAKI HIROYUKI; HIRUMA TAKASHI TEJIMA TOMOJI; MIYASHITA KAZUHISA; YAMADA TAKEMIKI; TAKAGI JUN	MITSUBISHI PLASTICS IND	Heat-shrinkable laminated film, molding using the same, heat-shrinkable label, and container provided with the molding or the heat-shrinkable label.
JP2008155385 A	20080710		JP20060343673 20061221	MATSUNAGA KEIJI	YAMATO ESURON KK	Food storage container and laminated film.
JP2008265117 A	20081106	JP5212685 B2 20130619	JP20070109996 20070419	UEKI TAKAYUKI; OSONE SATOSHI; MITA KOZO	DAINIPPON PRINTING CO LTD	Multilayered laminated film.
JP2009138085 A	20090625	JP5061868 B2 20121031	JP20070315382 20071206	MATSUMOTO HIROSHIGE; HOCHI MOTONORI; YOSHIDA TAKASHI	TORAY INDUSTRIES	Polylactic acid-based film.
JPH06256480 A	19940913		JP19930043904 19930304		TOYO BOSEKI	Biodegradable packaging film.
JPH06256481 A	19940913		JP19930045275 19930305	KIMURA KUNIO; ITO TAKESHI; AOYAMA TOMOHIRO; UNO KEIICHI	TOYO BOSEKI	Biodegradable agricultural film.
JPH06287347 A	19941011	JP3394063 B2 20030407	JP19930074228 19930331	SUZUKI KAZUHIKO; WATANABE TAKAYUKI; KITAHARA YASUHIRO; AJIOKA MASANOBU	MITSUI TOATSU CHEMICALS	Molded lactic-acid-based polymer foam and its production.

JPH07173271 A	19950711	JP3302145 B2 20020715	JP19930319488 19931220	KAMEOKA TAIJI; KASHIMA TAKESHI; AJIOKA MASANOBU; YAMAGUCHI TERUHIRO; SUZUKI KAZUHIKO	MITSUI TOATSU CHEM INC	Degradable film.
JPH07177826 A	19950718	JP3347440 B2 20021120	JP19930323740 19931222	SUGA KEIKO; IMON SHUHEI; MORIYA SHINOBU; KUROKI TAKAYUKI; SHINODA NORIMASA	MITSUI TOATSU CHEMICALS	Agricultural film.
JPH0811206 A	19960116		JP19940152525 19940705	TATEISHI KENJI; UEDA AKIHIKO	OKURA INDUSTRIAL CO LTD	Manufacture of biodegradable aliphatic polyester film.
JPH08150658 A	19960611		JP19940315987 19941125	AKAMATSU YOSHIMI	NIPPON SYNTHETIC CHEM IND	Inflation film forming method.
JPH08188706 A	19960723		JP19950035821 19950112	MORIKAWA AKIRA; SUGIMOTO MARIKO	GUNZE KK	Garbage bag formed of biodegradable plastic.
JPH0827296 A	19960130	JP3359744 B2 20021224	JP19940162464 19940714	SHINODA NORIMASA; MORITA KENJI; CHIKI KOICHI	MITSUI TOATSU CHEMICALS	Porous film and its production.
JPH08290526 A	19961105		JP19960058393 19960220; JP19950055082 19950220	YAMADA TOSHIO	NIPPON FOIL MFG	Aluminum-biodegradable plastic laminated body.
JPH09151310 A	19970610		JP19950253063 19950929; JP19950222126 19950830; JP19950244012 19950922; JP19950253064 19950929; JP19960215599 19960815	TOKUSHIGE YUJI; NAKAMURA NORIO; TANIFUJI YOICHI; UEDA SHUHEI	SHINETSU CHEMICAL CO	Polymer composition having biodegradability and shrink film.
JPH09169896 A	19970630		JP19960219701 19960821; JP19950245014 19950925; JP19950253066 19950929; JP19950267243 19951016; JP19950267244 19951016	TOKUSHIGE YUJI; OURA MAKOTO; NAKAMURA NORIO; UEDA SHUHEI	SHINETSU CHEMICAL CO	Biodegradable polymer composition and shrink film.
JPH09233956 A	19970909		JP19960043262 19960229	TASHIRO TAKESHI; YASUI MITSUO; OYAMA KANAKO; YAMAOKA HIROAKI; MIYAZAKI KEIKO	MITSUBISHI CHEM MKV CO; MITSUBISHI CHEM CORP	Expansion film for agriculture.

Continued

—Cont'd

Patent Number	Publication Date	Family Members	Priority Numbers	Inventors	Applicants	Title
JPH09235360 A	19970909	JP3211651 B2 20010925	JP19960043261 19960229	TASHIRO TAKESHI; YASUI MITSUO; OYAMA KANAKO; YAMAOKA HIROAKI; MIYAZAKI KEIKO; SUGIMOTO NOBUNARI	MITSUBISHI CHEM MKV CO; MITSUBISHI CHEM CORP; MITSUBISHI KAGAKU FOODS KK	Mulching film for agriculture.
JPH9263651 A	19971007	JP3772426 B2 20060510	JP19950319005 19951207; JP19960301768 19961113; JP19950309011 19951128; JP19960011782 19960126	KAKIZAWA YASUTOSHI; SHIKATA NORIKI	DAINIPPON INK & CHEMICALS	Foam and laminate.
KR101030231 B1	20110422		KR20100097470 20101006	JEON SEUNG HO; PARK JONG; LEE JONG SEONG	FOLLRI SCIEN TEC CO LTD	Low carbon environment-friendly polylactic acid film freshness-keeping film.
KR20090008110 A	20090121		KR20080035785 20080417	YOU YOUNG SUN; KIM MAN SOO; PARK KI MOON; CHEONG MYUNG SU	YOU YOUNG SUN; KIM MAN SOO	Nature biodegradable sheet manufactured by improved process and method for manufacturing the same.
KR20090008111 A	20090121	KR100955024 B1 20100427	KR20080035823 20080417	JIN MYONG SONR; YOU YOUNG SUN; PARK KI MOON; CHEONG MYUNG SU	ENFORECO CO LTD; YOU YOUNG SUN	Nature biodegradable sheet manufactured by improved process and method for manufacturing the same.
US20020052445 A1	20020502		US19980175562 19981020; US20000566625 20000508	TERADA SHIGENORI; TAKAGI JUN	TERADA SHIGENORI; TAKAGI JUN	Biodegradable film.
US2005287358 A1	20051229	US7368160 B2 20080506; CA2472420 A1 20051223; CA2472420 C 20111108	CA20042472420 2004062	INGLIS THOMAS L	INGLIS THOMAS L	An improved packaging film.
US2006045940 A1	20060302	WO2006026546 A2 20060309; WO2006026546 A3 20070426; US2010056689 A1 20100304; US2007054073 A1 20070308; US2008280081 A1 20081113; US8133558 B2 20120313; US7615183 B2 20091110;	US20040605151P 20040830; US20050209808 20050824; US20040609827P 20040915; US20050672515P 20050419	TWEED EDWARD C; STEPHENS HENRY M; RIEGERT THEODORE E	PLASTIC SUPPLIERS INC	Polylactic acid blown film and method of manufacturing same.

		MX2007002442 A 20071010; ES2374740 T3 20120221; EP1793994 A2 20070613; EP1793994 A4 20080903; EP1793994 B1 20111019; DK1793994 T3 20120206; DE202005022027 U1 20120720; CA2578635 A1 20060309; CA2578635 C 20110517; AT529242 T 20111115				
US2006051603 A1	20060309	WO2006031568 A2 20060323; WO2006031568 A3 20070222; RU2363586 C2 20090810; RU2007112465 A 20081010; KR20070106679 A 20071105 JP2008513234 A 20080501; EP1793995 A2 20070613; EP1793995 A4 20081224; CA2583529 A1 20060323; BRPI0515700 A 20080729; AU2005285159 A1 20060323	US20040608258P 20040909; US20050221175 20050907	CLEVELAND CHRISTOPHER S; REIGHARD TRICIA S	INT PAPER CO	Biodegradable paper-based cup or package and production method.
US2007116909 A1	20070524	WO2007061944 A2 20070531; US2011260355 A1 20111027; US8263197 B2 20120911; WO2007061944 A3 20071122; US2012316275 A1 20121213; US2010213202 A1 20100826; US7998545 B2 20110816; US7713601 B2 20100511; EP1992468 A2 20081119; EP1954571 A2 20080813; CA2630563 A1 20070531	US20050738029P 20051121; US20060561771 20061120	TWEED EDWARD CARL; MCDANIEL JOSEPH B	PLASTIC SUPPLIERS INC	Polylactic acid shrink films and methods of casting same.
US2008147034 A1	20080619	WO2008072114 A1 20080619; US8592641 B2 20131126; US2014023806 A1 20140123; MX2009006387 A 20090623; KR20090096454 A 20090910	US20060640109 20061215	WANG JAMES H; SHI BO	KIMBERLY CLARK CO	Water-sensitive biodegradable film.
US2009148713 A1	20090611	WO2009076458 A1 20090618; US7951438 B2 20110531; EP2222459 A1 20100901; EP2222459 A4 20121205	US20080332153 20081210; US20070012645P 20071210	LEE MARK S; CHANG KEUNSUK P	TORAY PLASTICS AMERICA INC	Biaxially oriented polylactic acid film with high barrier.
US2009155611 A1	20090618	US7678444 B2 20100316	US20070002495 20071217	EDFORD JR RICHARD A; LI WEI	INTERNATIONAL PAPER COMPANY	Thermoformed article made from renewable polymer and heat-resistant polymer.

Continued

—Cont'd

Patent Number	Publication Date	Family Members	Priority Numbers	Inventors	Applicants	Title
US2009326130 A	20091231	WO2010002668 A1 20100107; WO2010002668 A8 20110317; US2013253121 A1 20130926; US2013197161 A1 20130801; US2012296045 A1 20121122; US2012296044 A1 20121122; US8268913 B2 20120918; US8546490 B2 20131001; US8444905 B2 20130521; US8372917 B2 20130212; KR20110037928 A 20110413; JP2011526949 A 20111020; EP2296879 A1 20110323; CN101918211 A 20101215	US20080165037 20080630	LI FENGKUI; COFFY TIM J; DAUMERIE MICHEL	FINA TECHNOLOGY	Polymeric blends and methods of using same.
US2011237750 A1	20110929		US201113070970 20110324; US20100316857P 20100324	REN LIQUN; LOOS ROBERT	BASF SE	Process for film production.
US2011262720 A1	20111027	US2013149511 A1 20130613; US8389107 B2 20130305	US201113182767 20110714; US201113019060 20110201; US20090410018 20090324; US20080038971P 20080324; US20100364298P 20100714	RIEBEL MICHAEL J; RIEBEL MILTON	BIOVATION LLC	Cellulosic biolaminate composite assembly and related methods.
US2012142854 A1	20120607	WO2012078315 A1 20120614; TW201229105 A 20120716		BRANDON MATTHEW VINCENT; NATSUME YOSUKE	BONSET AMERICA CORP	Poly (lactic acid) shrink film.
US2013004760 A1	20130103	WO2013006464 A2 20130110	US201213538342 20120629 US201161503710P 20110701	PELLINGRA SALVATORE	PELLINGRA SALVATORE	Biodegradable moisture barrier film.
US2013029124 A1	20130131		US201213559058 20120726; US201161512935P 20110729	LOOS ROBERT; YANG XIN; AUFFERMANN JOERG; FREESE FRANZISKA	BASF SE	Biodegradable polyester foil.
US2676945 A	19540427		US19500190877 19501018	HIGGINS NORTON A	DU PONT	Condensation polymers of hydroxyacetic acid.
US2703316 A	19550301		US19510230079 19510605	SCHNEIDER ALLAN K	DU PONT	Polymers of high melting lactide.
US3116351 A	19631231		US19620225400 19620921	WOHLRABE FRANK C; MARK ARTHUR M; ROTH WILLIAM B; MEHLTRETTER CHARLES L		Process for production of amylose film.

US3275610 A	19660927		US19640354231 19640324	COTY VERNON F	MOBIL OIL CORP	Microbial synthesis of polymers.
US4045418 A	19770830		US19750544789 19750128	SINCLAIR RICHARD G	GULF OIL CORP	Copolymers of D,L-lactide and epsilon caprolactone.
US5443780 A	19950822	JPH0623836 A 19940201	JP19920182098 19920709; US19940265348 19940624	MATSUMOTO KIYOICHI; TAHARA SHU OZEKI EIICHI; OGAITO MAKOTO; KOBAYASHI MASAKAZU	SHIMADZU CORP	Oriented films of polylactic acid and methods of producing same.
WO02087851 A1	20021107	ZA200309278 A 20040929; US2004093831 A1 20040520; US7128969 B2 20061031; MXPA03009926 A 20040129; IL157964 A 20100217; EP1395415 A1 20040310; EP1395415 B1 20101222; CA2443161 A1 20021107; CA2443161 C 20110628; AU2002310868 B2 20071129; AU2002310868 B8 20021111; AT492389 T 20110115	DE2001121151 20010430; WO2002EP04443 20020423	BUSCH DETLEF; ROSENBAUM MARLIES; ROSENBAUM MANFRED	TRESPAPHAN GMBH	Method for the production of biologically-degradable packagings made from biaxially-drawn films.
WO02088230 A1	20021107	ZA200308081 A 20041117; US2004185282 A1 20040923; US6815079 B2 20041109; MXPA03009933 A 20040129; IL158424 A 20090901; ES2283572 T3 20071101; EP1385899 A1 20040204; EP1385899 B1 20070221; DE10121150 A1 20021107; CA2445845 A1 20021107; AU2002316857 B2 20070301; AT354607 T 20070315	DE2001121150 20010430	ROSENBAUM SONJA; HAEDE PETRA; BUSCH DETLEF; KOCHEM KARL-HEINZ	TRESPAPHAN GMBH	Opake Folie aus Polymilchsäuren. "Opaque film made of polylactic acids."
WO2004087812 A1	20041014	US2007032577 A1 20070208; US7718718 B2 20100518; KR20050120675 A 20051222; KR101045446 B1 20110630, JP4600278 B2 20101215; EP1609819 A1 20051228; EP1609819 A4 20060412; EP1609819 B1 20100929; CN1768115 A 20060503; CN1768115 B 20100623; AT482999 T 20101015	P20030090085 20030328	KANZAWA TAKESHI; KOBAYASHI SADAYUKI; YOSHIDA MINORU; SAKIDA FUMIE; KUMAKI JIRO	TORAY INDUSTRIES	Polylactic acid resin composition, process for producing the same, biaxially stretched polylactic acid film, and molded articles thereof.

Continued

—Cont'd

Patent Number	Publication Date	Family Members	Priority Numbers	Inventors	Applicants	Title
WO2006098159 A1	20060921	US2008213209 A 20080904; KR20070119632 A 20071220; DE112006000594 T5 20080131	JP20050071725 20050314; JP20050249361 20050830	KANAZAWA SHINICHI; KAWANO KIYOSHI	SUMITOMO ELEC FINE POLYMER INC	Process for producing crosslinked material of polylactic acid and crosslinked material of polylactic acid.
WO2006121118 A1	20061116	US2009074999 A1 20090319; US8470420 B2 20130625; TWI387534 B 20130301; KR20090086132 A 20090810; KR100967336 B1 20100705; KR20080011321 A 20080201; KR100955437 B1 20100504; EP1887029 A1 20080213; EP1887029 A4 20080709; CN102167893 A 20110831; CN102167893 B 20121024	JP20050138473 20050511; JP20050358106 20051212; JP20050378969 20051228; JP20050379196 20051228	Hiruma TAKASHI; YAMADA TAKEYOSHI; MIYASHITA YOU; SAWA KOUICHI; TANAKA KAZUYA; TAKAGI JUN	MITSUBISHI PLASTICS INC	Heat-shrinkable film, moldings and heat-shrinkable labels made by using the film, and containers made by using the moldings or fitted with the labels.
WO2009107425 A1	20090903	US2011027590 A1 20110203; JP2009202465 A 20090910; JP4972012 B2 20120711; EP2255951 A1 20101201; CN101945749 A 20110112	JP20080047985 20080228; WO2009JP50965 20090122	ABE SHUNSUKE	KUREHA CORP	Sequentially biaxially-oriented polyglycolic acid film, production process thereof and multi-layer film.
WO2010013483 A1	20100204	US2011190430 A1 20110804; EP2330157 A1 20110608; CN102112559 A 20110629	JP20080199314 20080801	NAKAMURA NOBUO	KANEKA CORP	Resin composition and sheet.
WO2010134454 A	20101125	US2012070679 A1 20120322; US8512852 B2 20130820; TW201105739 A 20110216; KR20120026039 A 20120316; EP2433796 A1 20120328; CN102438832 A 20120502	JP20090123851 20090522	SHIMIZU TOSHIYUKI; UNRININ TOSHIFUMI	TOYO BOSEKI	Polylactic acid resin composition and film.
WO2010151872 A1	20101229	US2010330382 A1 20101230	US20100824759 20100628; US20090220840P 20090626	DOU SHICHEN; CHANG KEUNSUK P	TORAY PLASTICS AMERICA INC	Biaxially oriented polylactic acid film with improved moisture barrier.
WO2011032727 A1	20110324	US2012213959 A1 20120823; EP2480411 A1 20120801; DE102009042008 A1 20110324; CA2774742 A1 20110324; AU2010294818 A1 20120503		SCHUHMANN MICHAEL; STARK KURT; SITZMANN STEFAN	HUHTAMAKI FORCHHEIM	Überwiegend biologisch abbaubare Trennfolie. "Predominantly biodegradable separating film."
WO2011082052 A1	20110707	US2012270978 A1 20121025; KR20120109571 A 20121008; JP2013515822 A 20130509; EP2519579 A1 20121107; CN102892820 A 20130123	US20090290356P 20091228	MYERS SASHA B; JENNEN JAY M; AUSEN RONALD W; SPAWN TERENCE D; ANDERSON KELLY S; FRANK JOHN W	3M INNOVATIVE PROPERTIES CO	Plasticized polylactide.

WO2011162046 A1	20111229	KR20130089159 A 20130809; EP2583994 A1 20130424; CN102892817 A 20130123	JP20110038040 20110224; JP20100140116 20100621	YAMAMURA GOUHEI; SAKAMOTO JUN; YAKUSHIDOH KENICHI; ENDO YOSHIKAZU	TORAY INDUSTRIES	Polylactic acid film.
WO2012023465 A1	20120223	US2013137788 A1 20130530; TW201219463 A 20120516; KR20130108277 A 20131002; EP2607415 A1 20130626; EP2607415 A4 20140101; CN103097441 A 20130508	JP20100182840 20100818	YAMAMURA GOUHEI; SAKAMOTO JUN; SUEOKA MASANORI; SHINNUMADATE HIROSHI	TORAY INDUSTRIES	Porous film.
WO2013038770 A1	20130321		JP20110197951 20110912	HIROTA MASAYUKI; YAMAMURA GOUHEI; SAKAMOTO JUN	TORAY INDUSTRIES	Film.
WO2013080788 A1	20130606		JP20110261452 20111130	YAKUSHIDOU KENICHI; TABATA HISATAKA; ISHII TAKESHI	TORAY INDUSTRIES	Polylactic acid resin sheet and moled body.
WO9400293 A	19940106	US5391423 A 19950221; TR27656 A 19950614; SG65587 A1 19990622; NO944985 A 19950224; NO300579 B1 19970623; MX9303853 A 19940531; KR100262356 B1 20000901; JPH08500062 A 19960109; HK1009643 A1 19990604; GR3026335 T3 19980630; FI946071 A 19941223; ES2113542 T3 19980501; EP0647184 A1 19950412; EP0647184 B1 19980311; EG20102 A 19970731; DK0647184 T3 19980427; DE69317423 T2 19980709; CN1085493 A 19940420; CN1068277 C 20010711; CA2138120 A1 19940106; CA2138120C 20000718; BR9306621 A 19981208; AU4533993 A 19940124; AU681589 B2 19970904; AT163883 T 19980315	US19920905057 19920626	WNUK ANDREW JULIAN; KOGER THURMAN JOHN II; YOUNG TERRILL ALAN	PROCTER & GAMBLE	Biodegradable, liquid impervious multilayer film compositions.

Continued

—Cont'd

Patent Number	Publication Date	Family Members	Priority Numbers	Inventors	Applicants	Title
WO9416000 A1	19940721	US5578382 A 19961126; US5534616 A 19960709; JPH08505415 A 19960611; JP3364494 B2 20030108; JPH08505415 A 19960611; FI953411 A 19950712; FI108460 B 20020131; EP0695321 A1 19960207; EP0695321 B1 19980701; EP0695321 B2 20021106, DE69411382 T2 19990204; DE69411382 T3 20031211; CA2153807 A1 19940721; CA2153807 C 20070313; AU5837694 A 19940815; AT167886 T 19980715; AU681862 B2 19970911	GB19930000554 19930113	WADDINGTON SIMON DOMINIC	ZENECA LTD	Polyhydroxyalkanoates and film formation therefrom.
WO9901278 A1	19990114	US2001000742 A1 20010503; US6322899 B1 20011127; JP2000516878 A 20001219; FI972638 A 19981220 FI110413 B 20030131; EP0918633 A1 19990602	FI19970002638 19970619	KARHUKETO HANNU; KORPELA HEIKKI	UPM KYMMENE OYJ	Plastic laminate.

Chapter 11

Manufacture of Fibers and Fabrics

11.1 FIBER FORMATION

Thermoplastic polymer fibers refer to elongated extrudates formed by passing a polymer through an orifice, such as a die. The polymer fibers include discontinuous fibers having a definite length and substantially continuous filaments. Filaments may have a length much greater than their diameter, such as a length to diameter ratio ("aspect ratio") greater than approximately 15,000–1, and in some cases, greater than approximately 50,000–1.

Fibers formed from biodegradable polymer compositions can have any desired configuration, including monocomponent, biocomponent, and multicomponent[1] (e.g., sheath-core configuration, side-by-side configuration, segmented pie configuration, and island-in-the-sea configuration) and/or multiconstituent[2] (e.g., polymer blend). Fibers may contain one or more additional polymers to further enhance strength and other mechanical properties. The fibers can be solid or hollow, and can have any cross-section, including circular, polygonal, elliptical, and multilobal.

The biodegradable thermoplastic fibers can be formed using a variety of conventional techniques well-known in the art, including melt spinning, spunbonding and melt blowing. Additional less common methods, which can still be practiced, include flash spun, dry spinning and wet spinning. Combinations of these three basic processes are often used.

In melt spinning, a melt processed biodegradable thermoplastic polymer is heated higher than its T_m and the molten polymer is forced through a spinneret. A spinneret is a die with many small orifices, which are varied in number, shape, and diameter. The jet of molten polymer is passed through a cooling zone where the biodegradable polymer solidifies and is then transferred to post-drawing and take-up equipment. In general, melt spinning is used to provide longer fibers for wovens and nonwovens. The fibers may also be cut to form staple fibers usually having an average fiber length in the range of 3–80 mm. The staple fibers may be incorporated into a nonwoven web, such as bonded carded webs, and through air-bonded webs. A typical melt spinning process is depicted in Figure 11.1.

The spunbonding process is often considered a type of melt spinning. A significant difference is that spunbonding involves air entrainment to draw the fibers rather than godet rolls typically seen in the melt spinning processes. A typical spunbonding process is depicted in Figure 11.2.

In melt blowing process, a high-velocity air blows the molten biodegradable thermoplastic polymer from an extruder die tip onto a conveyor or take-up screen to form fine fibers. Fibers prepared by melt blowing, in contrast, are generally finer in diameter but less oriented. A typical melt blowing process is depicted in Figure 11.3.

In dry spinning, the thermoplastic biodegradable polymer is dissolved in a solvent and the polymer solution is extruded under pressure through a spinneret. The jet of polymer solution is passed through a heating zone where the solvent evaporates and the filament solidifies.

In wet spinning, a biodegradable thermoplastic is also dissolved and the solution is forced through a spinneret that is submerged in a coagulation bath. As the polymer solution emerges from the spinneret orifices within the coagulation bath, the biodegradable polymer is either precipitated or chemically regenerated. Usually, all these processes need further drawing for useful properties to be obtained (e.g., to serve as textile fibers).

11.1.1 Poly(lactic acid)

Fiber-grade poly(lactic acid) (PLA) has adequate crystallinity, but a slow crystallization rate, under ordinary spinning conditions. Accordingly, fibers that have been spun and cooled still have tackiness among the fibers in the web accumulation process, and fibers constituting the web are bonded to each other to provide a nonwoven fabric that lacks flexibility.

The T_m of PLA is in the range of 150–180 °C and its use as a clothing fiber in the same manner as polyethylene terephthalate (PET) or nylon therefore requires that ironing be limited to relatively low temperatures, whereas its use as an industrial fiber has been hampered by its unsuitability for exposure to high temperatures of approximately 150 °C during production processes for rubber materials or resin-coated fabrics. Moreover, because PLA dissolves easily in ordinary organic solvents, such as chloroform, it cannot be used for purposes that involve contact with organic solvents, such as oils. PLA generally does not have good thermal dimensional stability. PLA usually undergoes severe heat shrinkage because of the relaxation of the polymer chain during downstream heat

---

[1] Fibers formed from at least two polymers (e.g., biocomponent fibers) that are extruded from separate extruders.

[2] Fibers formed from at least two polymers (e.g., biconstituent fibers) that are extruded from the same extruder.

Biopolymers: Processing and Products. http://dx.doi.org/10.1016/B978-0-323-26698-7.00011-8

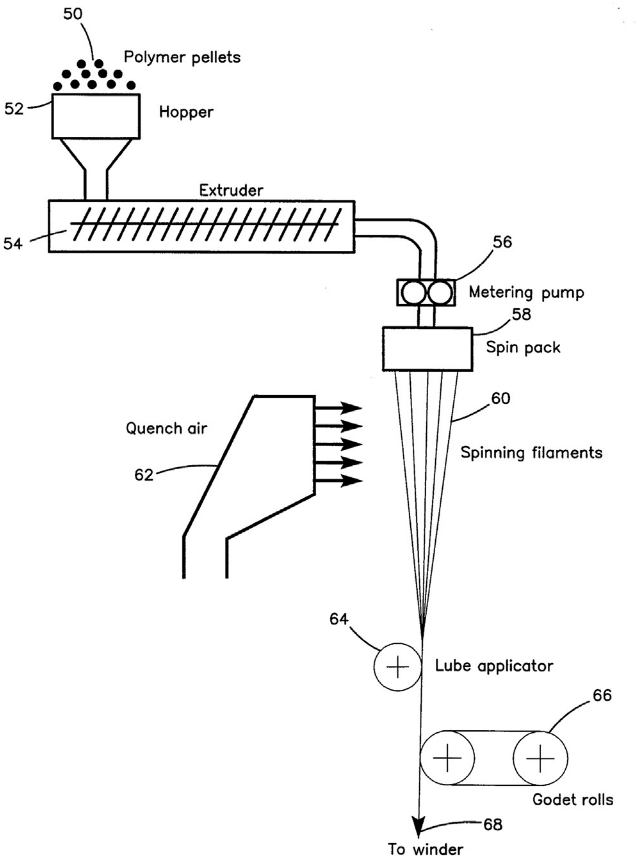


FIGURE 11.1 Melt spinning process (1998, **WO9850611** A1, CARGILL INC). 50, Polymer pellet; 52, Hopper; 54, Extruder; 56, Metering pump; 58, Spin pack; 60, Polymer fibers; 62, Quench system; 64, Lubricating roll; 66, Godet rolls; 68, Winder.

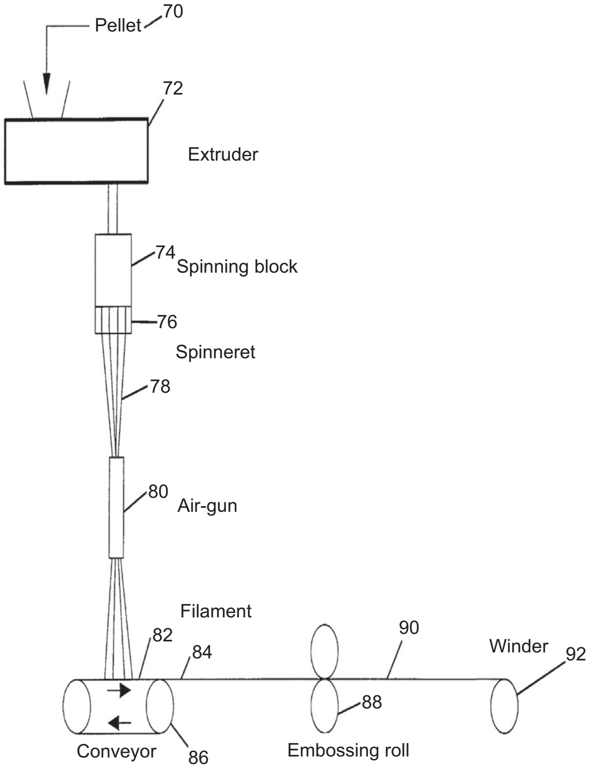


FIGURE 11.2 Spunbonding process (1998, **WO9850611** A1, CARGILL INC). 70, Pellets; 72, Extruder; 74, Spinning block; 76, Die or spinnerette; 78, Multiple fibers; 80, Air attenuator; 82, Belt; 84, Web; 86, Conveyer; 88, Embossing rolls; 90, Bonded web; 92, Winder.

treatment processes, such as thermal bonding and lamination, unless an extra step, such as heat setting, is taken. However, such a heat setting step generally limits the use of the fiber in *in situ* nonwoven forming processes, such as spunbond and melt blown, where heat setting is difficult to be accomplished (2004, **WO2004061172** A2, KIMBERLY–CLARK WORLDWIDE, INC).

Various studies on fibers made of stereocomplex PLA (scPLA) are also under way (2009, **WO2008029934** A1 TEIJIN LTD). scPLA fibers have been proposed, which exhibit improved heat resistance ironing durability that has been impossible to achieve with conventional PLA fibers (see Chapter 2: Properties; Sections 2.2.1 and 2.3.2). scPLA is formed when poly(L-lactic acid) (PLLA) and poly(D-lactic acid) (PDLA) are mixed together in a solution or molten state (see Chapter 1: Introduction; Section 1.4.1.1.1: Poly(lactic acid) (PLA)). This scPLA has a higher T_m than those of PLLA and PDLA and shows high crystallinity. Fibers have been made from the commercial product Biofront®[3] (Teijin Fibers), a heat-resistant scPLA (PLLA/PDLA, 50/50), with a $T_m = 210\,°C$, which is significantly higher than the T_m (170 °C) of conventional PLA. Biofront's extra heat resistance enables it to endure high-temperature, high-pressure dyeing, and Biofront® fabric finds uses in automotive interior materials (e.g., car seats for Mazda Motor Corp's Premacy Hydrogen RE hybrid automobile).

US4719246A (1988, DU PONT) discloses a scPLA fiber obtained by melt spinning a composition containing equimolar amounts of PLLA and PDLA. However, the scPLA fiber is unsatisfactory in terms of heat resistance and cannot be put to practical use (2009, **WO2008029934** A1 TEIJIN LTD).

The conventional methods for forming scPLA fibers use stretching and heat setting of amorphous unstretched filaments obtained by spinning blends of PLLA and PDLA, and in most cases heat setting is performed at a higher temperature than the T_m of the PLLA or PDLA homocrystals. However, when the heat setting is performed at a high temperature, partial melting of the filaments occurs, whereby the yarn becomes rough and hard, or is reduced in strength (**WO2008120807** A1 2008, TEIJIN LTD).

JP2003293220 A (2003, TORAY INDUSTRIES) discloses heat resistant PLA fibers with a low stereocomplex crystallization ratio of approximately 50% and a high tenacity of 4.5 cN/dtex, obtained by using a crystallized

---

[3] http://www.teijin.co.jp/english/news/2007/ebd070912.html.

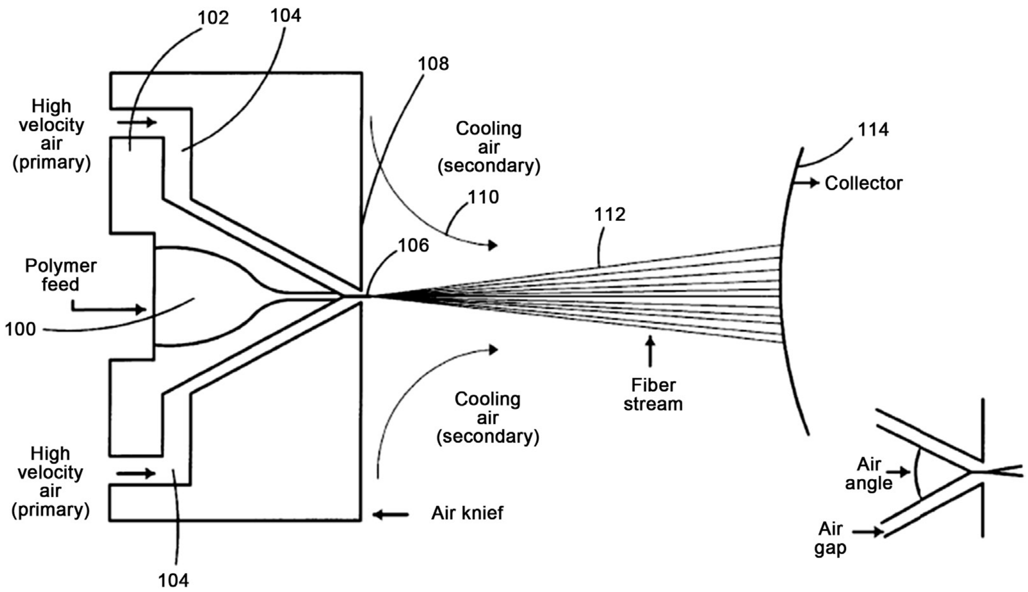


FIGURE 11.3 Melt blown process (1998, **WO9850611** A1, CARGILL INC). 100, Extruder; 102, Die; 104, High velocity air; 106, Attenuated fibers; 108, Die; 110, Secondary cooling medium; 112, Attenuated fiber; 114, Rotating drum.

unstretched filament with a crystallization ratio of 10–35% by high-speed spinning at a spinning speed of 4000 m/min, and subjecting it to (multistage) stretching to a factor of 1.4–2.3. However, because the ductility is <20%, the physical properties have been insufficient for clothing or industrial fibers. In addition, this process requires a spinning speed of at least 5000 m/min, and because spinning at such speeds can only be accomplished with special spinning equipment, problems still remain to be surmounted before it can be applied for industrial production (**WO2008120807** A1 2008, TEIJIN LTD).

JP2005023512 A (2005, TORAY INDUSTRIES) discloses a PLA fiber having two melting peaks derived from PLA homocrystals and stereocomplex crystals of $T_m \geq 190\,°C$, and a heat resistance at 200 °C, which is obtained by winding up an unstretched filament obtained by melt spinning at a spinning draft of ≥50 and a take-up speed of ≥300 m/min followed by stretching, or stretching to a stretch factor of 2.8 without winding, and then heat setting at a temperature of 120–180 °C. **WO2008120807** A1 (2008, TEIJIN LTD) comments on the above patent application that the fibers have sufficient practical strength without giving specific numerical values, and the heat resistance at 200 °C is merely a degree of heat resistance that prevents severe changes, such as fusion of fibers, or changes in fabric form after the fabric has been contacted with the surface of an iron at 200 °C for 30 s; but the patent application mentions that melting peaks for PLLA and PDLA single crystals are observed in differential scanning calorimetry, and therefore the heat resistance must be deemed insufficient because of melting of the single crystals.

According to **WO2008120807** A1 (2008, TEIJIN LTD), because scPLA fibers generally have a T_g of 60 °C, or approximately 8 °C lower than PET fibers, which are typically used as clothing fibers, they are more easily dyed than PET fibers with dispersed dyes at temperatures near 100 °C. However, the dye molecules that have become fixed in the fiber structure tend to escape to the outside, resulting in drawbacks, such as color crocking and discoloration, or in other words, poor washing durability. This tendency is accelerated in moist conditions.

There has been disclosed in **JP2003049374** A (2003, UNITIKA TEXTILES LTD) a method to counter such crocking behavior by adding a heat treatment step at 110–140° for 10–120 s between the dyeing step and reduction cleaning step of the PLA fiber, on the basis of the dyeing conditions, but a satisfactory solution has not been achieved.

Furthermore, PLA is naturally prone to hydrolysis that under dyeing conditions causes the amorphous sections of fibers to be hydrolyzed while the crystal sections selectively remain, thus creating dye-resistant regions in easily dyeable PLA fibers, and therefore creates the fibers that are uneven dyed. Moreover, PLA molecules have high light transmittance with virtually no absorption band in the region from the visible light range to the ultraviolet range of near 300 nm, and therefore are highly advantageous for optical applications, but because no shielding effect is provided by PLA molecules in dyed products, the dye molecules themselves are susceptible to decomposition and the sunlight fastness is insufficient for practical use. It has been proposed to use ultraviolet absorbers to overcome these drawbacks, but the use of such agents can potentially cause new problems, such as yellowing of the fibers.

WO2008120807 A1 (2008, TEIJIN LTD) discloses a scPLA is obtained by discharging a PLA composition (A) from a discharge hole with a pack temperature of 220–260 °C and an L/D of 2–10, rapidly cooling with cold air at below 50 °C after discharge, and spinning at a spinning draft of 0.1–50 and a spinning speed of 300–5000 m/min, with a yarn temperature of no higher than the crystallization start temperature at 3 m below the pack. The PLA composition (A) comprises a PLLA and a PDLA a weight ratio PLLA/PDLA of 10/90–90/10. The scPLA fiber has a degree of stereocomplex crystallization of 30–90%, a $T_m > 200\,°C$, a heat shrinkage factor of 0.1–15% at 150 °C, ironing resistance at 170 °C, a tenacity of at least 3.5 cN/dtex and a ductility of 20–50%.

11.1.2 Polyhydroxyalkanoates

Polyhydroxyalkanoates (PHA)s, such as poly(3-hydroxybutyrate) (P3HB) and poly(3-hydroxybutyrate-*co*-3-valerate) (PHBHV), are difficult to process into fibers, and nonwovens because of their thermal instability. Furthermore, the slow crystallization rates and flow properties of P3HB and PHBHV make fiber, and nonwoven processing difficult. Because of the slow crystallization rate, a fiber, or nonwoven, made from PHBHV will stick to itself even after cooling; a substantial fraction of the PHBHV remains amorphous and tacky for long periods. In spun fibers, the fiber bundle will likewise stick and collapse.

EP0104731 A2 (1984, ICI PLC) demonstrates in one of its embodiments a method for the production of P3HB fibers with a melt spinning machine, as shown in Figure 11.4, comprising the steps of: (i) melt extruding P3HB granules at a melt temperature of 185 °C at a rate of 0.28 g/min through a die (1) having a circular orifice of diameter 1.585 mm; (ii) bringing the molten extrudate (2) directly into a water bath (3) maintained at 60 °C and guided through bath (3) by guides (4, 5); (iii) taking up the resultant solidified monofilament (6) at a rate of 0.026 m/s by a taken up roller (7) and passed round a pin (8) heated to 120 °C: (iv) drawing the monofilament from the pin (8) into a fiber (9) by a second taken up roller (10): (v) positioning a plate (11) of length 20 cm maintained at 60 °C immediately below fiber (9) and between pin (8) and taken up roller (10); (vi) from taken up roller (10) winding up the fiber (9) on a reel (12). Heated plate (11) provides a heated zone above plate (11) wherein the fiber (9) drawn from pin (8) could be further crystallized. Heated pin (8) serves not only to heat the monofilament preform (6) to the drawing temperature, but also to localize the drawing position. The draw ratio is thus the ratio of the circumferential speeds of rollers (10) and (7).

JPS6169431 A (1986, TEIJIN LTD) discloses a method of spinning a PHA, which comprises heating P3HB or PHBHV at a temperature range of −40 °C below T_m and the T_m of the polyester, cooling the aliphatic polymer to below 100 °C for 1–120 s, and drawing the polymer 120%.

Furthermore, there are disclosures on methods for the production of PHA fibers, such as PHBHV comprising a pre-heating step before drawing, and a heating step after drawing so that the rapid cooling step and the drawing step are performed separately: **JPH05321025** A (1993); **JPH07300720** A (1995); **JPH08284016** A (1996) of CHUKOH CHEM IND and ISHIKAWA PREFECTURE.

The above methods cannot be applied with the spinning of poly(3-hxdroxy butyrate-*co*-3-hexanoate) (PHBHHx), because they have the problem that solidification does not proceed and end breakage or adhesion of fibers to the water bath guide is caused, resulting in unsuccessful fiber spinning (2002, **EP1266984** A1, KANEKA CORPORATION).

WO9520615 A1 (1995, PROCTER & GAMBLE) discloses a spinning method for the production of PHBHHx fibers and an example is given for the preparation of staple fibers having a length of 1.3–15 cm by jetting the fibers into from the nozzle of the extruder. There is no report on the process for preparing PHBHHx drawn filament (2002, **EP1266984** A1, KANEKA CORPORATION).

According to **EP1266984** A1 (2002, KANEKA CORPORATION), because PHBHHx does not have high crystallinity, such as P3HB or PHBHV, it is necessary to perform drawing by controlling the melt viscosity of the filament, solidifying the filament surface rapidly, and performing partial crystallization of the polymer rapidly, because the crystallization rate of PHBHHx is lower than that of P3HB or PHBHV. For this purpose, **EP1266984** A1 (2002, KANEKA CORPORATION) discloses a method for the production of PHBHHx fibers comprising the steps of: (1) preparing a melted filament by extruding PHBHHx from a melt extruder; (2) rapidly cooling the filament to at most the T_g of the polymer; (3) passing the filament through a

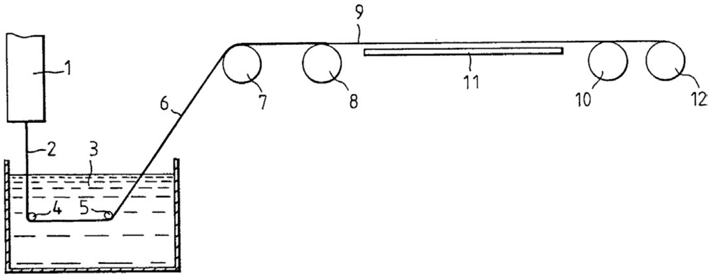


FIGURE 11.4 Schematic diagram of a fiber spinning machine (1984, **EP0104731** A2, ICI PLC). 1, Die; 2, Melt extrudate; 3, Water bath; 4, 5, Guides; 6, Monofilament; 7, 10, Taken up rollers; 8, Pin; 9, Fiber; 11, Heated plate; 12, Reel.

hot water bath adjusted to a water temperature, $T \geq T_g$; and drawing to produce a biodegradable fiber.

The technique is suitable for spinning not only PHBHHx but also PHAs containing units having a large number of methylene groups in the side chain. This is because thermoplastic polymers containing units having a large number of methylene groups in the side chain has low crystallization rate and tend to have slower progress of solidification. Thermoplastic polymers containing units having a small number of methylene groups in the side chain, such as P3HB and PHBHV have large crystallization degree and high crystallization rate, and therefore are unlikely to cause blocking.

11.1.3 Aliphatic-Aromatic Polyesters

Conventional aliphatic-aromatic copolyesters are not typically suitable for melt blowing processes, which require a low polymer viscosity for successful microfiber formation (2008, **WO2008008068** A1, KIMBERLY CLARK CO).

WO2008008068 A1 (2008, KIMBERLY CLARK CO) attempts to address this problem by disclosing a fiber made of a biodegradable aliphatic-aromatic copolyester terminated with an alkyl group, hydroxyalkyl group, or a combination thereof, wherein the copolyester has a melt flow index (MFI) of 5–500 g/10 min (measured with a load of 2160 g and a temperature of 190 °C in accordance with ASTM Test Method D1238-E). In one embodiment, the modified aliphatic-aromatic copolyester is prepared by melt blending an aliphatic-aromatic copolyester with an alcohol to initiate an alcoholysis reaction that results in a copolyester having one or more hydroxyalkyl or alkyl terminal groups. By selectively controlling the alcoholysis conditions (e.g., alcohol and copolymer concentrations, catalysts, and temperature), a modified aliphatic-aromatic copolyester may be achieved that has a molecular weight lower than the starting aliphatic-aromatic polymer. Such lower-molecular-weight polymers also have the combination of a higher MFI and lower apparent viscosity, which is useful in a wide variety of fiber forming applications, such as in the melt blowing of nonwoven webs.

11.1.4 Aromatic Polyesters (Bio-Based)

JP2003041435 A (2003, TEIJIN LTD) discloses a method for stably producing poly(trimethylene terephthalate) (PTT) staple fibers comprising the steps of: (1) mixing PTT and 1–10 wt% of PLA and melting; (2) discharging the molten mixture from a spinneret having hollow-forming discharging holes; (3) subjecting the extruded filaments to nonuniform cooling; (4) spun; (5) taken off; (6) drawing and (7) crimping by heat treatment. The mixture is used to prepare hollow, crimped staple fibers.

WO2007067435 A2 (2007, DU PONT) discloses a biconstituent filament comprising a PTT and approximately 0.5–18 wt% of the filaments of PLA. PTT is generally produced by the acid-catalyzed polycondensation of 1,3-propane diol and terephthalic acid/diester, with optional minor amounts of other monomers. A particular preferred PTT is one in which the 1,3-propane diol used to make the polymer comprises a 1,3-propane diol prepared by a fermentation process using a renewable biological source.

11.1.5 Starch

To produce biodegradable fibers, attempts have been made to process natural starch on standard equipment and existing technology known in the fiber industry. Because natural starch generally has a granular structure, it needs to be "destructurized" before it can be melt processed into fine denier filaments. Modified starch (alone or as the major component of a blend) has had poor melt extensibility, resulting in difficulty in successful production of fibers. In addition, starch fibers are difficult to spin and are virtually unusable to make nonwovens because of the low tensile strength, stickiness, and inability to be bonded to form nonwovens.

To produce starch-based fibers that have more acceptable processability and end-use properties, biodegradable polymers need to be combined with starch. However, the selection of a suitable biodegradable polymer for blending with starch is considered to be difficult for the following reasons: (1) the biodegradable polymer must have good spinning properties and a suitable T_m; (2) the T_m must be high enough for end-use stability to prevent melting or structural deformation, but not too high of a T_m to be able to be processable with starch without burning the starch (2002, **WO02090629** A1, PROCTER & GAMBLE).

WO02090629 A1 (2002, PROCTER & GAMBLE) discloses highly attenuated fibers, for nonwoven web and disposable articles, produced by melt spinning a composition comprising destructurized starch, one or two biodegradable thermoplastic polymer(s), and a plasticizer. Examples of commercially available starches include StarDri 100, StaDex 10, StaDex 15, StaDex 65 all (Stanley Manufacturing Co.). Preferably, one of the biodegradable thermoplastic polymers is a crystallizable PLA. Microfibrils of the biodegradable polymer are formed within the starch matrix of the highly attenuated fiber. A nonwoven web is prepared from the highly attenuated fibers. The highly attenuated fiber is formed from a cost-effective and easily processable composition made of natural starches and biodegradable polymers by using conventional processing equipment.

11.2 NONWOVEN

Nonwoven is a web having a structure of individual fibers that are randomly interlaid, but not in an identifiable manner as in a knitted fabric. Nonwoven webs include, for example, melt blown webs, spunbond webs, carded webs, wet-laid webs, airlaid webs, coform webs, and hydraulically entangled webs.

A nonwoven fabric is manufactured by accumulating a plurality of loose continuous filaments comprising a thermoplastic polymer on a support into a web form, and locally bonding the filaments to each other, in regions regularly separated from each other, at intersecting points of the filaments. The local bonding of the filaments can be effected by locally pressing the web at a temperature equal to or higher than the softening temperature, optionally the T_m, of the filaments. This type of nonwoven fabric is commonly referred to as a spunbond nonwoven fabric. The spunbond nonwoven fabric has not only a higher producibility than that of other nonwoven fabrics, but also high mechanical strength and flexibility and thus is widely used as a mulching sheet for agriculture and for other uses.

Over the centuries biodegradable nonwoven fabrics have been made from natural or regenerated fibers or filaments, examples of which include cotton, flax, hemp, ramie, wool, rayon, chitin, and alginic acid. However, these bio-based nonwoven fabrics, which are generally hydrophilic and water absorptive, are not suitable for several applications, such as disposable diaper top sheet. These nonwoven fabrics are much liable to deterioration in strength and dimensional stability under wet and moistened environmental conditions and, hence, find limited application in the general industrial material field. Furthermore, the nonwoven fabrics are not thermoformable because of their nonthermoplastic property and, hence, are inferior in processability.

Biodegradable polymer fibers for nonwoven articles are difficult to produce and pose additional challenges compared to films and laminates. This is because the material and processing characteristics for fibers are much more stringent than for producing films, blow-molding articles, and injection-molding articles. For the production of fibers, the processing time during structure formation is typically much shorter and flow characteristics are more demanding on the material's physical and rheological characteristics. The local strain rate and shear rate is much greater in fiber production than other processes. In addition, a homogeneous composition is required for fiber spinning. For spinning fine fibers, small defects, slight inconsistencies, or nonhomogeneity in the melt are not acceptable for a commercially viable process. The more attenuated the fibers, the more critical the processing conditions and selection of materials (2002, **WO02090629** A1, PROCTER & GAMBLE).

Various attempts have been made to produce nonwoven fabrics made of aliphatic polyester filaments. Of the available aliphatic polyesters, PLA, in particular, has a relatively high T_m, so that nonwoven fabrics composed of PLA filaments are possibly useful in applications that require heat resistance (2003, **US2003148688** A1, TOMOEGAWA PAPER CO LTD; UNITIKA LTD).

However, PLA nonwoven webs generally possess a low bond flexibility and high roughness because of the high T_g and slow crystallization rate of PLA. In turn, thermally bonded PLA nonwoven webs often exhibit low elongations that are not acceptable in certain applications, such as in an absorbent article. Likewise, although PLA may withstand high draw ratios, it requires high levels of draw energy to achieve the crystallization needed to overcome heat shrinkage. Plasticizers have been used in an attempt to reduce T_g and improve bonding and softness. But the addition of plasticizers causes other problems, such as degradation in melt spinning, reduction in melt strength and drawability, and an increased tendency to phase separate and migrate out of the fiber structure during aging, thus reducing plasticizer effectiveness over time (2012, **US2012289658** A1, KIMBERLY CLARK CO).

US2012289658 A1 (2012, KIMBERLY CLARK CO) attempts to solve the above problems by providing a PLA fiber that is formed from a thermoplastic composition comprising at least one PLA (55–97 wt%), at least one plasticizer (2–25 wt%), and at least one compatibilizer (1–20 wt%). The compatibilizer includes a polymer modified with a polar compound. The polar compound includes an organic acid, an anhydride of an organic acid, an amide of an organic acid, or a combination thereof. PLA is relatively nonpolar in nature and thus not readily compatible with polar plasticizers. When forming a polymer composition from such polymers, a separated interface may thus form between two phases, which deteriorates the mechanical properties of the resulting fibers. In this regard, the functionalized polymers are particularly effective for use in compatibilizing PLA with a plasticizer. Such a functionalized polymer may thus stabilize each of the polymer phases and reduce plasticizer migration. By reducing the plasticizer migration, the composition may remain ductile and soft. Furthermore, addition of the functionalized polymer may also promote improved bonding and initiate crystallization faster than conventional PLA fibers.

JPH07126970 A (1995, TOYO BOSEKI) and **JPH06212511** A (1994, UNITIKA LTD) disclose staple fiber nonwoven fabrics composed principally of PLA. However, the production of these staple fiber nonwoven fabrics involves many production steps from filament melt spinning to nonwoven fabric formation, thereby posing a limitation to reduction in the production costs.

Furthermore, **JPH0748769** A (1995, MITSUI TOATSU CHEMICALS), **JPH06264343** A (1994, TOYO BOSEKI) and **CA2127754** A1 (1995, FIBERWEB SODOCA SARL) suggest nonwoven fabrics produced from PLA filaments by the previously described spunbond technique in which filaments are melt extruded and deposited on a screen to form a web. According to **US2003148688** A1 (2003, TOMOEGAWA PAPER CO LTD; UNITIKA LTD), in **JPH0748769** A (1995) no specific description is given to the production process and the physical properties of the resulting nonwoven fabric. In **JPH06264343** A (1994), which pertains to a biodegradable filament aggregate for agricultural use, there is no detailed statement about critical production conditions, such as a filament drafting speed and the like, nor any teaching on the physical properties of the resulting nonwoven fabric. In **CA2127754** A1 (1995), there is no teaching that a PLA spunbond fabric with enhanced flexibility and mechanical strength was produced.

US2003148688 A1 (2003, TOMOEGAWA PAPER CO LTD; UNITIKA LTD) discloses a biodegradable nonwoven fabric, which is made of PLA filaments. The PLA is selected from PDLA, PLLA, and their copolymers, having $T_m \geq 100\,°C$. The PLA filaments have a birefringence of 10×10^{-3}–25×10^{-3}, a degree of crystallinity of 12–30%, and a crystal size of not greater than 80 Å as measured axially of the filaments. The nonwoven fabric has a shrinkage percentage in boiling water of not higher than 15%.

JP2007230284 A (2007, UNITIKA FIBERS LTD) discloses a surface member for an interior material formed by needle-punched nonwoven fabric using a core-sheath type composite short fiber, where the core part is made of PLA and the sheath part is made of aromatic polyester having higher T_m than PLA. PLA of the core part has a $T_m \geq 120°$ and a heat of melting, $\Delta H \geq 10\,J/g$.

Furthermore, **JP2005307359** A (2005, TORAY INDUSTRIES) discloses a nonwoven fabric produced from staple fibers of PLA (having a fiber length of 3–150 mm with a low dry-heat shrinkability that has undergone heat shrinkage in advance to reduce shrinkage during the nonwoven fabric production process). The PLA staple fiber nonwoven fabric has a dry heat shrinkage percentage (measured in accordance with JIS L 1913:1998 under dry heat-treating conditions at 150 °C for 30 min) within the range of 0.05–2%. The PLA staple fiber nonwoven fabric can be used as internal trim or door trim such as a ceiling material, a line carpet, an option mat or a trunk of automobiles. It is claimed that interior finishing materials for automobiles made of the disclosed PLA staple fiber nonwoven can withstand temperatures of 120–180 °C developed during their molding. On the other hand, the method described in **JP2005307359** A (2005) can effectively depress shrinkage, but the resulting materials are not sufficiently high in durability (2010, **WO2010137514** A1, TORAY INDUSTRIES).

JP2007314913 A (2007, TOABO MATERIAL CO LTD) discloses a needle-punched nonwoven fabric produced from PLA staple fiber and PTT fiber (>5 wt%). The disclosed nonwoven fabric is claimed to have improved wear resistance and moldability. The materials produced with the method described in **JP2007314913** A (2007) are not sufficiently high in durability when used for interior finishing of vehicles, and the PLA fibers can undergo fusion during molding. For the molding of interior finishing materials for automobiles, it is important not only to depress the shrinkage during molding, but also maintain a high elongation degree. In this respect, both the techniques described in **JP2007314913** A (2007) and **JP2005307359** A (2005) do not provide materials that can stretch sufficiently during molding.

WO2010137514 A1 (2010, TORAY INDUSTRIES) addresses these problems by disclosing a method of producing a needle-punched nonwoven fabric comprising: (1) blending a first group of short fibers (20–40 wt%) comprising PLA (end-capped with an epoxy compound) with a second group of short fibers (60–80 wt%) comprising PET to form blended fibers; (2) carding the blended fibers to form a plurality of fleece sheets; (3) stacking the fleece sheets; and (4) needle-punching the plurality of fleece sheets to form a nonwoven fabric. The needle-punched nonwoven fabrics are used as automotive interior material.

JPH0995849 A (1997, UNITIKA LTD) discloses a PLA continuous fiber nonwoven fabric, wherein the PLA constituting the continuous fibers is a polymer or a blend of polymers each having a $T_m \geq 100\,°C$ selected from PLLA or its copolymers with D-lactic acid or another hydroxyacid. However, the nonwoven fabric is constituted by a single component and thus has hard texture with poor flexibility (2010, **WO2010122806** A1, CHISSO CORP; CHISSO POLYPRO FIBER COMPANY L).

JPH07310236 A (1995, KANEBO LTD; SHIMADZU CORP) discloses heat-fusible composite fibers formed of two kinds of PLA having different $T_m s$. The composite fibers are claimed to be excellent in adhesion property, but the low T_m component functions as an adhesive component for all the fibers, and therefore, a nonwoven fabric produced from the fibers has hard texture with poor flexibility, as similar to a nonwoven fabric constituted by a single component (2010, **WO2010122806** A1, CHISSO CORP; CHISSO POLYPRO FIBER COMPANY L).

WO2010122806 A1 (2010, CHISSO CORP; CHISSO POLYPRO FIBER COMPANY L) discloses a nonwoven fabric containing at least two kinds of biodegradable fibers made of different biopolymers. The first biodegradable fiber is made of an aliphatic polyester or aliphatic copolyester each having a T_m that is higher than the T_m of the biopolymer making the second biodegradable fiber. Among the aliphatic polyesters and the aliphatic polyester copolymers used in the first fiber, PLA is most preferably used. The second fiber is made of a different type of aliphatic polyester, namely a poly(alkylene alkanoate) (PAA). Among the PAAs, poly(butylene succinate) (PBS) and poly(butylene succinate adipate) are preferred for enhancing the mechanical strength of the nonwoven fabric.

US6143947 A (2000, NODA ISAO) discloses nonwovens comprising fibers made of biodegradable copolyester, such as PHBHHx. The disclosed biodegradable nonwoven is used in an absorbent article comprising a liquid pervious top sheet, a biodegradable liquid impervious back sheet comprising the above fibers and/or nonwovens, and an absorbent core positioned between the top sheet and the back sheet.

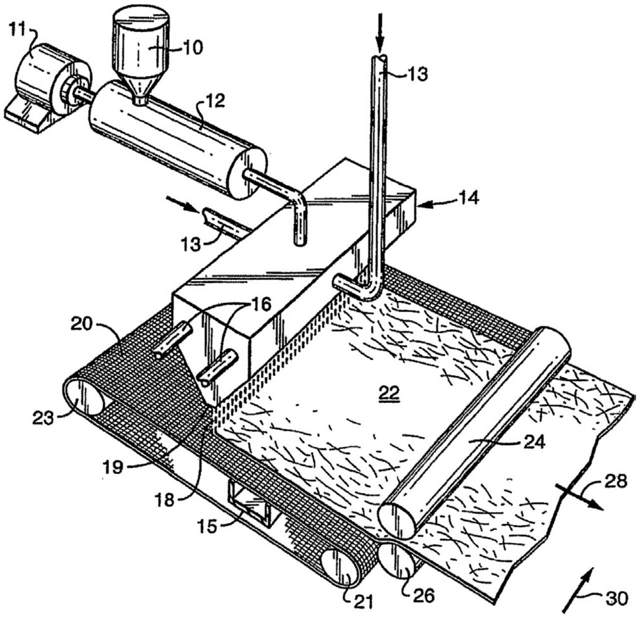


FIGURE 11.5 Nonwoven method for forming melt blown fibers (2008, **WO2008008068** A1, KIMBERLY CLARK CO). 10, Hopper; 11, Motor; 12, Extruder; 13, Conduits; 14, Die; 16, Heater; 18, Microfibers; 19, Orifice; 20, Foraminous surface; 21, 23, Rolls; 22, Web; 24, 26, Rolls; 28, Machine direction.

Example: Manufacture of compostable nonwoven fabric.

PHBHHx of composition 4 mol% 3-hexanoate/96 mol% 3-hydroxybutyrate is introduced into a single screw extruder (Rheomix Model 202, Paramus) with screw diameter of 0.75 in, a constant taper screw having a length to diameter ratio of 20/1, and a compression ratio of 3/1. The temperature of both heating zones of the extruder barrel is 25 °C above the T_m of PHBHHx. The extruder is equipped with a nozzle die containing five orifices of diameter 500 mm. The die is maintained at 20 °C above the melting temperature T_m) of the PHBHHx. The screw rpm is kept constant at 30 rpm. The molten polymer is forced through the die and the melted extruded fibers are led through a region where a rapid air stream is applied such that the polymer fibers elongate and thin to approximately one fifth of the diameter of the orifices (c. 100 mm). The fibers are collected on a cardboard mat. The mat is moved in a fashion so that a $10\times10\,\text{cm}^2$ area is covered uniformly with fibers. Collection of fibers on the mat continues, until there is approximately 0.5-cm thick fiber mat. A wide distribution of fiber lengths are obtained up several inches in length. Most fiber lengths (>50%) are in the range of 0.5–6 in. The mat is then transferred to a Carver Press (Fred S. Carver Inc.) and pressed at a 1000 lb (453.6 kg) force for 10 min at 5 °C below the T_m of PHBHHx. The resulting nonwoven sheet is removed from the press.

WO2008008068 (2008, KIMBERLY CLARK CO) discloses a nonwoven web prepared from melt blown or spunbond fibers made of modified aliphatic-aromatic copolyester fibers, as described in Section 11.4. Figure 11.5 is an illustrative example of the melt blown process used to form a nonwoven web from the modified aliphatic-aromatic copolyester fibers.

11.2.1 Carpets

Many carpets are used and consumed for helping the comfortable modern life. Carpets are generally bulky, difficult to be collected, and increase considerably the waste volume when disposed by land filling. The carpets are conventionally made of synthetic fibers such as polyamide fiber, polyolefin fiber, polyester fiber and the like, which are nonbiodegradable and remain in the environment for a long period of time unless they are burned. The disposal of the discarded carpets by incineration generates large quantities of heat, causes the emission of gas or black smoke and can shorten the service life of the incinerator. When poly(vinyl chloride) is used as backing layers for the carpet, dioxin may be generated when the backing layers are incinerated. For all these reasons, biodegradable fibers have been considered as alternatives for the production of carpets.

WO0065140 A1 (2000, UNITIKA LTD) discloses a tufted carpet using a base cloth constituted of a nonwoven fabric made of accumulated filaments formed of PLA. Each filament has a round cross-section, a birefringence[4] of 12×10^{-3}–30×10^{-3} and a crystallization degree of 15–25 wt%. The base cloth for the above described tufted carpet has a heat shrinkage of ≤1 wt% at 120 °C in 3 min in both directions of machine direction (MD) and cross direction (CD). If the cross-section of the filament is not round, it is not possible to measure the birefringence of the filament. In such a case the limitation for only crystallization degree is valid.

The base cloth used for the tufted carpet has required biodegradability, and, as a result, is not detrimental to the environment. Because of the PLA high stiffness, when this base cloth is tufted, it is difficult that filaments of the base cloth are stuck directly by tufting needles and as a result, the filament easily slips off a needle. Therefore, a damage given to fiber decreases, and mechanical strength of the tufted base cloth is maintained. When the final product is for example a tile carpet, it maintains stiffness, and may have an improvement in workability during the installation on the floor. When the above described filament has crystallization degree of 15–25 wt% and round cross-section, because this filament has birefringence of 12×10^{-3}–30×10^{-3}, it is apparent this filament has moderate stiffness and simultaneously the polymer constituting the filament is oriented enough. Accordingly the final product is claimed to have superior dimensional stability and mechanical property. The base cloth is also superior in thermal stability. Therefore, the

---

[4] Birefringence represents the degree of molecular orientation.

base cloth has durability to heat, without shrinking, given in the process where it is laminated or coated by the backing layer during the backing process, and where it is heated in the oven during backing layer hardening process after the layer is attached.

Several carpets made of crimped PLA filament yarns are known in the prior art. A conventional carpet using crimped PLA filament yarns has, however, such drawbacks that it lacks bulkiness, it is easily worn away and it is easily buckled. Because of these drawbacks, such a carpet has limited practical uses. This is because the filament yarn properties and crimp characteristics (e.g., tenacity or elongation) of the crimped PLA filament yarn are inferior to those of the currently available nylon, polypropylene, and polyester crimped filament yarn.

Several patents have attempted to handle the aforementioned problems. **JP2005008997** A (2005, TORAY INDUSTRIES) discloses a PLA crimped filament yarn for yarn-dyed carpet having the following characteristics: (1) tenacity of 1.3–3 cN/dtex; (2) percentage crimp elongation of 5–10%; (3) percentage crimp potentialization of 85–95%; and (4) tenacity retention ratio of 85–100% after a pressurized hot water treatment at 110 °C for 30 min. The disclosed PLA crimped filament yarns improve the defects of conventional PLA crimped yarns and carpets using the crimped yarns, especially the deterioration in the strength and crimping characteristics of the crimped yarn caused by a dyeing treatment, the lack of bulkiness, the durability of friction resistance, permanent setting resistance, and the like, as carpets.

JP2005048303 A (2005, TORAY INDUSTRIES) discloses a carpet made of spun-dyed PLA crimped yarns comprising 100–30,000 ppm of a colorant. The spun-dyed crimped yarn consists of PLA filaments, wherein the cross-section of each filament has an ellipticity of 3–8, as calculated from the ratio of the major axis of the filament to the minor axis thereof, and a filament fineness of 5–25 dtex. The disclosed spun-dyed PLA crimped yarns overcome the lowering of strength or crimp characteristics of the crimped yarn caused by dyeing and the obtained carpet has improved bulkiness, abrasion resistance and buckling resistance.

JP2005060850 A (2005, TORAY INDUSTRIES), which is a modification of the previous patent, discloses a carpet made of spun-dyed PLA crimped yarns comprising 100–30,000 ppm of a dye. The spun-dyed crimped yarn consists of PLA filaments, wherein the cross-section of each filament has an ellipticity of 1.5–5.5, a relative viscosity (η_r) of 8–30, an entangled number, and a entangled point tenacity each falling within a specified range. The spun-dyed PLA crimped yarn has the following characteristics: (1) tenacity of 1.3–3.5 cN/dtex; (2) percentage crimp elongation (CR) of 5–25%; (3) percentage crimp potentialization of 75–95%; (4) number of interlaced points of 3–25; and (5) strength of the interlaced points 0.05–2.0 cN/dtex.

JP2002248047 A (2002, UNITIKA FIBERS LTD) discloses a carpet in which the pile filament yarns, the base fabric and the backing film are made of an aliphatic polyester, especially PLA.

JP2003010030 A (2003, TOWA ORIMONO CO LTD; TORAY INDUSTRIES) discloses a carpet in which filament yarns made of PLA are used as pile yarns, ground yarns, and fabrics such as a base fabric and a back fabric, and an adhesive layer for joining the base fabric and the back fabric made of a PLA composition for joining the base fabric and the back fabric.

JP2006097166 A (2006, SUMINOE TEXTILE; NIPPON A & L KK) discloses a carpet, as shown in Figure 11.6, obtained by coating a back surface of a skin material layer (4), which is formed by using biodegradable fibers with the backing agent (6), which comprises an emulsion containing a polymer having adhesive properties and a pH of 4–7, and then drying the coated layer. The biodegradable fibers are composed of aliphatic polyesters, preferably PLA. The disclosed carpet is claimed to have good flexibility and texture, and further enough adhesion and durability.

WO2007029688 A1 (2007, SUMINOE TEXTILE) discloses a carpet comprising a spun-dyed, textured PLA filament yarn, wherein the filament has an approximately circular or circular cross-section and a relative viscosity of 2.5–3.8. The textured filament yarn contains a coloring agent (0.01–3 wt%) and meets the following characteristics: (1) tenacity of 1.7–3.5 cN/dtex; (2) elongation at break of 35–60%; (3) total fineness of 500–3500 dtex; (4) monofilament fineness of 2.5–25 dtex; (5) shrinkage ratio in boiling water of 2–8%; (6) dry heat crimp ratio (CR) of 5–25%; and (7) degree of deformation less than 1.5, wherein the degree of deformation is expressed by a ratio (B/A) between the diameter (A) of the inscribed circle and the diameter (B) of the circumscribed circle of the fiber cross-section. This cross-sectional configuration gives abrasion resistance to the filament yarn. The carpet is claimed to have excellent bulkiness, toughness, wearing resistance and buckling resistance.

JP2006068225 A (2006, ORIX INTERIOR CORP) discloses a mat which is effective in preventing slippage even when it is placed on a precise long cut pile carpet and used. In a mat, in which a backing lamina 11 of thermoplastic

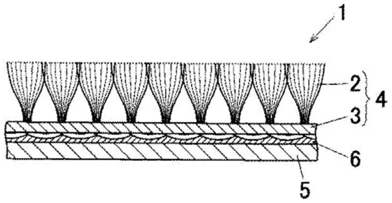


FIGURE 11.6 Carpet (2006, **JP2006097166** A, SUMINOE TEXTILE; NIPPON A & L KK). 1, Carpet; 2, Pile; 3, Primary base fabric; 4, Skin material layer; 5, Secondary base fabric; 6, Backing layer.

polymer is piled on a rear face of a pile fabric 10 and prongs 12 project at the required intervals on a surface of the backing lamina, the backing lamina 11 including the prongs is composed of polyester, the diameter (*d*) of the base 13 of the prong is set to 1 mm or more, the prong 12 is formed in a tip form, the height (*h*) of the prong is set to 5–15 mm and is 1–10 times of the diameter (*d*) of the base. The prongs 12 bite deep into a pile layer 16 without resistance as polyester is slippery and adamant, and the mat 18 cannot easily slip while placed on a precise long cut pile carpet. The backing lamina 11 and pile fabric 10 are preferably made of PLA or natural fiber.

JP2007270372 A (2007, UNITIKA LTD) provides a substrate cloth for a tufted carpet, which has a good thermal stability in producing the carpet and also excellent in heat resistance, and the tufted carpet using the same. This nonwoven fabric is composed of a conjugate filament (or biocomponent fiber) including an aliphatic-aromatic polyester copolymer and a PLA-based polymer. The PLA-based polymer forms at least a part of the fiber surface, and has a $T_m \geq 150\,°C$. The aliphatic-aromatic polyester copolymer has a repeating unit including a terephthalic acid and an aliphatic dicarboxylic acid as acid components, and an ethylene glycol and diethylene glycol as glycol components. The aliphatic-aromatic polyester copolymer has a higher T_m than that of the PLA-based polymer. The nonwoven fabric form is held by bonding the constituting fibers with each other by heat bonding. The fineness of the conjugate filament is ≥7 dtex and ≤12 dtex.

WO2007025582 A1 (2007, DS TEXTILE PLATFORM NV) discloses needle-punched carpets for intensive use, as well as methods of manufacture of the same. It is not possible to measure the birefringence of the filament. In such a case the limitation for only crystallization degree is valid. Carpets are substantially, and preferably completely biodegradable. A needle-punched carpet according to the present invention comprises a needle felt and at least one backing layer, wherein both the needle felt and at least one backing layer comprise at least 90 wt%, preferably at least 95 wt%, more preferably at least 98 wt% and most preferred 100 wt% of polymeric biodegradable material, for example PDLA and PLLA, respectively.

US2006257616 A1 (2006, STOWE PHARR MILLS INC D B A PH) discloses a carpet constructed from a biodegradable nonwoven face layer and a backing layer that is biodegradable and/or recyclable. The face layer comprises a needle-punched nonwoven web formed from a blend of different fiber types each of which is biodegradable, the blend comprising face fibers having a relatively high decomposition temperature and thermally activatable binder fibers having a thermal activation temperature lower than the decomposition temperature of the face fibers. The binder fibers bind to one another and to the face fibers. The face fibers can comprise one or more types of fibers that are biodegradable. Suitable fiber types include but are not limited to wool, hemp, cotton, jute, flax, kanaf, sisal, rayon, silk, and PLA. The binder fibers in some embodiments of the invention comprise low-melt PLA.

When a web made of PLA is thermally bonded or resin-bonded with an adhesive while controlling to prevent the flexibility from being impaired, the resulting nonwoven fabric becomes fluffy or inferior in mechanical strength, thereby failing to provide a nonwoven fabric that can be subjected to practical use (2010, **WO2010122806** A1, CHISSO CORP; CHISSO POLYPRO FIBER COMPANY L).

11.3 WOVEN/KNITTED

JP2004204365 A (2004, TORAY INDUSTRIES) discloses a soft woven or knitted fabric for bedding materials using a multifilament yarn composed of PLA. The PLA multifilament yarn contains a fatty acid bisamide and/or an alkyl-substituted fatty acid monoamide in an amount of 0.1–5 wt% on the basis of the whole fiber. The single filament fineness is 0.1–2.4 dtex. The disclosed PLA woven or knitted fabric is claimed to have excellent abrasion resistance and be gentle to the skin. Bedding materials using the woven knitted product include cover of sleeping bag, cradle, push chair, blanket, futon mattress, quilt, floor seat cushion, pillow, and bed pad.

JP2005146425 A (2005, KANEBO LTD; KANEBO SYNTHETIC FIBERS LTD) discloses a fibrous material for woven knitted product, containing preset amount of PLAs differing in molecular weight. In particular, the fibrous material contains PLA (5–50 wt%) with molecular weight of 10,000–50,000 and PLA (50–95 wt%) with molecular weight of 50,000–200,000. The fibrous material is claimed to have excellent stain resistance and inhibit water pollution. Woven knitted products using the PLA fibrous material include fishing net for marine culture and fishing implements, marine structure such as bottom portion of ship, undersea communication cable, transmission pipeline, observation buoy, float, oil fence, silt protector, bridge pier and wave-powered electricity generation buoy.

Example: PLA ($T_m = 168\,°C$ and molecular weight of 27,000) (10 wt%) and PLA ($T_m = 170\,°C$ and molecular weight of 140,000) (90 wt%) were mixed to obtain a polymer blend. The obtained polymer blend was melted at 220 °C, extruded, drawn and heat set at 130 °C to obtain 500 dtex monofilament. The tensile strength, elongation at break and shrinkage in boiling water of the obtained filament was 5.2 cN/dtex, 26.2% and 5.2%, respectively. A net made from the obtained monofilament had favorable stain resistance.

JP2009270228 A (2009, TEIJIN FIBERS LTD; TEIJIN LTD) discloses a heat storage interlining cloth comprising

PLA fibers containing a heat storage medium. The PLA fibers are composed of a PLA composition comprising: (1) PLLA, (2) PDLA, and (3) a specific phosphoric ester metal salt in an amount of 0.05–5 pbw on the basis of 100 pbw of the sum total of the components (1) and (2). The heat storage interlining cloth is claimed to have excellent heat storage properties without deteriorating fabric strength and heat resistance. The thermal storage agent is carbon black, zirconium carbide, titanium carbide, hafnium carbide, zirconium silicide, titanium silicide, titanium black, or hafnium silicide.

JP2009280932 A (2009, TEIJIN FIBERS LTD; TEIJIN LTD) discloses a water-absorbing woven or knitted fabric produced by using the same composition as the previous patent application and a cotton fiber from which cotton wax has been removed. The water-absorptive woven knitted product is used for textiles such as sporting clothes, underwear garment, gentleman garment, and women garment. Uses include vehicle interior material, flooring and sealing material, carpet, curtain, mat, spectacles wiping, tableware wiping, mouse pad, cap, and white board cleaner.

JP2010024576 A (2010, TEIJIN FIBERS LTD; TEIJIN LTD) discloses a PLA fabric used for woven knitted products like garments, comprising multifilament yarn formed from a similar PLA composition and having an apparent thick/thin ratio of 1.1 or more in which single filaments each having a random fineness distribution in the filament direction, and a thick part and a thin part of the multifilament yarn can be dyed in the same color. Preferably, the PLA composition contains 0.1–5 pbw of a carboxyl terminal sealing agent with respect to the total content of 100 pbw to the total content of 100 pbw of components (1) and (2).

JP2009133022 A (2009, UNITIKA FIBERS LTD) discloses a filter bag for beverages made of a woven fabric in which the monofilament yarns are arranged in warp yarns and weft yarns. The monofilament yarns are in a core-sheath conjugated form in which a scPLA having a $T_m \geq 180\,°C$ is arranged in a core part and an aliphatic polyester having a $T_m = 90–170\,°C$ is arranged in a sheath part. In the woven fabric, crossing points of the warp yarns with the weft yarns are heat-bonded with the molten polymer in the sheath part. The woven fabric is subjected to thermobonding in which the polymer of sheath portion melts along warp and weft direction. The edge portions of the filter bag are adhered by ultrasonic seal or heat seal.

DE102011121380 A1 (2013, NEXTRUSION GMBH) discloses an industrial fabric, such as woven or knitted fabric consisting of yarns or threads containing 80–99 wt% PET, polyamides or polyolefin such as polyethylene or polypropylene and 1–20 wt% PLA. The fabric is used for filtration sieves of papermaking device.

11.4 NANOFIBERS

WO2012029710 A1 (2012, UNIV OKAYAMA NAT UNIV CORP) discloses a method for producing a nanofiber of an aliphatic polyester using the apparatus of Figure 11.7 and comprising the following steps: (1) extruding an organic solvent solution (S) into filaments in an aqueous solution (W) including a surfactant (SF) and water, the organic solvent solution (S) including an aliphatic polyester (A0) or an oil-soluble low block copolymer (A) comprising a block derived from an aliphatic polyester (A1)

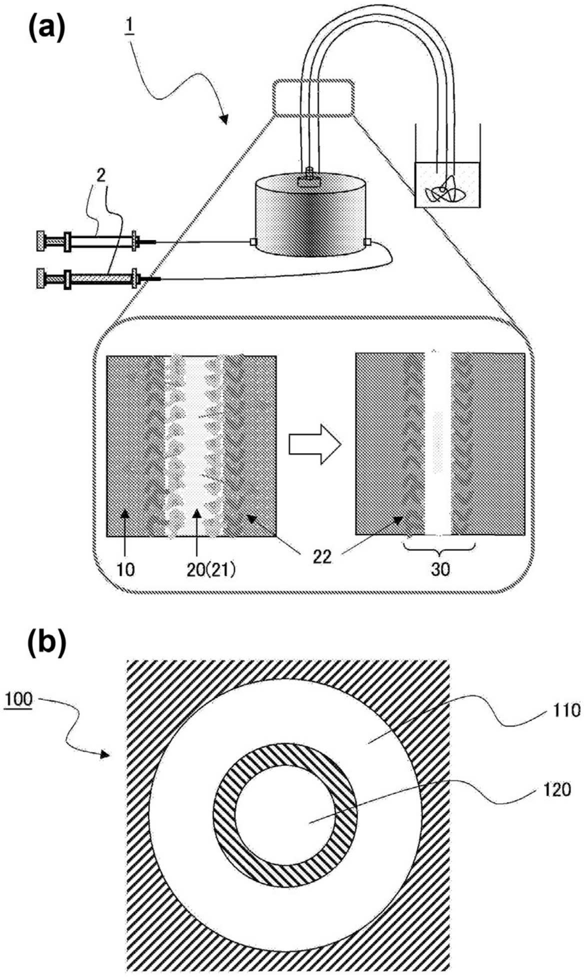


FIGURE 11.7 (a) Schematic view of a double-tube micro-nozzle apparatus (1) equipped with syringes (2) that is used in the production of nanofibers; (b) enlarged plan view of an opening of a double-tube micro-nozzle (100) of the apparatus (2012, **WO2012029710** A1, UNIV OKAYAMA NAT UNIV CORP). In the frame: an organic solvent (S1) (21) of an organic solvent solution (S) (20) extruded from an inner tube (120) is removed by being diffused into an aqueous solution (W) (10) with the result that molecules of a precipitated oil-soluble low block copolymer (A) (22) are aggregated to form nanofibers (30). 1, Double-tube micro-nozzle apparatus; 2, Syringes; 10, Aqueous solution (W); 20, Organic solvent solution (S); 21, Organic solvent (S1); 22, Oil-soluble low block copolymer (A); 30, Nanofibers; 100, Double-tube micro-nozzle; 110, Outer tube; 120, Inner tube.

and a block derived from a hydrophilic polymer (A2), and an organic solvent (S1); and (2) spinning organic solvent solution (S) to form filaments, while simultaneously diffusing or distilling the organic solvent (S1) within the organic solvent solution (S) into the aqueous solution (W). The aliphatic polyester (A0) or the aliphatic polyester (A1) is selected from PLA, PGA, PCL and PBS. The disclosed method does not require cumbersome steps such as steps involving stretching, is capable of performing operations at room temperature, and yields a higher productivity than conventional methods.

CN102071492 A (2011, UNIV JIANGNAN) discloses a method for preparing PLLA nanofibers with ultraviolet absorption performance, which belongs to the field of functional textile materials. The method is to uniformly mix an organic ultraviolet absorber (modified UV-O) with dichloromethane spinning solution of PLLA and adopt an electrostatic spinning technique to prepare the biodegradable PLLA nanofibers. The nanofibers are uniform in thickness and have high UV absorption performance. The absorption rate of UV light within a wavelength range from 200–350 nm is over 90%.

KR20120097948 A (2012, KUMOH NAT INST TECH ACAD COOP; WONBIOGEN CO LTD) discloses a method for fabricating a nano/micro hybrid fiber nonwoven fabric containing biodegradable polymers comprising the steps of: (1) dissolving two different biodegradable polymers in organic solvent to prepare each solution; (2) spinning the nanofibers and microfibers at both direction by electrospinning to prepare a nano/micro hybrid fiber sheet; and (3) removing residual solvent from the hybrid fiber sheet. The biodegradable polymers are poly(lactic-*co*-glycolic acid) and poly(ε-caprolactone) (PCL).

11.5 WEARING RESISTANCE OF FIBERS

The wearing or abrasion properties of PLA fibers have been described in Chapter 2: Properties; Section 2.3.1.1: Friction and wearing resistance. Here below, are provided additional information for improving the wearing resistance of PLA fibers.

JPH08183898 A (1996, SHIMADZU CORP; KANEBO LTD) discloses the addition of a fatty monoamide, expressed by the general formula $RCONH_2$, wherein R represents an alkyl group, to PLA fibers with the objective of suppressing the hydrolysis rate by imparting water repellency. PLA fibers in which a fatty monoamide had been added, however, wearing resistance and ability to smoothly pass through processing steps of PLA could not be improved on (2004, **WO2004020708** A1, TORAY INDUSTRIES).

PLA fiber having a fatty-acid monoamide, sometimes has a high b* value in fiber color system of L*a*b* and a strong tendency of a tincture of yellow. This is considered to be caused by that, in addition to the thermal degradation of the fatty-acid monoamide, which has a poor thermal resistance, the fatty-acid monoamide reacts with the carbonyl group of PLA in the melt molding to form a diacetamide group and as a result, the proportion of fatty monoamide that can function as smoothing agent in fibers of fatty monoamide decreases.

In some cases, when a fatty monoamide reacts with PLA, molecular chains of PLA end up cut and consequently molecular weight decreases, lowering the fiber properties. Moreover, fatty monoamides, having high sublimation property or low heat resistance, sometimes cause deterioration of the work environment through smoke, fouling of guides, rollers or the like through bleeding out, and deterioration of operating efficiency. Furthermore, bled out fatty monoamide condenses on the fiber surface, sometimes causing fiber property macula or dying macula.

WO2004020708 A1, (2004, TORAY INDUSTRIES) addresses the above problems by providing PLA fibers containing a fatty acid bisamide in an amount of 0.1–5 wt% in relation to the whole of fiber, said fatty acid bisamide having a $T_m \geq 100\,°C$ and being selected from the group consisting of ethylene-bis(stearamide), ethylene-bis(oleamide), ethylene-bis(erucamide) and *m*-xylylene-bis(stearamide); wherein said fiber are produced by a melt spinning method and have a b* value in fiber color system of L*a*b* in the range of −1 to 5 and a single fiber fineness of 0.1–10 dtex, and the fiber-constituting PLA is 40 eq/t or less in carboxyl end group amount.

As opposed to the conventional fatty acid monoamides, the selected fatty acid bisamides are claimed to have excellent thermal resistance, and because amide group has a low reactivity, a tincture of yellow of fiber is hard to be generated. The produced PLA fibers are claimed to have excellent wearing resistance and ability to smoothly pass through processing steps.

By specifying the b* value, which is an index of a color tone of a tincture of yellow, as five or less, the fiber can be widely used also in applications, in which the color tone is important, such as clothing materials, interior decoration and interior members of a vehicle. It is more preferable that b* value should be three or less.

Means of largely improving the wearing resistance of PLA fibers has been disclosed in a series of patents by TORAY INDUSTRIES described below. They aim to reduce abrasion by adding lubricants such as fatty acid bisamide to decrease the friction coefficient of the fiber surface. However, though these fiber materials work appropriately when applied stress is low, they are not sufficiently resistant adhesive wear when used in materials such as carpets that receive strong forces by users walking on them. Accordingly, PLA suffers destruction and, therefore, can be applied only to limited uses (2009, **WO2010074015** A1, TORAY INDUSTRIES).

JP2004091968 A (2004, TORAY INDUSTRIES) discloses a PLA fiber containing 0.1–5 wt% of a fatty acid bisamide and/or alkyl-substituted type fatty acid monoamide. The disclosed PLA fiber is claimed to have good wearing resistance and processability. **JP2004204406** A (2004, TORAY INDUSTRIES) is a modification of the previous patent application, and discloses a PLA staple fiber containing a fatty acid bisamide and/or an alkyl-substituted fatty acid monoamide in an amount of 0.1–5 wt% on the basis of the total fiber. The PLA staple fiber can be used as a binder fiber as it is, and a fiber structure such as spun yarn, nonwoven fabric and wadding can be produced by using the PLA staple fiber. The disclosed PLA staple fiber is claimed to have excellent slipperiness and provide various kinds of fiber structures such as spun yarn produced by using the PLA fiber. **JP2004204407** A (2004, TORAY INDUSTRIES) is another modification, and discloses a crimped PLA yarn for carpet composed of a PLA fiber and containing a fatty acid bisamide and/or an alkyl-substituted fatty acid monoamide in an amount of 0.1–5 wt% on the basis of the total fiber. The crimped yarn preferably has a crimp extension of 3–35%, a single fiber fineness of 3–35 dtex and a cross-section non-circularity of 1.1–8. The disclosed crimped yarn is claimed to give a carpet having excellent property to quickly recover the original state after removing the load applied to compress the carpet. **JP2006274520** A (2006, TORAY INDUSTRIES) is still another modification, and discloses a PLA fiber having a single fiber fineness of 0.1–3 dtex, and containing a bisamide and/or alkyl-substituted aliphatic monoamide in an amount of 0.5–1.5 wt% on the basis of the whole fiber. The disclosed PLA fiber is claimed to have excellent mechanical properties at high temperature, softness and wearing resistance and high productivity.

JP2004277931 A (2004, TORAY INDUSTRIES) discloses a PLA fiber comprising a fatty acid bisamide component and/or alkyl-substituted type fatty acid monoamide component, wherein the terminal carboxy groups are blocked with a carbodiimide compound. The disclosed PLA fiber is claimed to be excellent in wearing resistance and hydrolysis resistance, slight in yellowing tendency in itself, and also good in color developability when dyed. **JP2009084759** A (2009, TORAY INDUSTRIES) is a modification of the above patent applications, and discloses a high quality PLA staple fiber containing the same fatty acid bisamide and/or alkyl substituted monoamide, wherein carboxyl terminals are blocked by a carbodiimide compound and the presence ratio of devitrified fibers is 0–10%. The disclosed PLA staple fiber is claimed to be excellent in wearing resistance and hydrolysis resistance. **JP2009167539** A (2009, TORAY INDUSTRIES) is another modification of the previous patents applications, and discloses a PLA staple fiber in which the carboxyl groups of PLA chain ends are blocked with a trifunctional or multi-functional epoxy compound; the surfaces of the fibers are covered with a fatty acid bisamide and/or an alkyl substituted fatty acid monoamide. The disclosed PLA staple fiber is claimed to be excellent in hydrolysis resistance and dyeability.

JP2004218182 A (2004, TORAY INDUSTRIES) discloses a PLA false-twisted yarn containing a fatty acid bisamide and/or an alkyl-substituted fatty acid monoamide in an amount of 0.1–5 wt% on the basis of the whole fibers. The yarn has the following properties; tenacity at 90 °C, ≥0.3 cN/dtex, CR ≥ 10%, and ≤3/10 m number of non-untwisted spots. The disclosed PLA false-twisted yarn is claimed to be excellent in the ability to smoothly pass through the various processing steps, durable in application under high temperature environment and application, which requires abrasion resistance together with excellent dimensional stability and crimping property.

11.6 ANTISTATIC FIBERS

An aliphatic polyester is easily charged and the half-life of the built-up charge is long. Accordingly, a fibrous formed article obtained by processing an aliphatic polyester into a fiber is likely to be charged and, thus is not easy to use (see also Chapter 2: Properties; Section 2.3.4).

JPH09157954 A (1997, SHIMADZU CORP; KANEBO LTD) discloses an antistatic fiber obtained by combining an antistatic polymer (1) with a fiber-forming polymer (2) consisting essentially of an aliphatic copolyester in a single fiber (see Figure 11.8). The antistatic polymer (1) is obtained by mixing an aliphatic polyester such as a PGA with one or more compounds selected from the group consisting of a surfactant containing both a lipophilic group and a hydrophilic group, a 2–4C alkyl group-containing polyalkylene ether and a derivative of the polyalkylene ether and has a volume resistivity of $\leq 1 \times 10^{11}$ Ω-cm (or Ω-cm). The combining ratio (volume ratio) of the antistatic polymer (1) and the fiber-forming polymer (2) is preferably 10/90–60/40.

WO2006022430 A1 (2006, TEIJIN LTD) discloses a fiber structure containing 0.01–100 pbw of a phospholipid per 100 pbw of an aliphatic polyester such as PLA and

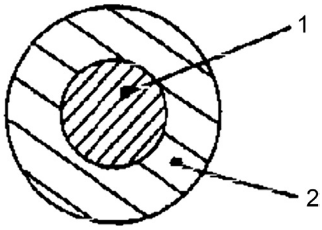


FIGURE 11.8 Cross-section view of an antistatic fiber (1997, **JPH09157954** A, SHIMADZU CORP; KANEBO LTD).

having an average fiber diameter of 0.05–50 µm. Preferably, the fiber structure has pores in the fiber surface and is suitably used as a base for cell cultivation. The patent application does not describe a fiber having antistatic properties.

WO2012023594 A1 (2012, TEIJIN LTD) discloses a low-charging fiber having an average surface porosity of less than 3% and made of a biodegradable polymer such as PLA that contains a specific amount of a phospholipid. The phospholipid is one of the following:

1. dilauroylphosphatidylcholine in an amount of 0.2–5 wt%,
2. dimyristoylphosphatidylcholine in an amount of 0.4 wt%,
3. dipalmitoylphosphatidylcholine in an amount of 1–5 wt%,
4. dioleoylphosphatidylcholine in an amount of 1–5 wt%, and
5. dioleoylphosphatidylethanolamine in an amount of 1–5 wt%, or
6. two or more of the phospholipids (1)–(5).

The disclosed fiber and fibrous article formed there are suitable for use as medical supplies, such as materials for the protection of the surface of organs or wound sites, covering materials, sealing materials, artificial dura mater, adhesion barriers, and hemostatic materials.

JP2004270094 A (2004, TORAY INDUSTRIES) discloses a biodegradable polyester short fiber composed of PLA and obtained by attaching an oil solution consisting essentially of a quaternary ammonium salt and an ester nonion to the surface of the fiber. The polyester short fiber is claimed to have excellent antimicrobial property and washing durability, good antistatic property, rust- and discoloration-preventing property, and biodegradability.

JP2004044002 A (2004, UNITIKA FIBERS LTD) discloses a base fabric for an antistatic belt, such as conveyance belt and transmission belt, comprising PLA-based fibers. It is preferable that the surface resistance of the base fabric is ≤1011 Ω (or Ohms) (measured in accordance with static electricity safety guideline structure standard AATCC-76, 84). The base fabric for the belt is, if necessary, coated with a rubber or a resin.

PATENTS

Patent Number	Publication Date	Family Members	Priority Numbers	Inventors	Applicants	Title
CA2127754 A1	19950203	JPH08246320 A 19960924; FR2709500 A1 19950310; ES2122205 T3 19981216; EP0637641 B1 19980902; EP0637641 A1 19950208; DK0637641 T3 19990531; DE69412948 T2 19990512; AT170575 T 19980915	JP19940200107 19940802; FR19930009649 19930802	BERTRAND ERIC; GUIPOUY PHILIPPE; LAUFFENBURGER PATRICK; EHRET PHILIPPE	FIBERWEB SODOCA SARL	Nonwoven containing an acid lactic polymer derivate, process of making and use thereof.
CN102071492 A	20110525		CN20101587649 20101206	DAN HUANG; HAO ZHU; CAIYING SHAO; YUN SHEN	UNIV JIANGNAN	Method for preparing polylactic acid (PLLA) nanofibers with ultraviolet (UV) absorption performance.
EP0104731 A2	19840404	US4537738 A 19850827; JPS5959419 A 19840405; JPH0263055 B2 19901227; EP0104731 A3 19850807; EP0104731 B1 19871125	GB19820024683 19820827	HOLMES PAUL ARTHUR	ICI PLC	3-Hydroxybutyrate polymers.
JP2002248047 A	20020903		JP20010048525 20010223	TSUGAWA HIROYUKI; HASEGAWA KENJI	UNITIKA FIBERS LTD	Biodegradable carpet.
JP2003010030 A	20030114		JP20010200712 20010702	KISHIGAMI KAZUHIKO; MATSUMURA KAZUYA	TOWA ORIMONO CO LTD; TORAY INDUSTRIES	Carpet.
JP2003041435 A	20030213	JP3806320 B2 20060809	JP20010225647 20010726	YAMADA TOSHIHIRO; AIDA HIRONORI	TEIJIN LTD	Method for producing polytrimethylene terephthalate staple fiber.
JP2003049374 A	20030221		JP20010234309 20010802	SHIMIZU TAKEO	UNITIKA TEXTILES LTD	Dyeing process for polylactic fiber.
JP2003293220 A	20031015	JP3966043 B2 20070829	JP20020096922 20020329	OCHI TAKASHI; KIMURA TOSHIAKI; MAEDA YUHEI	TORAY INDUSTRIES	Method for producing polylactic acid fiber having excellent heat resistance.
JP2003328229 A	20031119		JP20020131804 20020507	YAMAOKA TETSUJI; KIMURA YOSHIHARU	JAPAN SCIENCE & TECH CORP	Biodegradable porous ultrafine hollow fiber and method for producing the same.

Continued

—Cont'd

Patent Number	Publication Date	Family Members	Priority Numbers	Inventors	Applicants	Title
JP2004044002 A	20040212		JP20020201332 20020710	SAKOBE TADAYUKI; NAKAGAWA KUNIYOSHI; MATSUOKA EIICHI	UNITIKA FIBERS LTD	Base fabric for antistatic belt and industrial belt using the same.
JP2004091968 A	20040325	JP4114443 B2 20080709	JP20020254201 20020830	KIMURA TOSHIAKI; NONAKA SHUICHI; OCHI TAKASHI	TORAY INDUSTRIES	Polylactic acid fiber with high wear resistance and method for producing the same.
JP2004204365 A	20040722	JP4222023 B2 20090212	JP20020371669 20021224	MOCHIZUKI KATSUHIKO; KIMURA TOSHIAKI; SAKAI TAKAAKI	TORAY INDUSTRIES	
JP2004204406 A	20040722		JP20020377242 20021226	KIMURA TOSHIAKI; MAEDA YUHEI; MOCHIZUKI KATSUHIK	TORAY INDUSTRIES	Polylactic acid staple fiber and fiber structure composed thereof.
JP2004204407 A	20040722	JP4075611 B2 20080416	JP20020377243 20021226	KIMURA TOSHIAKI; OCHI TAKASHI; MAEDA YUHEI	TORAY INDUSTRIES	Crimped polylactic acid yarn for carpet.
JP2004218182 A	20040805	JP4059192 B2 20080312	JP20030417657 20031216; JP20020377241 20021226	SAKAI TAKAAKI; MOCHIZUKI KATSUHIKO; MAEDA YUHE	TORAY INDUSTRIES	Poly(lactic acid) false-twisted yarn and method for producing the same.
JP2004270094 A	20040930		JP20030064773 20030311	MAEDA KOICHIRO; YOKOYAMA MASAO; HOSOHARA SADAO	TORAY INDUSTRIES	Polyester short fiber.
JP2004277931 A	20041007		JP20030071467 20030317	KIMURA TOSHIAKI; MOCHIZUKI KATSUHIKO; MAEDA YUHEI	TORAY INDUSTRIES	Polylactic acid fiber and fibrous structure using the same.
JP2005008997 A	20050113	JP4254368 B2 20090415	JP20030171684 20030617	NISHIHATA SHINICHI; NISHIMURA MOTOKATSU	TORAY INDUSTRIES	Polylactic acid crimped yarn and method for producing the same, and carpet.
JP2005023512 A	20050127	JP4605640 B2 20110105	JP20040309035 20041025	MATSUMOTO HIROSHIGE; MAEDA YUHEI; ARANISHI YOSHITAKA	TORAY INDUSTRIES	Polylactic acid fiber.
JP2005048303 A	20050224		JP20030204343 20030731	INOUE SHOZO; HASHIMOTO KOJI; NISHIHATA SHINICHI	TORAY INDUSTRIES	Polylactate flat crimped yarn and carpet.

JP2005060850 A	20050310		JP20030207054 20030811	NISHIMURA MOTOKATSU; HASHIMOTO KOJI; INOUE SHOZO	TORAY INDUSTRIES	Spun-dyed polylactic acid crimped yarn and carpet using the same.
JP2005146425 A	20050609	JP4040567 B2 20080130	JP20030380765 20031111	KAJIYAMA HIROSHI; MUTAGAMI SHIYOUGO	KANEBO LTD; KANEBO SYNTHETIC FIBERS LTD	Polylactic acid fiber and woven or knit fabric made thereof.
JP2005307359 A	20051104		JP20040121472 20040416	NARITA SHUSAKU; YOKOYAMA MASAO; MITO OSAMU	TORAY INDUSTRIES	Polylactic acid staple fiber and staple fiber nonwoven fabric using the same fiber.
JP2006068225 A	20060316		JP20040254510 20040901	CHIGA KOJI	ORIX INTERIOR CORP	Mat.
JP2006097166 A	20060413		JP20040283324 20040929	YOSHIDA SHINJI; OTA SEIYA	SUMINOE TEXTILE; NIPPON A & L KK	Backing agent for carpet and carpet given by using biodegradable fiber.
JP2006274520 A	20061012	JP4604797 B2 20110105	JP20050100208 20050330	TAKANAGA HIDETOSHI; SAWAI YUMIKO	TORAY INDUSTRIES	Polylactic acid fiber, its package and method for producing the same.
JP2007230284 A	20070913		JP20060051862 20060228	YAMAMOTO HISAO	UNITIKA FIBERS LTD	Surface member for interior material of automobile.
JP2007270372 A	20071018		JP20060096192 20060331	MATSUNAGA ATSUSHI; MORIOKA TATSUTA	UNITIKA LTD	Substrate cloth for tufted carpet and tufted carpet using the same.
JP2007314913 A	20071206		JP20060145756 20060525	YAMADA TAKAYOSHI; HORIMOTO MASAKI	TOABO MATERIAL CO LTD	Needle punched non-woven fabric derived from vegetable, for automotive or industrial material.
JP2009084759 A	20090423		JP20070258391 20071002	KAWABATA HAYAHITO	TORAY INDUSTRIES	Polylactic acid staple fiber and method for making the same.
JP2009133022 A	20090618		JP20070308826 20071129	YAMADA FUTOSHI	UNITIKA FIBERS LTD	Filter bag for beverage.
JP2009167539 A	20090730	JP5200548 B2 20130605	JP20080004055 20080111	KAWABATA HAYAHITO	TORAY INDUSTRIES	Polylactic acid staple fiber and method for producing the same.

Continued

—Cont'd

Patent Number	Publication Date	Family Members	Priority Numbers	Inventors	Applicants	Title
JP2009270228 A	20091119		JP20080122324 20080508	YASUMITSU REI; TOYOHARA KIYOTSUNA	TEIJIN FIBERS LTD; TEIJIN LTD	Heat storage interlining cloth.
JP2009280932 A	20091203	JP5217056 B2 20130619	JP20080134087 20080522	YASUMITSU REI; TOYOHARA KIYOTSUNA	TEIJIN FIBERS LTD; TEIJIN LTD	Water-absorbing woven or knitted fabric and textile product.
JP2010024576 A	20100204		JP20080187105 20080718	FUKUNAGA SUKEFUMI; TOYOHARA KIYOTSUNA	TEIJIN FIBERS LTD; TEIJIN LTD	Polylactic acid fabric and clothing.
JPH05321025 A	19931207	JP2815260 B2 19981027	JP19920002297 19920109	YAMAMOTO TAKASHI; MAEKAWA YOSHIHIRO; SHINKAWA TAKEO	CHUKOH CHEM IND; ISHIKAWA PREFECTURE	Production of yarn.
JPH06212511 A	19940802	JP3880073 B2 20070214	JP19930022109 19930113	MOCHIZUKI MASATSUGU; KAN YOSHIHIRO; TAKAHASHI SHUJI; KANEMOTO NAOTAKA	UNITIKA LTD	Biodegradable staple fiber.
JPH06264343 A	19940920	JP3711409 B2 20051102	JP19930050881 19930311	ITO TAKESHI; AOYAMA TOMOHIRO; KIMURA KUNIO; UNO KEIICHI	TOYO BOSEKI	Biodegradable fiber aggregate for agricultural use.
JPH07126970 A	19950516	JP3319531 B2 20020903	JP19930276787 19931105	KITAMURA MAMORU	TOYO BOSEKI	Biodegradable nonwoven fabric.
JPH07300720 A	19951114	JP2883809 B2 19990419	JP19940089526 19940427	YAMAMOTO TAKASHI; KIMIZU MITSUGI; MAEKAWA YOSHIHIRO; SHINKAWA TAKEO	CHUKOH CHEM IND; ISHIKAWA PREFECTURE	Biodegradable fiber and its production.
JPH07310236 A	19951128	JP3355026 B2 20021209	JP19940129565 19940518	YOSHITOME HIDEO; OSAKI TAKUJI; KONDO YOSHIKAZU; KAJIYAMA HIROSHI; MATSUI MASAO; KOSEKI EIICHI; FUJII YASUHIRO	KANEBO LTD; SHIMADZU CORP	Thermofusible polylactic acid fiber.
JPH0748769 A	19950221	JP3329350 B2 20020930	JP19930276385 19931105; JP19920301192 19921111; JP19930134425 19930604	SHINODA NORIMASA; OTAGURO MASAZO; FUNAE AKIHIRO; IIMURO SHIGERU; TANIGUCHI KEIKO; MORIYA SHINOBU; WASHINO MASAHIRO	MITSUI TOATSU CHEMICALS	Degradable nonwoven fabric and its production.

JPH08183898 A		JP3419575 B2 20030623	JP19940327439 19941228	MATSUI MASAO; FUJII YASUHIRO; KOSEKI HIDEKAZU; KONDO YOSHIKAZU; HIRAI YOSHIAKI	SHIMADZU CORP; ANEBO LTD	
JPH08284016 A	19961029	JP2892964 B2 19990517	JP19950080511 19950405	YAMAMOTO TAKASHI; KIMIZU MITSUGI; MAEKAWA YOSHIHIRO; SHINKAWA TAKEO	CHUKOH CHEM IND; ISHIKAWA PREFECTURE	Biodegradable fiber.
JPH09157954 A	19970617		JP19950316909 19951205	MATSUI MASAO; KOSEKI HIDEKAZU; KONDO YOSHIKAZU; KAJIYAMA HIROSHI	SHIMADZU CORP; KANEBO LTD	Antistatic fiber.
JPH0995849 A	19970408	JP3434628 B2 20030811	JP19950251679 19950929	NAGAOKA KOICHI; MATSUOKA FUMIO; ICHINOSE NAOJI	UNITIKA LTD	Nonwoven fabric of polylactate-based filament and its production.
JPS6169431 A	19860410	JPH0263056 B2 19901227	JP19840191834 19840914	SAIKI NORITSUGU; IBA NOBORU; KONISHI TADASHI	TEIJIN LTD	Stretching method of poly(beta-hydroxy-butyric acid) molded product.
KR20120097948 A	20120905		KR20110017540 20110228	KWON OH HYEONG; KIM CHEOL JOO; KIM YOUNG JIN; KIM WON IL	KUMOH NAT INST TECH ACAD COOP; WONBIOGEN CO LTD	Nano/micro hybrid fiber nonwoven fabric using biodegradable polymers and method for preparing the same.
US2002192456 A1	20021219	WO03078493 A2 20030925; WO03078493 A3 20040122; US2008132134 A1 20080605; US2009325444 A1 20091231; AU2003225805 A1 20030929; AU2003225805 A8 20030929	US20010275631P 20010315; US20020097439 20020315	MASHBURN LARRY E; HARRISON WILLIAM H; PATTERSON THOMAS E	MASHBURN LARRY E; HARRISON WILLIAM H; PATTERSON THOMAS E	Carpet backings prepared from vegetable oil-based polyurethanes.
US2003148688 A1	20030807	US6607996 B1 20030819	US19990351413 19990709; US19960715900 19960919; JP19950256079 19951003; JP19950251679 19950929; JP19950256083 19951003; JP19990009965 19990119; JP19950256080 19951003	MATSUNAGA MAMIKO; MATSUNAGA ATSUSHI; NAGAOKA KOICHI	TOMOEGAWA PAPER CO LTD; UNITIKA LTD	Biodegradable filament nonwoven fabric and method of producing the same.

Continued

—Cont'd

Patent Number	Publication Date	Family Members	Priority Numbers	Inventors	Applicants	Title
US2006257616 A1	20061116	WO2006124349 A2 20061123; WO2006124349 A3 20070125	US20050127417 20050512	HENDRIX JAMES E; GOSNEY H W	STOWE PHARR MILLS INC D B A PH	Renewable nonwoven carpet.
US2012289658 A1	20121115	US8461262 B2 20130611		MCENEANY RYAN J; TOPOLKARAEV VASILY A; HE AIMIN	KIMBERLY CLARK CO	Polylactic acid fibers.
US4719246 A	19880112	JPS63241024 A 19881006; CA1292818C 19911203	US19860944588 19861222	MURDOCH JOSEPH R; LOOMIS GARY L	DU PONT	Polylactide compositions.
US6143947 A	20001107		US19990385791 19990830; US19960593027 19960129	NODA ISAO	PROCTER & GAMBLE	Fibers, nonwoven fabrics and absorbent articles comprising a biodegradable polyhydroxyalkanoatecomprising 3-hydroxybutyrate and 3-hydroxyhexanoate.
WO0065140 A1	20001102	JP4623833 B2 20110202; EP1130149 A1 20010905; EP1130149 A4 20050914; EP1130149 B1 20090617	JP19990117884 19990426	MATSUNAGA ATSUSHI; WATANABE TOMOKO; MATSUNAGA MAMIKO	UNITIKA LTD	Ground fabric for tufted carpet and tufted carpet made using the ground fabric.
WO02090629 A1	20021114	US2005026529 A1 20050203; US2002188041 A1 20021212; US6946506 B2 20050920; US2003109605 A1 20030612; US6890872 B2 20050510; JP2004533551 A 20041104; JP4119756 B2 20080716; EP1397537 A1 20040317; EP1397537 B1 20080109; EP1397537 B2 20110323; DE60224530 T2 20081224; DE60224530 T3 20111013; CA2446092 A1 20021114; CA2446092 C 20061114; AU2002309683 B2 2000707; AT383462 T 20080115	US20010852889 20010510	BOND ERIC BRYAN; AUTRAN JEAN PHILIPPE MARIE; MACKEY LARRY NEIL; NODA ISAO; O'DONNELL HUGH JOSEPH	PROCTER & GAMBLE	Fibers comprising starch and biodegradable polymers.

WO2004020708 A1	20040311	US2011165370 A1 20110707; US8101688 B2 20120124; US2005203258 A1 20050915; TWI321600 B 20100311; KR20050058484 A 20050616; EP1548161 A1 20050629; EP1548161 A4 20080820; EP1548161 B1 20100825; CN1678777 A 20051005; CN100429338 C 20081029	JP20020254201 20020830; JP20020377241 20021226	KIMURA TOSHIAKI; NONAKA SHUICHI; OCHI TAKASHI; SAKAI TAKAAKI; MOCHIZUKI KATSUHIKO; MAEDA YUHEI	TORAY INDUSTRIES	Polylactic acid fiber, yarn package, and textile product.
WO2004061172 A2	20040722	WO2004061172 A3 20040923; US6953622 B2 20051011; MXPA05006874 A 20050816; KR20050088141 A 20050901; JP2006512506 A 20060413; EP1576213 A2 20050921; BR0317787 A 20051122; AU2003293173 A1 20040729; AU2003293173 A8 20040729; AR042799 A1 20050706	US20020331197 20021227	TSAI FU-JYA DANIEL; WERTHEIM BRIGITTE C	KIMBERLY–CLARK WORLDWIDE, INC	Biodegradable bicomponent fibers with improved thermal-dimensional stability.
WO2006022430 A1	20060302	JP4354996 B2 20091028	JP20040246432 20040826	FUKUHIRA YUKAKO; KITAZONO EIICHI; KANEKO HIROAKI	TEIJIN LTD	Fiber structure containing phospholipid.
WO2007025582 A1	20070308	US2009221204 A1 20090903; EP1762655 A1 20070314; EP1920106 A1 20080514; EP1920106 B1 20090729; CA2620378 A1 20070308; AT437992 T 20090815	EP20050018883 20050831	DE SAEDELEIR DIRK	DS TEXTILE PLATFORM NV	Biodegradable needle punch carpets.
WO2007029688 A1	20070315	US2009208695 A1 20090820; EP1956120 A1 20080813; EP1956120 A4 20100721;	JP20050258632 20050907; JP20050286452 20050930; JP20050286444 20050930	FUNATSU KENICHI; OKAMOTO YOSHIHIKO; HAYASHI YOSHIKI; YOSHIDA HIROJI	SUMINOE TEXTILE	Spun-dyed, crimped polylactic acid fiber, method for manufacture thereof, and carpet.
WO2007047844 A2	20070426	WO2007047844 A3 20070705	US20050728537P 20051020; US20050731189P 20051028	RANDALL BRIAN S; EVANS PAUL D JR; HAMMEL WALLACE J	COLLINS & AIKMAN FLOORCOVERING	Floor covering formed from a renewable resource derivative.
WO2007067435 A2	20070614	WO2007067435 A3 20070816; US2007128436 A1 20070607; US8066923 B2 20111129; US2010105841 A1 20100429; US7666501 B2 20100223; KR20080074206 A 20080812; JP2009518555 A 20090507;	US20050296157 20051207	KURIAN JOSEPH V; GODWIN RICHARD E; CHANG JING C	DU PONT	Poly(trimethylene terephthalate)/poly(alpha-hydroxy acid) bi-constituent filaments.

Continued

—Cont'd

Patent Number	Publication Date	Family Members	Priority Numbers	Inventors	Applicants	Title
		EP1957582 A2 20080820; CN101326056 A 20081217; CN101321828 A 20081210; CN101321828 B 20120704; CA2628565 A1 20070614; BRPI0620556 A2 20111116; AU2006322085 A1 20070614				
WO2008008068 A1	20080117	US2009291607 A1 20091126; US2014065914 A1 20140306; MX2009000526 A 20090127; EP2041341 A1 20090401; EP2041341 A4 20091216; EP2041341 B1 20101103	WO2006US27337 20060714	WANG JAMES H; HE AIMIN	KIMBERLY CLARK CO	Biodegradable aliphatic-aromatic copolyester for use in nonwoven webs.
WO2008029934 A1	20080313	US2010004362 A1 20100107; US8299148 B2 20121030; TW200831725 A 20080801; MX2009002380 A 20090320; KR20090048612 A 20090514; JP5023065 B2 20120912; EP2060665 A1 20090520; EP2060665 A4 20091111; CN101528994 A 20090909; CA2662400 A1 20080313; BRPI0716443 A2 20130917 AU2007292008 A1 20080313	JP20060238928 20060904	IKEGAME MIDORI; MATSUDA TAKAAKI; TO SHIN	TEIJIN LTD	Polylactic acid fiber and method for producing the same.
WO2008120807 A1	20081009	US2010130699 A1 20100527; TW200909512 A 20090301; KR20100016017 A 20100212; EP2138542 A1 20091230; CN101679733 A 20100324	JP20070093076 20070330; JP20070093073 20070330	IKEGAME MIDORI; TOYOHARA KIYOTSUNA; KURIHARA HIDESHI	TEIJIN LTD	Polylactic acid composition and fiber composed of the same.
WO2010074015 A1	20100701	US2011262683 A1 20111027; TW201031700 A 20100901; KR20110098970 A 20110902; JP2010150721 A 20100708; CN102325931 A 20120118	JP20080332097 20081226	MOCHIZUKI KATSUHIKO; KATO YASUUMAZAWA; SADANORI; ONOUE YOSUKE	TORAY INDUSTRIES	Polymer alloy fiber and fiber structure.
WO2010122806 A1	20101028	US2012064789 A1 20120315; TW201038786 A 20101101; KR20120012780 A 20120210; JP2010255135 A 20101111; EP2422005 A1 20120229; EP2422005 B1 20131204; CN102395720 A 20120328	JP20090106234 20090424	IWATA JUNJI; MATSUDA YASUSHI; KOJIMA MITSURU	CHISSO CORP; CHISSO POLYPRO FIBER COMPANY L	Biodegradable nonwoven fabric and fiber product using the same.

WO2010137514 A1	20101202	US2012064791 A1 20120315; JP2010270425 A 20101202; EP2436814 A1 20120404; EP2436814 A4 20130508; CN102395719 A 20120328	JP20090125712 20090525	MATSUMURA KAZUYA; KAJIYAMA HIROSHI; NARITA SHUSAKU; YOKOI SEIJI; ISHII SHUNTARO	TORAY INDUSTRIES	Needle-punched nonwoven fabric.
WO2012023594 A1	20120223	US2013137803 A1 20130530; MX2013001128 A 20130312; EP2607529 A1 20130626; EP2607529 A4 20130626; CN103025933 A 20130403; CA2807164 A1 20120223; AU2011291705 A1 20130314	JP20100181761 20100816; WO2011JP68728 20110812	KAGEYAMA YUKAKO; HONDA SUSUMU; SATAKE MAKOTO; KANEKO HIROAKI	TEIJIN LTD	Low-chargeable fibers and process for production thereof.
WO2012029710 A1	20120308	US2013157367 A1 20130620; EP2612959 A1 20130710; EP2612959 A4 20140122; CN103154338 A 20130612	JP20100192223 20100830	ONO TSUTOMU; KIMURA YUKITAKA	UNIV OKAYAMA NAT UNIV CORP	Nanofibers with excellent biodegradability and biocompatibility and method for producing the same.
WO9520615 A1	19950803	US5502116 A 19960326; US5536564 A 19960716; SK96996 A3 19970604; SG47812 A1 19980417 RU2144047 C1 20000110; PL315682 A1 19961125; PL181098 B1 20010531; NZ279627 A 19980626 MX9603065 A 19970628; JPH09508424 A 19970826; ID23288 A 19950810; FI962996 A 19960726; ES2251716T T3 20060501; EP0741753 A1 19961113; EP0741753 B1 20051228; DE69534715 T2 20060831; CZ9602211 A3 19970115; CN1139936 A 19970108; CN1071341 C 20010919; CA2181795 A1 19950803; CA2181795 C 20010424; AT314410T T 20060115; AU1680995 A 19950815; AU703156B B2 19990318; BR9506664 A 19970916	US19940189029 19940128	NODA ISAO	PROCTER & GAMBLE	Biodegradable copolymers and plastic articles comprising biodegradable copolymers of 3-hydroxyhexanoate.

Continued

—Cont'd

Patent Number	Publication Date	Family Members	Priority Numbers	Inventors	Applicants	Title
WO9704036 A1	19970206	MX9800592 A 19981129; KR100266488 B1 20000915; JPH11510194 A 19990907; JP4113989 B2 20080709; ES2162088 T3 20011216; EP0839170 A1 19980506; EP0839170 B1 20011017; EP1132446 A2 20010912; EP1132446 A3 20030604; EP1132446 B1 20060823; DE69636485 T2 20070419; DE69616067 T2 20020711; CA2226864 A1 19970206; CA2226864 C 20030520; AU6499896 A 19970218; AT207104 T 20011115; AT337382 T 20060915	US19950001274P 19950720	NODA ISAO	PROCTER & GAMBLE	Nonwoven materials comprising biodegradable copolymers.
WO9850611 A1	19981112	US6506873 B1 20030114; PT977912 E 20050228; NZ501274 A 20010629; NO995357 A 20000103; NO315906 B1 20031110; KR20010012198 A 20010215; KR100504214 B1 20050728; JP2001522412 A 20011113; JP4093595 B2 20080604; HK1025607 A1 20050324; ES2230689 T3 20050501; EP0977912 A1 20000209; EP0977912 B1 20040922; DE69826457 T2 20051013; CN1259176 A 20000705; CA2287952 A1 19981112; CA2287952 C 20061128; BR9815471 A 20020213; BR9815471 B1 20090113; AU7259698 A 19981127; AU742248 B2 20011220; AT277208 T 20041015	US19970850319 19970502	RYAN CHRISTOPHER MICHAEL; BUEHLER NANCY UZELA; GESSNER SCOTT LOUIS; BROSCH ANDREA LEE	CARGILL INC	Degradable polymer fibers.

Chapter 12

Manufacture of Biocomposites

12.1 GENERAL

In addition to blending a biopolymer with other (bio) polymer(s), other ways of improving the physical and thermomechanical properties of a biopolymer include the addition of various inorganic or organic fillers in the form of loose or coherent particles or fibers to the biopolymer base; and the bonding of a preformed biopolymer to the same or other solid material.

The quality of a polymer composite of the first type is affected by several factors, including the following: (1) tensile modulus, tensile strength, heat resistance, and other thermophysical properties of the fillers and polymers used; (2) size and shape of the filler particles (for fibers, the aspect ratio); (3) the total amount of filler used; (4) orientation of the embedded fillers; (5) intimacy of mixing of fillers throughout the polymeric matrix (distribution of fillers and dispersion of filler aggregates); and (6) the interfacial adhesion between the filler surface and the surrounding matrix (2011, **US2011319509** A1, POLYNEW INC).

Among the most important factors are the level of both distributive and dispersive mixing as well as the interfacial adhesion between the polymer and the filler. When a hydrophilic filler is mixed with a hydrophobic polymer, a lack of dispersion and interfacial adhesion is observed, and sometimes poorly dispersed fillers do not improve the properties, but result in deterioration of the properties instead. These effects are often overcome through the use of a surface modifying agent. For example, in glass and mineral fillers, the use of a silane surface or coupling agents is widely practiced, and these agents are available with a wide range of chemical functionalities that enable compatibilization with many different polymers. However, such surface or coupling agents are based on non-renewable resources, are often not biodegradable, can be noxious or toxic, and are relatively expensive. These and other drawbacks limit coupling agent applications in low-cost articles, such as food packaging (2011, **US2011319509** A1, POLYNEW INC).

Another important factor is the particle size of fillers. It is known that inorganic fillers, which are generally in the form of a powder or slurry, if they are simply added and mechanically stirred in a polymer matrix, they are prone to aggregation. The problem becomes severe when the particle size of the inorganic filler is in the nanodomain (see also Chapter 5: Compounding; Section 5.1: General).

A composite consisting of a biopolymer as a matrix material and a filler as reinforcement material is termed a biocomposite. The biopolymer refers to bio-based polymers (biodegradable and non-biodegradable alike) and biodegradable fossil fuel–derived polymers: Chapter 1: Introduction; Section 1.2: Definition of terms. Fillers used as biocomposite reinforcement material include inorganic, vegetable, and animal fiber/particles, as well as fiber/particles derived from renewable or fossil fuel resources.

The techniques used to manufacture biocomposites are based largely on existing techniques for processing conventional or composite polymers. These include extrusion, press molding, injection molding, compression molding, resin transfer molding, sheet molding compounding, hand lay-up, filament winding and pultrusion, and others [1].

12.2 REINFORCING BIOPOLYMERS WITH LOOSE OR COHERENT FIBROUS MATERIAL

Adding fibers into polymers can significantly improve the mechanical properties of the polymers in question. Natural and synthetic fibers have been used to this effect. Natural fibers include mineral (e.g., carbon or glass), vegetable, and animal fibers, and are incorporated in the polymer matrix to increase stiffness and reduce cost. Synthetic fibers include fibers made of polymers derived from fossil fuel and renewable resources.

12.2.1 With Carbon Fibers

JP2001329072 A (2001, TORAY INDUSTRIES) discloses a carbon fiber–reinforced polymer biocomposite comprising a carbon fiber, which has a crystal size in the range of 1.4–4.5 nm, and a biodegradable polymer, such as poly(lactic acid) (PLA). The carbon fiber reinforced polymer biocomposite is claimed to have high electroconductivity, thin wall moldability (a flowability at the time of molding), and high mechanical characteristics. The composite can be used to make molded products, such as housing of electronic appliances/equipment, and for industrial fields, such as space and aeronautical navigation, motor vehicle industry, sports, and industrial article manufacture.

JP2004231910 A (2004, TOYO INK MFG CO) discloses a molded product made of a biodegradable polymer composition comprising the following: a biodegradable polymer (97–30 wt%) and carbon fiber (3–70 wt%), wherein the carbon fiber is bundled by the biodegradable polymer along its longitudinal direction and the mean fiber length is

Biopolymers: Processing and Products. http://dx.doi.org/10.1016/B978-0-323-26698-7.00012-X

4.0–12.0 mm. The biodegradable polymer is selected from PLA, poly(ε-caprolactone) (PCL), polyhydroxyalkanoates (PHA)s, poly(alkylene alkanoate)s (PAA)s, starch, and modified starch; a preferred PAA is poly(butylene succinate-*co*-adipate) (PBSA).

Example: Carbon fiber (50 wt%), having a fiber diameter of 7 μm and fiber bundle of 7000, was bonded with PBSA (50 wt%), which had a melting temperature (T_m) of 96 °C and melt flow index (MFI) of 2 g/10 min. The obtained strand was cut. A carbon fiber polymer composition of 2 mm length was obtained. PBSA (90 wt%) was blended with the organic fiber resin composition (10 wt%) and molded using an injection-molding machine. The obtained plate-shaped molded product had a tensile-yielding strength of 25 MPa. The carbon fiber in the molded product had a fiber length of 1.36 mm and a standard deviation of 0.964.

CN1850300 A 2006 (2006, UNIV ZHEJIANG) discloses a biodegradable composite comprising PLA (80–90 wt%), hydroxyl apatite (8.8–19.2 wt%), and carbon fibers (0.8–1.2 wt%).

JP2008274228 A (2008, NEC CORP) discloses a biodegradable composite comprising a biodegradable polymer as a matrix, a fibrous filler, and a low-molecular-weight biodegradable polymer, which is partially bonded with the matrix polymer and/or surface functional group of the fibrous filler. The fibrous filler is carbon fiber. The surface functional group of the fibrous filler is an oxygen-containing group obtained by performing a gaseous phase thermal oxidation process of the fibrous filler. The low-molecular-weight biodegradable polymer is selected from PLA, PCL, poly(3-hydroxybutyrate) (P3HB), poly(butylene succinate) (PBS), cellulose acetate, or starch. The matrix polymer is of the same nature as the low-molecular-weight biodegradable polymer, and is preferably PLA.

TW201005031 A (2010, YONGYU APPLIED TECHNOLOGY MATERIAL CO LTD) discloses a PLA-based composition containing high-performance vapor-grown carbon fibers (0.1–1.5 wt%), at least one inorganic filler, and a biodegradable filler. The PLA-based composition may further include an engineering plastic (<30 wt%).

CN102532832 A (2012, HEFEI GENIUS NEW MAT CO LTD) discloses a biodegradable composite comprising PLA (50–95 pbw), modified carbon fiber (5–50 pbw), antioxidant (0.05–1 pbw), and photostabilizer (0.05–1 pbw). The modified carbon fiber is prepared as follows: (1) mixing carbon fiber (1 pbw) and oxidant solution (5–50 pbw), (2) performing ultrasonic treatment for 30–240 min at 30–90 °C, (3) rinsing with deionized water for three to five times; and (4) vacuum drying for 24–48 h at 60–150 °C. The oxidant solution is sulfuric acid, nitric acid, and/or perchloric acid. The carbon fiber is chopped carbon fiber, including polyacrylonitrile carbon fiber. The carbon fiber has a diameter of 1–100 μm and a length of 1–10 mm.

The PLA/carbon fiber composite can be used for packing food, fast food lunch box, non-woven fabric, industrial and civil cloth, agricultural fabric, health care fabric, cloth, anti-UV radiation fabric, tent cloth, or hygiene product.

DE102011011173 A1 (2012) and **DE102011017126** A1 (2012) of SCHWEMMER MARTIN disclose a molded part comprising carbon fibers and a hardened matrix material containing acrylic resin (30–95 wt%) and PLA (2–60 wt%). The manufacturing process of the molded part comprises the following steps: (1) providing a molding tool and/or a base body; (2) optionally disposing carbon fibers or carbon fiber mats in the molding tool and/or the base body; (3) adding and/or applying a viscous matrix material comprising acrylic resin and PLA into the molding tool and/or to the base body by pouring, injecting, coating, spraying, or dipping; and (4) hardening the matrix material using UV light and/or heating. The molded part can be useful for lightweight construction, preferably for automobiles and airplanes, and is produced with low material and manufacturing costs; it claims to exhibit improved resistance to weathering, sunlight, and scratch resistance, have an improved glossy surface without lacquering, and be biodegradable.

JP2013194175 A (2013, TEIJIN LTD) discloses the manufacture of a biodegradable composite obtained by adhering a biodegradable polymer with a conductive fiber, impregnating the polymer with the fiber by microwave irradiation, and heating. The conductive fiber is carbon fiber. The biodegradable polymer is preferably PLA or stereocomplex PLA (scPLA).

12.2.2 With Glass Fibers

JPH0841214 A (1996, SHIMADZU CORP) discloses a glass fiber'–reinforced biodegradable polymer obtained by reinforcing an aliphatic polyester, such as PLA, with glass fibers. The glass fibers are oxynitride glass fibers, preferably containing ≤70 wt% of an alkali (alkaline earth) metal, such as lithium, sodium, potassium, magnesium, calcium, strontium, or barium. The composite has a sufficient reinforcing effect, promoting its biodegradation after being discarded.

JP2004175831 A (2004, FUJITSU LTD) discloses a housing for an electronic device made of a composition comprising PLA, glass fibers, and a phosphate flame retardant. The housing is claimed to have high strength, excellent moldability, flame retardancy, and biodegradability.

JP2007070517 A (2007, NAGASE CHEMTEX CORP; NITTO BOSEKI CO LTD) discloses a method for producing a fiber-reinforced PCL-based sheet by impregnating a reinforcing fiber of a length ≥10 mm with a PCL varnish, which is formed by dissolving a PCL of a number average molecular weight (M_n) of 20,000–100,000 in a solvent and adding an organic peroxide, evaporating the solvent, and molding the sheet by applying heat and pressure. The molded product can be used in sports products, construction materials, leisure equipment, toys, models, and domestic electrical appliances.

Example: PCL (Placcel® H5, Daicel) (1000 g) of $M_n = 50,000$ and cellosolve acetate (2333 g) were added to a flask, heated, stirred at 80 °C, and dissolved completely. Then, the mixture was cooled at 60 °C and followed by addition of an organic peroxide: 2,5-dimethyl-2,5-bis (t-butylperoxy)hexyne-3 (Perhexyne 25B, Nippon Oils and Fats Co., Ltd.) (10 g) to obtain a PCL varnish (35 wt%). The obtained varnish was impregnated into a glass fiber fabric (WF230, Nitto Boseki Co., Ltd.) and dried at 120 °C for 10 min to obtain a sheet material. The obtained sheet material was heat pressed at 150 °C for 30 min to obtain a glass fiber–reinforced PCL composite. The glass fiber–reinforced PCL composite had a flexural (or bending) elastic modulus of 7.3 GPa and a flexural (or bending) strength of 99.6 MPa (measured according to JISK7017).The gel portion amount of composite material when extracting in 100 °C cyclohexanone for 24 h was 71%.

RTP Company (USA) introduced in the market a range of glass fiber–reinforced PLA compound grades having glass fiber loadings of 10–40 wt% (RTP 2099 X 121249 and RTP 2099 X 126216) [2]. The new materials are claimed to provide greater strength, stiffness, and thermal performance in durable and semidurable applications. In comparison with unmodified PLA, the glass fiber–reinforced compound has nearly twice the tensile strength at 114 MPa, and its heat deflection temperature (HDT) has increased by nearly 93 °C. The application of nucleation packages speeds crystallization, increasing temperature performance and allowing quicker part ejection. RTP claims that this results in PLA injection molding cycle times similar to polypropylene and acrylonitrile-butadiene-styrene copolymer [3].

Glass fiber is harmful to human body and is difficult to recycle, thus causing several energy and environmental problems. There is a trend, therefore, to reduce the use of glass fibers in biocomposites by using natural fiber reinforcements instead.

12.2.3 With Vegetable or Animal Fibers

Vegetable fibers occur spontaneously in nature and/or are cultivated as an agricultural activity and found practically in all the regions of the world, under different forms of vegetation. The vegetable fibers are also known as cellulosic fibers, because cellulose (the linear β-(1,4)-glucan that constitutes the major part of the plant cell wall) is their main chemical component, or as lignocellulosic fibers, considering that most of the fibers contain lignin, which is a natural polyphenolic polymer. The wood residues (alias lignocellulosic fillers) are commercially known as wood flour or wood dust.

Biocomposites prepared until now and used in the art use mostly powders or fibers derived from wood-based and non–wood-based natural fiber materials as cellulose-based reinforcements. Natural fibers have low abrasion resistance, superior toughness, high specific rigidity, and light weight (i.e., ≥30% weight reduction) compared with glass, thus enabling an 80% reduction in production energy. In particular, the cost of natural fibers is only approximately 1/4 of glass fibers. Furthermore, these biocomposites contribute to energy saving based on an increase (1.6%) in fuel efficiency on being applied for components of automobiles (2008, **WO2008050945** A1, KOREA ENERGY RESEARCH INST). However, the properties of cellulose-based reinforcements depend on growth conditions, growth sites, and growth periods of woods or natural fibers. In particular, because the composition and size of fibers are different in each site, the properties of raw fibers used as reinforcements are sometimes different in each site. In addition, other problems of cellulose-based reinforcements are damage to forests caused by the use of wood-based reinforcements and adverse effects associated with cultivation of non–wood-based specific plants, such as flax or hemp (e.g., use of pesticides and occupation of fertile land), which are mainly used for biocomposites as reinforcements (2008, **WO2008050945** A1, KOREA ENERGY RESEARCH INST).

The reinforcement of thermoplastic biopolymers with vegetable fibers and/or fillers is a complex process because of the hygroscopic and hydrophilic nature of the lignocellulosic fibers. The tendency of the lignocellulosic fibers to absorb humidity generates the formation of gases during processing. For articles molded by injection molding, the formation of gases causes problems, because the volatile gases remain trapped within the mold cavity during the injection molding cycle. If the material is not adequately dried before the processing, there will occur the formation of a product with porosity and with microstructure similar to a structural expanded material. This distribution of porosity is influenced by the processing conditions (pressure, time, and temperature) and, consequently, will jeopardize the mechanical properties of the modified material. The presence of the absorbed water can also aggravate the thermal degradation of the cellulosic material. The hydrolytic degradation, which is enhanced when the melted polymer temperature reaches 200 °C, is accompanied by the release of volatile substances. Therefore, drying of the vegetable fibers and/or fillers is necessary before mixing with the biopolymer. A typical drying procedure of vegetable fibers and/or fillers is 24 h, at 60 °C, in an oven with circulation of air (**WO2007095709** A1 20070830 (2007), PHB IND SA).

JPH09169897 A (1997, UNITIKA LTD) discloses a biodegradable fiber-reinforced molding obtained by dispersing 100 pbw of aliphatic polyester powder and/or fibers and 5–500 pbw of highly heat-resistant biodegradable reinforcing fibers having a mean length of 1–50 mm, preferably together with a binder, in a liquid medium, removing the liquid medium to form a sheet, drying the sheet, heating it at a temperature, $T > T_m$ of the polyester, and compressing it. Examples of aliphatic polyesters include PBS, poly(ethylene succinate) (PES), and poly(butylene adipate). Examples of highly heat-resistant biodegradable reinforcing fibers include vegetable fibers (e.g., cotton, flax, ramie, hemp, Manila hemp, kapok, and pulp), regenerated fibers (e.g., wool, silk, viscose rayon, Bemberg rayon, polynosic rayon, and solvent spinning rayon), and vinylons fibers. The biodegradable fiber reinforced molding has sufficient strength during its service life, decomposes in the natural environment when discarded, and is heat resistant by using biodegradable reinforcing fibers. The biodegradable fiber reinforced molding can be used in various applications, but because its physical properties are not sufficient compared with the general-purpose polymer, there is a limit to the application deployment.

Some exemplary commercial biocomposite products are Terralene® WF 3516 and Terralene® WF 6534 of FKuR Kunststoff GmbH (DE). Both biocomposites products are based on polyethylene derived from renewable resources (green polyethylene of BRASKEM SA) and contain wood fibers and functional additives. Terralene® WF 3516 and WF 6534 contain a low amount of wood fibers; Terralene® WF 5525 contains a medium amount of wood fibers and functional additive (see also Chapter 1: Introduction, Table 1.13).

JP2001335710 A (2001, CHIBA INST TECHNOLOGY) discloses a biodegradable fiber-reinforced composite obtained by mixing 100 pbw aliphatic polyester with 5–100 pbw cellulose fiber composed of hard linen fiber having a fiber length of 3–10 mm, and compression molding the mixture at 100–300 °C. The aliphatic polyester is preferably PBS or PBSA. The cellulose fiber is selected from Manila, sisal, and New Zealand hemp. The biodegradable fiber-reinforced composite has an improved mechanical strength without decrease in biodegradability.

WO0206023 A1 (2002, BIO DEG MOULDINGS PTY LTD) discloses a composition for forming a wood substitute, the composition comprising 30–70 vol% of a high-molecular-weight (M_w of 40,000–300,000) aliphatic polyester and the balance a comminuted cellulose-containing plant material. The aliphatic polyester is preferably PBS or PBSA. The cellulose-containing plant is selected from the epidermis or cortex of a plant, or is seed coat material. Specific examples of suitable plant material are nutshells (e.g., pecan nutshells and peanut shells) and other cellulose-containing waste material (e.g., sugar cane bagasse).

Example: PBSA (Bionolle® 3020, Showa Highpolymer Co. Ltd.) (402 g) was heated until liquefied; then, comminuted pecan nutshells (125 g) were added, and a homogeneous mixture was formed by hand mixing. The pecan nutshells had been comminuted using an electric blender to produce a powder. The composition so formed was a reddish brown plasticine-like paste. The paste composition (500 g) was immediately compression molded into bowls of approximately 70 mm in diameter, and the molded products were cooled under running water to room temperature. The product had the appearance, feel, and weight characteristics of timber, yet was stronger than Australian hardwood. The product was biodegradable when buried or exposed to soil and other compost material. When combusted, the product did not give off toxic fumes or release any detectable harmful products into the environment.

JP2005307078 A (2005, SEKISUI CHEMICAL CO LTD) discloses a method for the fabrication of a biocomposite by melting and kneading vegetable fibers with a biodegradable polymer within a temperature range of −25 to 30 °C of the decomposition starting temperature (T_{ds}) of the vegetable fiber. The vegetable fibers have an average fiber length of 10–2000 μm and an average fiber diameter of 5–500 μm. The biodegradable polymer has a $T_m < T_{ds} + 30°$. A preferred biodegradable polymer is PBS (GSpla®, Mitsubishi Chemical Co).

WO2005078018 A1 (2005, UNIV MICHIGAN STATE) discloses a method for the fabrication of a biocomposite by extruding PHA, maleic anhydride–grafted PHA, and dried cellulose fiber. The fibers react with the grafted PHA, which acts as a compatibilizer. Preferably, the fiber is bast or leaf fiber or any other cellulosic filler or fiber; more preferably, the fiber is hemp, kenaf, sisal, flax, henequen or pineapple leaf fiber, native grass fiber, synthetic cellulose fiber, or wood flour. The amount of the cellulose fiber is varied 5–50 wt% (see also Chapter 7: Chemical Treatment; Section 7.1: Chemical Modification). Preferred PHAs are as follows: P3HB, poly(3-hydroxyvalerate), poly(3-hydroxypropionate), poly(3-hydroxyhexanoate) (PHHx), poly (3-hydroxyoctanoate), poly(3-hydroxydecanoate), poly (3-hydroxyundecanoate), poly(3-hydroxydodecanoate), and poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate) (PHBHV).

CN101503521 A (2009, UNIV SHANGHAI JIAOTONG) discloses a method for the fabrication of a biocomposite comprising the following steps: (1) vacuum drying PHBHV, PBS, and cellulose fibers; (2) melt mixing PBS and the cellulose fibers in a two-roll mixing mill in a weight ratio of 1/1–1/2 to prepare a masterbatch; (3) adding 50–80 pbw of PHBHV, 50–20 pbw PBS, and 5–20 pbw of the masterbatch to a homomixer for evenly mixing; and (4) adding the mixture to a Banbury mixer for melt mixing to obtain a strengthened and toughened biodegradable biocomposite. The biocomposite can have impact strength up to 105 J/m, tensile strength up to 32 MPa, and bending strength up to 45.9 MPa (see also Chapter 5: Compounding; Section 5.4: Making Masterbatches).

WO2007095709 A1 (2007, PHB IND SA) discloses a biodegradable composition comprising the following: (1) P3HB or its PHBHV; (2) at least one other biodegradable polymer, such as PLA, PCL, or poly(butylene adipate-*co*-terephthalate) (PBAT); and (3) at least one additive of the type of vegetable fillers and vegetable fibers, and optionally, nucleant, thermal stabilizer, or processing aid. The natural fibers are selected from sisal, sugarcane bagasse, coconut, piasaba, soybean, jute, ramie, and curaua (*Ananas lucidus*), and are present in the composition in an amount of 5–70 wt%, more preferably, of 10–60 wt%. The natural fillers are selected from wood flour or wood dust, starches, and rice husk, and are present in the composition also in an amount of 5–70 wt%, more preferably, of 10–60 wt%. The biodegradable composition can be used in the manufacture of injected packages for food or cosmetics, tubes, technical pieces, and several injected products.

WO2008050945 A1 (2008, KOREA ENERGY RESEARCH INST) discloses a biocomposite prepared from a seaweed fiber reinforcement obtained by solvent extraction and decoloration by means of high-temperature elevated-pressure molding and a method for preparing the biocomposite. The method, as outlined in Figure 12.1, comprises the following steps: (S100) drying seaweed fiber; (S101) crushing the seaweed fiber; subjecting the seaweed fiber again to drying; (S102) grinding and dissociating into fine seaweed fiber particles; (S200) dehydrating a biodegradable polymer (e.g., PBS) by drying; (S201) grinding the polymer into a powdery form; (S300) mixing the seaweed fiber (20–60 wt%) with the dried polymer powder to prepare an integral mixture of the seaweed fiber and the polymer powder; (S400) filling a metal mold with the mixture; and (S500) compressing the mold at a pressure of 1000 psi (6.89 MPa) for 10–15 min at a high temperature (135–180 °C).

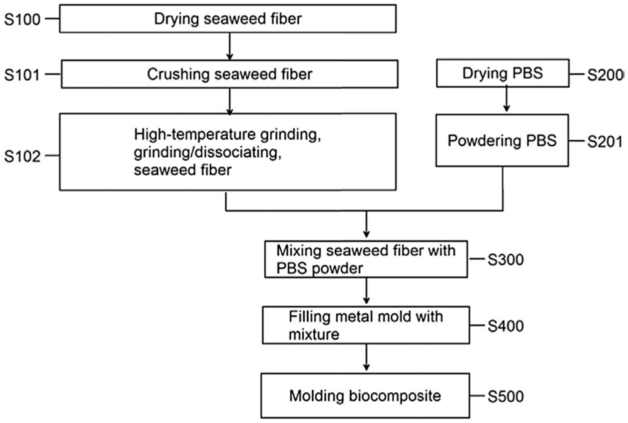


FIGURE 12.1 Flow chart showing the method steps for preparing a biocomposite from seaweed fibers (2008, **WO2008050945** A1, KOREA ENERGY RESEARCH INST). PBS, poly(butylene succinate).

Of seaweeds, red algae contain a great deal of a fiber known as "endofiber" and have a uniform diameter size of several microns. Red algae have crystallinity similar to cellulose fibers, and bleached red algae exhibit superior thermal stability, compared with cellulose fibers.

KR20080036854 A (2008, KOREA ENERGY RESEARCH INST) discloses an alternative biocomposite comprising a biodegradable polymer (e.g., PBS) and fibers extracted from red algae. Preferably, the fiber extracted from red algae is bleached, has better thermal stability than that of cellulose, and has crystallinity similar to that of cellulose.

KR100836271 B1 (2008, KOREA ENERGY RESEARCH INST) discloses a method for manufacturing an electronic parts case using a biocomposite reinforced with sea algae fibers. The method of manufacturing the electronic parts case is similar to the one described in previous patent application **WO2008050945** A1.

WO2013029018 A1 (2013, ALGIX LLC) discloses in one of its embodiments a biocomposite comprising a macrophyte biomass (10–85 wt%) and a biodegradable polymer (90–15 wt%). The biodegradable polymer is selected from P3HB, PHHx, PHV, and thermoplastic starch. A macrophyte as used herein refers generally to a macroscopic fresh or brackish water aquatic plant that is composed of multicellular specialized tissues with highly differentiated forms. The macrophyte biomass comprises at least one of duckweed, water fern, water lettuce, water hyacinth, water milfoil, pond weed, southern naiad, water weeds, horn wort, water lily, pond lily, water willow, broadleaf arrowhead, orontium, and hydrilla. The macrophyte biomass preferably has an average particle of 1–300 μm.

JP2000160034 A (2000, NIPPON CATALYTIC CHEM IND) discloses a biodegradable composite comprising bamboo fibers or bundles in a biodegradable polymer. The biodegradable polymer is preferably an aliphatic polyester, such as PES. The biodegradable polyester has a M_n of 30,000–200,000. The diameter of a bamboo fiber or a fiber bundle is preferably 7–15 μm, and the length is preferably 100 times or over of the diameter. The combining ratio of the fiber of fiber bundle is preferably 5–100 pbw on the basis of 100 pbw the biodegradable polymer.

Nishino et al. [4] describe a biocomposite in which a non-woven fabric prepared from kenaf bast is combined with PLA by a wet process having both high mechanical properties and heat resistance. Kenaf grow rapidly and, in certain cases, its growth is approximately 10 cm per day. In this way, kenaf has a fast photosynthetic rate and, thus, can absorb a large amount of carbon dioxide; therefore, it is attracting attention as one of the means to simultaneously solve the global problems of global warming caused by carbon dioxide and deforestation.

WO2004063282 A1 (2004, NEC CORP) discloses a fiber-reinforced biodegradable polymer composition suitable for production of molded items, such as electric and electronic apparatus products. A biodegradable polymer composition comprises kenaf fibers wherein the content of kenaf fibers is in the range of 10–50 wt%. The biodegradable polymer is preferably PLA. The average fiber length (number-average fiber length of fibers excluding fragments) of kenaf fibers is preferably in the range of 100 μm to 20 mm, and the kenaf fibers preferably contain kenaf fibers of 300 μm to 20 mm fiber length. The kenaf fibers are preferably fibers produced from the bast part of kenaf.

JPH10273582 A (1998, OKURA INDUSTRIAL CO LTD) discloses a biodegradable polymer composition containing 1–30 pbw of plant fiber powder crushed to a fiber length of 200 μm or less, 99–70 pbw of aliphatic polyester resin, such as PLA, and an alkaline earth metal oxide. By blending inexpensive plant fiber, the cost of the composition can be reduced and the biodegradation rate of the plant fiber composition can be increased. The vegetable fiber is most preferably one derived from coconut husks. When the amount blended of plant fiber is 1 wt% or less, the effect of the invention cannot be obtained, and when the amount is 30 wt% or more, the fluidity of the composition is decreased and the molding processability is poor. The alkaline earth metal oxide is exemplified by BeO, MgO, CaO, SrO, or BaO. The amount of the alkaline earth metal oxide added is rather larger on the basis of the amount stoichiometrically equivalent to the moisture, which the vegetable fiber carries into the composition when the molding temperature is high or when the required rate of biodegradation is high. On the other hand, the amount of the alkaline earth metal oxide added is rather smaller when the molding temperature is low or when the required rate of biodegradation is low.

JP2002069303 A (2002, MASARU O; IBB KK) discloses a method of effective use of plant fiber, which has been conventionally discarded, by mixing 40–60 wt% of plant fiber, such as straw, crushed to 60–100 mesh (150–250 μm) with 60–40 wt% of PLA and calcium bicarbonate and subjecting the mixture to injection molding. The obtained molding has reduced manufacturing cost and does not cause environmental pollution when discarded.

Li et al. [5] prepared composites of biodegradable poly(propylene carbonate) (PPC) reinforced with short *Hildegardia populifolia* natural fiber by melt mixing, followed by compression molding. Tensile tests showed that the stiffness and tensile strength of the composites increased with an increasing fiber content. However, the elongation at break and the energy to break decreased dramatically with the addition of short fiber. Scanning electron microscopy observations indicated good interfacial contact between the short fiber and PPC matrix. Thermogravimetric analysis revealed that the introduction of short *Hildegardia populifolia* fiber led to a slightly improved thermooxidative stability of PPC.

CN102504503 A (2010, GUANGZHOU ZHUOYANG NEW MATERIAL TECHNOLOGY CO LTD) discloses a keratin-reinforced and fireproof-modified PLA. The keratin fiber is obtained by degreasing, decoloring, and oxidizing (e.g., pig hair, ox hair, chicken feather, duck feather, or human hair), and crushing the modified surface into 10–10,000 meshes sieve; adding a modification reagent into the keratin fiber in a weight ratio of 10/0.5–10/2, uniformly stirring at high speed at room temperature, sealing at 40–60 °C and thermally insulating for 2–4 h to obtain modified keratin fiber, press filtering, and extruding to obtain filter cake. The reinforced PLA comprises the following components: modified keratin fiber (5–50 wt%) as basic unit, PLA (40–90 wt%), long-chain aliphatic amide compound (1–10 wt%), impact modifier (0.1–4 wt%), bio-UV stabilizer (0.1–4 wt%), and natural antioxidant (0.01–0.1 wt%). The keratin-reinforced PLA is useful (e.g., sheets for producing foam products), comprises modified keratin fiber, PLA, aliphatic amide compound, impact modifier, UV stabilizer, and natural antioxidant. The modified PLA is useful in sheets, boards, tubes, and section bars for producing foam products, extrusion molding products, blister products, injection molding products, film-blowing products, and plastic-rolling products in large scale.

12.2.4 With Synthetic Polymeric Fibers or Their Mixtures

WO2007015371 A1 (2007, UNITIKA LTD) discloses a PLA-based composition comprising a crosslinked PLA (70–99 pbw) and a high-strength fiber (1–30 pbw). The resin composition is obtained by mixing PLA and a (meth) acrylic acid ester compound in the presence of a peroxide, together with a high-strength fiber. The high-strength fiber is an aramid fiber and/or a liquid crystal polymer (LCP) fiber. To improve the mechanical strength and heat resistance, a glass fiber (1–50 pbw) may be added to the PLA-based composition.

Example: PLA (PLA 6201D, Nature Works having an MFI = 10 g/10 min and $T_m = 168\,°C$) containing LCP fiber was cooled, solidified, and pelletized. Crosslinked PLA (90 pbw) obtained using polyethylene glycol dimethacrylate (1), di-t-butyl peroxide (1), and glycerin-diacetomonocaprylate (2.5 pbw) was extruded. Furthermore, ethylene glycol dimethacrylate (0.22 pbw), di-t-butyl peroxide (0.45 pbw), FT592 (glass fiber, Asahi Fiber Glass Co., Ltd) (5 pbw), and the PLA pellets (5 pbw) were mixed and pelletized. The pellets were dried at 70 °C for 24 h and injection molded. The molded product had a heat deformation temperature of 80 °C (as measured by ISO 75), a Charpy impact value of 11.3 kJ/m^2 (as measured by SO 179), a bending elastic modulus of 6.1 GPa, and a bending fracture distortion of 4% (both measured by ISO 178), and claimed to exhibit biodegradability, moisture resistance, moldability, and flexibility.

12.2.5 With Pretreated Fibers

The natural fibers and/or natural fillers can be surface treated to improve the compatibility between the matrix and fibers and/or fillers by generating a more active interface, which facilitates the stress transfer from the matrix to the fiber. The efficiency of the treatment is evaluated by quantitative techniques of surface analysis and/or by the performance of the composite.

JP2007154002 A (2007, TOYODA GOSEI KK) discloses a PLA composition in which at least part of the carboxyl terminal group of PLA is blocked with a carbodiimide compound, a crystal nucleating agent, reinforcing fibers surface treated with a coupling agent, and inorganic particles also surface treated with a coupling agent. The concentration of the residual monomer derived from the PLA in this PLA-based resin composition is 2000 ppm or less. The claimed PLA composition enables improvement of crystallinity and thermal deformation resistance and insurance of good hydrolysis resistance, and its molded article.

12.3 REINFORCING BIOPOLYMERS WITH FILLERS

12.3.1 With Inorganic Fillers

JP2002105298 A (2002, SHIMADZU CORP) discloses a PLA composition composed of PLA and inorganic filler having an aspect ratio of five or more in an amount of 1-30 wt%, more preferably 5–15 wt%. The inorganic filler component is surface treated with a silane coupling agent.

12.3.2 With Organic Fillers

US2012202925 A1 (2012, SRUBAR III WILFRED V; BILLINGTON SARAH L) discloses a biocomposite that includes a matrix composed of a PHA, such as PHBHV, and a filler composed of particles dispersed in the matrix. The particles are composed of naturally derived materials, have a microporous microstructure, have a hygroscopic expansion of at most 2%, and have diameters within the range of 0.1–1.0 mm. The filler preferably amounts at most 30 vol%, and more preferably 15–25 vol% of the composite material. The biocomposite has improved durability and service life when exposed to environmental moisture, while also having mechanical properties suitable for use as a building material. The biocomposite material may also take the form of a coating on a building material or other article. The biocomposite coating is claimed to avoid the detrimental environmental effects of conventional moisture sealants, serve as a moisture reservoir coating to protect the underlying structural material, and do not affect the biodegradability of the underlying material. Moreover, after absorption of moisture in a humid environment, the composite material may later serve as a humidifier in dry environments.

In preferred embodiments of the invention, the particulate filler is made of ground bone meal, powdered pumice, or a mixture of the two. Ground bone meal is an industrial byproduct of the food industry that is largely disposed as waste. Ground pumice is a lightweight, naturally occurring aggregate. These filler materials have various advantageous features. Tensile tests of the PHBHV-bone meal composite reveal that bone meal filler makes the composite stiffer than the pure PHBHV. Moreover, data revealed that the moisture absorption rate in bone meal composites was twice that of pure PHBHV. As a result, these fillers avoid the adverse effects of exposure to environmental moisture that damage composites using natural fibers. Bone meal is also relatively inexpensive, has a low density, and is naturally derived.

12.3.3 Nanobiocomposites

Nanocomposites represent an alternative approach for improving the properties of a biopolymer. Many researchers have examined the potential for nanoparticles reinforcement of biopolymers, with mixed degrees of success [6–11]. Biopolymer-based nanocomposites have been reported to have improved physical, mechanical, and thermal properties, including barrier properties, tensile strength, and thermal stability, respectively [12]. Substantial savings to the costs and the weight of the materials can also be achieved. It has been estimated that a nanocomposite with a nanofiller content of 4 wt% provides equivalent mechanical properties compared with a conventional microcomposite with a microfiller content of 20 wt% [13]. However, the polymer nanocomposites did not live up to the expectations because they did not provide substantial improvements to the mechanical properties of materials in comparison to the conventional microcomposites. The main reason the mechanical properties of polymer nanocomposites still fall short of their theoretically predicted values is the inherent tendency of the nanoparticles to aggregate and/or agglomerate, and their inability to disperse homogeneously within the polymer matrix.

12.3.3.1 Inorganic Nanofillers/Nanofibers

Most inorganic nanofillers, such as clay nanoparticles, are hydrophilic, whereas the major aliphatic polyesters, in particular PLA, are hydrophobic. Therefore, most inorganic nanofillers are surface treated to render them hydrophobic e.g., fumed silica treated with silicone oil or hexamethyl disiloxane (e.g., Aerosil®, Evonik Industries AG). Numerous efforts have been made to solve the previously mentioned problems. A variety of nanofiller dispersion methods, such as in situ polymerization [6], solution intercalation method in N-dimethylacetamide [7], and melt intercalation technique using modified montmorillonite [6,14], have been applied. Biodegradable nanocomposites were prepared on the basis of PLA and montmorillonite clay with stacked intercalated and partially exfoliated morphologies [8].

KR100655914 B1 (2006, SK NETWORKS CO LTD) discloses a biodegradable nanocomposite comprising the following: 70–95 wt% of an aliphatic polyester and 5–30 wt% of a powder of layered inorganic silicate comprising muscovite and/or phlogopite dispersed in oil. The dispersion of the powder of layered inorganic silicate in oil improves dispersibility with the biodegradable polymer and enables penetration of the oil into the pores between the layers of the powder of layered inorganic silicate, thereby further expanding the pores or interlayer spacing. The aliphatic polyester is selected from PLA, poly(glycolic acid) (PGA), PCL, and P3HB; preferably, PLA is used. The method for preparing the biodegradable nanocomposite is outlined in Figure 12.2.

KR20060003580 A (2006, TORAY SAEHAN INC) discloses a biodegradable polyester composition comprising 40–95 wt% PLA, 5–60 wt% aliphatic-aromatic polyester, and 0.1–10 wt% inorganic nanoparticles modified with various intercalating agents. Suitable inorganic nanoparticles are montmorillonite, hectorite, saponite, atapulgite, sepiorite, and vermiculite. The intercalating agents are selected from alkylene glycols, such as ethylene glycol, propylene glycol, and tetramethylene glycol.

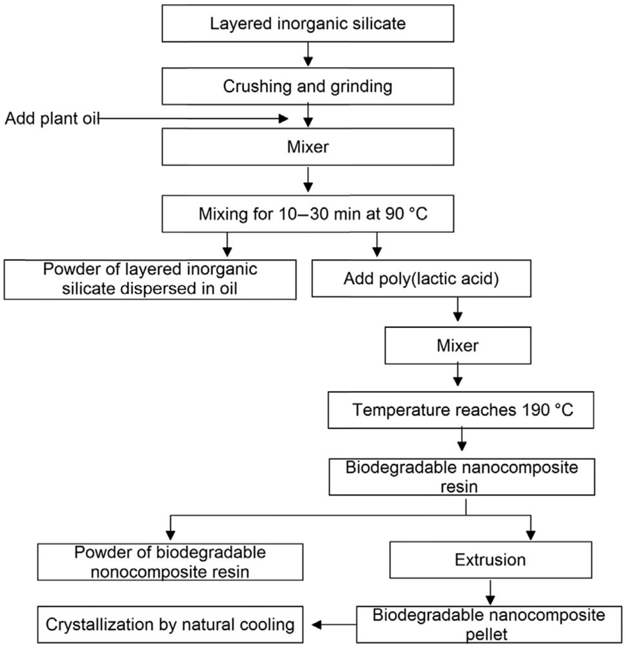


FIGURE 12.2 Flow chart illustrating the method for preparing a biodegradable nanocomposite (2006, **KR100655914** B1, SK NETWORKS CO LTD).

WO03022927 A1 (2003, UNITIKA LTD) discloses a biodegradable polymer composition for molding comprising 100 pbw of a biodegradable polyester containing at least 50 pbw of PLA having a $T_m \geq 160°$, and an MFI of 0.1–50 g/10 min under 21.2 load, and 0.1–20 pbw of a phyllosilicate containing primary-tertiary amine salt, quaternary ammonium salt, or phosphonium salt bonded as ions. For improvement of the dispersibility of the phyllosilicate in the biodegradable polyester, at least 0.1–10 pbw of a compound selected from a polyalkylene oxide, an aliphatic polyester, a polyalcohol ester, and a polycarboxylic acid ester having an affinity for both the biodegradable polyester and the phyllosilicate having a boiling point of at least 250 °C, and a M_n of 200–50,000 may be added as a compatibilizer. The phyllosilicate is preferably dispersed in the biodegradable polyester in a completely exfoliated state in which the layers of the phyllosilicate are exfoliated from each other, in an intercalated state in which molecules of the polymer are intercalated between the layers, or in a mixed state in which the exfoliated state and the intercalated state are present. From a quantitative point of view, the average thickness of single and multiple layers of the phyllosilicate is preferably 1–100 nm, more preferably 1–50 nm, and most preferably 1–20 nm. The interlayer distance of the phyllosilicate is preferably 2.5 nm or higher.

WO2007022080 A2 (2007, UNIV MICHIGAN STATE) discloses a biopolymer composition of nanocomposite structure comprising three materials: (1) a bio-based biopolymer, such as PLA or P3HB; (2) a fossil fuel–derived biopolymer, such as PBAT; and (3) a fatty acid triglyceride quaternary ammonium salt modified nanoclay to develop a high-barrier, biodegradable material for packaging. An exemplary nanocomposite is formed by melt compounding particularly by extrusion, poly(L-lactic acid) (PLLA) with (PBAT) with Cloisite® 25A/30B (injection-molded rigid samples).

CN101469072 A (2009, SHENZHEN ECOMANN BIOTECHNOLOGY CO LTD) discloses a melting intercalation method for the preparation of a PHA/montmorillonite nanocomposite comprising the following steps: (1) preparing a graft polymer of PHA through an initiator under the condition of melting, (2) preparing a masterbatch comprising the grafted PHA as matrix and organically modified montmorillonite as a filling component, and (3) melting and blending the masterbatch and PHA to prepare the composite material. The interval of a montmorillonite layer of the prepared composite material is 1–5 nm. The montmorillonite has the advantage of dispersion evenness, good material mechanical property, better heat resistance, and film-forming property.

US2012289618 A1 (2012, KOREA INST SCI & TECH) discloses a method of preparing a biodegradable nanocomposite, including the following steps: (1) putting two kinds of single-phase biodegradable polymers (namely, poly(D-lactic acid) (PDLA) and PLLA), a clay, and a small amount of organic solvent into a reactor; (2) injecting a supercritical fluid into the reactor and applying a predetermined temperature and pressure; (3) uniformly mixing the single-phase polymers and clay to form a stereocomplex (or stereoisomeric) composite and causing a dispersion reaction of the clay; and (4) collecting the PLA/clay nanocomposite. The nanosized clay used as a filler is preferably a clay mineral having a layered structure in which oxide layers having a negative charge are laminated to one another, and may be a natural clay or synthetic clay having a thickness of approximately 1 nm, a length of approximately 2180 Å, and an aspect ratio of approximately 2000 for each layer. More specifically, the clay compound may be a phyllosilicate having a negative charge made of aluminum silicate or magnesium silicate layers, or potassium or sodium phyllosilicates filled with sodium ions (Na^+) or potassium ions (K^+) between phyllosilicate layers. The phyllosilicates are preferably selected from montmorillonite, hectorite, saponite, beidellite, nontronite, vermiculite, volkonskoite, sauconite, fluorohectorite, magadite, kaolinite, and halloysite. The PLA/clay nanocomposite has the form of a particle or porous foam (see Chapter 5: Compounding; Section 5.3.1: With Inorganic Compounds).

WO2013005914 A1 (2013, GLOTECH CO LTD) discloses the molding of a bone-fixing composite material useful for repairing osseous fracture in human skull. The molding is obtained by: (1) mixing nanocarbon particles whose end is substituted by amine or amide, and a biodegradable biopolymer at constant temperature, in an extruder; (2) heat kneading; (3) extruding through stretching; (4) continuously cooling; and (5) injection molding into desired shape. The biodegradable polymer is selected from PGA, PDLA, PLLA, PCL, polyesteramide, polyoxalate, aliphatic polycarbonate, poly(glutamic-*co*-leucine), and their copolymers. The amount of nanocarbon granules is 0.1–10 wt% with respect to biodegradable organic polymer. The composite is claimed to have excellent dispersibility, biodegradability, biocompatibility, impact strength, and tissue affinity, improves mechanical strength and physicochemical properties of the bone, and prevents adverse effects, such as corrosion of bone by acid and inflammation.

CN102167894 A (2011, CHANGCHUN APPLIED CHEMISTRY) discloses a PLA/graphene nanocomposite preparation method thereof, wherein the graphene oxide accounts for 0.1–5 wt% of the PLA (see Chapter 5: Compounding; Section 5.4: Making Masterbatches). The prepared PLA/graphene nanocomposite had a tensile strength up to 79 MPa, a tensile elastic modulus up to 3100 MPa, a notch impact strength up to 12 kJ/m^2, and a HDT up to 95 °C.

CN103030791 A (2013, UNIV HEBEI TECHNOLOGY) discloses a method of fabricating a PLA/nanodiamond composite with a solvent backflow method comprising the following steps: (1) add a PLA aqueous solution and nanodiamond to a reactor; (2) ultrasonic dispersing the mixture at room temperature for 1 h; (3) add a catalyst and an organic solvent and stir at 150 °C for 12–48 h; (4) remove the solvent and water generated by reaction by reduced pressure distillation; and (5) dissolve the reacted product with acetone, precipitate with distilled water, and dry to obtain the PLA/nanodiamond composite. The nanocomposite comprises the various components in the following proportions: 10 wt% of PLA aqueous solution, 0.01–0.50 wt% of nanodiamond, 0.035–0.06 wt% of catalyst (e.g., stannous octoate), and 10–15 wt% of solvent (e.g., toluene, xylene, or diphenyl ether). The solvent backflow method used is lower in reaction temperature, simple in equipment, easy and simple to operate, and easy to implement. The thermostability of PLA is improved substantially. Both the 5% weight loss temperature and the 10% weight loss temperature of the composite increase approximately by 40 °C, whereas the complete decomposition temperature is increased by 60 °C.

Most of the natural polymers, such as starch, cellulose, chitin, lignin, and keratin, are polar, and thus compatible with the natural clay. Yet, the incorporation of the natural clay particles on these biopolymers to produce nanocomposites does not provide satisfactory properties because the main matrix is moisture sensitive and the melt strength of the resulting product becomes poor at high clay loading, making the extrusion process and blown molding difficult.

DE19504899 A1 (1996, NAT INST RES INORGANIC MAT) discloses a method for the production of a porous body of polysaccharide/clay composite by: (1) rapidly freezing an aqueous solution of starch, Na alginate, carboxymethylcellulose (CMC), or a derivative thereof, and a clay solution; and (2) vacuum drying the frozen product without melting the ice. The clay has a size of at most 2 μm, and is selected from montmorillonite, saponite, beidellite, kaolinite, allophane, or bentonite, or a synthetic clay. The polysaccharide/clay composite can be used as a shock-absorbing, heat insulator, or sound-absorbing material. The presence of clay provides high compression strength when compared with other commercially available foamed polymers.

EP1134258 A1 (2001, TNO) discloses a biodegradable nanocomposite comprising a natural polymer, a clay, and, optionally, a plasticizer. The natural polymer is selected from starch, cellulose, chitosan, alginic acid, inulin, pectin, and derivatives and combinations thereof. The clay has a cation exchange capacity of 50–200 meq/100 g, and is preferably a smectite-like clay mineral. The nanocomposite is obtained by preparing a suspension of the clay in water and extruding the suspension together with the natural polymer and the plasticizer at elevated temperature (35–200 °C). The clay suspension is ion exchanged with a modifying agent, the modifying agent being a surfactant having from 6 to 16 carbon atoms, a functionality compatible with the natural polymer and an ammonium, phosphonium, or sulfonium group. However, this nanocomposite generally has a poor melt strength to be used in blown film applications, and because it has a natural polymer matrix, it is permeable to moisture and soluble in water, which decrease their shelf life and makes the composite film unsuitable for packaging purposes (2007, **EP1860138** A1, 2007, SABANCI UNIVERSITESI).

EP1860138 A1 (2007, SABANCI UNIVERSITESI) discloses a method for preparing biodegradable nanocomposite granules, comprising the following steps:

1. Dissolving a natural polymer selected from starch, chitosan, carbohydrates, keratin, cellulose, proteins, and derivatives thereof, such as CMC, ester-grafted chitosan, or PLA in a solvent.
2. Adjusting the pH of the solution to acidic.
3. Adding 2–50 wt% natural clay on the basis of the weight of the natural polymer.
4. Stirring the solution to obtain a natural polymer/clay nanocomposite precipitate.
5. Melt blending the natural polymer/clay nanocomposite in an extruder at a suitable temperature of 110–250 °C with a synthetic polymer selected from polyethylene oxide, low-density polyethylene, high-density polyethylene, polypropylene, and the combination thereof, and any polyolefin having a T_m lower than the degradation temperature of the natural polymer.
6. Granulating the obtained material a pelletizer.

The method comprises an optional step of adding 25–80 wt% plasticizer on the basis of the weight of the natural polymer. The clay is selected among naturally occurring smectite clays having a layered structure and a cation exchange capacity of 30–250 mEq/100 g. The weight ratio of the amount of clay to the amount of polymeric matrix is 1–10 wt%, preferably 1–5 wt%.

12.3.3.2 Organic Nanofillers/Nanofibers

Except the inorganic nanofillers/nanofibers, there are also reports of using cellulose nanowhiskers for the reinforcement of PLA [15]. The cellulose nanowhiskers were pretreated with poly(vinyl alcohol) (PVOH) for improving the dispersion of the nanofibers in the matrix. When an extruder was fed with a mixture of nanofibers and PVOH in the form of both spray-dried powders and suspension, a phase separation occurred consisting of a PVOH phase, in which most of the nanofibers were concentrated, and a PLA phase.

Petersson et al. [16] describe a method for the production of nanocomposites on the basis of a PLA matrix reinforced with cellulose nanowhiskers by means of casting. The nanofibers were subjected to a treatment with tert-butanol or with a surfactant to disperse them in the solvent, and they were subsequently incorporated into the PLA matrix through the technique of casting using chloroform as a solvent. However, it was not possible to completely prevent the agglomeration of the crystals (2011, **WO2011138485** A1, CONSEJO SUPERIOR INVESTIGACION).

Oksman et al. [17] describe a method for producing a reinforced polymer comprising PLA and a microcrystalline cellulose reinforcing material. The reinforcement material was subjected to a treatment with N,N-dimethylacetamide (DMAc) and lithium chloride (LiCl) to partially separate the cellulose nanofibers. The suspension of nanofibers was mixed with the polymeric matrix in an extruder using the technique of melt mixing. The treatment with DMAc/LiCl causes the degradation of nanocomposites at high temperatures. In addition, the dispersion of the nanofibers is not complete and, therefore, there was not a considerable improvement in the mechanical properties (2008, **US2008108772** A1, NTNU TECHNOLOGY TRANSFER AS).

Grunert et al. [18] describe a method for the incorporation of bacterial cellulose nanofibrils in a cellulose acetate butyrate matrix (CAB) by means of casting. The cellulose nanofibers showed a tendency to agglomerate. By means of chemical modification of the surface of the nanofibers (trimethylsilylation), the dispersion was improved. However, the chemically modified nanofibers had worse reinforcement properties (2011, **WO2011138485** A1, CONSEJO SUPERIOR INVESTIGACION).

US2008108772 A1 (2008, NTNU TECHNOLOGY TRANSFER AS) discloses a method for producing a nanocomposite by mixing a dispersion comprising a plasticizer and cellulose nanowhiskers into CAB. The nanowhiskers dispersion is pumped into an extruder together with CAB. The extrusion process will thoroughly mix the cellulose whiskers into the CAB matrix, thus providing a homogeneous mixture being highly reinforced.

WO2011138485 A (2011, CONSEJO SUPERIOR INVESTIGACION) discloses a method for producing a nanocomposite comprising the following steps: (1) mixing of a nanoreinforcement with a polymeric matrix in liquid state; (2) electrospinning of the dispersion obtained in (1); and (3) melt mixing of the product obtained in step (2) with a polymeric matrix equal to or different from the one used in step (1). The polymer matrix can be a biodegradable polymer. The nanoreinforcement is selected from spherical, fibrillar, tubular, lamellar nanostructures or any of their combinations. In a preferred embodiment, the fibrillar nanostructure is made of cellulose.

Example: Incorporation of plant cellulose nanofibers in PLA by melt mixing.

Plant cellulose nanofibers extracted from highly purified cellulose were lyophilized and dispersed in water by means of the application of ultrasound. They were then centrifuged at 12,500 rpm, 15 °C and 20 min, the water was removed from the supernatant by means of decanting, and the water was replaced by acetone, which was replaced later using the same method by chloroform (solvent used for PLA). This cycle was repeated four times to ensure the complete substitution of the solvent and, therefore, obtaining plant cellulose nanofibers disperse in the non-polar solvent chloroform. The solution of chloroform with cellulose nanofibers was used to dissolve the PLA pellets, so the final concentration of nanofibers with respect to the weight of PLA in the solution was set at 8%. To improve the electrospinning of the matrices, 20% polyethylene glycol and 80% PLA were added, such that both materials represent 5–6 wt% of the chloroform. The solution is introduced in 5-mL glass syringes connected through Teflon tubes to several 0.9-mm-diameter stainless steel needles. The needles are connected to an electrode that, in turn, is connected to a power source of 0–30 kV. A voltage of 12 kV is applied, and the solution is pumped through said needles with a flow of 0.6 mL/h. The counter electrode is connected to a plate (collector) covered with aluminum foil, where the electrospun structures are collected, being the distance between needle and plate of approximately 12 cm. The process is performed at room temperature. In this way, PLA electrospun structures that contain disperse plant cellulose nanofibers are obtained.

12.4 MANUFACTURE OF PREPREGS

The term prepreg as used herein means a fiber structure that has been impregnated with a resin before curing the composition.

DE102011016918 A1 (2012, FRAUNHOFER GES FORSCHUNG) discloses in one of its embodiments a prepreg made of a solvent-free epoxy resin mixture containing components made of renewable resources (≥70 wt%). The epoxy resin mixture comprises at least one multifunctional glycidyl compound made of renewable resources (20–90 wt%) as a crosslinking component and at least one multifunctional aromatic monomer with phenolic hydroxyl groups and their multifunctional oligomers and/or polymers (10–80 wt%) as a crosslinking agent, and/or an activator for crosslinking. The crosslinking agent comprises polymeric lignin and its derivatives, preferably lignin from combined processes, sulfur-free lignins and tannins; polymers, preferably oligomers obtained by extraction with aqueous and/or organic solvents; and/or polymers obtained by chemical degradation of the polymer and monomers with at least two hydroxyl groups, preferably pyrogallol. The epoxy resin is free of bisphenol A.

CN103061162 A (2013, SHANGHAI GENIUS ADVANCED MAT) discloses a biodegradable composite prepreg cloth comprising a modified PLA (40–70 wt%) and vegetable fiber. The preparation method comprises the following steps: (1) conducting a continuous drying treatment on vegetable fiber; (2) immersing the fiber with molten-modified PLA; (3) coating the modified PLA on the surface of the vegetable fiber; and (4) rolling, cooling, and winding to obtain the prepreg cloth.

12.5 BONDING PREFORMED BIOPOLYMERS TO THE SAME OR OTHER SOLID MATERIAL

There are numerous applications where it is advantageous to bond biopolymers to another material or themselves. For example, by laminating different types of films, such as a polyolefin film having good water vapor barrier property and flexibility on PLA films, the shortcomings of PLA films may be compensated. For the laminate to be functional, it is essential that both of these substrates are not delaminated during use. However, both of these substrates barely adhere to each other (see also Chapter 10: Manufacture of Films/Laminates; Section 10.2: Laminates).

The ability of biopolymers to bond to other materials is controlled by a variety of factors, including surface chemistry, topography (on the nanoscale, microscale, and macroscale), and wettability of both surfaces to be bonded. This also applies when both materials are polymeric, or one material is a polymer and the other can be metal, ceramic, composite, paint, adhesive, biological material, glass or rubber in a solid, particulate, fibrous, textile, gel, slurry or liquid form, or a combination thereof. Examples of adhering techniques to bond the two surfaces, of which at least one is composed of a biopolymer, include the use of an adhesive medium, the treatment of at least one of the surfaces by physical (e.g., heat, solvent/swelling agent, roughening, or coating) or chemical (e.g., etching or grafting) means (see Chapter 8: Surface Treatment).

12.5.1 Using Adhesives

For the purpose of improving the adhesion between a PLA film (I) and a polyolefin film (II), a modified polyolefin adhesive layer (e.g., ethylene-vinyl acetate copolymer) has been used between the layers (I) and (II) (2006, **JP2006326952** A, MITSUBISHI PLASTICS IND). In another example, a polypropylene-based adhesive composition has been used for the adhesion of layers (I) and (II) (2009, **JP2005263997** A, MITSUI CHEMICALS INC). However, no hitherto known adhesives have attained sufficient adhesiveness with respect to the adhesive strength between a PLA substrate and a polyolefin substrate, and disadvantageously delamination or the like occurs during the use of products obtained through adhesion (2009, **WO2009104372** A1, UNITIKA LTD).

WO2009104372 A1 (2009, UNITIKA LTD) discloses a resin composition that forms an adhesive layer between a PLA base layer and a polyolefin base layer. The resin composition contains a modified polyolefin (a) and a terpene resin (b), and the weight (a)/(b) is of 20/80–99/1. Alternatively, the resin composition may contain 10–90 wt% of PLA (c), 5–89 wt% of a modified polyolefin (a), and 1–80 wt% of a hydrogenated petroleum resin (d), with the total of the resins being 100 wt%.

JP2004237543 A (2004, KUREHA CHEMICAL IND CO LTD) discloses an adhesive resin layer inserted between a PGA layer and an epoxidized polyolefin layer to bond the two layers. The adhesive resin layer is composed of a carboxyl-modified polyolefin.

WO0001530 A1 (2000, ENSO OYJ) discloses a biodegradable polymer-coated paper or paperboard consisting of an outer layer containing PLA, the weight of which is at most approximately 20 g/m^2, and of an adhesive layer that binds the outer layer to a paper or paperboard and is preferably of biodegradable copolyester, such as poly(tetramethylene adipate-*co*-terephhalate) (e.g., Eastar™ 14766, Eastman Chemical Company) that is coextruded with PLA.

JP2007307719 A (2007, TOYOTA MOTOR CORP) discloses a method of bonding PLA-based parts using a PLA-based adhesive sheet arranged between the PLA-based parts, whereas the interfaces in contact with the PLA-based parts and the PLA-based adhesive sheet are heated to a temperature, $T > T_m$ of PDLA or PLLA. When the PLA-based parts contain PDLA as a main component, the adhesion sheet contains PLLA as a main component. When the PLA-based parts contain PLLA as a main component, the adhesion sheet contains PDLA as a main component. The PLA-base parts are preferably composite materials of PLA and biodegradable fibers and have concaves (i.e., gaps) between the fibers at the surface contacting the PLA-based parts. The softened adhesive sheet is made to penetrate into the concave portion, whereas the adhesive sheet is arranged and joined between the PLA-based parts. The concave portion is non-perforated hole or through hole.

JPH11124443 A (1999, KYODO PRINTING CO LTD) discloses the manufacture of a biodegradable plastic card by coating vinyl chloride–vinyl acetate resin on two biodegradable polyester core sheets, which are then thermocompression bonded. The plastic card can be used, for example, as an identity card, membership card, or credit card.

EP0576993 A2 (1994, MITSUI TOATSU CHEMICALS) discloses in one of its embodiments a method for adhering a PLA-based film to an aluminum foil or shaped form with a biodegradable adhesive. Exemplary adhesives that can be used include gelatin, starch paste, and low-molecular-weight PLA. However, such metalized PLA-based films are not always suitable in many packaging applications demanding high-moisture barrier properties.

Example: A 30 wt% aqueous gelatin solution was coated as an adhesive on an aluminum foil having dimensions of 150 mm in length, 150 mm in width, and 7 μm in thickness. The coated surface was superimposed on a PLA film of thickness of 30 μm. The overlapped film was pressed overnight under pressure of 1 kg/cm^2 (98 kPa). Adhesion between the aluminum foil and the polymer film was good. A composite film thus obtained had good surface gloss, high transparency, and high strength.

12.5.2 Using Heat

EP0576993 A2 (1994, MITSUI TOATSU CHEMICALS) discloses in one of its embodiments a method for bonding a PLA-based film to an aluminum foil or shaped form by heat pressing.

Example: A PLA film was superimposed on an aluminum foil having dimensions of 150 mm in length, 150 mm in width, and 7 μm in thickness, and hot pressed at 175 °C for 5 min under the pressure of 30 kg/cm^2 (2.94 MPa). Adhesion between the aluminum foil and the polymer film was good. The composite film thus obtained had good surface gloss, high transparency of a resin layer, and high strength.

12.5.3 Using Surface Treatment

The various surface treatment techniques used to improve the adhering properties of a biopolymer are described in Chapter 8: Surface Treatment.

PATENTS

Patent No.	Publication Date	Family Members	Priority Numbers	Inventors	Applicants	Title
CN101469072 A	20090701	CN101469072 B 20120502	CN20081142367 20080812	XIANGNAN ZHANG; MIN LI; CHAOQUN LI	SHENZHEN ECOMANN BIOTECHNOLOGY CO LTD	Preparation of polyhydroxy-alkanoate/montmorillonite intercalation type nano composite material.
CN101503521 A	20090812		CN2009147049 20090305	QINGWEN GUAN; SHIFENG WANG; RUYIN WANG; YONG ZHANG; YINXI ZHANG	UNIV SHANGHAI JIAOTONG	Preparation of high-strength high-ductility biodegradable composite material.
CN102167894 A	20110831	CN102167894 B 20130102	CN2011125309 20110124	PENGYANG DENG; YUAN YIN; CHUNBAI ZHENG	CHANGCHUN APPLIED CHEMISTRY	Graphene/polylactic acid composite material and preparation method thereof.
CN102504503 A	20120620	CN102504503 B 20130605	CN20111292129 20110929	DEMING XIE; ZHUOHUA TAN	GUANGZHOU ZHUOYANG NEW MATERIAL TECHNOLOGY CO LTD	Full-biodegradation ceratin fiber reinforced and fireproof modified polylactic acid material and preparation method thereof.
CN102532832 A	20120704		CN20101609464 20101228	ZHENMING CHEN	HEFEI GENIUS NEW MAT CO LTD	Polylactic acid/carbon fiber composite material and preparation method thereof.
CN103030791 A	20130410		CN20121575500 20121226	ZHANG QINGXIN; LIU RUOJIN; NIU CHUNLIANG; ZHAO FENGHUA; YU XIAOYAN; ZHANG LIZHEN	UNIV HEBEI TECHNOLOGY	Method of fabricating poly-lactic acid/diamond nano composite with solvent backflow method.
CN103061162 A	20130424		CN20111318964 20111019	LIU MIMI	SHANGHAI GENIUS ADVANCED MAT	Biodegradable composite prepreg cloth, and preparation method and device for the same.
CN1850300 A	20061025	CN100427153 C 20081022	CN2006150190 20060404	SHEN LIE PENG	UNIV ZHEJIANG	Composite biological material and preparing method.
DE102011011173 A1	20120816		DE20111011173 20110214		SCHWEMMER MARTIN	Formteil mit Carbonfasern. "Molded part with carbon fibers."

Continued

—Cont'd

Patent No.	Publication Date	Family Members	Priority Numbers	Inventors	Applicants	Title
DE102011016918 A1	20121018		DE20111016918 20110413	ENGELMANN GUNNAR; GANSTER JOHANNES	FRAUNHOFER GES FORSCHUNG	Lösungsmittelfreie Epoxidharzmischung, verfahren zu deren Herstellung sowie deren Verwendung. "Solvent free epoxy resin mixture, process of manufacture and use."
DE102011017126 A1	20121018		DE20111017126 20110414		SCHWEMMER MARTIN	Formteil mit Carbonfasern. "Molded part with carbon fibers."
DE19504899 A1	19960328	US6228501 B1 20010508; JPH0892417 A 19960409; JP2636186 B2 19970730; DE19504899 B4 20060420	JP19940256186 19940926	NAKAZAWA HIROMOTO; OHTA SHUN-ICHI	NAT INST RES INORGANIC MAT	Porösen Körper aus Polysaccharid oder Polysaccharid-Ton-Komposit und Verfahren für dessen Herstellung. "Porous body of polysaccharide or polysaccharide-clay composite, and process for its production."
EP1134258 A1	20010919	WO0168762 A1 20010920; US2003180524 A1 20030925; US6811599 B2 20041102; ES2225503 T3 20050316; EP1263871 A1 20021211; EP1263871 B1 20040908; DE60105398 T2 20050922; AU4286701 A 20010924; AT275603 T 20040915	EP20000200896 20000313; WO2001NL00206 20010313	FISCHER HARTMUT RUDOLF; FISCHER SABINE	TNO	Biodegradable thermoplastic material.
EP1860138 A1	20071128	US2008033093 A1 20080207	EP20060404001 20060525	MENCELOGLU YUSUF ZIYA; INCEOGLU FUNDA	SABANCI UNIVERSITES	Biodegradable thermoplastic nanocomposite polymers.
JP2000160034 A	20000613		JP19980333603 19981125	FUJII TORU; SHO KENGYO; ITO HIROSHI	NIPPON CATALYTIC CHEM IND	Biodegradable composite material.
JP2001329072 A	20011127	JP4581181 B2 20101117	JP20000151333 20000523	SAWAOKA RYUJI; OHARA HARUO; WADAHARA EISUKE	TORAY INDUSTRIES	Carbon fiber reinforced resin composite, molded article, and method for recovery of carbon fiber.
JP2001335710 A	20011204		JP20000155718 20000526	TAKEISHI HIROYUKI; SHIBATA MITSUHIRO; YOSOMIYA RYUTOKU	CHIBA INST TECHNOLOGY	Composite material and method for producing the same.

JP2002069303 A	20020308		JP20000262506 20000831	OMORI TAKEMITSU	MASARU O; IBB KK	Molding of vegetable fiber.
JP2002105298 A	20020410	JP3716730 B2 20051116	JP20000298817 20000929	HORIBE YASUMASA; KANAMORI KENJI	SHIMADZU CORP	Lactic acid resin composition.
JP2004175831 A	20040624	JP3971289B B2 20070905	JP20020340331 20021125	KIMURA KOICHI; NAKAMURA TAKAMITSU; FUJIWARA TAKAYUKI	FUJITSU LTD	Resin housing.
JP2004231910 A	20040819		JP20030025344 20030203	UCHIDA NOBUYUKI; NAKANO MASARU; SAWADA SEIJI; KOBAYASHI YOSHIHIKO; KOIDE MASASHI	TOYO INK MFG CO	Fiber-containing thermoplastic resin composition and use of the same.
JP2004237543 A	20040826	JP4588980 B2 20101201	JP20030028508 20030205	SATO TAKU; ITO DAISUKE; AMANO YOSHIKAZU	KUREHA CHEMICAL IND CO LTD	Multi-layer resin structure.
JP2005263997 A	20050929	JP4328244 B2 20090909	JP20040079280 20040318	YASUI SHIGEYUKI; OTA SEIJI	MITSUI CHEMICALS INC	Propylene-based adhesive polymer composition and laminate thereof.
JP2005307078 A	20051104		JP20040128348 20040423	KORI TOMOYUKI	SEKISUI CHEMICAL CO LTD	Method for producing biodegradable resin composite material and method for molding the same.
JP2006326952 A	20061207	JP4632866 B2 20110223	JP20050151831 20050525	YAMADA TAKEMIKI; MIYASHITA AKIRA	MITSUBISHI PLASTICS IND	Heat shrinkable laminated film and molding, heat shrinkable label, and container using the film.
JP2007070517 A	20070322	JP4815171 B2 20111116	JP20050260459 20050908	NISHIDA HIROFUMI; HIRAYAMA NORIO	NAGASE CHEMTEX CORP; NITTO BOSEKI CO LTD	Method for producing a fiber-reinforced polycaprolactone.
JP2007154002 A	20070621		JP20050349728 20051202	MIZUNO KATSUTOSHI; ANDO YOJI; SHICHIDA HIROAKI	TOYODA GOSEI KK	Lactic acid based resin composition and its molded article.
JP2007307719 A	20071129	JP4650339 B2 20110316	JP20060136216 20060516	MIYAKE YUICHI; YONEHARA HIROSHIGE	TOYOTA MOTOR CORP	Biodegradable resin member joining method.
JP2008274228 A	20081113		JP20070090570 20070330; JP20080053304 20080304	BUN SEINICHI; ICHI MASATOSHI; NAKAMURA AKINOBU	NEC CORP	Reinforced resin composition.

Continued

—Cont'd

Patent No.	Publication Date	Family Members	Priority Numbers	Inventors	Applicants	Title
JP2013194175 A	20130930		JP20120064050 20120321	ISHINAGA J	TEIJIN LTD	Manufacture of composite material.
JPH04334448 A	19921120	JP2513091 B2 19960703	JP19910135754 19910510	KOSEKI HIDEKAZU	SHIMADZU CORP	Biodegradable composite material and manufacture thereof.
JPH0841214 A	19960213		JP19940197729 19940729	OTA MASAAKI; KOSEKI HIDEKAZU	SHIMADZU CORP	Glass fiber-reinforced plastic.
JPH09169897 A	19970630		JP19950348248 19951219	MUKAI KATSUYUKI; YAMADA YOSHIHISA; SAWARA TETSUYA	UNITIKA LTD	Biodegradable fiber reinforced molding and its production.
JPH10273582 A	19981013	JP3634937 B2 20050330	JP19970077268 19970328	TANAKA SUMINORI	OKURA INDUSTRIAL CO LTD	Biodegradable resin composition.
JPH11124443 A	19990511		JP19970290077 19971022	NANJO RYOJI	KYODO PRINTING CO LTD	Production of biodegradable card.
KR100655914 B1	20061204	WO2007086623 A1 20070802	KR20060008907 20060127	LEE JAE SIK; JANG YUN SUK	SK NETWORKS CO LTD	Biodegradable nanocomposite.
KR100836271 B1	20080610		KR20070050532 20070523	HAN SEONG OK; KIM HONG SOO; YOO YOON JONG; SEO YEONG BUM; LEE MIN WOO	KOREA ENERGY RESEARCH INST	Electronic parts case using biocomposites reinforced with sea algae fiber.
KR20060003580 A	20060111	KR100657936 B1 20061214	KR20040052511 20040707	KIM SANG PIL; PARK BYUNG SIK; YOON CHANG WON; PARK YANG HO	TORAY SAEHAN INC	Biodegradable polyester resin composition containing nano particles.
KR20080036854 A	20080429	KR100867424 B1 20081106	KR20060103643 20061024	HAN SEONG OK; KIM HONG SOO; YOO YOON JONG; SEO YEONG BUM; LEE MIN WOO	KOREA ENERGY RESEARCH INST	Biocomposites reinforced with red algae fiber and method of manufacturing biocomposites with highly dispersed reinforcements using high temperature milling technique.
TW201005031 A	20100201		TW20080127009 20080716	WANG CHUN-SHAN; HUANG YA-JEN; LIN WEN-JOUE; LI KUAN-JU; KO KAI-JEN; TAN YEN-CHU	YONGYU APPLIED TECHNOLOGY MATERIAL CO LTD	PLA resin composition containing high performance VGCF and method for producing the same.

US2008108772 A1	20080508	WO2008056989 A2 20080515; WO2008056989 A3 20080717	NO20060005147 20061108	OKSMAN KRISTIINA; BONDESON DANIEL; SYRE PEDER	NTNU TECHNOLOGY TRANSFER AS	Nanocomposites based on cellulose whiskers and cellulose plastics.
US2011319509 A1	20111229		US201113070378 20110323; US20100316758P 20100323	DORGAN JOHN R; BRAUN BIRGIT	POLYNEW INC	Polymer composites incorporating stereocomplexation.
US2012202925 A1	20120809	US2013295376 A1 20131107; US8507588 B2 20130813; US2012202925 X6 20130813	US201213367900 20120207; US201161440386P 20110207	SRUBAR III WILFRED V; BILLINGTON SARAH L	UNIV LELAND STANFORD JUNIOR	PHBV/ground bone meal and pumice powder engineered biobased composite materials for construction.
WO0001530 A1	20000113	ZA200100251 A 20021004; US6645584 B1 20031111; PT1094944 E 20050228; JP2002519222 A 20020702; JP4664502 B2 20110406; FI981558 A 20000108; FI112624 B 20031231; ES2226410 T3 20050316; EP1094944 A1 20010502; EP1094944 B1 20040929; DE69920703 T2 20060216; CA2336898 A1 20000113; CA2336898 C 20070529; AU5040799 A 2000-01-24; AU750072 B2 2002-07-11; AT277758 T 2004-10-15	WO1999FI00597 19990706; FI19980001558 19980707	KUUSIPALO JURKKA; NEVALAINEN KIMMO; PENTTINEN TAPANI	ENSO OYJ	Compostable coated paper or paperboard, a method for manufacturing the same and products obtained thereof.
WO0206023 A1	20020124	US2004028927 A1 20040212; US6835764 B2 20041228; NZ523669 A 20030429; JP2004503415 A 20040205; HK1059414 A1 20060818; EP1309434 A1 20030514; EP1309434 A4 20040310; EP1309434 B1 20061018; DE60123968 T2 20070614; CN1447738 A 20031008; CN1230288 C 20051207; CA2415642 A1 20020124; AU7220601 A 20020130; AU2001272206 B2 20030529; AT342793 T 20061115	AU2000PQ08805 2000071; WO2001AU00853 20010713	LECKEY RICHARD ANTHONY; HILL ALLAN LEON SYDNEY; REICHLE ALAN JOHN	BIO DEG MOULDINGS PTY LTD	Biodegradable composition and products prepared therefrom.

Continued

—Cont'd

Patent No.	Publication Date	Family Members	Priority Numbers	Inventors	Applicants	Title
WO03022927 A1	20030320	US2005043462 A1 20050224; US7173080 B2 20070206; JP4334345 B2 20090930	JP20010270434 20010906	YAMADA KAZUNOBU; UEDA KAZU; OGAMI AKINOBU; MATSUOKA FUMIO; HAYASE SHIGERU; YANO TAKUMA; YOSHIMURA KAZUKO; OKAMOTO MASAMI	UNITIKA LTD	Biodegradable resin composition for molding and molded object obtained by molding the same.
WO2004063282 A1	20040729	US2006147695 A1 20060706; US7445835 B2 20081104; JP2011063821 A 20110331; JP2005105245 A 20050421; EP1589076 A1 20051026; EP1589076 A4 20060208	JP20030003856 20030110; JP20030407799 20031205; JP20110001172 20110106	SERIZAWA SHIN; INOUE KAZUHIKO; ICHI MASATOSHI	NEC CORP	Kenaf fiber-reinforced resin composition.
WO2005078018 A1	20050825	US2005215672 A1 20050929	US20040543825P 20040211	MOHANTY AMAR K; DRZAL LAWRENCE T; DESAI SHROJAL M; MISRA MANJUSRI; MULUKUTLA PRASAD	UNIV MICHIGAN STATE	Anhydride functionalized polyhydroxyalkanoates, preparation and use thereof.
WO2007015371 A1	20070208	EP1911809 A1 20080416; EP1911809 A4 20100519; US2009093575 A1 20090409; KR20080039336 A 20080507; JP5246645 B2 20130724; CN101175819 A 20080507; CN101175819 B 20120523	JP20050239243 20050822; JP20050223530 20050802	KABASHIMA YOHEI; KAWADA KEN-ICHI	UNITIKA LTD	Resin compositions, method of producing the same and molded article obtained therefrom.
WO2007022080 A2	20070222	WO2007022080 A3 20071115; US2007037912 A1 20070215; US7619025 B2 20091117	US20050707625P 20050812	MOHANTY AMAR K; PARULEKAR YASHODHAN; CHIDAMBARAKUMAR MARIAPPAN; KOSITRUANGCHAI NAPAWAN; HARTE BRUCE R	UNIV MICHIGAN STATE	Biodegradable polymeric nanocomposite compositions particularly for packaging.
WO2007095709 A1	20070830	US2009018235 A1 20090115; JP2009527594 A 20090730; DOP2007000034 A 20070915; CA2641924 A1 20070830; BRPI0600683 A 20071120; AU2007218993 A1 20070830	BR2006PI00683 20060224; WO2007BR00045 20070223	NASCIMENTO JEFTER FERNANDES; PACHEKOSKI WAGNER MAURICIO; AGNELLI JOSE AUGUSTO MARCONDES	PHB IND SA	Environmentally degradable polymeric composition and process for obtaining an environmentally degradable polymeric composition.

WO2008050945 A1	20080502	US2009197994 A1 20090806; JP2010502811 A 20100128; JP4971449 B2 20120711; EP2079794 A1 20090722; EP2079794 A4 20091028; EP2079794 B1 20120125; AT542852 T 20120215	KR20060103643 20061024; KR20070050532 20070523	HAN SEONG-OK; KIM HONG-SOO; YOO YOON-JONG; SEO YEONG-BUM; LEE MIN-WOO	KOREA ENERGY RESEARCH INST	Seaweed fiber-reinforced biocomposite and method for producing the same using high-temperature grinding.
WO2009104372 A1	20090827	US2010279135 A1 20101104; US8114522 B2 20120214; JP4726989 B2 20110720; EP2246402 A1 20101103; EP2246402 A4 20110216; EP2246402 B1 20130814	JP20080038796 20080220; JP20080038797 20080220	KITORA YUJI; KAWAHARA MITSUHIRO; UEDA KAZUE	UNITIKA LTD	Resin composition, laminate using the same, and molded body using the laminate.
WO2011138485 A1	20111110	US2013085212 A1 20130404; EP2567936 A1 20130313; EP2567936 A4 20130313; ES2369811 A1 20111207; ES2369811 B1 20121015	ES20100030663 20100504	LAGARON CABELLO JOSE MARIA; MARTINEZ SANZ MARTA; LOPEZ RUBIO AMPARO	CONSEJO SUPERIOR INVESTIGACION	Procedure for the obtainment of nanocomposite materials.
WO2013005914 A1	20130110	KR20130005389 A 20130116	KR20110066736 20110706	PARK JONG SOON; KIM O JIN; HEO SU HAK; JEONG HYE KYUNG	GLOTECH CO LTD	Biodegradable polymer for fixing bones in which chemically-treated nanocarbons are added.
WO2013029018 A1	20130228	US2013220173 A1 20130829	WO2012US52380 20120824	SHARMA SURAJ; HUNT RYAN W; ZELLER MARK ASHTON	ALGIX LLC	Macrophyte-based composition.

REFERENCES

[1] Fowler PA, Hughes JM, Elias RM. Biocomposites: technology, environmental credentials and market forces. J Sci Food Agric 2006;86:1781–9.

[2] RTP Company. Eco solutions/bioplastic compounds. http://web.rtp-company.com/info/data/bioplastics/.

[3] Blog "Bioplastic innovation". In: Bourg V, Chivrac F, Berthé V, editors. Glass fibre-reinforced bioplastic PLA with improved strength and thermal performance/injection moulding cycle times reduced; August 24, 2011. http://bioplastic-innovation.com/?s=glass+fibre&blogsub=confirming#subscribe-blog.

[4] Nishino T, Hirao K, Kotera M, Nakamae K, Inagaki H. Kenaf reinforced biodegradable composite. Compos Sci Technol 2003;63:1281–6.

[5] Li X, Meng Y, Wang S, Rajulu AV, Tjong S. Completely biodegradable composites of poly (propylene carbonate) and short, lignocellulose fiber Hildegardia populifolia. J Polym Sci B Polym Phys 2004;42:666–75.

[6] Paul M-A, Alexandre M, Degée P, Henrist C, Rulmont A, Dubois P. New nanocomposite materials based on plasticized poly(L-lactide) and organo-modified montmorillonites: thermal and morphological study. Polymer 2003;44:443–50.

[7] Chang J-H, An YU, Sur GS. Poly(lactic acid) nanocomposites with various organoclays. I. Thermomechanical properties, morphology, and gas permeability. J Polym Sci B Polym Phys 2003;41:94–103.

[8] Feijoo JL, Cabedo L, Giménez E, Lagaron JM, Saura JJ. Development of amorphous PLA-montmorillonite nanocomposites. J Mater Sci 2005;40:1785–8.

[9] Sinha Ray S, Okamoto M. Polymer/layered silicate nanocomposites: a review from preparation to processing. Prog Polym Sci 2003;28:1539–641.

[10] Sinha Ray S, Maiti P, Okamoto M, Yamada K, Ueda K. New polylactide/layered silicate nanocomposites. 1. Preparation, characterization, and properties. Macromolecules 2002;35:3104–10.

[11] Okamoto K, Sinha Ray S, Okamoto M. New poly(butylene succinate)/layered silicate nanocomposites. II. Effect of organically modified layered silicates on structure, properties, melt rheology, and biodegradability. J Polym Sci B Polym Phys 2003;41:3160–72.

[12] Arora A, Padua GW. Review: nanocomposites in food packaging. J Food Sci 2010;75:R43–9.

[13] Kontou E, Niaounakis M, Georgiopoulos P. Comparative study of PLA nanocomposites reinforced with clay and silica nanofillers and their mixtures. J Appl Polym Sci 2011;122:1519–29.

[14] Lepoittevin B, Devalckenaere M, Pantoustier N, Alexandre M, Kubies D, Calberg C, et al. Poly(ε-caprolactone)/clay nanocomposites prepared by melt intercalation: mechanical, thermal and rheological properties. Polymer 2002;43:4017–23.

[15] Bondeson D, Oksman K. Polylactic acid/cellulose whisker nanocomposites modified by polyvinyl alcohol. Compos Part A Appl Sci Manuf 2007;38:2486–92.

[16] Petersson L, Kvien I, Oksman K. Structure and thermal properties of poly(lactic acid)/cellulose whiskers nanocomposite materials. Compos Sci Technol 2007;67:2535–44.

[17] Oksman K, Mathew AP, Bondeson D, Kvien I. Manufacturing process of cellulose whiskers/polylactic acid nanocomposites. Compos Sci Technol 2006;66:2776–84.

[18] Grunert M, Winter W. Nanocomposites of cellulose acetate butyrate reinforced with cellulose nanocrystals. J Polym Environ 2002;10:27–30.

Chapter 13

Coating Compositions

13.1 GENERAL

This chapter is dedicated to coating compositions based on biopolymers applied to any type of substrates; and it shall be distinguished from the coating compositions of Chapter 8: Surface treatment, wherein any type of material, including biopolymers, is applied to a biopolymer substrate.

The term “coating,” as used herein, refers to both a layer exclusively on the surface of a substrate as well as a layer that to some degree penetrates the substrate.

Different coatings are used in huge quantities to coat paper, cardboard, textiles, wood, metals, and polymers. With the coating, one strives to improve the product properties of the substrate, such as barrier properties, for example water or fat retention, and special durability properties, e.g., water resistance. The coatings usually comprise a viscous three-component system: a film-forming binder, a colorant, and a volatile solvent. These coatings are used either as solutions or dispersions in the coating applications. The binders in most coatings are either polymers or monomers or oligomers, which are further polymerized and/or crosslinked.

13.2 THERMOPLASTIC COATING COMPOSITIONS

13.2.1 Polyhydroxyalkanoate(s)

Aqueous latexes of either crystalline or moderately noncrystalline polyhydroxyalkanoates (PHAs) such as poly(3-hydroxybutyrate-*co*-hydroxyvalerate) (PHBHV) are known to form cohesive coatings on nonfibrous substrates if they are heated to temperatures of 100 °C or more.

Amorphous PHA aqueous suspensions (which also are referred to as amorphous PHA latexes or emulsions) have been found to be particularly useful in, for example, architectural paints (1996, **GB2291648** A, TAYLOR PHILIP LOUIS), cathode-ray tube metallization lacquers (1996, **WO9617369** A1, COOKSON PLC), and coatings for paper (1991, **CA2076038** A1 and 1991, **WO9113207** A1, PULP PAPER RES INST; UNIV MCGILL), cellulose or nonwoven objects (1996, **WO9624682** A1, ZENECA LTD), and paints for wood, glass, or plastic (**WO9600263** A1, 1996, STICHTING ONDERZOEK EN ONTWIKKELING NOORD NEDERLAND).

DE4040158 A1 (1992, DANUBIA PETROCHEM DEUTSCHLAND) discloses the coating of one or both faces of carrier sheet(s) with an aqueous dispersion of a PHA such as poly(3-hyroxybutyrate) (P3HB) or PHBHV optionally with other thermoplastic polymers; followed by drying to remove the dispersion agent preferably with heating, at a temperature at which coating sinters or melts with film formation. The other thermoplastic polymers are polyolefins, polyesters, or polyamides. The coating composition contains no solvent residues and can be formed as porous, gas-, and air-permeable coating. It can be used in pharmaceutical and foodstuff industries, particularly for packaging medicinal and hygiene applications (e.g., wound dressings). However, the coating composition is not totally biodegradable because of the presence of nonbiodegradable thermoplastic polymers. The preparation of the PHA aqueous dispersion is described in Chapter 4: Emulsions/Dispersions/Solutions/Gels; Section 4.1: Making Emulsions and Dispersions.

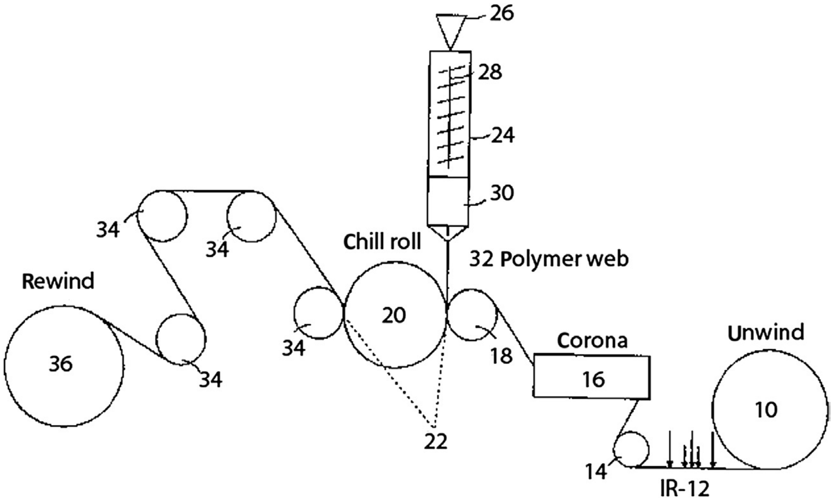
A coating film formed by applying an aqueous dispersion containing a PHA such as P3HB and PHBHV has little elongation and is brittle, and when applied to paper, sheet, or film, there is the problem of cracks, which occur by folding (2004, **WO2004041936** A, KANEKA CORP). **WO2004041936** A (2004, KANEKA CORP) uses instead an aqueous dispersion of poly(3-hydroxybutyrate-*co*-3-hydroxyhexanoate) having an average particle size of 0.1–50 μm and molecular weight (M_w) of 50,000–3,000,000 for forming a coating film, which is claimed to be flexible, have favorable elongation, and be strong to folding when applied in coatings, adhesives, fiber processing, sheet film processing, and paper processing (see also Chapter 4: Emulsions/Dispersions/Solutions/Gels; Section 4.1.3: Non-solvent destructuring methods).

PHA coatings are typically made by melting and extruding the melt through a die onto a substrate such as paper or board. Extrusion coating of PHA polymers, however, has typically required coextrusion with a non-PHA polymeric sacrificial layer such as polyethylene, resulting in a coated material that comprises a paper layer, a PHA layer, and a sacrificial layer. The use of a sacrificial layer during PHA processing has been necessary to provide sufficient melt stability and adhesion of the PHA coating to the paper surface and to allow the coatings to be processed at commercially desirable line speeds. Typically, the sacrificial layer is subsequently stripped from the PHA coated paper.

WO9904948 A1 (1999, MONSANTO CO) discloses an object that is extrusion coated with a molten PHA such as PHBHV. The melted PHA is extruded via die in the form of

Biopolymers: Processing and Products. http://dx.doi.org/10.1016/B978-0-323-26698-7.00013-1

FIGURE 13.1 Diagram of the melt-coating process for coating paper or paperboard with PHA (1999, **WO9904948** A1, MONSANTO CO). 10, Reel; 12, Infrared heater; 14, Roller; 16, Corona treatment facility; 18, Roller; 20, Chill roller; 22, Contacting zone; 24, Melt extruder; 26, Hopper; 28, Screw; 30, Die; 32, Web; and 34, Roller.



a polymer web. Figure 13.1 shows a typical melt extrusion–coating process for coating paper or paperboard with PHA in which uncoated paper or board unwinding from reel (10) is dried by infrared heater (12) and passed via roller (14) to a corona treatment facility (16) for oxidizing and preparing functional groups on the paper that facilitates coating and adhesion of the resulting coat; feedstock of the PHA composition is introduced via the hopper (26) into extruder (24) and processed by heated screw (28), which melts the PHA, for example at a temperature typically in the range of 160–210 °C, and causes the melted PHA to be extruded via die (30) in the form of a polymer web (32). Polymer web (32) and paper from facility (16) are passed between the roller (18) and chill roller (20) maintained at a temperature between 50 and 60 °C, and roller (34) which together form a cooling and contacting zone (22) under conditions of temperature, pressure, and contact time in the zone for producing coated paper of desired characteristics. The coated paper can be further air cooled by passing over rollers (34) and wound onto the take-up reel (36).

The initial molecular weight of the PHA and the time and temperature at which the PHA is molten are such that the PHA coating has a molecular weight above 125,000 g/mol. The PHA coating composition is claimed to have improved properties suitable for applications in which excellent heat sealability and moisture resistance is desired.

PHAs frequently exhibit an unacceptable degree of neck-in during extrusion operations, which can severely limit the yield of the final product. Neck-in refers to a contraction of the melt width upon leaving the die and represents the difference between the width of the die and the width of the polymeric coating on the substrate. Neck-in contraction generally increases with increasing line speeds, temperatures, and air gaps. **WO9914268** A1 (1999, MONSANTO CO) discloses that neck-in in the desirable range for commercial production of PHA-derived films and paper coatings can be achieved if the polymeric melt that is extrusion-coated contains branched PHA. The disclosed composition comprises PHA and 0.001–0.5 wt% of a free radical initiator, preferably a peroxide, wherein the peroxide is dicumyl peroxide, dibenzoyl peroxide, or 2,5-bis(*t*-butylperoxy)-2,5-dimethylhexane.

13.2.2 Poly(Lactic Acid)

Poly(lactic acid) (PLA) has been used to coat paper products (1994, **WO9407949** A1; 1998, **WO9853141**, A1, CARGILL INC). PLA is advantageous because, once it is separated from the paper, it can be composted. Alternatively, the entire coated paper product can be composted. PLA has reasonably good moisture and gas barrier properties adequate for many applications. Use of PLA as food packaging material coating is known, e.g., from **WO9631303** A1 (1996, YHTYNEET PAPERITEHTAAT OY) and **WO9631347** A1 (1996, ZENECA LTD; YHTYNEET PAPERITEHTAAT OY) that describe a grease-resistant paper intended for food stuff packaging where PLA is mentioned as one possible material for the biodegradable polymer coating. The coating on the paper can consist of one biodegradable polymer layer or of a layered structure of two, even three, layers on top of one another where the different layers have their own functions. The object was to produce a packaging paper that was at the same time grease-, aroma-, gas-, and water-vapor proof and biodegradable.

JPH0978494 A (1997, MITSUI TOATSU CHEMICALS) discloses an aqueous dispersion for paper coating comprising: (1) particles of a PLA copolymer having a diameter of 0.1–50 μm and weight-average molecular weight, $M_w \leq 50{,}000$; (2) a water-soluble polymer such as poly(vinyl alcohol) or carboxymethyl cellulose; and (3) a filler such as kaolin or calcium, in an amount of 5–80 wt% of the total amount of components (1) and (3). The composition for aqueous paper coating is applied in an amount of 1–100 g/m^2 to one surface of a substrate containing cellulose fiber and the composition is heat-treated at a temperature, $T > T_g$, the glass transition temperature of the PLA copolymer (a) or above to form a coating layer to provide the objective-coated paper. The coated paper is claimed to have sufficient strength and water permeability, and superior impression properties in printing, including inking, ink setting, and high strength in printing, and sufficient biodegradability (see also Chapter 4: Emulsions/Dispersions/Solutions/Gels; Section 4.1.2: Thermo-Mechanical Methods).

JP2003321600 A (2003, ARAKAWA CHEM IND) discloses a coating containing a PLA aqueous emulsion. This PLA aqueous emulsion is characterized by containing a rosin-based resin. The PLA aqueous emulsion is produced by emulsifying a mixture of the PLA with a rosin-based resin in water (see also Chapter 4: Emulsions/Dispersions/Solutions/Gels; Section 4.1.1.1: Emulsification-Evaporation Technique).

There have been also efforts to use stereocomplex PLA (scPLA) as a coating material. However, it is difficult to coat the surface of molded product with csPLA dissolved in a solvent such as chloroform, because the csPLA is apt to precipitate. Furthermore, the csPLA is hardly soluble in most kind of solvents and is difficult to make a coating (2006, **WO2006088241** A1, TEIJIN LTD; MUSASHINO KAGAKU KENKYUSHO; MUTUAL CORP; YOSHIHARU KIMURA).

WO2006088241 A1 (2006, TEIJIN LTD; MUSASHINO KAGAKU KENKYUSHO; MUTUAL CORP; YOSHIHARU KIMURA) discloses a method for the manufacture of a csPLA coating film comprising the steps of:

1. preparing an aqueous emulsion of poly(L-lactic acid) (PLLA) and an aqueous emulsion of poly(D-lactic acid) (PDLA);
2. mixing them together to prepare a mixed emulsion;
3-i. applying the mixed emulsion to a substrate; and
3-ii. drying the coating film of the mixed emulsion.

It is considered that the scPLA is formed in the drying step (3-ii). PLLA and PDLA are rarely miscible with each other in the mixed emulsion because of the presence of an emulsifier. However, after the mixed emulsion is applied to a substrate, they become miscible with each other in the step of drying (3-ii) and heating the coating film to form an scPLA. The stereocomplex is formed not at the time of application but at the time of drying after application. That is, a stereocomplex can be formed *in situ*. Therefore, the coating agent has an advantage that it can be easily applied and can be kept as well.

The weight ratio of PLLA to PDLA (PLLA/PDLA) in the mixed emulsion (2) is preferably 40/60–60/40, more preferably 45/55–55/45. The mixed emulsion has an average particle diameter of preferably 0.05–2 μm, more preferably 0.07–0.5 μm in an O/W form. The mixed emulsion may be cast by extruding it from a die or by doctor blade coating or spin coating. Examples of the substrate include glass plates, metal plates, and polymer plates. The drying step may be carried out at room temperature under atmospheric pressure. The thickness of the film obtained by this method is preferably 5–200 μm, more preferably 10–100 m.

Extrusion coating and proximity coating are two fairly common methods for coating paper. Both methods can be practiced for applying a PLA composition to a substrate. In general, extrusion coating is meant to include various types of paper-coating processes using an extruder to force polymer through a die and includes, for example, curtain coating. Proximity coating generally refers to applications that provide a die in contact with the substrate. The coating is typically supplied with a melt pump or with an extruder/melt pump combination. In general, proximity coating is used for the application of pressure sensitive adhesives to a substrate (1998, **WO9853141**, A1, CARGILL INC).

To process PLA on commercial extrusion coating equipment, the PLA should have good melt elasticity. This is because it is desirable to extrude and draw down thin coatings of PLA with minimal neck-in at high velocities at the high temperatures required for good adhesion to paper (1999, **WO9950345** A1, CARGILL INC).

According to **WO9950345** A1 (1999, CARGILL INC) linear PLA is generally not suitable for processing on conventional paper coating equipment. It is believed that the reason for this is that linear PLA does not possess the melt elasticity needed to provide commercially acceptable throughput at acceptable levels of neck-in and coating stability. Linear PLA will generally have a molecular weight distribution with a polydispersity index of less than 2.2 and a M_z molecular weight (M_n) of about 3. This equates to a low degree of chain entanglement and a low melt elasticity. **WO9950345** A1 (1999) discloses that the melt elasticity can be increased by broadening the molecular weight distribution. Bridging and branching are preferred methods, which increase chain entanglement and broaden the molecular weight distribution.

PLA is stiff and brittle, has a fairly high T_m and poor heat sealing ability. As a result, it requires a high extrusion temperature and a fairly large layer thickness for managing its adherence to the fiber substrate of a packaging material. However, at high temperatures, PLA runs a risk of degrading, and in extrusion, the molten web tends to experience occurrences of tearing along its edges and the extruded layer is easily left with pin holes. As a solution to these problems, **WO0001530** A1 (2000, ENSO OYJ) discloses an inner adhesion layer to be coextruded together with an outer PLA layer as shown in Figure 13.2, and consisting of a biodegradable polymer, examples of which including some commercial aliphatic copolyesters (e.g., Eastar™ 14766, Eastman Chemical Co.), cellulose esters, and poly(ester amide)s (e.g., BAK® 402-005 and BAK® 2195, Bayer). These have enabled facilitating the extrusion of PLA and reaching adhesion that prevents detachment of the coating from the fiber substrate by peeling.

The coextrusion of PLA with a biodegradable polymer layer functioning as adhesive on paper or paperboard prevents the detachment of the coating from the fiber substrate by peeling.

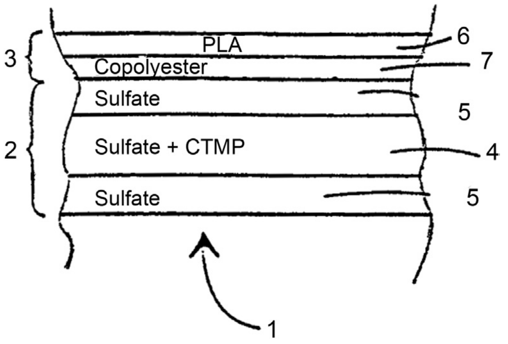


FIGURE 13.2 Schematic representation of a coated paperboard (2000, **WO0001530** A1, ENSO OYJ). 1, Paperboard; 2, Trilayered fiber structure having a thicker middle layer (4), and thinner outer layers (5) of sulfate mass on both sides of the middle layer (4); 3, Biodegradable polymer coating composed of an outer layer (6), which comprises PLA and of an adhesive layer (7) that is coextruded with the former and is of biodegradable polymer and binds the PLA onto the sulfate mass layer (5); 4, Middle fiber layer (sulfate mass and CTMP); 5, Sulfate mass layer; 6, PLA; 7, Copolyester.

WO2012120199 A1 (2012, STORA ENSO OYJ; NEVALAINEN KIMMO) is a modification of the previous patent application and discloses a heat-sealable biodegradable packaging material useful in a closed product package comprising a fiber substrate, obtained by the addition of a minor amount of an acrylic copolymer additive (<10 wt%) to the PLA coating layer. The acrylic copolymer is ethylene-butyl acrylate-glycidyl methacrylate terpolymer.

WO2012158511 A1 (2012, TALEYARKHAN RUSI P; BAKKEN ALEXANDER CHARLES; GRIMES THOMAS FRANCIS; HUME NICHOLAS EDWARD) discloses a PLA coating having a hardness as measured on the Shore D scale of 75–85. The PLA coating composition can contain 1–10 wt% of triallyl isocyanurate with respect to PLA. The method for forming the hard PLA coating involves the following steps: (1) melt PLA powder; (2) heat a wood product to degas; (3) transfer liquid PLA to the wood product through dipping or scooping; (4) form PLA into roughly sheet-like shape; (5) place metal sheet over the PLA surface; (6) apply heat and pressure; and (7) remove the metal sheet. The PLA coating is used, for example, in the manufacture of flooring and furniture, and it is claimed to impart excellent abrasion resistance, impact resistance, and scratch resistance.

13.2.3 Starch

Starch and starch derivatives are used as binders in single paints, which, by definition, are paints containing no synthetic binders. **WO9712946** A1 (1997, BERNACCHIA IDA) discloses the use of potato flour and starch pastes, in addition to the use of milk casein (e.g., proteins, egg yolks), in water-based exterior and interior wall paints. Overall, up to 30% of natural binders are used in that case. **DE10100667** A1 (2002) and **EP1477535** A1 (2004) of ARTUR FISCHER TIP GMBH & CO KG also use starch as a binder in single-paint systems. The paint is in the form of a crayon (10) and is held so that it can slide in a tube (16) having a tapered end; see Figure 13.3.

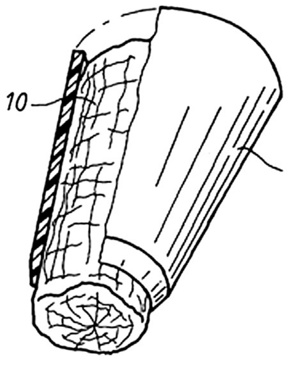


FIGURE 13.3 Starch-based paint in the form of a crayon (2002, **DE10100667** A1, FISCHER ARTUR). 10, Crayon; 16, Tube.

WO03043815 A1 (2003, US AGRICULTURE) discloses the coating of articles produced from hydrophobic polymers (e.g., polyethylene) with a hot aqueous solution of starch (0.5–5 wt%) to render the surfaces hydrophilic. The starch coating is claimed to be extremely adherent to the hydrophobic plastic surfaces under both wet and dry conditions, and permit the surface to be uniformly wet with water.

WO2010059562 A1 (2010, SUN CHEMICAL CORP) discloses a coating or printing ink composition comprising one or more hydrolyzed starch, starch derivative, or chemically modified starch, wherein at least one of the starches either has a number average molecular weight, $M_{\text{n}} < 100{,}000$ or had a $M_{\text{n}} < 100{,}000$, which has been increased to greater than about 100,000 by chemical modification. A preferred low-molecular-weight starch is maltodextrin. The starch coating can be oil-based, solvent-based, aqueous, or solventless and can be applied on a variety of substrates.

WO2013041561 A1 (2013, NOVAMONT) discloses an aqueous polymer dispersion for coating paper substrates comprising destructurized starch in a form complexed with at least one polymer containing groups of different hydrophilicity intercalated in the backbone or outside the backbone, said dispersion having dynamic viscosity of 10–500 mPa s and a solid content of 5–55 wt%. The polymers containing groups of different hydrophilicity intercalated outside the backbone are preferably copolymers of ethylene with vinyl alcohol and/or with acrylic acid.

13.2.4 Cellulose Derivatives

WO2010085569 A1 (2010, BIOSPHERE IND LLC) discloses a biodegradable coating composition for use with a starch-based composition comprising: (1) a cellulose ester or a biodegradable polymer; (2) a wax; (3) a plasticizer; and (4) a solvent. Various types of cellulose esters can be used as a base for a biodegradable and compostable coating. Preferred cellulose esters used in some embodiments of the present invention include cellulose acetate propionate (CAP), cellulose acetate butyrate (CAB), cellulose acetate (CA), and nitrocellulose. In some embodiments where an ovenable coating is desired, the preferred cellulose esters are CAP, CAB, and CA. The coating composition is used to coat biodegradable articles such as containers to increase the moisture resistance, thus allowing use in high-moisture applications. The coating composition can be applied without the need to coat at elevated temperature or prolonged drying or heating above the melting temperature of the wax. The coating is preferably solvent-borne. Suitable solvents include methyl acetate, ethyl acetate, propyl acetate, butyl acetate, ethanol, propanol, acetone, water, hydrocarbons, and the like in various proportions as required for solubility and coatability of the ingredients. It is preferred that the solvents be nonhazardous air pollutants and be obtainable from nonpetroleum sources. Especially preferred are ethanol/*n*-propyl acetate and *i*-propanol/methyl acetate. Acetone, methyl acetate, and *t*-butyl acetate are also preferred because they are typically exempt from volatile organic compound regulations.

13.3 POWDER COATINGS

Powder coatings are finely pulverized polymeric compositions in the form of dry, free-flowing, fine powder that melts and flows at elevated temperatures to produce a smooth coated surface when applied to a substrate. Protective surface coatings based on powder coatings are particularly useful in view of environmental compliance in that powder paints ordinarily do not contain organic solvents or emit organic compounds upon baking or heat curing.

EP1484371 A2 (2004, ROHM & HAAS) discloses a powder coating composition comprise one or more than one finely divided polymer chosen from a partially degradable aliphatic–aromatic copolyester, a mixture of a cyclic oligomeric polyester, a ring opening polymerization catalyst and a degradable polyester, a degradable ultraviolet curable polyester, and mixtures thereof. A preferred aliphatic aromatic copolyester is poly(butylene adipate-*co*-terephthalate). The composition enables the formation of a thin, water-resistant coating, which is claimed to have excellent appearance properties, thereby lowering the cost of making the degradable coating. The composition further offers an immediate advantage of reducing scrap through reclaiming of powder material.

JP2008138060 A (2008, MEIDENSHA ELECTRIC MFG CO LTD) discloses a biodegradable powder coating composition consisting of poly(butylene succinate). The powder coating is used to isolate an electrical conductor. The conductor is preheated in advance and immersed in fluidized bed of the polymer powder, where the polymer powder is fused on the surface of the conductor.

13.4 TEMPORARY OR STRIPPABLE COATINGS

This type of coatings refers to coatings that are peelable or releasable as coherent films from a substrate.

WO2007052587 A1 (2007, KANSAI PAINT CO LTD) discloses an aqueous dispersion composition for forming strippable coating films comprising a biodegradable polymer such as PLA, a water-dispersible powder polymer, and optionally a plasticizer.

JP2006160867 A (2006, KANSAI PAINT CO LTD) discloses a releasable film forming coating composition comprising an aqueous dispersion of PLA (a) and a plasticizer (b) having a viscosity of at least 25 mPa s at 25 °C, wherein the plasticizer (b) is contained in an amount of 1–40 pbw per 100 pbw solid content of PLA (A). The releasable film forming coating composition protects temporarily the surface of, for example, a structure, can allow the easy removal of graffiti or posters, and is useful as a stain removing agent for an old coated surface or an uncoated surface.

WO2009024812 A1 (2009, INNOVIA FILMS LTD) discloses a sealable, peelable (strippable) film formed by coating a cellulosic substrate with a coating solution of a copolyester of lactic acid and ε-caprolactone (poly(lactide-*co*-ε-caprolactone)). Suitable copolymers for use in the coating composition singly or as part of a suitable blend include Vyloecol™ BE-450, Vyloecol™ HYD-306, Vyloecol™ BE-910, Vyloecol™ BE-400, and Vyloecol™ BE-410 (Toyobo Co., Ltd) and mixtures thereof. The coating composition comprises preferably nitrocellulose (<40 wt%), wax and antiblocking agent.

The various types of biodegradable polymer coating compositions are summarized in Table 13.1.

TABLE 13.1 Various Types of Biodegradable Polymer Coating Compositions Disclosed in Patents

Biodegradable Polymer	Other Components	Type of Coating	Function	Patent
PHA (P3HB, P3HV, PHBHV)		Aq. dispersion	Architectural paints	**GB2291648** (1996, ATAYLOR PHILIP LOUIS)
PHA		Aq. dispersion	Cathode-ray tube metallization lacquers	**WO9617369** A1 (1996, COOKSON PLC)
PHA (P3HB, P3HV, PHBHV)		Aq. dispersion	Paper coating	**CA2076038** A1 (1991); (1991, **WO9113207** A1, PULP PAPER RES INST; UNIV MCGILl)
PHA		Aq. dispersion	Coating cellulose or nonwoven	**WO9624682** A1 (1996, ZENECA LTD)
PHA containing unsaturated groups		Aq. dispersion	Food packaging	**WO9600263** A1 (1996, STICHTING ONDERZOEK EN ONTWIKKELING NOORD NEDERLAND)
PHA		Aq. dispersion	Paint for wood, glass, polymer	**US6024784** A (2000, INST VOOR AGROTECH ONDERZOEK)
PHA (P3HB, PHBHV)		Aq. dispersion	Packaging medicinal and hygiene items	**DE4040158** A1 (1992, DANUBIA PETROCHEM DEUTSCHLAND)
PHBHV		Melt extrusion	Paper coating	**WO9904948** A1 (1999, MONSANTO CO)
PHA (PHBHV)	Free radical initiator (e.g., peroxide)	Melt extrusion		**WO9914268** A1 (1999, MONSANTO CO)
PHBHx		Aq. dispersion	Paper and film coating	**WO2004041936** A (2004, KANEKA CORP)
PLA	PVOH, CMC; filler (kaolin, calcium); multi-layered structure	Aq. dispersion	Paper coating	**JPH0978494** A (1997, MITSUI TOATSU CHEMICALS)
PLA	Rosin	Aq. emulsion	Water resistance, transparency	**JP2003321600** A (2003, ARAKAWA CHEM IND)
PLA		Emulsion containing water and at least two organic solvents of boiling point >100 °C (e.g., diethylene glycol butyl methyl ether/propylene glycol monomethyl ether)	Adhesiveness, external appearance, and hardness	**JP2011089006** A (2011, FUJITSU LTD)
PLA	Plasticizer (1–40 pbw)	Aq. dispersion	Strippable coating film	**JP2006160867** A (2006, KANSAI PAINT CO LTD)
PLA	Water-dispersible powder polymer; opt plasticizer	Aq. dispersion	Strippable coating film	**WO2007052587** A1 (2007, KANSAI PAINT CO LTD)
PLCL	Nitrocellulose (<40 wt%)	Org. solution	Strippable coating film	**WO2009024812** A1 (2009, INNOVIA FILMS LTD)

TABLE 13.1 Various Types of Biodegradable Polymer Coating Compositions Disclosed in Patents—cont'd

Biodegradable Polymer	Other Components	Type of Coating	Function	Patent
scPLA (PLL/PDLA 45/55–55/45)		Aq. dispersion	Paper coating and coating of biodegradable polymer moldings	**WO2006088241** A1 (2006, TEIJIN LTD; MUSASHINO KAGAKU KENKYUSHO; MUTUAL CORP; YOSHIHARU KIMURA)
PLA having polymerizable (meth) acryloyl group	Surface-modified metal oxide particles	Polymn.	Protective coating (scratch resistance, surface hardness)	**JP2012067157** A (2012, NIDEK KK; KYOTO INST OF TECHNOLOGY)
PLA		Melt extrusion	Paper coating	**WO9407949** A1 (1994); **WO9853141** A1 (1998, CARGILL INC)
PLA		Melt extrusion	Paper coating	**WO9950345** A1 (1999, CARGILL INC)
PLA	Multilayered structure	Melt extrusion	Paper coating	**WO0001530** A1 (2000, ENSO OYJ)
PLA	Multilayered structure	Melt extrusion	Paper coating	**WO2012120199** A1 (2012, STORA ENSO OYJ; NEVALAINEN KIMMO)
PLA	Acrylic copolymer additive (e.g., ethylene-butyl acrylate-glycidyl methacrylate terpolymer); multilayered structure	Melt extrusion	Paper coating	**WO9631303** A1 (1996, YHTYNEET PAPERITEHTAAT OY); **WO9631347** A1 (1996, ZENECA LTD; YHTYNEET PAPERITEHTAAT OY)
PLA	Triallyl isocyanurate (1–10 wt%)	Melt extrusion	Abrasion resistance, impact resistance and scratch resistance to floor and furniture	**WO2012158511** A1 (2012, TALEYARKHAN RUSI P; BAKKEN ALEXANDER CHARLES; GRIMES THOMAS FRANCIS; HUME NICHOLAS EDWARD)
PDLA	Cu_2O (100 pbw); ethyl acetate (140 pbw)	Organic solution	Antifouling paint (ships, sea water inlet tubes and fishing net)	**JP2004277748** A (2004, TOYO BOSEKI)
PGA		Melt extrusion	Underwater antifouling coating	**WO2011132537** A1 (2011, KUREHA CORP)
PBS		Powder coating	Electrical insulator	**JP2008138060** A (2008, MEIDENSHA ELECTRIC MFG CO LTD)
PBAT		Powder coating	Water resistance and strength to biodegradable substrates (e.g., starch food containers)	**EP1484371** A2 (2004, ROHM & HAAS)
CAP, CAB, CA, NC	Wax; plasticize; solvent (e.g., ethanol/*n*-propyl acetate, *i*-ropanol/methyl acetate)	Organic solution	Moisture resistance	**WO2010085569** A1 (2010, BIOSPHERE IND LLC)

Continued

TABLE 13.1 Various Types of Biodegradable Polymer Coating Compositions Disclosed in Patents—cont'd

Biodegradable Polymer	Other Components	Type of Coating	Function	Patent
Starch (potato, flour and starch pastes), milk casein, egg yolks	Pigments; inorganic binder (borax, kalinite, calcite, kaolin, slaked lime, mica and talc, sea salt and boron salts); additives (vegetable oils, citrus-fruit juices, wine vinegar and natural waxes)	Aq. dispersion	Architectural paints	**WO9712946** A1 (1997, BERNACCHIA IDA)
Starch		Aq. dispersion	Rendering hydrophilic surfaces of hydrophobic polymer substrates	**WO03043815** A1 (2003, US AGRICULTURE)
Starch		Oil-based, solvent-based, aqueous, solventless	Paper, paper board, film, etc.	**WO2010059562** A1 (2010, SUN CHEMICAL CORP)
Destructurized starch in complexed form	Preferably ethylene-acrylic acid copolymer; ethylene-vinyl alcohol copolymer	Aq. dispersion	Paper coating	**WO2013041561** A1 (2013, NOVAMONT)
Starch		Crayon	Artist's paints; toys	**DE10100667** A1 (2002); **EP1477535** A1 (2004, ARTUR FISCHER TIP GMBH & CO KG)
Oxidized polysaccharide (starch, cellulose, chitin and chitosan)	Cpd. having at least two reactive functional groups: Isocyanate, epoxy, carbodi-imide, oxazolone, and/or amino group	Aq. solution or dispersion	Sealer, primer, anchor-coat agent	**JP2008239830** A (2008, TOPPAN PRINTING CO LTD)
Chitosan Cu(I) complex	Fe_2O_3; (5–25% w/v) acetic acid (1–3%)		Antifouling paint for impregnating nets	**WO2010032197** A1 (2010, UNIV CONCEPCION)

CA, Cellulose acetate; CAB, Cellulose acetate butyrate; CAP, Cellulose acetate propionate; CMC, Carboxymethyl cellulose; NC, Nitrocellulose; P3HB, Poly(3-hydroxybutyrate); P3HV, Poly(3-hydroxyvalerate); PBAT, Poly(butylene adipate-*co*-terephthalate); PBS, Poly(butylene succinate); PLCL, Poly(lactide-*co*-caprolactone); PDLA, D- and L- lactic acid; PGA, Poly(glycolic acid); PHA, Polyhydroxyalkanoate; PHBHx, Poly(3-hydroxybutyrate-*co*-3-hydroxyhexanoate); PHBHV, Poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate); PLA, Poly(lactic acid); PVOH, Poly(vinyl alcohol); scPLA, Stereocomplex PLA.

PATENTS

Patent Number	Publication Date	Family Members	Priority Numbers	Inventors	Applicants	Title
CA2076038 A1	19910822	US5451456 A 19950919; CA2076038 C 20010327	CA19902076038 19900221; WO1990CA00058 19900221	MARCHESSAULT ROBERT HENRY; LEPOUTRE PIERRE F; WRIST PETER E	PULP PAPER RES INST; UNIV MCGILL	Poly-β-hydroxyalkanoates for use in fiber constructs and films.
DE10100667 A1	20020711		DE2001100667 20010109	FISCHER ARTUR	ARTUR FISCHER TIP GMBH & CO KG	Paint comprises a starch material as a basic substance to which a pigment is added.
DE4040158 A1	19920617		DE19904040158 19901215	HAEUBL GEORG; SCHEUCHENSTUHL WILLIBALD; ESTERMANN ROBERT; HRABAK OTTO; KROATH HANS	PCD PETROCHEMIE DANUBIA DEUTSCHLAND	FläChenförmiger Gegenstand aus einer mit Polyhydroxyalkanoat-dispersion beschichteten Trägerschicht. “Flat article obtained by coating carrier sheet with dispersion of polyhydroxyalkanoate.”
EP1477535 A1	20041117	DE10321616 A1 20041202	DE2003121616 20030513	FISCHER ARTUR	ARTUR FISCHER TIP GMBH & CO KG	Verfahren zur Herstellung von Malfarbe. “Process for the preparation of artist’s paint.”
EP1484371 A2	20041208	US2004247807 A1 2004120; EP1484371 A3 20050209	US20030476122P 20030605	ANNAN NIKOI; HORINKA PAUL R; TULLOS TINA L; ZIMMERMAN SCOTT ALLEN	ROHM & HAAS	Degradable powder coatings, methods and apparati for powder coating biodegradable substrates and products produced thereby.
GB2291648 A	19960131	WO9603468 A1 19960208; JPH10503227 A 19980324; GB2291648 B 19981125; EP0772654 A1 19970514; EP0772654 B1 20010613; DE69521321 T2 20011031; AU3114095 A 19960222	GB19940014922 19940725	TAYLOR PHILIP LOUIS	ICI PLC	Coating compositions containing poly hydroxyalkanoates.
JP2003321600 A	20031114	JP3775668 B2 20060517	JP20020127744 20020430	TAKAGI YOSHINORI; TSUSHIMA YOSUKE	ARAKAWA CHEM IND	Polylactic acid aqueous emulsion, method for producing the same and coating containing the polylactic acid aqueous emulsion.
JP2004277748 A	20041007	JP3773057 B2 20060510	JP20040144730 20040514	MIYAMOTO TAKASHI; UNO KEIICHI	TOYO BOSEKI	Manufacturing method of hydrolyzable polyester resin.
JP2006160867 A	20060622	JP4819350 B2 20111124	JP20040353728 20041207	INOUE TAKESHI; SUZUKI KENYA; SUGISHIMA MASAMI	KANSAI PAINT CO LTD	Releasable film forming composition.
JP2008138060 A	20080619		JP20060325142 20061201	KURATA YASUYUKI	MEIDENSHA ELECTRIC MFG CO LTD	Insulating polymer material composition and conductor.
JP2008239830 A	20081009		JP20070083181 20070328	OMORI YUMIKO	TOPPAN PRINTING CO LTD; TOYO BOSEKI; TOYO INK MFG CO	Aqueous coating composition, composite sheet, decorative sheet and decorative material.

Continued

—Cont'd

Patent Number	Publication Date	Family Members	Priority Numbers	Inventors	Applicants	Title
JP2011089006 A	20110506		JP20090243091 20091022	TAKEUCHI FUMIYO; KIMURA KOICHI	FUJITSU LTD	Coating material and electronic equipment.
JP2012067157 A	20120405		JP20100211688 20100922	KOIDE S; YAMADA Y	NIDEK KK; KYOTO INST OF TECHNOLOGY	Resin composition.
JPH0978494 A	19970325	JP3523944 B2 20040426	JP19950235165 19950913	TAKAGI MASATOSHI; MINAZU HIROSHI; AJIOKA MASANOBU; YAMAGUCHI TERUHIRO	MITSUI TOATSU CHEMICALS	Composition for aqueous paper coating and coated paper obtained by coating of the same composition.
US6024784 A	20000215	NL1008497 C2 19990907	NL19981008497 19980305	BUISMAN GODEFRIDUS JOHANNES HE; CUPERUS FOLKERT PETRUS; WEUSTHUIS RUUD ALEXANDER; EGGINK GERRIT	INST VOOR AGROTECH ONDERZOEK	Poly(3-hydroxyalkanoate) paint and method for the preparation thereof.
WO0001530 A1	20000113	ZA200100251 A 20021004; US6645584 B1 20031111; PT1094944 E 20050228; JP2002519222 A 20040929; FI981558 A 20010502; FI112624 B1 20031231; ES2226410 T3 20050316; EP1094944 A1 20010502; EP1094944 B1 20040929; DE69920703 T2 20060216; CA2336898 A1 20000113; CA2336898 C 20070529; AU5040799 A C1920000124; AU750072 B2 20020711; AT277758 T 20041015	FI19980001558 19980707	KUUSIPALO JURKKA; NEVALAINEN KIMMO; PENTTINEN TAPANI	ENSO OYJ	Compostable coated paper or paperboard, a method for manufacturing the same and products obtained thereof.
WO03043815 A1	20030530	US2003096126 A1 20030522; US7052776 B2 20060530; US6709763 B2 20040323; AU2002348306 A1 20030610;	US20010989365 20011120	FANTA GEORGE F; FELKER FREDERICK C	US AGRICULTURE	Formation of hydrophilic polysaccharide coatings on hydrophobic substrates.
WO03068289 A1	20030821	ZA200406448 A 20060531; US2007071926 A1 20070329; US7419709 B2 20080902; US2007071879 A1 20070329; US7364768 B2 20080429; US2003219562 A1 20031127; US7160592 B2 20070109; US2008160166 A1 20080703; SI1492581 T1 20070430; SI1764118 T1 20101130; RU2004124718 A 20050410; RU2308976 C2 20071027; PT1492581 E 20070228;	US20020357573P 20020215	YPACEK FRANTISEK; LAPCIKOVA MONIKA; MACHOVA LUDKA	YPACEK FRANTISEK; LAPCIKOVA MONIKA; MACHOVA LUDKA	Polymer coating for medical devices.

		PT1764118 E 20100927; PL371517 A1 20050627; NZ534682 A 20061027; NO20043843 A 20040914; MXPA04007898 A 20050620; KR20040097126 A 20041117 JP2005516736 A 20050609; JP4472348 B2 20100602; HU0402591 A2 20050928; HK1072205 A1 20070209; HK1107286 A1 20101126 ES2276084 T3 20070616; ES2349424 T3 20110103; EP1764118 A2 20070321; EP1764118 A3 20080625; EP1764118 B1 20100825; EP1492581 A1 20050105; EP1492581 B1 20061220; DK1492581 T3 20070430; DK1764118 T3 20101108; DE60310540 T2 20071004; CY1107549 T1 20130313; CN1633313 A 20050629; CN1279984 C 20061018 CA2476431 A1 20030821; CN1911460 A 20070214 AT348643 T 20070115; AU2003215495 A1 20030904; AU2003215495 B2 20080814; AT478696 T 20100915				
WO2004041936 A1	20040521	US2006258833 A1 20061116; US7491754 B2 20090217; JP4553733 B2 20100929; EP1566409 A1 20050824; CA2503590 A1 20040521, BR0315787 A 20050913; AU2003277546 A1 20040607	JP20020325984 20021108	SENDA KENICHI; MIKI YASUHIRO	KANEKA CORP	Aqueous dispersion of biodegradable polyester and method for production thereof.
WO2006088241 A1	20060824	US2008161505 A1 20080703; KR20070105990 A 20071031; EP1849833 A1 20071031; EP1849833 A4 20100811; CN101124280 A 20080213; CA2598470 A1 20060824	JP20050080382 20050220	KIMURA YOSHIHARU	TEIJIN LTD; MUSASHINO KAGAKU KENKYUSHO; MUTUAL CORP; KIMURA YOSHIHARU	Process for producing polylactic acid.
WO2007052587 A1	20070510	JP2010018640 A 20100128	JP20050315674 20051031	INOUE TAKESHI; SUZUKI KENYA; SUGISHIMA MASAMI; MATSUOKA HIROYUKI; SAIKA MASAAKI	KANSAI PAINT CO LTD	Aqueous dispersion composition for forming strippable coating film.

Continued

—Cont'd

Patent Number	Publication Date	Family Members	Priority Numbers	Inventors	Applicants	Title
WO2009024812 A1	20090226	US2012201983 A1 20120809; US2011008555 A1 20110113; US8182889 B2 20120522; EP2181145 A1 20100505; EP2181145 B1 20110420; AT506395 T 20110515	GB20070016456 20070823	CHAPALAIN FLORIAN	INNOVIA FILMS LTD; CHAPALAIN FLORIAN	Packaging article.
WO2010032197 A1	20100325		CL20080002791 20080917	CARDENAS TRIVINO GALO	UNIV CONCEPCION	Anti-fouling paint composition based on a chitosan/copper (i) complex and method for preparing same.
WO2010059562 A1	20100527	EP2356184 A1 20110817; US2011229700 A1 20110922; CA2743866 A1 20100527	US20080115659P 20081118	TROUTMAN MALISA; BIENKOWSKI IRENA; HARRIS NICOLE; TRUNCELLITO-SIMONI JEANNETTE	SUN CHEMICAL CORP; TROUTMAN MALISA; BIENKOWSKI IRENA; HARRIS NICOLE; TRUNCELLITO-SIMONI JEANNETTE	Printing ink and coating compositions containing derivatives of starch and modified starch.
WO2010085569 A1	20100729	US2010203348 A1 20100812; US8563140 B2 20131022 TW201114852 A 20110501; KR20110117183 A 20111026; JP2012515835 A 20120712; EP2389421 A1 2011130; EP2389421 A4 20130821; CN102348772 A 20120208; CA2750273 A1 20100729; AU2010206743 A1 20110901	US20090227744P 20090722; US20090258537P 20091105; US20090146280P 20090121	DELLINGER DAVID A; HELOU ELIE; SPEER DREW V; SCHWARK DWIGHT W	BIOSPHERE IND LLC	Moisture resistant coating.
WO2011132537 A1	20111027		JP20100097310 20100420	YAMANE KAZUYUKI; SUZUKI TAKEHISA	KUREHA CORP	Underwater antifouling material, melt-moulded article and coating material.
WO2012120199 A1	20120913	EP2683623 A1 20140115; CN103429503 A 20131204	FI20110005226 20110307	NEVALAINEN KIMMO	STORA ENSO OYJ; NEVALAINEN KIMMO	Heat sealable biodegradable packaging material, its manufacturing method and a product package made therefrom.
WO2012158511 A1	20121122	EP2707222 A1 20140319; CA2836044 A1 20121122	US201261595991P 20120207; US201161485733P 20110513	TALEYARKHAN RUSI P; BAKKEN ALEXANDER CHARLES; GRIMES THOMAS FRANCIS; HUME NICHOLAS EDWARD	TALEYARKHAN RUSI P; BAKKEN ALEXANDER CHARLES; GRIMES THOMAS FRANCIS; HUME NICHOLAS EDWARD	Polylactic acid-based coating and uses thereof.
WO2013041561 A1	20130328		IT2011MI01680 20110919; IT2012MI01253 20120718	BASTIOLI CATIA; CAPUZZI LUIGI; MAGISTRALI PAOLO	NOVAMONT SPA	Stable aqueous disersios comprising complexed starch.

WO9113207 A1	19910905		WO1990CA00058 19900221; CA19902076038 19900221	MARCHESSAULT ROBERT HENRY; LEPOUTRE PIERRE F; WRIST PETER E	PULP PAPER RES INST; UNIV MCGILL	Poly-β-hydroxyalkanoates for use in fiber constructs and films.
WO9407949 A1	19940414	US5475080 A 19951212; US5338822 A 19940816; US5981694 A 19991109; US5798436 A 19980825; US5763564 A 19980609; US5773562 A 19980630; US5585191 A 19961217; US5539081 A 19960723; US6121410 A 20000919; US6143863 A 20001107; US6197380 B1 20010306; US5446123 A 19950829; US5484881 A 19960116; US5536807 A 19960716; US6093791 A 20000725; PT615532 E 20001130; NZ257216 A 19961028; NO942035 A 19940713; NO309042 B1 20001204; MX9306143 A 19940630; JPH07504227 A 19950511; JP3436368 B2 20030811; JPH07504939 A 19950601; DK0615532 T3 20001016; DE69328822 T2 20010125; CA2124846 A1 19940414; CA2124846 C 20090519; BR9305657 A 19961126; AU5350294 A 19940426; AU660266 B2 19950615; AT193718 T 20000615	US19920955690 19921002	GRUBER PATRICK RICHARD; KOLSTAD JEFFREY JOHN; HALL ERIC STANLEY; EICHEN CONN ROBIN SUE; RYAN CHRISTOPHER M	CARGILL INC	Melt-stable lactide polymer composition and process for manufacture thereof.
WO9600263 A1	19960104	US5958480 A 19990928; US6410096 B1 20020625; NO965492 A 19961223; NL9401037 A 19960201; EP0766719 A1 19970409; AU2684095 A 19960119	NL19940001037 19940623	EGGINK GERRIT; NORTHOLT MARTIN DINANT	STICHTING ONDERZOEK EN ONTWIKKELING NOORD NEDERLAND	Method for producing a biologically degradable polyhydroxyalkanoate coating with the aid of an aqueous dispersion of polyhydroxyalkanoate.
WO9617369 A1	19960606	US5874124 A 19990223; JPH10510394 A 19981006; EP0795190 A1 19970917; EP0795190 B1 19990217; DE69507898 T2 19991007; AU3932395 A 19960619	GB19940024175 19941130	ADEBAYO ADELAIDE TITILAYO OLUR; WAGLAND ALISON MARY; SAVILL KAREN	COOKSON PLC	Process for metallizing phosphor screens.
WO9624682 A1	19960815	US5977250 A 19991102; JPH11500613 A 19990119; EP0808373 A1 19971126; EP0808373 B1 19990506; DE69602351 T2 19991125; AU4631196 A 19960827; AT179757 T 19990515	GB19950002531 19950209; GB19950009857 19950516; GB19950002521 19950209; GB19950002522 19950209	GEORGE NEI; HAMMOND TIMOTHY; LIDDELL JOHN MACDONALD; SATGURUNATHAN RAJASINGHAM; TURNER PETER DERYCK	ZENECA LTD	Latex of polyhydroxyalkanoate.

Continued

—Cont'd

Patent Number	Publication Date	Family Members	Priority Numbers	Inventors	Applicants	Title
WO9631303 A1	19961010	JPH11509142 A 19990817; FI951637 A 19961007; EP0831996 A1 19980401; AU5277696 A 19961023	FI19950001637 19950406	KARHUKETO HANNU; KUUSIPALO JURKKA] MONTADOR JAMES HENRY	YHTYNEET PAPERITEHTAAT OY	Packaging material.
WO9631347 A1	19961010	JP2002503160 A 20020129; EP0819058 A1 19980121; CA2217640 A1 19961010; AU5159896 A 19961023	FI19950001637 19950406; GB19950007263 19950407	WADDINGTON SIMON DOMINIC; MONTADOR JAMES HENRY; KUUSIPALO JURKKA TAPANI; KARHUKETO HANNU TAPANI	ZENECA LTD; YHTYNEET PAPERITEHTAAT OY	Composite laminate.
WO9712946 A1	19970410	US5972093 A 19991026; PT866839 E 20021129; ITBO950462 A1 19970401; EP0866839 A1 19980930; EP0866839 B1 20020626; DE69622040 T2 20030206; AU6943196 A 19970428; AT219786 T 20020715	IT1995BO00462 19950929	MOSCA ROBERTO	BERNACCHIA IDA	Paint and use thereof.
WO9853141 A1	19981126	US6183814 B1 20010206; NZ501695 A 20030725; NO995734 A 20000124; JP2002513449 A 20020508; EP0981666 A1 20000301; CA2291172 A1 19981126; CA2291172 C 20080415; BR9809136 A 20011204; AU7586298 A 19981211 AU733819 B2 20010524;	US19970862612 19970523	NANGERONI JAMES FRANCIS; HARTMANN MARK H; IWEN MATTHEW L; RYAN CHRISTOPHER M; KOLSTAD JEFFREY J; MCCARTHY KEVIN T	CARGILL INC	Polylactide coated paper.
WO9904948 A1	19990204	US6025028 A 20000215; EP0998381 A1 20000510; EP0998381 B1 20031119; EP0998381 B2 20100505; DE69819902 T2 20040902; DE69819902 T3 20101104; AU8506898 A 19990216; AT254531 T 20031215	US19970053724P 19970725	ASRAR JAWED; PIERRE JEAN R; D'HAENE POL	MONSANTO CO	Polyhydroxyalkanoate coatings.

WO9914268 A1	19990325	US6096810 A 20000801; US6201083 B1 20010313; EP1023378 A1 20000802; EP1023378 B1 20020626; DK1023378 T3 20021014	US19970059670P 19970918	ASRAR JAWED; D'HAENE POL	MONSANTO CO	Modified polyhydroxyalkanoates for production of coatings and films.
WO9950345 A1	19991007	US6114495 A 20000905; US6353086 B1 20020305; JP2002509968 A 20020402; HK1036466 A1 20090206; EP1070097 A1 20010124; CN1299393 A 20010613; CN100379806 C 20080409; CA2325046 A1 19991007; CA2325046 C 20090310; BR9909283 A 20001226; BR9909283 B1 20090505	US19980053836 19980401	KOLSTAD JEFFREY J; WITZKE DAVID ROY; HARTMANN MARK H; HALL ERIC STANLEY; NANGERONI JAMES FRANCIS	CARGILL INC	Lactic acid residue containing polymer composition, product method for preparation and use.

Chapter 14

Inks

14.1 INKS IN GENERAL

Ink is a colloid formulation, comprising colorant(s), vehicle or binder (alias varnish), solvent, and additives. Inks include dye-based inks with dyes dissolved in solvents and pigment-based inks with solid pigments dispersed in liquid. Out of consideration for the environment, water-based pigment or dye inks are used almost exclusively in desk printer for home or office. The advantages of water-based inks include high safety, high quality of output, and capability of printing in vivid color. The main disadvantages of the water-based inks are long drying time, poor weather resistance, poor blocking resistance, poor abrasion resistance, and poor printing quality. By using special additives, such as high-molecular-weight resins, waxes, and other materials, and techniques, several of the properties of water-based inks were improved, but at the expense of the overall cost.

Most of the commercial inks contain resins that are derived from fossil-fuel resources, and are nonbiodegradable. Although the amount of ink is relatively small with respect to the mass of the printed material, the requirement of complete biodegradability also makes it necessary for inks to be completely biodegradable. Such as with the adhesives, conventional inks used for the printing of packaging materials, such as paper and paper carton, can contaminate the recycling process and affect the quality of the recycled paper. Numerous efforts have been made, therefore, to develop formulations of biodegradable resin-based inks.

Printing can be done by any conventional technique known in the art, including ink jet printing, flexographic printing, gravure printing, offset printing (lithography), spin coating, letter press printing, thermal transfer printing, screen printing (serigraphy), and electrophotographic printing (xerography).

14.2 JET PRINTING INKS

Ink jet printing is a nonimpact method for producing images by the deposition of ink droplets, after ejection from a small orifice, in a pixel-by-pixel manner to an image-recording substrate in response to digital signals. The inks used in the various ink jet printers can be classified as either pigment or dye based. A pigment is a colorant that is insoluble in the carrier medium, but is dispersed or suspended in the form of small particles, often stabilized against flocculation and settling by the use of dispersing agents. A dye is a colorant that is dissolved in the carrier medium. In either case, the carrier medium can be a liquid or a solid at room temperature.

EP0613927 A2 (1994, CANON KK) discloses a water-based ink for ink jet printing comprising a biodegradable polymer linked to a solubilizing group of a water-soluble dye by coordination bonding. The biodegradable polymer can be chosen from among the organic acid salts of cationic chitosans (e.g., chitosan acetate) and cationic starches; other polymers include vinylbenzyl-type cationic polymers, acrylic acid-type cationic polymers, polyamine sulfones, and polyarylamines. The water-based ink composition comprise at least 67 wt% of water.

WO2012150349 A2 (2012, MARKEM IMAJE; DE SAINT-ROMAIN PIERRE) discloses a biodegradable ink composition for ink jet printing, liquid at room temperature, comprising the following:

1. A binder comprising at least 0.5 wt% relative to the total weight of the ink, of at least one biodegradable polymer having a weight average molecular weight (M_w) of less than 70 kDa, preferably less than 60 kDa, more preferably less than 50 kDa, further preferably less than 40 kDa, expressed as polystyrene equivalents.
2. An organic vehicle or solvent comprising, preferably consisting of, one or more organic solvent compound (s), and optionally water.
3. At least 0.1 wt% relative to the total weight of the ink composition of one or more dye(s) and/or pigment (s).

The biodegradable polymer is chosen from among polyhydroxyalkanoates (PHAs), polyesteramides, poly(glycolic acid) (PGA), PLA, poly(ε-caprolactone) (PCL), and the copolymers thereof; and aliphatic copolyesters, such as succinates, adipates, and terephthalates; and wherein the ink composition has a viscosity of 1–20 mPa s, preferably of 2–10 mPa s at 20 °C. The liquid ink composition is used for the ink jet marking or printing of a large variety of supports, substrates, and objects, whether porous or nonporous, both using the so-called "deflected continuous ink jet" technique and the so-called "drop on demand" technique.

EP1256606 A2 (2002, CANON KK) discloses a pigment ink with at least part of surfaces of pigment particles covered with a PHA and a medium for dispersion of the color material. In addition, microcapsulated pigment with

Biopolymers: Processing and Products. http://dx.doi.org/10.1016/B978-0-323-26698-7.00014-3

various kinds of properties can be obtained by subjecting the PHA to chemical modification. Furthermore, by introducing a graft chain into the PHA, for example, it is possible to obtain a microcapsulated pigment with at least part of the pigment covered by PHA having various kinds of properties derived from the graft chain. In addition, by crosslinking the PHA, it is possible to obtain a microcapsulated pigment with at least part of the pigment covered with PHA having wanted physicochemical properties (e.g., mechanical strength, chemical resistance, and heat resistance). The microcapsulated pigment is claimed to exhibit satisfactory dispersibility in the absence of surfactant in water-based, oil-based, and both water- and oil-based ink compositions by appropriately selecting the composition of PHA. Because of the reduced particle size, the microcapsulated pigment is excellent in density, fineness, transparency, coloring, and color-rendering properties, and has excellent dispersibility and dispersion stability with time. The pigment ink is useful for ink jet printing applications.

GB2461147 A (2009, SERICOL LTD) discloses an ink jet ink composition comprising a solvent blend containing a biosolvent and a dibasic ester, a carrier resin, a colorant, and an organomodified polysiloxane. The biosolvent may be a solvent derived from renewable resources and may comprise soy methyl ester, lactate esters (e.g., ethyl lactate, PHAs, terpenes, and nonlinear alcohols), and D-limonene. The dibasic ester may be a di(C1-C4 alkyl) ester of a dicarboxylic acid having three to eight carbon atoms, such as esters of succinic acid, glutaric acid, and adipic acid. The organomodified polysiloxane may be a polyether modified polysiloxane. The carrier resin may be nitrocellulose.

DE10256492 A1 (2003, HUECK FOLIEN GMBH) discloses a biodegradable printing ink composition comprising the following: (a) casein (5–30 wt%), starch (5–30 wt%), hydroxycellulose (5–35 wt%), or poly(vinyl alcohol) (PVOH) (5–35 wt%); (b) pigment (5–80 wt%); and (c) solvent (15–87 wt%). The pigment (b) is colored and is inorganic (specifically, titanium dioxide, zinc sulfide, kaolin, and aluminum, chromium, or silicon oxide) or organic (specifically, phthalocyanine blue, i-indolidine yellow, or dioxazine violet). The printing ink is used in the production of coated carriers with exactly dimensioned uncoated areas (e.g., areas with codes, script, or patterns). Typical applications are in security documents and data carriers.

WO0190262 A2 (2001, VIDEOJET TECHNOLOGIES INC) discloses an ink jet ink composition suitable for use in continuous ink jet printing comprising a liquid vehicle, a binder resin, a colorant, and optionally a surfactant. The liquid vehicle includes an organic solvent or blend of solvents, and the binder resin can be nitrocellulose.

US2007043145 A1 (2007, ELECTRONICS FOR IMAGING INC) discloses ink jet ink formulations incorporating cellulose derivatives, nitrocellulose, and cellulose acetate butyrate as binding agents.

14.2.1 Hot Melt Inks

Another type of ink useful in ink jet printing comprises the so-called hot melt inks (alias solid phase change inks, solid inks, or thermoplastic inks). These inks, being solids, must be melted before being ejected from the printer as a liquid, which solidifies on the relatively cool surface of the substrate. Hot melt inks contain a "phase change agent" that enables the ink to exist in a solid phase at ambient temperatures, but also exist in the liquid phase at the elevated operating temperature of an ink jet printing device. At the deposit operating temperature, droplets of liquid ink are ejected from the printing device and, as the ink is jetted towards or contacts the surface of the recording substrate, either directly or via an intermediate heated transfer belt or drum, the ink quickly solidifies to form a predetermined pattern of solidified ink drops. Hot melt inks have also been used in other printing technologies, such as gravure printing. Hot melt inks are considered to be an environmentally conscious way to print because of the cartridge-free design, minimal packaging, nearly waste-free printing process, and safe, toxin-free solid ink sticks. However, hot melt inks may also cause certain problems, such as the following: (1) increased accumulation in greenhouse gases and/or accumulation of nonbiodegradable materials and (2) ink shrinkage (the purging of excess ink) caused by formation of air bubbles in jet lines. These issues may be due to the presence of fossil fuel–based products, such as waxes in the solid ink, which can lead to poor abrasion resistance, poor adhesion, and poor fold resistance. Although present hot melt inks are useful for their intended purposes, it is better to provide a hot melt ink wherein a major proportion of the ink is derived from renewable resources and is, thus, environmentally friendly (2011, **US2011130502** A1, XEROX CORP).

EP0371627 A2 (1990, ICI PLC) discloses, in one of its embodiments, a method of printing in which a hot melt ink composition is melted and ejected from a small orifice in the form of small drops directed towards a substrate on which an image is to be formed. It is characterized in that the hot melt ink composition comprises either a solution or a dispersion of a dye or a finely divided pigment in a halogenated hydrocarbon having a melting temperature, $T_m \geq 50\,°C$, or a colored condensation polymer obtained by reacting a polymerizable lactone or a hydroxyalkanoic acid with a dye containing at least one active hydrogen atom. A preferred polymerizable lactone for preparing the colored condensation polymers is ε-caprolactone, and a suitable hydroxyalkanoic acid is ω-hydroxydodecanoic acid.

US2011130502 A1 (2011, XEROX CORP) discloses a hot melt ink composition comprising at least one colorant and an ink vehicle. The ink vehicle further comprises at least one poly(3-hydroxyheptanoate-*co*-3-hydroxynonanoate) copolymer.

14.3 FLEXOGRAPHIC INKS, GRAVURE INKS, AND SCREEN INKS

In flexographic printing, a flexographic plate of plastic or rubber with raised images or text is used. That plate is attached to a roller. Ink is applied on the plate using a second roller, and a third roller keeps the printing substrate pressed against the flexographic plate while the substrate is being passed between them.

There are five basic types of inks commonly used in flexographic printing. Primarily, the inks can be divided into solvent- and water-based inks. In addition, there are electron beam curing inks with a photoreactive vehicle ink that dries or sets, under the influence of beams of electrons, and ultraviolet (UV) curing inks, as well as the more rare two-part chemically curing inks. Similarly, as for ink jet inks, the binders used for the flexographic inks are typically derived from fossil fuel resources and cellulose; the cellulose-based binders are represented by nitrocelluloses and fine chemical–type cellulose-acetate derivatives (2013, **WO2013038068** A1, TEKNOLOGIAN TUTKIMUSKESKUS VTT).

A water-based flexographic ink composition generally comprises a pigment, a polymer resin, a binder or wax, an organic solvent, and water. Flexographic inks are composed of nonbiodegradable pigments and polymer resins that generally accumulate in post-treated sludge resulting from the de-inking processes, or are buried in soils when the final product is disposed therein. Conventional flexographic ink compositions are normally made of acrylic-, methacrylic-, epoxy-, or styrene-based polymer resins. Actually, acrylic and epoxy resins are present in 90 wt% of the flexographic ink compositions. There are trends in the last years to replace the conventional resins with biodegradable ones. In addition, there are efforts to decrease the content of volatile organic solvent to limit their impact on the environment. Nowadays, water-based flexographic inks usually contain 5–20 wt% of organic solvents. Although they are harmful, they cannot easily be eradicated because they help to reduce the drying time of the ink once it is applied on a surface (paper, cardboard, or plastic) (2003, **WO03062334** A1, BIOMATERA INC). The physical properties of inks for printing by flexography, such as viscosity and conductivity, are fundamentally different from those of inks that can be projected by an ink jet.

WO2013038068 A1 (2013, TEKNOLOGIAN TUTKIMUSKESKUS VTT) discloses an ink composition comprising a liquid medium, pigment particles, and at least one binder forming a suspension, characterized in that said ink composition contains a wood-based polysaccharide binder, selected from the group of nanocellulose, hemicelluloses, celluloses, and derivatives and combinations thereof. It is preferred that the polysaccharide binder is present in an amount efficient for modifying the rheology of the composition. Thus, the polysaccharide binder forms at least 10 wt%, preferably 15–100 wt% of the total weight of the binder of the ink composition. The polysaccharide binder forms at least 1 wt%, preferably 5–60 wt%, of the total weight of the ink composition. The ink composition can be used in the ink jet and particularly in flexographic printing applications.

JPH0892518 A (1996, TOYO BOSEKI) discloses a biodegradable ink composition comprising the following: (1) a PLA having a molar ratio (L/D) of the L-lactic acid to D-lactic acid of 1–9, a reduced viscosity (η_{sp}/C) of 0.4–1.5 dL/g, and a glass transition temperature (T_g) of 35–60 °C; (2) an ink pigment; and (3) a solvent. No organic halogenous solvents are used; preferably, the solvent is selected from methyl ethyl ketone, ethyl acetate, toluene, or isopropyl alcohol. The ink composition is used especially for flexography printing.

JP2002097359 A (2002, TOYO BOSEKI) discloses a biodegradable ink composition comprising a PLA dissolved in a solvent. The PLA contains 80–100 mol% of lactic acid units in which the molar ratio (L/D) of L-lactic acid to D-lactic acid is 1–9.

Example: L-lactide (100 g), D,L-lactide (100 g), and tin octylate (50 mg) were added to a flask, and ring-opening polymerization was performed for 1 h at 190 °C under a nitrogen atmosphere to obtain PLA. The PLA (100 g) was dissolved in toluene (200 g), and the solution was dispersed in titanium oxide (100 g) and diluted with ethylacetate (100 g) to obtain a white ink. The ink obtained was printed in a PLA film with a flexographic press. The ink was claimed to have excellent printing property, adhesivity, scratch resistance, and biodegradability.

WO03062334 A1 (2003, BIOMATERA INC) discloses an essentially water-based biodegradable ink composition for flexographic printing in which the biodegradable binders are in a dispersed form in an aqueous medium (namely, in the form of suspensions in water of latex type). The flexographic ink composition comprises a biodegradable polymer selected from the group consisting of PHA, PLA, poly(lactic-*co*-glycolic acid), PGA, PCL, poly(butylene succinate) (PBS), or a derivative or a mixture thereof.

JPH08319445 A (1996, TOPPAN PRINTING CO LTD) discloses a biodegradable ink composition, essentially for gravure or screen printing (serigraphy) in which the biodegradable binder is PLA, PCL, or PVOH. When the binder resin contains PCL or PLA, the solvent is selected from toluene, xylene, acetone, methyl ethyl ketone, cyclohexanone, dioxane, tetrahydrofuran, methyl isobutyl ketone, *N*-dimethylformamide, butyl cellosolve, ε-caprolactone, n-butyl acetate, ethyl cellosolve acetate and isophorone. These solvents may be used in accordance with the printing method. For example, the use of toluene, xylene, acetone, methyl ethyl ketone, cyclohexanone, dioxane, *N*,*N*-dimethylformamide, tetrahydrofuran, and methyl isobutyl ketone is preferred when gravure printing is used. Furthermore, the use of butyl cellosolve, ε-caprolactone, *n*-butyl acetate, ethyl cellosolve acetate and isophorone, is preferred in the case of screen printing. When the binder resin is PVOH, the solvent contains water.

JP2001294792 A (2001, TOYO INK MFG CO) discloses a biodegradable ink comprising at least one biodegradable polymer chosen from PLA, cellulose acetate, PVOH, PCL, PBS, poly(ethylene succinate) (PES), and an edible colorant. The ink composition is used especially for flexography printing.

Example: A rotogravure ink was prepared by mixing PLA (12 pbw), methyl ethyl ketone (13 pbw), toluene (10 pbw), and carotene (10 pbw) obtained from carrot. The above gravure ink was applied on a PLA film. The embedded printed matter was evaluated after a year. The base material film did not change its original form.

JP2002069341 A (2002, TOYO BOSEKI; TOPPAN PRINTING CO LTD; TOYO INK MFG CO) discloses an ink composition comprising the following: an aliphatic polyester containing a tertiary-amino group in its main chain, an ink pigment, and a solvent. The biodegradable polyester contains preferably ≥80 mol% of lactic acid residue in which the molar ratio (L/D) of L-lactic acid to D-lactic acid is 1–9. The biodegradable ink composition can be used for printing labels and wrapping films, especially biodegradable films, such as PLA films, as base materials and as paper ink. The ink is applied by the gravure method.

JP2002069352 A (2002, TOYO BOSEKI; TOPPAN PRINTING CO LTD; TOYO INK MFG CO) discloses a modified ink composition comprising an aliphatic polyester containing a bivalent metal in its main chain, as shown in Scheme 14.1, an ink pigment, and a solvent.

$$-\mathrm{OR_1COO-MOCOR_2\text{-}O}- \qquad (1)$$

$$-(\text{-}\mathrm{CO{-}R_3{-}O}\text{-})_n \qquad (2)$$

SCHEME 14.1 Chemical formulae of an aliphatic polyester containing a bivalent metal in its main chain (2002, **JP2002069352** A, TOYO BOSEKI; TOPPAN PRINTING CO LTD; TOYO INK MFG CO). R_1, R_2, R_3, each a ≤20C alkylene group; M, divalent metal; *n*, integer (≥1).

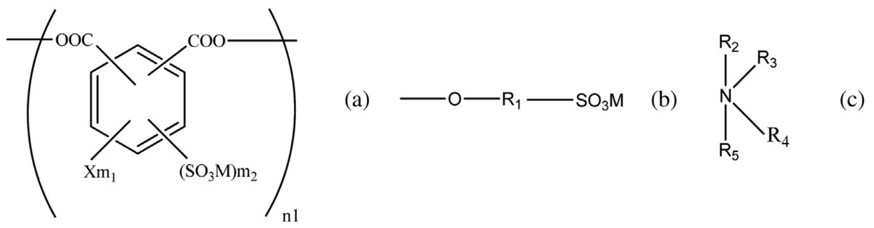
JP2003147248 A (2003, TOYO BOSEKI; TOPPAN PRINTING CO LTD; TOYO INK MFG CO) discloses another modified ink composition comprising an aliphatic polyester containing a sulfonate group (1), as shown in Scheme 14.2, an ink pigment, and a solvent. The disclosed ink composition is claimed to have dispersibility of the ink pigment and ink stability superior to those of a conventional PLA ink.

JP2010174170 A (2010, TOYO BOSEKI) discloses a binder for a PLA-based aqueous ink. The binder for the aqueous ink contains a copolymerized polyurethane resin having, in the molecule, PLA segments and metal sulfonate groups containing segments. The aqueous ink has such self-emulsifying function as to enable a stable water-based emulsion to be formed even if no emulsifier is added.

JP2002356640 A (2002, TOYO BOSEKI; TOPPAN PRINTING CO LTD; TOYO INK MFG CO) discloses an ink composition comprising an aliphatic polyester, an ink pigment, and a solvent. The aliphatic polyester comprises PLA segments and polyglycerol segments, the degree of polymerization of the polyglycerol segment being 3–20; contains ≥80 mol% of lactic acid units, the molar ratio (L/D) of L-lactic acid to D-lactic acid being 1–9; has a reduced viscosity (η_{sp}/C) of 0.3–1.0 dL/g; a T_g of 40–60 °C; and a hydroxyl group concentration of 100–500 eq/10^6 g. The ink is applied by the gravure method.

JP2003182266 A (2003), **JP2003165570** A (2003), and **JP2003175569** A (2003) of TOYO BOSEKI; TOPPAN PRINTING CO LTD; TOYO INK MFG CO use similar ink compositions comprising, as a binder, an aliphatic polyester containing PLA segments and polyglycerol segments for printing a biodegradable film that forms either a heat-shrinkable packaging (bag) or a releasable sheet. The ink is applied by the gravure method.

JP2008013657 A (2008) and **JP2008013658** A (2008) of SAKATA INKS disclose aqueous ink compositions comprising a colorant, a binder resin, and an aqueous medium containing water. As the binder resin, a PLA aqueous dispersion, which is prepared by dispersing PLA or a PLA-PCL copolymer in an aqueous medium in the presence of



SCHEME 14.2 Chemical formula of a metal sulfonate group containing aliphatic polyester (2003, **JP2003147248** A TOYO BOSEKI; TOPPAN PRINTING CO LTD; TOYO INK MFG CO). (a): aliphatic polyester containing a sulfonate group; X: ≤20C alkyl group, a cycloalkyl group, an aryl group, an arylalkyl group, hydrogen, hydroxy group, nitro group, amino group, an acyl group, sulfonic acid group, an alkoxy group, or a halogen; M: lithium, sodium, potassium, or an amine represented by formula (c); In (c): R_2–R_5 are each independently hydrogen, an alkyl group, a phenyl group, or a benzyl group; m_1 is an integer of 0–3; m_2, an integer of 1–4; m_1 and m_2 satisfy the relation of $1 \leq m_1 + m_2 \leq 4$; n_1, integer of ≥ and/or In (b): R_1: ≤ 20C alkylidene group; M: lithium, sodium, potassium, or an amine represented by formula (c), including a sulfonic acid–containing structure.

a poly(ethylene oxide-*co*-propylene oxide) having a weight average molecular weight (M_w) of 5000–50,000 and an HLB of 11–20, is used. The aqueous-printing-ink compositions are used in flexographic printing or gravure printing.

JP2002179971 A (2002, TOYO INK MFG CO; TOYO FOOD COLOR & CHEMICAL CO) discloses a biodegradable printing ink composition comprising a natural pigment, such as a chlorophylline-based pigment as the colorant component and casein as the binder component. The ink composition is used especially for flexography printing.

Example: Copper chlorophylline sodium (4 pbw), water (12 pbw), ethanol (70 pbw), zein (2 pbw), and propylene glycol (2 pbw) were mixed and dissolved, and the printing ink was obtained. The printing ink was printed on a PBS film of 25–35 µm thickness using a photogravure printing machine. A print with favorable peeling strength was obtained.

JP2002249696 A (2002, TOYO INK MFG CO; TOYO FOOD COLOR & CHEMICAL CO) discloses a printing ink for biodegradable films comprising a chlorophylline-based pigment, shellac, and an ethanol/water mixed solvent. The ink contains also 5–25 wt% calcium carbonate ($CaCO_3$). A preferred ink is rotogravure ink or flexographic ink. The printing ink is made of natural products and is, thus, harmless to the human body and environment.

JP2002105371 A (2002, TOYO INK MFG CO) discloses a biodegradable ink composition consisting of the following: (1) 50–80 wt% of a nitrocellulose, (2) 5–25 wt% of an alkyd resin, and (3) 15–45 wt% of a plasticizer. The ink composition is used especially as a rotogravure ink.

JP2004238564 A (2004, DAINICHISEIKA COLOR CHEM) provides a biodegradable ink composition comprising PCL, a pigment, and an organic solvent (e.g., ethyl acetate). The ink is useful for the flexographic or gravure printing of biodegradable polymer films and paper.

JP2004168798 A (2004, DAINICHISEIKA COLOR CHEM) discloses a biodegradable printing ink composition comprising a starch fatty acid ester, a pigment, and an organic solvent (e.g., ethanol). The esterification degree of the starch fatty acid ester with respect to fatty acid is at least 40%. The ink is useful for the flexographic or gravure printing of biodegradable polymer films and paper.

GB2456564 A (2009, SUN CHEMICAL LTD) discloses an ink composition comprising a solvent (e.g., water, ethanol, or ethyl acetate), a binder resin (e.g., polysaccharide, rosin, shellac, soybean protein, zein corn protein, or shellac), and a pigment (e.g., talc, chalk, or kaolin). In the case of water-based inks, preferred binder resins are shellac, polysaccharide, arabinogalactan, a soybean protein, or rosin. In the case of solvent-based inks, preferred resins are shellac, zein corn protein, tree rosin sandarac, or dammar. The resin is preset in an amount of 1–20 wt%. The ink is useful in flexographic printing.

Screen printing is done with plastisol, a complex mixture of vinyl resin, a plasticizer, and one or more pigments. Fusion of freshly printed plastisol into a dried film requires exposure of the screen printed fabric to temperatures exceeding 165 °C. This increases the cost of the screen printed product and consumes energy. Moreover, dried plastisols are not biodegradable, and some of the components used in conventional screen printing are hazardous. Screen printing generates waste, which often contains hazardous materials, creating disposal problems (1996, **US5521233** A, SHIFRIN SHARI).

US5521233 A (1996, SHIFRIN SHARI) discloses a biodegradable air drying screen printing ink, which is free of plastisol. The ink includes a base made of water and a colloidal gum, preferably sodium alginate (0.37 vol%). A naturally occurring binder is added to the base, preferably natural latex (8–20 vol%). The ink also includes one or more pigments (0.2–2 vol%) made from natural ingredients, preferably plants or insects.

14.4 ELECTROPHOTOGRAPHIC TONERS

Electrophotographic toners are used in copying machines and printers. The electrophotographic process forms an image on a recording medium, such as paper or a sheet, through a charging step, an exposure step, a developing step, a transferring step, and a fixing step. In the charging step, a surface of a photoreceptor is evenly charged. In the exposure step, the charge photoreceptor is exposed to light so that an electrostatic latent image is formed on the surface of the photoreceptor. In the developing step, a developer adheres to the electrostatic latent image formed on the surface of the photoreceptor to thereby form a visualized image. In the transferring step, the visualized image formed on the surface of the photoreceptor is transferred to the recording medium. In the fixing step, the visualized image transferred to the recording medium is fixed by heat, pressure, and the like. Through the described steps, an image is formed on the recording medium in the electrophotographic printer.

US5004664 A (1991, XEROX CORP) discloses a toner composition comprising a biodegradable polyester, preferably PHA, copolymers, or blends thereof, and pigment particles, preferably carbon black, magnetite, mixtures, or magenta, cyan, and/or yellow pigments. The tone composition is prepared by extruding PHA blended with polyethyloxazoline, poly(vinyl pyrrolidone), PVOH, or other water-soluble polymer, grinding, then removing the water-soluble polymer with water, followed by filtration and an electrostatic imaging method using the claimed toner. Preferred PHAs are P3HB and poly(3-hydroxybutyrate-*co*-3-valerate) (PHBHV). The toner is useful for conventional electrostatic imaging. The biodegradable composition enables the easy de-inking of papers by soil enzymes. The toner also provides stable triboelectric performance and good image quality.

Conventionally, to improve the fixing strength of a toner for electrophotography, a binder resin having low molecular weight or a wax having a low T_m have been used. Most of the binder resins, which account for 70% of constituents of a toner, are manufactured by using raw material derived from fossil fuel resources (2009, **US2009170020** A1, SHARP KK). Synthetic resins, such as styrene-acryl copolymers, have the problem that hazardous chemicals, such as styrene and xylene, used in the polymerization process remain in the final product. Furthermore, although waste toner from copying machines and printers of the electrophotography systems are being collected recently, most of the collected toner is incinerated or buried as industrial wastes. Also, the handling of an all-in-one type toner cartridge containing a developer and a waste toner box is troublesome when it is recycled (2001, **EP1107069** A1, OMOEGAWA PAPER CO LTD; SHIMADZU CORP; TOYOTA MOTOR CO LTD). Therefore, numerous efforts have been made to replace the conventional binder resins for toners with resins derived from renewable resources.

EP1107069 A1 (2001, OMOEGAWA PAPER CO LTD; SHIMADZU CORP; TOYOTA MOTOR CO LTD) discloses an electrophotographic toner comprising, as a binder resin, a resin that contains PLA and a terpene phenol copolymer. The toner is claimed to exhibit an enhanced low-temperature toner fixing property.

US2009170020 A1 (2009, SHARP KK) discloses an electrophotographic toner comprising the following: (1) toner base particles containing a colorant and a binder resin, wherein the binder resin contains a PLA copolymer (20–50 wt%) and an amorphous polyester resin; and (2) a mixed oxide of aluminum oxide (35–50 wt%) and silicon dioxide (35–50 wt%) added to the toner base particles. The toner is claimed to exhibit excellent fixing property, chargeability, color reproducibility, and long-term stability.

JP2010175841 A (2010, CASIO ELECTRONICS CO LTD; CASIO COMPUTER CO LTD) discloses an electrophotographic toner containing PLA as a binder resin. The electrophotographic toner is prepared by kneading a raw material mixture, including a binder resin containing PLA with a molecular weight of 5000–50,000, thermally processing the kneaded mixture at a temperature, T, in the range $T_g < T < T_m$, and pulverizing the thermally processed kneaded mixture.

JP2006111836 A (2006, KOTOBUKI SEIHAN PRINTING CO) discloses a biodegradable offset ink prepared by heating in the temperature range of 150–300 °C three components of a PLA, a rosin, and a drying oil varnish. The drying oil used is linseed oil, tung oil, sesame oil, rapeseed oil, cotton seed oil, or the like. The biodegradable offset ink is claimed to have excellent biodegradability and give printed matters with good physical properties and good deinking ability.

14.5 COLOR CHANGING INKS

Color changing inks contain chemical compounds (dyes or pigments) that are sensitive to variations in temperature or radiation. Currently, there are two main groups of color changing inks: thermochromic, which change color in response to temperature fluctuations; and photochromic, in response to variations in exposure to UV light, primarily sunlight. Known thermochromic inks often include leuco dyes that change from a particular color at low temperature to colorless at a high temperature (e.g., red at 29 °C and colorless at >32 °C). Depending on the application, color changing inks can be applied with several printing processes, including flexography, gravure offset lithography, and screen printing.

CN103305053 A (2013, KUNSHAN XIANGHUAJING BIOTECHNOLOGY CO LTD) discloses a temperature-sensitive, color-change, water-based ink and a preparation process of the ink. The water-based ink is characterized by comprising a reversible temperature-sensitive, color-change composite pigment, a colloid stabilizer, a water-soluble organic solvent, de-ionized water, a thickener, a surfactant, and other functional additives. The carrier resin is a polyethylene glycol–modified PLA. The water-based ink can be used for avoiding the defect of poor dispersion stability of the color-change pigment in the water-based ink, is good in biodegradability, and is widely applied to the fields of functional electronic ink, functional textile coatings, and writing ink.

14.6 WRITING INKS

JPH08302265 A (1996, PENTEL KK) discloses an ink for ball point pen comprising the following: (1) organic solvent (30–70 wt%), such as ethylene glycol monophenyl ether or benzyl alcohol; (2) coloring material (10–45 wt%) colorant composed of a dye or a pigment; (3) resin, such as rosin; and (4) 1,3-dimethyl-2-imidazolidinone (5–30 wt%).

KR20090073824 A (2009, KAWK NO YUN (KR); LEE CHUL KYU) discloses an aqueous ink composition for marker pen comprising the following: (a) distilled water (30–40 wt%), (b) semisynthetic cellulose-based polymer (3–7 wt%), (c) white pigment (12–18 wt%), (d) emulsifier (20–30 wt%), (e) potassium aluminum sulfate (1–3 wt%), (f) polyethylene glycol (3–7 wt%), (g) dispersing agent (3–7 wt%), (h) anti-settling agent (2–4 wt%), and (i) release agent (3–7 wt%). The emulsifier (d) consists of compounds of edible glycerol and polysorbate. The semisynthetic cellulose polymer (b) is chosen from methyl cellulose, hydroxyethyl cellulose, hydroxypropyl cellulose, hydroxypropylmethylcellulose, hydroxypropylethyl cellulose, and carboxymethyl cellulose. The aqueous ink composition is claimed to be eco-friendly, have excellent erasability, and prevent strains and spots on a writing board formed of non-absorptive material.

WO2013053774 A2 (2013, SOJASUN TECHNOLOGIES) discloses an ink, useful in official document or bank note for unforgeable printing and/or writing, comprising a solvent, a coloring agent (1–1.5 wt%), a wetting agent (1–12 wt%), and a photoluminescent marker (1–5 wt%). The solvent is selected from water, vegetable oil, and natural resin. The vegetable oil comprises soy oil, broccoli oil, sunflower oil, rapeseed oil, wheat germ oil, corn oil, palm oil, olive oil, linseed oil, hemp oil, or jojoba oil. The wetting agent is soy lecithin. The photoluminescent marker includes a lanthanide.

Example: A typical composition comprises the following: refined soybean oil (up to 100 wt%), glycerol (15 wt%), soybean membrane (5 wt%), ultramarine blue-54 (1–5 wt%), ultramarine blue (1–5 wt%), brilliant blue (1–5 wt%), photoluminescent marker (5 wt%), kappa carrageenan (0.1–1 wt%), hydrophilic clay (0.5–2 wt%), and starch (0.5–5 wt%).

PATENTS

Patent Number	Publication Date	Family Members	Priority Numbers	Inventors	Applicants	Title
CN103305053 A	20130918		CN20131282565 20130708	XU DAN; WANG DONGHAI	KUNSHAN XIANGHUAJING BIOTECHNOLOGY CO LTD	Temperature-sensitive color-change water-based ink taking biodegradable resin as carrier and preparation process of ink.
DE10256492 A1	20030925		AT20010001919 20011207	HAMMERL STEFANIE; REICH PETER; HILBURGER JOHANN; KAMMERER HANS HERMANN	HUECK FOLIEN GMBH	Biologisch abbaubare Druckfarbe. "Biodegradable printing inks."
EP0371627 A2	19900606	US5102448 A 19920407 JPH02200475 A 19900808; EP0371627 A3 19911023	GB19880027781 19881128	PARTON BRIAN; GUNN DONALD MURRAY	ICI PLC	
EP0613927 A2	19940907	EP0613927 A3 19950524; EP0613927 B1 20000823; US5713991 A 19980203; US5579038 A 19961126; DE69425599 T2 20010419	JP19930041374 19930302; JP19930119850 19930521	KIMURA ISAO	CANON KK	Recording apparatus and ink employing biodegradable substance.
EP1107069 A1	20010613	US2001003636 A1 20010614, US6432600 B2 20020813; JP2001166537 A 20010622; JP3785011 B2 20060614; EP1107069 B1 20040331; DE60009428 T2 20050217	JP19990352412 19991210	OKUYAMA HISASHI; HORIBE YASUMASA; SUWA YOSHIHITO	OMOEGAWA PAPER CO LTD; SHIMADZU CORP; TOYOTA MOTOR CO LTD	Toner for electrophotography.
EP1256606 A2	20021113	EP1256606 A3 20030924; EP1256606 B1 20060308; US2003203987 A1 20031030; US6916861 B2 20050712; KR20020083949 A 20021104; JP2003012984 A 20030115; DE60209587 T2 20060817	JP20010133550 20010427; JP20010210050 20010710	NOMOTO TSUYOSHI; YANO TETSUYA; KOZAKI SHINYA; HONMA TSUTOMU	CANON KK	Pigment containing ink and production method thereof.
GB2456564 A	20090722		GB20080000975 20080118	NIX CARLTON	SUN CHEMICAL LTD	Environmentally friendly printing ink compositions.
GB2461147 A	20091230	GB2461147 B 20100616	GB20080009139 20080520; GB20080010033 20080602	RUSSELL CHRISTINE	SERICOL LTD	Inkjet printing ink composition and method.

JP2001294792 A	20011023		JP20000114512 20000417	KANO FUMIHISA	TOYO INK MFG CO	Biodegradable covering agent and covered material.
JP2002069341 A	20020308		JP20000258828 20000829	MIYAMOTO TAKASHI; ITO TAKESHI; SHINO KATSUYA; SHIBAZAKI SATOKO; HOTTA YASUNARI; WATANABE JIRO; KATO SHUNICHI; ICHIKAWA YOSHITO; WATANABE FUMIO	TOYO BOSEKI; TOPPAN PRINTING CO LTD; TOYO INK MFG CO	Ink composition.
JP2002069352 A	20020308	JP4795518 B2 20111019		MIYAMOTO TAKASHI; ITO TAKESHI; SHINO KATSUYA; SHIBAZAKI SATOKO; HOTTA YASUNARI; WATANABE JIRO; KATO SHUNICHI; ICHIKAWA YOSHITO; WATANABE FUMIO	TOYO BOSEKI; TOPPAN PRINTING CO LTD; TOYO INK MFG CO	Ink composition.
JP2002097359 A	20020402	JP3558060 B2 20040825	JP20010279205 20010914	MIYAMOTO TAKASHI; KIMURA KUNIO; ITO TAKESHI; AOYAMA TOMOHIRO; YUUCHI MINAKO; HOTTA SEISHI; UNO KEIICHI	TOYO BOSEKI	Dissolved product of biodegradable polyester.
JP2002105371 A	20020410		JP20000301568 20001002	KURIHASHI TOR; HIGO YUKIKO WATANABE FUMIO	TOYO INK MFG CO	Ink binder, ink composition and biodegradable printing film.
JP2002179971 A	20020626		JP20000383036 20001218	KONO MONICHIRO; KANO FUMIHISA	TOYO INK MFG CO; TOYO FOOD COLOR & CHEMICAL CO	Printing ink.
JP2002249696 A	20020906		JP20000399926 20001228; JP20000383037 20001218	KONO MONICHIRO; KANO FUMIHISA	TOYO INK MFG CO; TOYO FOOD COLOR & CHEMICAL CO	Printing ink for biodegradable plastic film.

Continued

—Cont'd

Patent Number	Publication Date	Family Members	Priority Numbers	Inventors	Applicants	Title
JP2002356640 A	20021213	JP4891490 B2 20120307	JP20010162909 20010530	MIYAMOTO TAKASHI; ITO TAKESHI; SHINO KATSUYA; KATO TAKEO; KAKU TOSHIYUKI; OKADA TAKU; OKUYAMA KAZUNORI	TOYO BOSEKI; TOPPAN PRINTING CO LTD; TOYO INK MFG CO	Ink composition.
JP2003147248 A	20030521	JP3962576 B2 20070822	JP20010351765 20011116	MIYAMOTO TAKASHI; HOTTA YASUNARI; KAKU TOSHIYUKI; OKUYAMA KAZUNORI; SUZUKI AKIRA	TOYO BOSEKI; TOPPAN PRINTING CO LTD; TOYO INK MFG CO	Ink composition.
JP2003165570 A	20030610	JP3992966 B2 20071017	JP20010366514 20011130	MIYAMOTO TAKASHI; HOTTA YASUNARI; KAKU TOSHIYUKI; OKUYAMA KAZUNORI; SUZUKI AKIRA	TOYO BOSEKI; TOPPAN PRINTING CO LTD; TOYO INK MFG CO	Packaging material.
JP2003175569 A	20030624	JP3942883 B2 20070711	JP20010378547 20011212	MIYAMOTO TAKASHI; HOTTA YASUNARI; KAKU TOSHIYUKI; OKUYAMA KAZUNORI; SUZUKI AKIRA	TOPPAN PRINTING CO LTD; TOYO BOSEKI; TOYO INK MFG CO	Biodegradable releasable sheet.
JP2003182266 A	20030703		JP20010381159 20011214	MIYAMOTO TAKASHI; HOTTA YASUNARI; KAKU TOSHIYUKI; OKUYAMA KAZUNORI; SUZUKI AKIRA	TOYO BOSEKI; TOPPAN PRINTING CO LTD; TOYO INK MFG CO	Printed matter.
JP2004168798 A	20040617	JP4190261 B2 20081203	JP20020332787 20021115	SAKAI SHIGEKAZU	DAINICHISEIKA COLOR CHEM	Printink ink.
JP2004238564 A	20040826		JP20030031005 20030207	SAKAI SHIGEKAZU	DAINICHISEIKA COLOR CHEM	Ink composition.
JP2006111836 A	20060427		JP20040325698 20041012	NAITO IKUO; SAWADA HIDEYUKI	KOTOBUKI SEIHAN PRINTING CO	Biodegradable offset ink.
JP2008013657 A	20080124		JP20060185972 20060705	UENO YOSHIAKI; TAKAHASHI RYOTA; OZAWA NORIAKI; HIROSE TADASHI	SAKATA INKS	Biodegradable aqueous printing ink composition.

JP2008013658 A	20080124		JP20060185973 20060705	UENO YOSHIAKI; TAKAHASHI RYOTA; OZAWA NORIAKI; HIROSE TADASHI	SAKATA INKS	Polylactic acid/ polycaprolactone copolymer aqueous dispersion composition and its use.
JP2010174170 A	20100812		JP20090019777 20090130	KITSUMOTO HIROTOSHI; AKASHINA NAOKO	TOYO BOSEKI	Binder for polylactic acid-based aqueous ink, aqueous emulsion, and aqueous ink.
JP2010175841 A	20100812		JP20090018526 20090129	MAEDA MASAHIRO; YAMAZAKI YUTAKA; TSUBAKI TADAHIRO; SUGA YUTA	CASIO ELECTRONICS CO LTD; CASIO COMPUTER CO LTD	Electrophotographic toner and method of manufacturing the same.
JPH08302265 A	19961119	JP3312213 B2 20020805	JP19950129799 19950428	IWATA MASAHIRO; OGAWA ASUKA	PENTEL KK	
JPH08319445 A	19961203	JP4088980 B2 20080521	JP19950255709 19950906; JP19950091869 19950323	ITO NORIYUKI; IMAI TOSHIFUMI; KAWAMOTO KENJI; RI KANSHIN	TOPPAN PRINTING CO LTD	
JPH0892518 A	19960409	JP3493744 B2 20040203	JP19940226531 19940921	MIYAMOTO TAKASHI; KIMURA KUNIO; ITO TAKESHI; AOYAMA TOMOHIRO; YUUCHI MINAKO; HOTTA SEISHI; UNO KEIICHI	TOYO BOSEKI	Biodegradable ink.
KR20090073824 A	20090703	KR100945060 B1 20100305	KR20070141884 20071231	KAWK NO YUN; LEE CHUL KYU	KAWK NO YUN; LEE CHUL KYU	Aqueous ink composition using food material for marker pen and method of preparing the same.
US2007043145 A1	20070222	WO2007021377 A2 20070222; WO2007021377 A3 20080724; US7919543 B2 20110405; EP1957589 B1 20100310; AU2006280452 A1 20070222	US20050708614P 20050816; US20060353754 20060214	BECK CHARLES; MILLS STEPHEN	ELECTRONICS FOR IMAGING INC	Inkjet inks, methods for applying inkjet ink, and articles printed with inkjet inks.
US2009170020 A1	20090702	US8153343 B2 20120410; JP2009162957 A 20090723; JP4610603 B2 20110112; CN101470366 A 20090701; CN101470366 B 20120307	JP20070341458 20071228	KUBO MASAHIKO; ARIYOSHI SATORU	SHARP CORP	Toner, two-component developer, developing device, and image forming apparatus.

Continued

—Cont'd

Patent Number	Publication Date	Family Members	Priority Numbers	Inventors	Applicants	Title
US2011130502 A1	20110602	US8002399 B2 20110823; KR20110063345 A 20110610; JP2011116984 A 20110616; DE102010061931 A1 20110630; CN102086322 A 20110608; CA2722282 A1 20110602	US20090629411 20091202	TUREK CAROLINE M; MCANENEY LANNEN GWYNNE EVELYN; ALLEN C GEOFFREY NESS EVERETT ALAN	XEROX CORP	Solid inks incorporating a polyhydroxyalkanoate compound for enhanced properties.
US5004664 A	19910402		US19890316070 19890227	FULLER TIMOTHY J; MARCHESSAULT ROBERT H; BLUHM TERRY L	XEROX CORP	Toner and developer compositions containing biodegradable semicrystalline polyesters.
US5521233 A	19960528		US19950386109 19950209	SHIFRIN SHARI	SHIFRIN SHARI	Biodegradable air drying screen printing ink.
WO0190262 A2	20011129	WO0190262 A3 20020404; US6726756 B1 20040427; EP1294814 A2 20030326; AU5862501 A 20011203	US20000578702 20000526	ZOU WAN KANG; ZHU LINFANG; ZHAN XUEDONG; XIAO FENGFEI; WANG XIAOMANG	VIDEOJET TECHNOLOGIES INC	
WO03062334 A1	20030731	US2005215662 A1 20050929; US7588632 B2 20090915; RU2004124243 A 20050527; RU2398806 C2 20100910; JP2005515290 A 20050526; ES2271522 T3 20070416; EP1470199 A1 20041027; EP1470199 B1 20060809; DE60307423 T2 20070503; CN1643092 A 20050720; CN100419034C 20080917; CA2473519 A1 20030731; AU2003201583 B2 20090226; AT335795 T 20060915	US20020350347P 20020124	MASARO LAURENT; LAPOINTE PATRICK; GAYET JEAN-CHARLES JACQUES	BIOMATERA INC	Biodegradable flexographic ink.
WO2012150349 A2	20121108	WO2012150349 A3 20121227; US2014050868 A1 20140220; FR2974811 A1 20121109; EP2705096 A2 20140312; CN103429675 A 20131204	FR20110053874 20110505; US201161512184P 20110727	DE SAINT-ROMAIN PIERRE	MARKEM IMAJE	Biodegradable liquid ink composition for ink jet printing.
WO2013038068 A1	20130321		FI20110005909 20110916	ILMONEN ANU; KELA LAURA; JOKIAHO KATJA	TEKNOLOGIAN TUTKIMUSKESKUS VTT	Method of printing.
WO2013053774 A2	20130418	WO2013053774 A3 20130815; FR2981359 A1 20130419; FR2981359 B1 20131108	FR20110059312 20111014	EFSTATHIOU THEO; CLANCHIN OLIVIER	SOJASUN TECHNOLOGIES	Encre biodégradable pour impression et/ou écriture infalsifiable. "Biodegradable ink for unforgeable printing and/or writing."

Chapter 15

Adhesive Compositions

15.1 CLASSIFICATION OF ADHESIVES

An adhesive is a material that joins two other materials, called adherents, together. Adhesives are widely used for various commercial applications such as product assembly and packaging. Generally an adhesive is applied as a liquid, preferably of a low viscosity. The adhesive wets the adherent surface and may flow into the crevices in the adherent surfaces. In many cases, the liquid form of the adhesive is obtained by heating the adhesive to the point that flow occurs, dissolving or dispersing the material in a solvent, or starting with liquid monomers or oligomers that polymerize or react after application; usually, the adhesive then solidifies by cooling, solvent evaporation, reaction, or the like to provide the necessary strength to resist shearing forces (1997, **WO9704036** A1, PROCTER & GAMBLE).

Adhesives are classified by different classification systems. Therefore, adhesives can be classified by origin (i.e., natural or synthetic); by the type of polymers (i.e., thermoplastic, thermosetting, or elastomeric); by the method of adhesion; by their starting physical state; or by their reactivity. The biodegradable adhesives of the present study follow the last system and are organized into reactive and nonreactive adhesives according to the following scheme. It is noted that an adhesive can fall under more than one category; e.g., a pressure-sensitive adhesive can be also a hot melt adhesive, or a reactive adhesive can also be a water-based adhesive.

Classification scheme of adhesives

- Nonreactive adhesives
  - Drying adhesives
    - Water-based adhesives
    - Solvent-based adhesives
  - Pressure-sensitive adhesives
  - Hot melt adhesives
- Reactive adhesives
  - One-component reactive adhesives
  - Multi-component reactive adhesives

The method of using these adhesives and the choice of adhesive will depend upon the material to which the adhesive is applied and the application intended.

Most of the commercial adhesives consumed annually are derived from fossil fuel resources [1,2]. One disadvantage of conventional adhesives is their lack of biodegradability. Although the amount of adhesive required to bond two substrates is relatively small, the requirement of complete biodegradability also makes it necessary for adhesives to be completely biodegraded. Conventional HMAs used in packaging materials can contaminate the recycling process. Adhesive residues can also create pinholes, cause printability problems, or degrade the appearance of recycled paper [3].

15.2 NONREACTIVE ADHESIVES

15.2.1 Drying Adhesives

The adhesives of this category are applied either as aqueous dispersions or in the form of solutions. When using an aqueous dispersion or solution, heating is preferred to expedite drying or "setting" of the adhesive.

15.2.1.1 Water-Based Adhesives

Water-based dispersion adhesives refer to adhesives that are prepared or dispersed as larger polymer particles in an aqueous medium. In addition to their economic advantage, aqueous dispersions containing 40–50% solids have lower viscosity than solutions, even if the solids are high molecular-weight polymers.

WO9710292 A1 (1997, JAPAN CORN STARCH CO LTD) discloses in one of its embodiments the use of an aqueous dispersion of starch derivative as adhesive.

WO9704036 A1 (1997, PROCTER & GAMBLE) discloses in one of its embodiments an aqueous dispersion of polyhydroxyalkanoate (PHA) such as poly(3-hydroxybutyrate-*co*-octanoate) (PHBO) to be used as an adhesive in nonwovens. PHA is initially dissolved in an organic solvent (e.g., chloroform, 1,2-dichloroethane and the like), and emulsified in water with the aid of sonicator. An emulsifier, e.g., oleylethoxylate (Volpo™-20, Croda, Inc.), can be used in the mixture to stabilize the emulsion. The organic solvent is subsequently evaporated from the emulsion to obtain an aqueous dispersion of the copolymer binder.

WO9502649 A1 (1995, ZENECA LTD) discloses a method of bonding two or more articles together using an adhesive composition comprising at least one PHA, wherein the PHA is applied to one or more of the articles as a latex of particles of PHA in water, placed between the articles to be bonded, and the articles are subjected to pressure to set the adhesive, optionally at elevated

Biopolymers: Processing and Products. http://dx.doi.org/10.1016/B978-0-323-26698-7.00015-5

temperatures. The adhesive is believed to set by crystallization. The PHA is poly(3-hydroxybutyrate) (P3HB) or poly(3-hydroxybutyrate-*co*-valerate) (PHBHV) and has a relatively high level of crystallinity, for example more than 30%, especially 50–90%, in the absence of plasticizer.

WO02088271 A1 (2002, ECOSYNTHETIX INC) discloses a biodegradable adhesive comprising a latex of cross-linked starch micro- and/or nanoparticles and a biocide. The biocide is a nontoxic biocide selected from potassium sorbate, benzoic acid, and/or sodium bisulfate. The starch used to generate the crosslinked particles have a high amylopectin content (>95% amylopectin, <5% amylose). The starch micro- and nanoparticles have a diameter of 400 nm–100 μm and less than 400 nm, respectively. The adhesive is totally biodegradable, and has a shelf-life stability in excess of 6 months. The strength of an adhesive layer exceeds that of an adhesive layer formed from a typical poly(vinyl acetate) glue, a synthetic adhesive derived from fossil fuel–derived resources. The adhesive resists the growth of fungi, molds and yeast for at least 6 months. The adhesive is used as biodegradable alternative to poly(vinyl acetate) latex adhesive for school label, packaging and glue applications.

CN102627935 A (2012, CHANGSHA LEYUAN CHEMICAL TECHNOLOGY CO LTD) discloses an aqueous emulsion poly(lactic acid) (PLA) adhesive for forming cigarette filter comprising, per 100 pbw of adhesive, 5–45 parts of polyethylene glycol–grafted PLA copolymer, 5–40 parts of vinyl acetate grafted starch, and 0.5–30 parts of ethylene-vinyl acetate copolymer; the polyethylene glycol chain segment in the polyethylene glycol grafted PLA copolymer is 0.5–30% of the total weight of the polymer; and the grafting rate of the vinyl acetate in the vinyl acetate grafted starch is 0.5–5%. The aqueous emulsion–type PLA adhesive is claimed to have high bonding fastness, adjustable filter rod hardness as well as good molding performance, and enhances the filter rod absorbing and harm-reducing property.

WO2010142507 A2 (2010, KITOZYME S A) discloses an adhesive composition comprising: (1) a chitin and/or chitosan containing material (>10 wt%), wherein said chitin and/or chitosan containing material are not photochemically crosslinked; (2) a polar solvent (>10 wt%), preferably water; and (3) an adhesive-enhancing agent (<60 wt%), wherein said adhesive-enhancing agent comprises granules of chitin or of chitin-glucan having an average granule size lower than 1000 μm, preferably between 10 and 250 μm. The chitin and/or chitosan containing material comprises a compound selected from the group comprising chitin, chitin-glucan, chitosan, chitosan-glucan, derivatives thereof, and any combinations thereof; said chitosan derivatives or said chitosan-glucan derivatives are chitosan polymers or chitosan-glucan copolymers that are covalently coupled to PLA or an amino-alkyl such as amino-ethyl. The adhesive composition can be used as gluing composition, in particular in wound-healing and/or surgical applications.

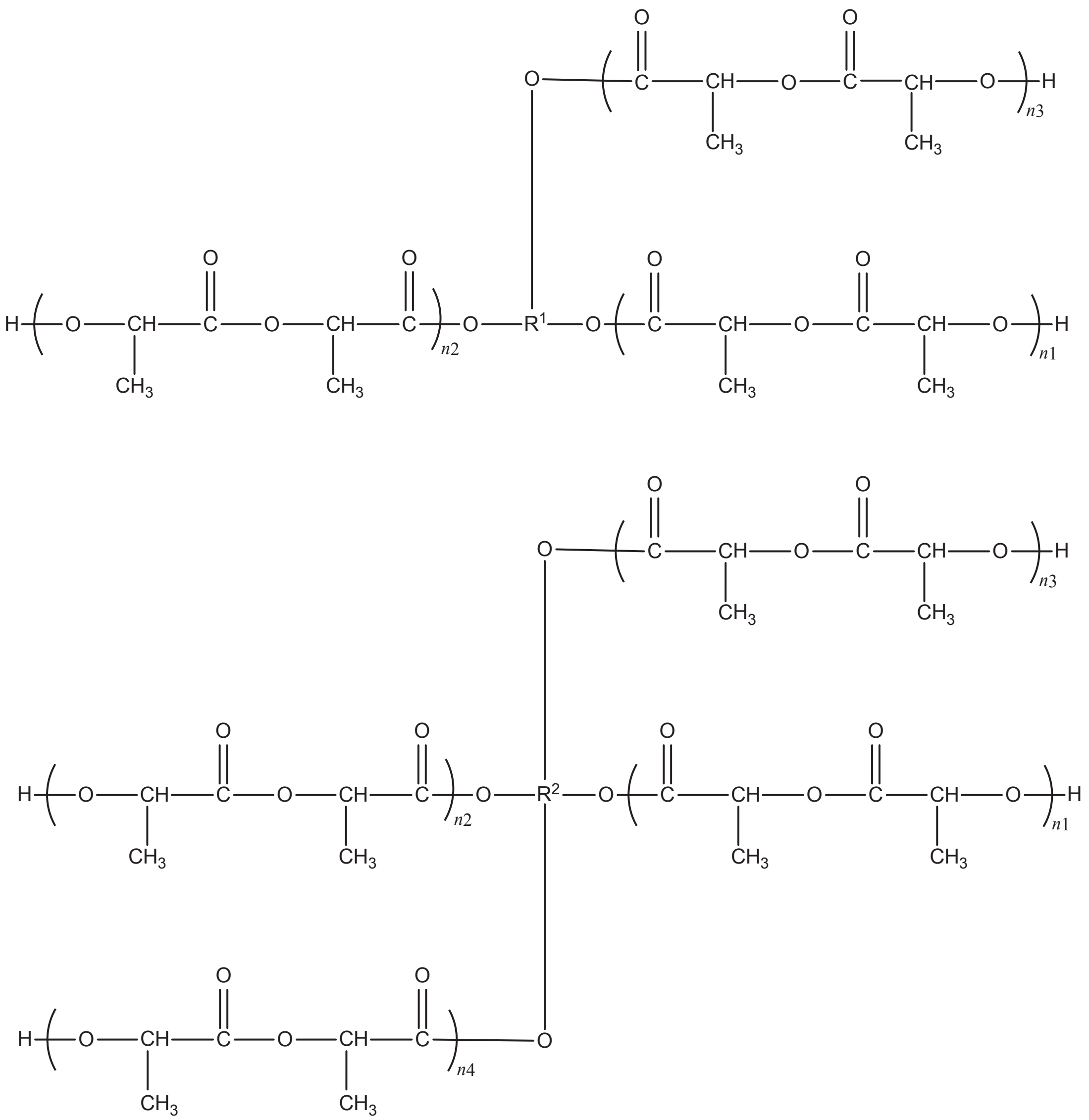
15.2.1.2 Solvent-Based Adhesives

Solvent-based adhesives refer to adhesives containing polymers dissolved in solvents.

DE19615151 A1 (1997, BIOTEC BIOLOG NATURVERPACK; BAYER AG) discloses a compostable adhesive comprising a solution of 1–70 wt%, preferably 8–50 wt%, with respect to the polymer constituent, of biodegradable polymers selected from the group consisting of thermoplastic aliphatic or partially aromatic polyester urethanes, aliphatic or aliphatic-aromatic polyester carbonates, and aliphatic or partially aromatic polyester amides. Preferably, the biodegradable polymer comprises 0.1–5 wt% branching agents selected from the group consisting of trifunctional alcohols, tetrafunctional alcohols, and trifunctional carboxylic acids. The solvent is selected from the group consisting of acetone, ethyl acetate, isopropanol, methanol, dichloromethane, chloroform, tetrahydrofuran, ethanol, toluene, and mixtures containing at least one of these solvents. The disclosed adhesive is used for the adhesive bonding of compostable materials such as paper or cardboard, while retaining the compostability of the composite material as a whole.

JP2011252102 A (2011, KONISHI CO LTD; OSAKA MUNICIPAL TECHNICAL RES INST) discloses a solvent-based adhesive containing a three- or four-branched PLA as represented by chemical formulae 1 and 2 of Scheme 15.1, and having a number average molecular weight of $M_n \geq 40{,}000$. It is preferable that the ratio of the weight average molecular weight (M_w) to the number average molecular weight (M_n), M_w/M_n, is within the range of 1.07–1.16. The method for producing the adhesive is characterized by obtaining a PLA by polymerizing a lactide in the presence of a polymerization catalyst and a tetrahydric or trihydric alcohol, and then dispersing or dissolving the PLA into an organic solvent such as acetone or dichloromethane. The polymerization catalyst is preferably 4-dimethylaminopyridine and 4-dimethylaminopyridinium triflate. The tetrahydric alcohol is pentaerythritol, and the trihydric alcohol is trimethylolpropane. The PLA adhesive is used for adhering PLA films and molded products. The branched PLA macromolecules are prone to entangle with each other and thus endow the adhesive with a high adhesive strength.

WO2004076583 A1 (2002, METABOLIX INC) discloses a solvent-based adhesive comprising a PHA (e.g., P3HB or PHBHV) or a blend of PHAs (e.g., P3HB and poly(hydroxy octanoate) (PHO)). The solvent comprises an organic solvent or a mixed solvent system. The mixed solvent system comprises water and a water immiscible organic solvent. The adhesive composition can comprise various additives such as tackifier, crosslinking agent, initiator, colorant, wax, stabilizer, or plasticizer.



SCHEME 15.1 Three- and four-branched poly(lactic acid) (PLA) represented by formulae 1 and 2, respectively (2011, **JP2011252102** A, KONISHI CO LTD; OSAKA MUNICIPAL TECHNICAL RES INST). R^1, Trimethylolpropane residue; R^2, Pentaerythritol residue.

15.2.2 Pressure-Sensitive Adhesives

Pressure-sensitive adhesives (PSAs) are a distinct category of adhesive, which, in dry (solvent free) form, are aggressive and permanently tacky at room temperature and adhere to a variety of surfaces without the need of more than pressure. They do not require activation by water, solvent, or heat. PSAs have been designed for either permanent or removable applications. Commercially available PSAs often include polymers such as natural rubber, polyacrylonitrile, polyacrylic, polyisobutylene, silicone, and polystyrene. Typically, these PSAs are derived from fossil fuel resources, have favorable adhesive properties, are low in cost and are easily processed. However, many of the conventional PSAs are not biodegradable. Such PSAs are thus limited in their use in biomedical applications and other applications for which a biocompatible or biodegradable PSA would be useful.

JPH08157798 A (1996) and **JPH11158452** A (1999) of NITTO DENKO CORP disclose a PSA prepared by mixing 100 pbw of a biodegradable polyester, whose main chain has a poly(ε-caprolactone) (PCL) structure and a $M_w \geq 10{,}000$, with 0.5–6 wt% (based on the polyester) of a polyfunctional compound (e.g., an aliphatic polyisocyanate compound) having functional groups reactive with the hydroxyl or carboxyl groups of the polyester as a crosslinking agent to cross-link and chain-extend the polyester to a suitable degree to bring the insoluble content to 10 wt% or higher. Thus, the heat resistance of the composition is enhanced. The biodegradable polyester is synthesized from poly(ε-caprolactone diol) or its derivative having a $M_n \geq 400$ as the essential component, a diol component containing 20 wt% or lower other diol, and an aliphatic dicarboxylic acid component (e.g., succinic acid). The PSA composition is claimed to be excellent tackiness and heat resistance.

JP2004231797 A (2004, TOYO BOSEKI) discloses a biodegradable PSA containing as essential components: (1) an aliphatic polyester containing at least 55 wt% of PLA having a molar ratio (L/D) of L-lactic acid to D-lactic acid of 0.11–9, and a reduced viscosity in the range of 0.2–1.0 dl/g; (2) a natural product-based tackifying resin; and (3) a polyfunctional isocyanate. An adhesive varnish is prepared by dissolving the previously mentioned composition in a nonhalogenated solvent. However, the adhesive strength of the disclosed PSA is not sufficiently prevented from increasing, so that it has the problem of staining of the adherend. In general, even if a large amount of a crosslinking agent is added, the gel fraction of conventional PSAs produced from natural resources does not sufficiently increase—namely the adhesive strength does not decrease, so that surface-protecting PSA sheets produced therewith cannot be peeled off after use, and an adhesive deposit is formed on the adherend to cause a problem such as staining of the adherend (2011, **WO2011049111**, NITTO DENKO CORP).

JP2006070091 A (2006, DAINIPPON PRINTING CO LTD) discloses a biodegradable PSA comprising PLA, a glass transition temperature (T_g)–reducing agent composed of a raw material having biodegradability and a tackifier.

JP2006131705 A (2006, DAINIPPON INK & CHEMICALS) discloses a biodegradable PSA comprising: (1) an aliphatic polyester prepared by reacting lactic acid as a main material and (2) a rosin or a rosin derivative, wherein the lactic acid is composed of L-lactic acid and D-lactic acid in a molar ratio (L/D) of 1–9, the M_n of the aliphatic polyester resin (A) is 10,000–120,000 and the T_g is from −5 to −60 °C.

According to **WO2010016514** A1 (2010, NITTO DENKO CORP; TOYO BOSEKI), it is difficult for the PSAs which use a PLA-based polymer, as disclosed in the past three patent applications, to obtain sufficient pressure-sensitive adhesion properties.

WO2010016514 A1 (2010, NITTO DENKO CORP; TOYO BOSEKI) discloses a PSA composition comprising a polyester and a crosslinking agent. The polyester comprises 10–50 mol% of a lactic acid unit, 50–90 mol% of a dibasic acid unit, and a glycol unit; the molar ratio of the dibasic acid unit to the glycol unit is 1/0.8–1/1.2 wherein the dibasic acid unit includes a dimer acid, the polyester has T_g of −70 to −20 °C, a M_w of 20,000–300,000 and a hydroxyl value of 1–100 mg KOH/g. The crosslinking agent is a polyvalent isocyanurate. A PSA layer and a PSA sheet can be obtained from the same composition. The PSA sheet includes a pressure-sensitive film and a PSA tape.

JP2007070422 A (2007, SHOWA HIGH POLYMER CO LTD) discloses a biodegradable PSA based on a polyester polyurethane having a $M_w > 400{,}000$, a $T_m \leq -10$ °C and a $T_g \leq -30$ °C. The polyester polyurethane is obtained by an addition reaction of a polyisocyanate (e.g., hexamethylene diisocyanate) for molecular chain extension to an aliphatic polyester obtained by condensation of a dicarboxylic acid, a glycol (e.g., 3-methyl-1,5-pentane diol) and 0.01–10 mol%, based on the dicarboxylic acid, of a triol (trimethylol propane). This PSA has the disadvantage that is meltable at high temperatures, which is detrimental to the bondability of the adhesive (2013, **DE102012202822** A1, TESA SE).

WO0234857 A2 (2002, METABOLIX INC) discloses in one of its embodiments an adhesive comprising a PHA and optionally a tackifying agent and a wax. Preferably, up to about 60 wt% of the HMA can be the tackifying resin and up to about 40 wt% of the composition can be the wax component. In addition, a reactive monomer or oligomer can be included in the HMA composition. A method is provided for making the PHA by combining a PHA as a latex with a resin emulsion or a wax emulsion and spray drying the blend without the need for a hot melt compounding process.

15.2.2.1 Pressure-Sensitive Adhesive Sheets (Tapes)

PSA sheets, tapes, labels, and the like, each of which comprises a substrate in the form of a film, tape, a film or a label, etc., and an adhesive layer formed on the substrate, are conventionally known. Examples of adhesive tapes include a single-sided adhesive tape comprising a release agent layer formed on one surface of an adhesive tape substrate and an adhesive layer formed on the other surface of the substrate; and a double-sided adhesive tape comprising a double-sided adhesive tape main body that has an adhesive tape substrate bearing adhesive layers on both surfaces thereof and a double-sided release tape having a release tape substrate bearing release agent layers on both surfaces thereof, which adheres to one of the surfaces of the adhesive tape main body.

PSA tapes are stored or are on the market as rolls formed by winding those tapes around a paper core or a plastic core. In the case of the single-sided adhesive tape, the adhesive tape itself is rolled up via its release agent layer so that the adhesive layers are not directly brought into contact with each other. In the case of the double-sided tape, the double-sided adhesive tape main body is rolled up via the release tape so that the adhesive layers are not directly brought into contact with each other.

PSA tapes have been used also for masking, in which PSA tapes are bonded to adherends and then peeled off when coating operation is completed. Generally known masking tapes are composed of a backing and a PSA layer formed on one side of the backing. Such masking PSA tapes should exhibit adherability when attached in layers and should exhibit adherability to the pressure-sensitive adhesive layer of the tapes (adherability to their own backside). Therefore a release-treated layer is provided in a PSA tape so that adherability can be provided between its own backside and the pressure-sensitive adhesive layer. In general, a masking PSA tape is wound into a roll for storage, and in this form, the PSA adhesive layer is placed on the backside of the tape so that the pressure-sensitive adhesive layer is temporarily protected by the backside of the tape. When used, the PSA tape is unwound. In this process, unwinding should be performed smoothly. Even when the masking PSA tape has reliable adherability to its own backside, an excessively large force can be applied to the tape being unwound so that a problem such as breakage, curling, or kinking of the tape may occur in the process of unwinding the tape, because the pressure-sensitive adhesive layer of the tape is bonded to its own backside. Such a large tape-unwinding force can also cause the problem of low workability. In addition, the masking PSA tapes are not used in final products and generally peeled off and incinerated after they are used during processing, transportation and so on. Therefore, because there has been a concern about the depletion of fossil resources or the increase in carbon dioxide from combustion of fossil resources, which is a cause of global warming, they are required to be produced using plant-derived alternative materials, which are so-called carbon neutral, so that measures can be taken against that (2011, **WO2011049115** A1, NITTO DENKO CORP).

JPH09125016 A (1997, SUNSTAR INC) discloses a biodegradable PSA tape comprising: (1) a tape substrate consisting essentially of a biodegradable polyester such as PLA or poly(glycolic acid) and (2) a tacky adhesive such as an acrylic emulsion, a solvent-based acrylic or a rubber-based tacky agent. The adhesive force of the tacky adhesive (2) to the tape substrate (1) is ≥500 fg/in. (193 N/m) in one surface of the component (a) and ≤500 fg/in. (193 N/m) in the other surface thereof. The tear strength is 100–1000 g. The adhesive tape is easily dissolved in an alkali solution, thus not interfering with the recycling treatment of paper.

JPH10237401 A (1998, SHINETSU POLYMER CO) discloses a biodegradable PSA tape by applying a biodegradable PSA onto the surface of a biodegradable base film prepared from a composition comprising 100 pbw of an aliphatic polyester and 10–150 pbw of a surface-treated filler. The aliphatic polyester is selected from poly(alkylene dicarboxylate)—a polycondensate from a polycarboxylic acid and a polyhydric alcohol—a ring-opening polymerization product of a cyclic ester and a polycondensate of a hydroxy acid. The biodegradable PSA is prepared by compounding isobutylene rubber and natural rosin or the like. As a filler, use is made of an inorganic filler such as calcium carbonate, a ceramics balloon, or the like, which has been surface-treated with an epoxy silane or a titanate coupling agent, and an organic filler such as starch or the like, which has been surface-treated with a surfactant such as acetylene glycol. The biodegradable PSA tape finds use in agricultural applications.

EP1816174 A2 (2007, LOGO TAPE GES FUER SELBSTKLEBE) discloses a biodegradable PSA tape (A), comprising: (a) a film material comprising a blend of PLA and at an aromatic–aliphatic copolyester (blend ratio: 2/3 PLA to 1/3 copolyester), a plasticizer, and at least one inorganic filler (−20 wt%) for control of its deep-drawing properties. A preferred aliphatic-aromatic copolyester is poly(butylene adipate-*co*-terephthalate), and especially the commercial product Ecoflex® (BASF). The filler is preferably a mixture of talc and chalk, each at 6–10 wt%. The biodegradable adhesive tape is useful as labels for packaging.

JP2007308626 A (2007, NITTO DENKO CORP) discloses a low moisture permeability PSA sheet comprising an adhesive layer including a polyester polymer having an alkyl group in a molecular side chain obtained by condensation reaction between a dicarboxylic acid (e.g., a dimer acid) and a diol (e.g., a dimer diol), both derived from renewable resources, and having a water vapor permeability of 200 g/m^2 or lower. The diol is 9–11 mol eq to 10 mol eq of the dicarboxylic acid. The PSA sheet is suitable for sealing electronic components and dried food.

WO2011049111 A1 and **WO2011049115** A1 (2011) of NITTO DENKO CORP discloses a PSA sheet for surface protection (masking) comprising a substrate and, formed on at least one surface (backing) thereof, a PSA layer formed from a polyester-based PSA composition comprising a biodegradable polyester and a crosslinking agent as described in **WO2010016514** A1 (2010, NITTO DENKO CORP; TOYO BOSEKI). The polyester comprises 10–50 mol% of a lactic acid unit, 50–90 mol% of a dibasic acid unit, and a glycol unit, and the molar ratio of the dibasic acid unit to the glycol unit is 1/0.8–1/1.2, wherein the dibasic acid unit includes a dimer acid. The polyester has a T_g of −70 to −20 °C and a M_w of 20,000–200,000. The polyester-based PSA composition of each patent has a hydroxyl value of 20–60 and <5 mg-KOH/g, and a gel content of 85–99 and 40–90 wt%, respectively. The substrate is preferably biodegradable. The method of forming the PSA layer is based on known PSA sheet-manufacturing methods, examples of which include: a method of applying a PSA composition (a solution of a PSA composition in a solvent or a hot melt of a PSA composition) to the substrate (backing) and drying the coating to form a PSA layer; a method of transferring a formed PSA layer; a method of extruding and applying a PSA layer-forming material onto the substrate (backing); a method of extruding the substrate (backing) and a PSA layer in two or more layers; and a method of laminating the substrate (backing) with a single PSA layer. A coextruding method may also be used, in which a thermoplastic polymer substrate (backing) and a PSA layer are extruded in two or more layers by inflation molding or T-die molding. The PSA sheet may also include a PSA film, a PSA tape, or the like.

WO2011049116 A1 (2011, NITTO DENKO CORP) discloses a thermally removable PSA sheet comprising a substrate and a PSA layer that is provided on the backing and contains an expanding or foaming agent such as thermally expandable microspheres. The PSA layer is formed from a polyester-based PSA composition comprising a polyester and a crosslinking agent as described in **WO2010016514** A1 (2010, NITTO DENKO CORP; TOYO BOSEKI) or **WO2011049111** A1 (2011, NITTO DENKO CORP). The thermally removable pressure-sensitive adhesive sheet combines tackiness with peelability after use. Specifically, they are so designed that after they achieve the object of adhering to an adherend, their pressure-sensitive adhesive layer, which contains an expanding or foaming agent such as thermally expandable microspheres, expands or foams when heated, so that the surface of the pressure-sensitive adhesive layer is deformed to have asperities, which reduces the area of adhesion to the adherend and thus reduces the adhesive strength, so that the adherend can be easily separated. Therefore, they are used for a variety of purposes, such as fixation (e.g., temporary fixation) of electronic components or materials during processing thereof and fixation (e.g., temporary fixation) of products during distribution such as transportation or conveyance. In contrast to conventional thermally removable pressure-sensitive adhesive sheets, which are mostly incinerated after they are used, during processing, transportation and so on, the disclosed thermally removable pressure-sensitive adhesive sheet is biodegradable.

A series of patents: **JP2012111203** A (2012), **JP2012111204** A (2012), **JP2012111205** A (2012), **JP2012111206** A (2012), **JP2012111207** A (2012), **JP2012111208** A (2012), **JP2012111217** A (2012), **JP2012111914** A (2012), **JP2012111915** A (2012), **JP2012111916** (2012), **JP2012111918** A (2012), **JP2012111919** (2012), **JP2012116888** A (2012), **WO2012070526** A1 (2012) and **CN103228713** A (2013) of NITTO DENKO CORP disclose biodegradable PSA tapes having a PLA-based substrate film. Suitable commercial products of PLA are: Lacea® H-400 and Lacea® H-100, each from Mitsui Chemicals Inc.; and Terramac® TP-4000 and Terramac® TE-4000, each from Unitika Ltd. In an embodiment, the PLA-based film may further include a fluoropolymer. The tetrafluoroethylene polymer is preferably a homo- or copolymer of tetrafluoroethylene. The fluoropolymer increases the melt tension of PLA, enables orientation-induced crystallization typically in a flow field of a melt film formation, and thereby promotes the crystallization of PLA. The PLA prevents the substrate film from being melted or deformed even at high temperature exceeding 100 °C, and furthermore, during production or processing of the adhesive film, there is no breakage or tearing when the film is rolled into a roll.

DE102012202822 A1 (2013, TESA SE) discloses a PSA useful in a single- or double-sided adhesive tape comprising an amorphous PLA, which is present in an amount of at least 40 wt%. For improving the cohesion of the adhesive the PSA can be crosslinked, either by irradiation (e.g., electron beams, ultraviolet (UV) radiation), or by using a crosslinker (e.g., an isocyanate compound, hydrazide, nitrene).

Example: Amorphous PLA (BE-910, Toyobo) (30 g) and tetrahydrofuran (70 g) were weighed into a screw-cap bottle. The glass was covered with a lid and then placed on a roller bench and homogenized for 24 h, such that a clear solution had formed. The solution thus obtained was subsequently coated with a laboratory coating unit with coating bar onto 35 μm thick corona pretreatment PLA film with a coat weight of 50 g/m^2. The material thus obtained was dried at room temperature for 10 min. Then drying was carried out for 10 min in an oven at 60 °C.

15.2.3 Hot Melt Adhesives

Hot Melt Adhesives (HMAs) are typically applied to a substrate while in its molten state and cooled to harden the adhesive layer. The major advantage of HMAs is the lack of a carrier fluid that eliminates the need for drying the adhesive film once it is applied to the substrate. This elimination of the drying step overcomes hazards associated with solvent usage and also allows for faster production line speeds and lower transportation costs. Depending on the desired use, the degree of tack of HMAs may be varied over a wide range to produce HMAs varying from pressure-sensitive to non–pressure-sensitive in character. Non–pressure-sensitive HMAs are used, for example, in bookbinding, bag ending, and case and carton sealing. Pressure-sensitive HMAs—the so-called hot melt pressure-sensitive adhesive—are used in particular in disposables such as diapers, sanitary products, and the like, where room temperature tack and long open time are often required.

Conventional HMAs are based on fossil fuel–derived polymers such as polyethylene, ethylene-vinyl acetate, styrenic block copolymers, and polypropylene. These compositions are further tackified, plasticized, and reinforced with a variety of resins, oils, and waxes that are derived from both fossil fuel and naturally occurring feedstocks such as wood, gum, and tall oil rosin and terpenes. These conventional compositions are generally very resistant to degradation once the articles employing them are disposed of.

It has been suggested to use various biodegradable polymers such as PLA and PHBHV in HMAs. However, these biodegradable adhesives have inferior mechanical and thermal stability when compared with other conventional HMAs [3]. One effort to manufacture partially biodegradable adhesives is disclosed in **US5169889** A (1992, NAT STARCH CHEM INVEST), which describes an HMA composition prepared from 20–98 wt% of PHBHV (e.g., BIOPOL®); 2–80 wt% of a polar tackifier having a Ring and Ball softening point

>60 °C (ASTM E–26); 0–50 wt% of a plasticizer; 0–30 wt% of a wax diluent; 0–3 wt% of a stabilizer; and 0–20 wt% of a compatible polymer. The same applies *mutatis mutandis* to the HMA compositions disclosed in **US5252646** A (1993), **WO9410257** A1 (1994), and **US5312850** A (1994) of NAT STARCH CHEM INVEST by replacing PHBHV with PLA or a copolymer of lactide (>20 mol%) with glycolide or ε-caprolactone. The HMAs disclosed in the previously mentioned patent applications of NAT STARCH CHEM INVEST are not fully biodegradable because the tackifiers and plasticizers used in the polymer blend are not biodegradable (1995, **WO9510577** A1, FULLER H B LICENSING FINANC).

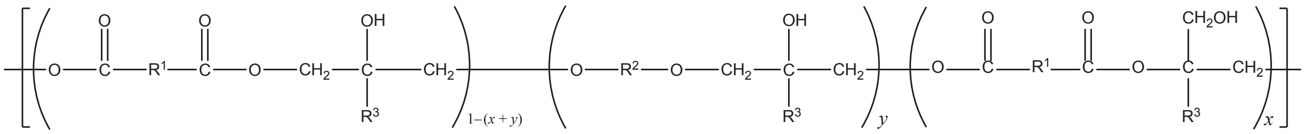
EP0741177 A2 (1996, NAT STARCH CHEM INVEST) discloses an HMA composition comprising: (1) 10–90 wt% of a biodegradable thermoplastic polymer selected from the group consisting of PLA, PHBHV, hydroxypropyl cellulose, cellulose, or starch esters having a degree of substitution less than 2.5; (2) 5–80 wt% of sucrose benzoate as a tackifier; (3) 0–80 wt% of a plasticizing diluent selected from the group consisting of phthalate plasticizers, benzoate plasticizers, phosphate plasticizers, poly(ethylene glycols) and derivatives thereof, liquid rosin derivatives having Ring and Ball melting temperatures below about 60 °C, and vegetable and animal oils and the polymerization products thereof; (4) 0–50 wt% of a wax selected from the group consisting of *N*-(2-hydroxy-ethyl)-12-hydroxy stearamide, hydrogenated castor oil, oxidized synthetic waxes, polyethylene oxide having a $M_w > 1000$ and functionalized synthetic waxes; and (5) 0–3 wt% of an antioxidant.

EP0741178 A2 (1996, NAT STARCH CHEM INVEST) discloses a biodegradable HMA composition comprising: (1) 10–90 wt% of a thermoplastic methylol polyester, which is the reaction product of at least one dicarboxylic acid with a diglycidyl ether, a diglycidyl ester, or a combination thereof—see Scheme 15.2; (2) 0–90% by weight of a compatible tackifier (preferably a sucrose benzoate); (3) 0–80 wt% of a compatible plasticizer (preferably a diethylene glycol benzoate); and (4) 0–50 wt% of a compatible wax diluent (preferably hydrogenated castor oil, *N*,*N′*-ethylenebisstearamide or *N*-(2-hydroxyethyl)-12-hydroxy stearamide) and 0–3 wt% of a stabilizer. The use of certain hydroxy functional polyesters as the base polymers in HMAs provides adhesives with improved thermal stability. Because of the polarity of the base polymers, they are also highly compatible with other biodegradable ingredients and may be formulated with various additives to provide a range of pressure sensitive to non–pressure-sensitive HMAs for environmentally sensitive applications.

The adhesives are useful as pressure sensitive or non–pressure-sensitive adhesives in packaging and carton sealing, bookbinding, laminating tissue layers in wipers, paper towels, toilet tissue. and so on, assembly or construction of disposable sanitary pads, diapers, hospital gowns, bed pads, etc., especially where flexible film substrate(s) are bonded to tissue, nonwoven, polyolefin, or other flexible polymeric film substrate(s) or bonding elastic to polyethylene, polypropylene, or nonwoven substrate to impart elongation resistant gathers thereto, and for end or perimeter sealing. No indication is given with respect to the biodegradability of the final composition; e.g., according to standard EN ISO 14,855 (2009, **FR2927629** A1, BOSTIK SA).

WO9510577 A1 (1995, FULLER H B LICENSING FINANC) discloses a biodegradable HMA composition by combining PLA with a tackifying resin based on PLA having a low molecular weight (<20,000). The adhesive material can be made pressure sensitive pressure sensitive adhesive (hot melt pressure-sensitive adhesive) and can be made entirely biodegradable by combining the polyester polymer with other biodegradable/compostable ingredients. The biodegradable HMA can be used, for example, in packaging as a substitute for nonbiodegradable materials made from commercial polymers that resist attack by bacteria, fungi, and other microbial populations. Although the HMA composition is claimed to be fully biodegradable, no indication is given with respect to the biodegradability of the final composition; e.g., according to standard EN ISO 14855 (2009, **FR2927629** A1, BOSTIK SA). Furthermore, HMA compositions containing PLA are not suitable for food packaging because they have the drawbacks of being rather stiff and having a heat-reactivation temperature that is too high for the intended applications.

EP1236753 A1 (2002, HYCAIL B) addressed the problem of the brittleness of PLA by coupling flexible aliphatic polyesters to PLA, whereby the polyester groups act as a flexibilizing coupler or linker. The produced block copolymer comprises 50–99 wt% PLA having a M_w of 500–50,000 g/mol, to which chains a flexibilizing aliphatic polyester (e.g., PCL) having a M_w of 200–50,000 g/mol is coupled, wherein the amount of aliphatic polyester in the copolymer is 1–50 wt%. The block copolymer may, for example, be in the shape of a star having a core of flexible polyester moiety at



SCHEME 15.2 Thermoplastic methylol polyester (1996, **EP0741178** A2, NAT STARCH CHEM INVEST). R^1, R^2 are a divalent organic moiety which is predominantly hydrocarbon, R^3 is hydrogen or lower alkyl, y is a fraction from 0 to 0.5, and x is a fraction from about 0.05 to about 0.4.

the core, whereas the arms are formed by the PLA oligomers. Alternatively, the compound may be in the form of a partial network containing flexible polyester stars connected by PLA chains. The block copolymer is used as an HMA that is biodegradable and more flexible than the prior art. Also, the produced block copolymer provides for an improvement in at least some of the other properties of biodegradable HMAs including: open time (defined as the time in which the hot melt still retains its adhesive character; after this time, no substantial adhesion occurs), T_g (which should be decreased), and UV curability, when applicable.

WO2005056680 A1 (2005, BIOMET DEUTSCHLAND GMBH) discloses a biodegradable or resorbable HMA based on ε-caprolactone copolymers or polymer blends of ε-caprolactone copolymers and PCL and having a T_m of 57–100 °C. The HMA is used for temporary bonding of biological tissue with special materials in medical applications.

Example: A polymer blend of $T_m = 69.2\,°C$ consisted of PCL of $M_w = 65{,}000$ (35 wt%), poly(D-lactide-*co*-ε-caprolactone) of $M_w > 100{,}000$ (65 wt%), and carboxymethylstarch (10 wt%).

FR2927629 A1 (2009, **FR2927629** A1, BOSTIK SA) discloses a biodegradable HMA comprising: (A) 45–55 wt% of a (co)polymer selected from (a1) PCL, (a2) polyesters resulting from condensation of dicarboxylic acid and diol, and (a3) copolymers of (a1) and (a2); (B) 25–35 wt% of an adhesive agent selected from natural or modified rosin, terpene resins, or natural terpene based copolymers; (C) 10–25 wt% of a stiffening agent selected from wax, preferably optionally hydroxylated amide waxes, hydrogenated castor oil, optionally oxidized and functionalized synthetic waxes, polyethylene oxide; and (D) 3–7 wt% of one or more additives.

WO9704036 A1 (1997, PROCTER & GAMBLE) discloses in one of its embodiments an HMA of PHA such as PHBO to be used as an adhesive in nonwovens.

Example: PHBO (50:50) may be used as an HMA in the following manner. About 1 g of PHBO (50:50) is placed between two polymer films, such as poly(vinyl alcohol) (PVOH), P3HB, or any other PHA that has a melting temperature at least 10 °C higher than PHBO (50/50). The films/adhesive assembly is placed in a Carver Press (Fred S. Carver Inc.) and is then pressed at a temperature 5 °C above the T_m of PHBO. After compression at 2000 lb (907 kg) force for 30 min, the pressure is released and the bonded film assembly is allowed to cool to room temperature.

WO2012030819 A1 (2012, SURMODICS PHARMACEUTICALS INC) discloses a PSA comprising a poly(D,L-lactide-*co*-glycolide-*co*-ε-caprolactone) terpolymer having a $M_w \leq 140{,}000$ Da and a polydispersity index of less than 2.0. The PSA can be part of an article comprising a release liner adhered to a surface of the terpolymer PSA. The terpolymer can also be applied to an implant device.

US4833036 A (1989, ARCO CHEM TECH) discloses a poly(alkylene carbonate)-based HMA. The poly(alkylene carbonate) (also called aliphatic polycarbonate) is produced by copolymerization of carbon dioxide (CO_2) with one or more epoxides. A poly(alkylene carbonate) can contain up to 50 wt% CO_2 or CO and sequester the harmful greenhouse gas permanently from the environment (see Chapter 1: Introduction; Section 1.6: Aliphatic Polycarbonates). An aliphatic polycarbonate possesses also unique properties in various adhesive applications because of the presence of polar groups in the backbone. The polar/nonpolar balance can be easily adjusted to the desired level for any specific applications by using different epoxides in different ratios. The adhesive is claimed to have good adhesion to surfaces to which adhesion is difficult. An adhesive bond is formed by placing the above HMA formulation between two sheets of mild steel (preferably covered with a fluoropolymer or poly(ethylene terephthalate)) and pressing them hot.

15.3 REACTIVE ADHESIVES

Reactive adhesives (also called chemically hardening or curable adhesives) require a chemical reaction for bonding two surfaces. These adhesives are classified into one- and two-component reactive adhesives (e.g., heat or light-cured) and have been used in applications where substrates require substantial permanency and high strength adherence. For optical product applications (e.g., glazings), curable adhesives have been desirable because they can provide optically clear, strongly adhered laminates (e.g., layered substrates).

15.3.1 One-Component Reactive Adhesives

Single-component adhesives are further classified into heat cure, moisture cure, radiation cure adhesives, and anaerobic adhesives. These adhesives are primarily used in the automotive industry, optics, microelectronics, and medical industries.

Ono et al. [4] describe a chitosan containing both azide and lactose moieties (Az-CH-LA) which is then photo crosslinked by application of a UV irradiation resulting in an insoluble hydrogel. The modified chitosan (Az-CH-LA) requires illumination with UV light for generating highly reactive nitrene groups that will react with each other or with amino groups of the chitosan (or tissue proteins) resulting in covalent linkage (chemical crosslinks) between molecules or with tissue proteins providing adhesive properties. A composition containing the photochemically crosslinked insoluble hydrogel in water showed adhesive properties comparable to fibrin glues when tested in experiments consisting in testing the adhesion of two pieces of ham together (2010, **WO2010142507** A2, KITOZYME S A). In another example, **US2005112182** A1 (2005, UNIV TOTTORI) provides an *N*-alkyl chitosan derivative having an ultra-violet ray-curable functional group capable of forming a polymer upon irradiation with ultraviolet rays usable as an adhesive or a film or a covering agent.

JPH1160716 A (1999, MITSUI CHEMICALS INC) discloses a biodegradable adhesive obtained by photopolymerization crosslinking of an aliphatic polyester containing an aliphatic unsaturated polybasic acid as a polymer constituting component. The aliphatic polyester contains one or more kinds of aliphatic unsaturated polybasic acids such as fumaric acid. The adhesive is claimed to have stable quality, excellent waterproof and strong adhesive strength, and is useful as an adhesive for biodegradable film, nonwoven fabric, etc.

15.3.2 Multi-component Reactive Adhesives

Urethane adhesive, epoxies, and silicon adhesive are various types of two-component adhesives. However, none of these multireactive adhesives is biodegradable.

WO9603159 A1 (1996, MINNESOTA MINING & MFG) discloses an adhesive composition that may be used to bond or seal tissue in vivo. The adhesive composition is readily formed from a two-component mixture that includes a first part of a protein, preferably a serum albumin protein, in an aqueous buffer having a pH in the range of about 8.0–11.0 and a second part of a water-compatible or water-soluble bifunctional crosslinking agent. When the two parts of the mixture are combined, the mixture is initially a liquid that cures in vivo on the surface of tissue in less than about 1 min to give a strong, flexible, pliant substantive composition that bonds to the tissue and is absorbed in about 4–60 days. The adhesive composition may be used either to bond tissue, to seal tissue, or to prevent tissue adhesions caused by surgery.

Crosslinking agents include compounds of the formula:

$$\mathrm{G-LM-PEG-LM-G}$$

wherein,

PEG is a polyethylene glycol or polyoxyethylene chain portion;

G is an activated leaving group portion group such as a succinimidyl, maleimidyl, phthalimidyl, or alternatively, nitrophenyl, imidazolyl, or tresyl leaving groups; and

LM is a linking moiety, such as a carbonate, dicarbonate, monoester, diester, or oligomeric diradical fragment that binds the PEG-portion and the leaving group portion G.

15.4 BIO-BASED ADHESIVES

15.4.1 Proteins

Proteins have been used to make adhesives. Proteins derived from plant and animals have been used traditionally for wood bonding and for preparing wood laminates [1]. Blood proteins, soybean protein, and casein derived from milk have been used as adhesive for many applications [5]. Soy proteins have been also used as binders in the manufacture of paper composites, particleboards, and veneer bonding [6,7]. **US2010089287** A1 (2010, THAMES SHELBY F; RAWLINS JAMES W; FERGUSON RICHARD C; MENDON SHARATHKUMAR K) uses an enzymatically modified soy protein, preferably an urease enzyme for such modification. The urease modification disclosed is claimed to yield improvements in adhesive solid content and particleboard internal bond values, both of which are highly desirable attributes for such adhesive compositions. Particleboards produced using the soybean protein–based adhesive are claimed to perform as well as or better than commercial particleboards.

Proteins, such as collagen and albumin, crosslinked with aldehyde are already used and commercialized (gelatin-resorcinol-formaldehyde, GRF glue, or French glue). Concern regarding the toxicity of the crosslinking agents used in this technology has frequently been raised. Moreover, the mammalian origin of both collagen and albumin constitutes a major concern for approval onto the market due to pronounced risks of allergenic, immunogenetic, or infectious related diseases.

Natural polyphenolic adhesive proteins secreted by organisms such as mussels (*Mytilus edulis*) as well as their synthetic analogues have raised interest recently because of their ability to adhere to a variety of surfaces under water when crosslinked. The catechol functionality of L-3,4-dihydroxyphenylalanine (DOPA) residues is thought to be responsible for adhesion and crosslinking of the mussel adhesive proteins [8]. Another key ingredient in the mussel adhesive is iron [9]. Iron binds to the DOPA residues, thereby bringing together multiple protein strands [9–11]. Subsequent protein oxidation and metal reduction enables protein–protein crosslinking and possibly protein–surface adhesion [9,12]. The mussel obtains iron by filtering it directly from its surrounding water.

The possibility to harvest natural polyphenolic adhesive proteins is small as the amount of adhesive protein that can be directly gained from marine organisms, such as the mussel, is quite small and expensive to extract [13]. Efforts have also been made to create adhesives that mimic nature's adhesion mechanisms. Man-made mussel adhesives could be used for the creation of durable marine adhesives or medical adhesives in surgery wound closure, nerve reconstruction, or when one might need a scaffold upon which to grow cells and build new tissue [13]. Some of these novel adhesives may seem to work from a macroscopic point of view, but have been little studied microscopically to obtain a better understanding of the origin of the adhesiveness of these adhesive proteins [14]. Furthermore, the cost effectiveness and in some cases the use of toxic crosslinkers may compromise such approaches (2010, **WO2010142507** A2, KITOZYME S A; PRAVATA LAURENT).

15.4.2 Starch

Starch has been used since old times to make adhesives, especially for bonding paper or paper board. **US2051025** A (1936, STEIN HALL MFG CO), **US3355307** A (1937, STEIN HALL MFG CO), and **US3487033** A (1969, CORN PRODUCTS CO) are some old patents disclosing starch-based adhesives used for making corrugated paperboard. Imam et al. [15] described an adhesive composition comprising starch and PVOH, the composition further comprising a melamine resin. The pressing temperature needed was very high. A general problem encountered with prior art starch–based adhesive compositions is the viscosity increase already at moderate dry contents. Too high of a viscosity makes spreading of an adhesive composition difficult. A sufficient dry content is generally needed to obtain good adhesive properties such as adhesive strength and no spring back at compression molding.

Starch has very poor shelf-life stability. The reason for short shelf-life stability of aqueous starch dispersions is: (1) starch adhesive solutions and pastes have a strong tendency to gel or retrograde, with stabilities in the order of hours or days; and (2) starch adhesive in water provides a good growth medium for fungi and bacteria (2002, **WO02088271** A1, ECOSYNTHETIX INC). Starch has been chemically modified or blended with other material to improve its viscosity, tackiness and fluid properties. There is a modified type of starch starch-borate that is used in paper, packaging, and textile applications [1].

15.4.3 Chitin, Chitosan

Chitosan, chitin, and chitin-glucan copolymers are natural polysaccharides, readily available in massive quantities, and present unique characteristics often not found for synthetic polymers (see Chapter 1: Introduction; Section 1.11.3: Chitin, Chitosan). Adhesive compositions comprising chitosan, chitin, or derivatives thereof have been reported in the literature (see also Section 15.3.1). Chitin- and chitosan-based adhesive compositions find applications in the medical and surgical field. An important drawback of some of these adhesive is that they do not allow the compositions to be detached and/or repositioned, e.g., onto a living tissue or organ (2010, **WO2010142507** A2 2010, KITOZYME S A; PRAVATA LAURENT).

WO2010142507 A2 (2010, KITOZYME S A; PRAVATA LAURENT) discloses an adhesive composition comprising more than 10 wt% of a chitin- and/or chitosan-containing material provided in a polar solvent, preferably water, wherein said chitin and/or chitosan containing material are not photochemically crosslinked. The chitin- and/or chitosan-containing materials comprise a compound selected from chitin, chitin-glucan, chitosan, chitosan-glucan, derivatives thereof, and any combinations. The chitosan derivatives or said chitosan-glucan derivatives, respectively, are chitosan polymers or chitosan-glucan copolymers that are covalently coupled to aliphatic polyesters, and preferably to PLA.

15.4.4 Natural Resins

Natural resin-based adhesives have also been formulated from components in the forestry industry. A representative example of these adhesives is lignin, which is the binder that holds cellulose and hemicellulose together. Lignin is an amorphous polyphenolic polymer of phenylpropane units, which are crosslinked to each other by a variety of different chemical bonds (see Chapter 1: Introduction; Section 1.12: Lignin). The use of lignin eliminates the need for relatively expensive phenol resins. Special formulations have been prepared with the combinations of tannins with melamine formaldehyde, phenol formaldehyde, and isocyanates. Adhesives using sulfite waste liquor from the forest industry have also been developed as a particleboard adhesive [13].

A common natural-based adhesive is made from rosin, which is derived from the oleoresin of the pine tree. This material is used either in solvent solution or as an HMA. A rosin-based adhesive has poor resistance to water and oxidation. Bond strengths are moderate and develop rapidly; thus, this adhesive is often used for temporary fastening.

Bio-based raw materials are now finding their way into adhesives applications where recycling and environmental concerns are important. Examples include a family of reactive, sugar-based monomers called Ecomer® (EcoSynthetix Inc.). The sugar used to produce EcoMer® is derived from annually renewable resources, such as glucose or dextrose from cornstarch. Copolymerization of these monomers with acrylic monomers has resulted in waterborne sugar-based acrylic adhesives. These adhesives are being used in environmentally benign, self-adhesive postage stamps.

PATENTS

Patent Number	Publication Date	Family Members	Priority Numbers	Inventors	Applicants	Title
CN102627935 A	20120808	CN102627935 B 20130925	CN20121080011 20120323	KAIBING HUANG; WEI LI; JIAN WANG; TAO LUO	CHANGSHA LEYUAN CHEMICAL TECHNOLOGY CO LTD	"Biodegradable aqueous emulsion-type polylactic acid adhesive and its preparation method."
CN103228713 A	20130731		WO2011JP76794 20111121; JP20100264415 20101126; JP20100264416 20101126; JP20100264417 20101126; JP20100264418 20101126; JP20100264419 20101126; JP20100264420 20101126; JP20100264421 20101126; JP20100264422 20101126; JP20100264423 20101126; JP20100264424 20101126	ENDO A; GOMI A; HAYASHIUCHI R; ISHIGURO S; RINNAI R; SEKIGUCHI Y; SENDA H; TAKAHIRA H; YOSHIE S	NITTO DENKO CORP	Polylactic acid film or sheet.
DE102012202822 A1	20130829	EP2647682 A1 20131009	DE201210202822 20120224	SCHUEMANN UWE; SPIES MANFRED; IHRIG RALF	TESA SE	Biologisch abbaubarer Haftklebstoff. "Biodegradable adhesive agent."
DE19615151 A1	19971023	WO9740114 A1 19971030; US6307003 B1 20011023; JP2000508699 A 20000711; EP0894122 A1 19990203; CA2251821 A1 19971030; AU2693997 A 19971112; AU729239 B2 20010125	DE1996115151 19960418	WESTEPPE UWE; POMMERANZ WINFRIED; LÖRCKS L JÜJRGEN; SCHMIDT HARALD; IDEL KARSTEN-JOSEF; GRIGAT ERNST; SCHULZ-SCHLITTE WOLFGANG	BIOTEC BIOLOG NATURVERPACK; BAYER AG	Kompostierbarer Klebstoff. "Compostable adhesive."
EP0741177 A2	19961106	US5574076 A 19961112; EP0741177 A3 19970319; EP0741177 B1 19990303; DE69601590 T2 19991021	US19950433285 19950503	SHARAK MATTHEW L; PAUL CHARLES W	NAT STARCH CHEM INVEST	Sucrose benzoate as a tackifier for water sensitive or biodegradable hot melt adhesives.
EP0741178 A2	19961106	US5583187 A 19961210; EP0741178 A3 19970423; CA2175735 A1 19961104; AU699166 B2 19981126	US19950433578 19950503	SHARAK MATTHEW L; PAUL CHARLES W; RAY-CHAUDHURI DILI K	NAT STARCH CHEM INVEST	Hot melt adhesives based on hydroxy-functional polyesters.

Continued

—Cont'd

Patent Number	Publication Date	Family Members	Priority Numbers	Inventors	Applicants	Title
EP1236753 A1	20020904	WO02070583 A2 20020912; WO02070583 A3 20021128; WO02070583 A8 20031113; US2004143072 A1 20040722; US2007243374 A1 20071018; US7868101 B2 20110111; US7465770 B2 20081216; PT1366104 E 20080418; ES2299555 T3 20080601; EP1366104 A2 20031203; EP1366104 B1 20080109; DK1366104 T3 20080526; DE60224505 T2 20081127; AU2002236346 A1 20020919; AT383386 T 20080115	EP20010200800 20010302	LEWIS DAVID N; SCHUTTE GERRIT; WESTERHOF HENK; JANSSEN JANE; KELLY WILLIAM E	HYCAIL B V	Environmentally degradable polymeric compounds, their preparation and use as hot melt adhesive.
EP1816174 A2	20070808	EP1816174 A3 20090218; EP1816174 B1 20130501; DE202006001693 U1 20060330	DE20062001693 U 20060201	WESSELMANN ULRICH; MOELLER MICHAEL; CHRISTIANSEN FREYA	LOGO TAPE GES FUER SELBST-KLEBE	Biodegradable adhesive film based on renewable raw materials.
FR2927629 A1	20090821	WO2009115672 A1 20090924; US2010330315 A1 20101230; US8067492 B2 20111129; FR2927629 B1 20110729; EP2245102 A1 20101103; CN102007192 A 20110406	FR20080000809 20080214	ROBERT CHRISTOPHE	BOSTIK SA	Compositions adhésives thermofusibles biodégradable. "Biodegradable hot melt compositions."
JP2002371259 A	20021226	JP4745540 B2 20110810	JP20010181768 20010615	DOI YUKIO; ISHIOKA RYOJI	SHOWA HIGHPOLYMER	Biodegradable aqueous-dispersion-type adhesive composition.
JP2003301152 A	20031021	JP4242109 B2 20090318	JP20020108631 20020411	INAGAKI MADOKA; TSURUSAKI YOSHIYUKI	UNITIKA LTD	Pressure-sensitive adhesive tape.
JP2004231797 A	20040819		JP20030022278 20030130	MIYAMOTO TAKASHI; MORIMOTO OSAMU	TOYO BOSEKI	Biodegradable adhesive, varnish and laminate using the same.
JP2006070091 A	20060316		JP20040252460 20040831	MIZUNO UTAKO	DAINIPPON PRINTING CO LTD	Adhesive and adhesive member.
JP2006131705 A	20060525		JP20040320459 20041104	SAWAMURA SHINYA; SHIRAKI YASUICHIROU	DAINIPPON INK & CHEMICALS	Biodegradable adhesive and pressure-sensitive adhesive label using the same.

JP2007070422 A	20070322		JP20050257260 20050906	ISHII AKIRA; DOI YUKIO; NISHIIKE HARUKI	SHOWA HIGHPOLYMER	Biodegradable polyester polyurethane.
JP2007308626 A	20071129	JP4871436 B2 20120208	JP20060140071 20060519	TAKAHIRA HITOSHI; HAYASAKA KENJI	NITTO DENKO CORP	Low moisture permeability pressure-sensitive adhesive sheet.
JP2011252102 A	20111215		JP20100127750 20100603	AGARI Y; ARISAWA S; HIRANO H; KADOTA J	KONISHI CO LTD; OSAKA MUNICIPAL TECHNICAL RES INST	Polylactic acid-based adhesive and method for producing the same.
JP2012111203 A	20120614		JP20100264418 20101126	ENDO A; GOMI A; HAYASHIUCHI R; ISHIGURO S; RINNAI R; SEKIGUCHI Y; SENDA H; TAKAHIRA H; YOSHIE S	NITTO DENKO CORP	
JP2012111204 A	20120614		JP20100264419 20101126	ENDO A; GOMI A; HAYASHIUCHI R; ISHIGURO S; RINNAI R; SEKIGUCHI Y; SENDA H; TAKAHIRA H; YOSHIE S	NITTO DENKO CORP	Separator.
JP2012111205 A	20120614		JP20100264420 20101126	ENDO A; GOMI A; HAYASHIUCHI R; ISHIGURO S; RINNAI R; SEKIGUCHI Y; SENDA H; TAKAHIRA H; YOSHIE S	NITTO DENKO CORP	Separator.
JP2012111206 A	20120614		JP20100264424 20101126	ENDO A; GOMI A; HAYASHIUCHI R; ISHIGURO S; RINNAI R; SEKIGUCHI Y; SENDA H; TAKAHIRA H; YOSHIE S	NITTO DENKO CORP	Protective film.

Continued

—Cont'd

Patent Number	Publication Date	Family Members	Priority Numbers	Inventors	Applicants	Title
JP2012111207 A	20120614		JP20100264425 20101126	ENDO A; GOMI A; HAYASHIUCHI R; ISHIGURO S; RINNAI R; SEKIGUCHI Y; SENDA H; TAKAHIRA H; YOSHIE S	NITTO DENKO CORP	Protective film.
JP2012111208 A	20120614		JP20100264425 20101126	ENDO A; GOMI A; HAYASHIUCHI R; ISHIGURO S; RINNAI R; SEKIGUCHI Y; SENDA H; TAKAHIRA H; YOSHIE S	NITTO DENKO CORP	Protective film.
JP2012111217 A	20120614		JP20100264421 20101126	ENDO A; GOMI A; HAYASHIUCHI R; ISHIGURO S; RINNAI R; SEKIGUCHI Y; SENDA H; TAKAHIRA H; YOSHIE S	NITTO DENKO CORP	Adhesive tape or sheet.
JP2012111914 A	20120614		JP20100264415 20101126	ENDO A; GOMI A; HAYASHIUCHI R; ISHIGURO S; RINNAI R; SEKIGUCHI Y; SENDA H; TAKAHIRA H; YOSHIE S	NITTO DENKO CORP	Polylactic acid film or sheet.
JP2012111915 A	20120614		JP20100264416 20101126	ENDO A; GOMI A; HAYASHIUCHI R; ISHIGURO S; RINNAI R; SEKIGUCHI Y; SENDA H; TAKAHIRA H; YOSHIE S	NITTO DENKO CORP	Polylactic acid film or sheet.

JP2012111916 A	20120614		JP20100264417 20101126	ENDO A; GOMI A; HAYASHIUCHI R; ISHIGURO S; RINNAI R; SEKIGUCHI Y; SENDA H; TAKAHIRA H; YOSHIE S	NITTO DENKO CORP	Polylactic acid film or sheet.
JP2012111918 A	20120614		JP20100264422 20101126	ENDO A; GOMI A; HAYASHIUCHI R; ISHIGURO S; RINNAI R; SEKIGUCHI Y; SENDA H; TAKAHIRA H; YOSHIE S	NITTO DENKO CORP	Adhesive tape or sheet.
JP2012111919 A	20120614		JP20100264423 20101126	ENDO A; GOMI A; HAYASHIUCHI R; ISHIGURO S; RINNAI R; SEKIGUCHI Y; SENDA H; TAKAHIRA H; YOSHIE S	NITTO DENKO CORP	Adhesive tape or sheet.
JP2012116888 A	20120621		JP20100265580 20101129	ENDO A; GOMI A; HAYASHIUCHI R; ISHIGURO S; RINNAI R; SEKIGUCHI Y; SENDA H; TAKAHIRA H; YOSHIE S	NITTO DENKO CORP	Adhesive tape or sheet.
JP2012116889 A	20120621		JP20100265581 20101129	ENDO A; GOMI A; HAYASHIUCHI R; ISHIGURO S; RINNAI R; SEKIGUCHI Y; SENDA H; TAKAHIRA H; YOSHIE S	NITTO DENKO CORP	Protective film.

Continued

—Cont'd

Patent Number	Publication Date	Family Members	Priority Numbers	Inventors	Applicants	Title
JPH08157798 A	19960618		JP19940330729 19941206	TOKUNAGA YASUYUKI; ANDO MASAHIKO; YAMANAKA TAKESHI; HIKOSAKA WAKA; KOJIMA MAKOTO	NITTO DENKO CORP	Pressure-sensitive polyester adhesive composition.
JPH09125016 A	19970513		JP19950303862 19951027	SANADA AKIRA	SUNSTAR INC	Biodegradable tacky tape.
JPH10237401 A	19980908	JP3938609 B2 20070627	JP19970040522 19970225	MITSUHASHI KIMIYUKI; KOBORI TADASHI; GONDA TAKASHI	SHINETSU POLYMER CO	Biodegradable pressure-sensitive adhesive tape.
JPH11158452 A	19990615		JP19970327500 19971128	HIKOSAKA WAKA; ANDO MASAHIKO; TOKUNAGA YASUYUKI; YAMANAKA TAKESHI	NITTO DENKO CORP	Biodegradable pressure-sensitive adhesive composition and pressure-sensitive adhesive sheet prepared therefrom.
JPH1160716 A	19990305	JP3698533 B2 20050921	JP19970155272 19970612; JP19970304603 19971106; JP19960295044 19961107	HIGUCHI CHOJIRO; KASHIMA TAKESHI; TAKAGI MASATOSHI; TERADO YUJI; AJIOKA MASANOBU	MITSUI CHEMICALS INC	Biodegradable adhesive and its production.
US2005112182 A1	20050526	JP2005154477 A 20050616; CA2468929 A1 20050520; CA2468929 C 20080311	JP20030391221 20031120	MINAMI SABURO]; RENBUTSU EIKO; OMURA YOSHIHIKO; NAKATSUBO FUMIAKI; OKAMOTO YOSHIHARU; SAIMOTO HIROYUKI; SHIGEMASA YOSHIHRO	UNIV TOTTORI	Medical adhesive and medical covering agent using ultraviolet ray curable chitosan derivative.
US2010089287 A1	20100415		US20090586739 20090925	THAMES SHELBY F; RAWLINS JAMES W; FERGUSON RICHARD C; MENDON SHARATHKUMAR K	THAMES SHELBY F; RAWLINS JAMES W; FERGUSON RICHARD C; MENDON SHARATHKUMAR K	Soy protein adhesive and uses thereof.

US2051025 A	19360818		US19360035764 19360617	BAUER JORDAN V	STEIN HALL MFG CO	Method of making ply board.
US2102937 A	19371221		US19350033206 19350726	BAUER JORDAN V	STEIN HALL MFG CO	Plyboard adhesive.
US3487033 A	19691230	NL6814218 A 19690409; JPS5233137 B1 19770826; GB1239636 A 19710721; FR1585311 A 19700116; ES358639 A1 19700616 DK143450 B 19810824; DK143450 C 19811228 DE1800834 A1 19690508; DE1800834 B2 19770623; BE721809 A 19690404	US19670672691 19671004	MCELMURY DONALD E; FISCHER AUGUST C JR	CORN PRODUCTS CO	Single ungelatinized starch-component-corrugating adhesive.
US4833036 A	19890523		US19880171335 19880321	CANNARSA MICHAEL J; KESLING JR HAVEN S; HOSTETLER DONALD E; COOPER TERENCE A; SUN HSIANG-NING	ARCO CHEM TECH	Polyalkylene carbonate hot melt adhesive.
US5169889 A	19921208	JPH05271638 A 19931019; JPH0662928 B2 19940817; ES2067437 T1 19950401; ES2067437 T3 19951101; EP0553394 A1 19930804; EP0553394 B1 19950726; DK0553394 T3 19950911; DE553394 T1 19950803; DE69203713 T2 19960111; CA2079535 A1 19930728; AU643154 B2 19931104	US19920826571 19920127	KAUFFMAN THOMAS; BRADY FRANCIS X; PULETTI PAUL P; RAYKOVITZ GARY	NAT STARCH CHEM INVEST	Poly hydroxybutyrate/hydroxyvalerate based hot melt adhesive.
US5252646 A	19931012		US19920968564 19921029	IOVINE CARMINE P; KAUFFMAN THOMAS F; SCHOENBERG JULES E; PULETTI PAUL P	NAT STARCH CHEM INVEST	Polylactide containing hot melt adhesive.
US5312850 A	19940517		US19930000153 19930104	IOVINE CARMINE P; KAUFFMAN THOMAS F; SCHOENBERG JULES E; PULETTI PAUL P	NAT STARCH CHEM INVEST	Polylactide and starch containing hot melt adhesive.

Continued

—Cont'd

Patent Number	Publication Date	Family Members	Priority Numbers	Inventors	Applicants	Title
WO02088271 A1	20021107	US2004231559 A1 20041125; US6921430 B2 20050726; MXPA03010031 A 20040227; JP2005505639 A 20050224; JP4490633 B2 20100630; ES2266506 T3 20070301; EP1383847 A1 20040128; EP1383847 B1 20060712; DE60213080 T2 20070111; CA2445885 A1 20021107; CA2445885 C 20101207; CN1524115 A 20040825; CN100378186 C 20080402; BR0209393 A 20050419; AU2002309622 B2 20070906; AT332949 T 20060815	US20010288259P 20010502	BLOEMBERGEN STEVEN; KAPPEN FRANS; BEELEN BRIGIT	ECOSYNTHETIX INC	Environmentally friendly biopolymer adhesives and applications based thereon.
WO0234857 A2	20020502	WO0234857 A3 20030109; US2002068810 A1 20020606; US7094840 B2 20060822; US2006247390 A1 20061102; JP2004512419 A 20040422; ES2362405 T3 20040422; EP1330503 A2 20030730; EP1330503 B1 20110525; AU2582702 A 20020506; AT510898 T 20110615	US20000243818P 20001027	WHITEHOUSE ROBERT S; HONG LUHUA; DAUGHTRY SEAN	METABOLIX INC	Compositions comprising low molecular weight polyhydroxyalkanoates and methods employing same.
WO2004076583 A1	20040910	WO2004076582 A1 20040910; US2010305280 A1 20101202; US7928167 B2 20110419; PT1603987 E 20111110; JP2006519293 A 20060824; JP2006518799 A 20060817; JP2011140656 A 20110721; JP5079321 B2 20121121; JP4724111 B2 20110713; HK1084687 A1 20111223; HK1085504 A1 20080620; ES2297385 T3 20080501; ES2371069 T3 20111227; EP2241605 A2 20101020; EP2241605 A3 20120321; EP1935945 A1 20080625; EP1603987 A1 20051214; EP1603987 B1 20110803; EP1601737 A1 20051207; EP1601737 B1 20071031; DE602004009764 T2 20080828; AT377060 T 20071115; AT518932 T 20110815	EP20040713313 20040220; US20030449187P 20030221	WHITEHOUSE ROBERT S	METABOLIX INC	PHA blends.

WO2005056680 A1	20050623	EP1692224 A1 20060823; DE10358779 A1 20050728; DE10358779 B4 20070906	DE2003158779 20031212	NIES BERTHOLD; SCHILKE FRANK; DAUM LUDWIG	BIOMET DEUTSCHLAND GMBH	Biodegradable hot melt adhesive.
WO2010016514 A1	20100211	US2011135924 A1 20110609; JP2010037463 A 20100218; EP2311896 A1 20110420; CN102119186 A 20110706; CN102119186 B 20130515	JP20080203352 20080806	TAKAHIRA HITOSHI; YOSHIE SATOMI; NAKAJIMA TADASHI; FUNAOKA DAIKI; SHIMENO KATSUYA	NITTO DENKO CORP; TOYO BOSEKI	Polyesters, polyester compositions, adhesive compositions, adhesive layers and adhesive sheets.
WO2010142507 A2	20101216	WO2010142507 A3 20110224; US2012053261 A1 20120301; EP2429598 A2 20120321	EP20090160133 20090513	PRAVATA LAURENT	KITOZYME S A	Adhesive composition.
WO2011049111 A1	20110428	US2012202058 A1 20120809; JP2011088958 A 20110506; EP2492325 A1 20120829; CN102575132 A 20120711	JP20090241717 20091020	NITTO DENKO CORP; TAKAHIRA HITOSHI; YOSHIE SATOMI	NITTO DENKO CORP	Pressure-sensitive adhesive sheet for surface protection.
WO2011049115 A1	20110428	US2012208017 A1 20120816; JP2011088957 A 20110506; EP2492327 A1 20120829; EP2492327 A4 20130522; CN102575131 A 20120711	JP20090241674 20091020	SATOMI YOSHIE; HITOSHI TAKAHIRA	NITTO DENKO CORP	Pressure-sensitive adhesive tape for masking.
WO2011049116 A1	20110428	US2012208015 A1 20120816; JP2011088959 A 20110506; EP2492328 A1 20120829; CN102549094 A 20120704; CN102549094 B 20131106	WO2010JP68457 20101020; JP20090241721 20091020	HITOSHI TAKAHIRA; SATOMI YOSHIE	NITTO DENKO CORP	Thermally removable pressure-sensitive adhesive sheet.
WO2012030819 A1	20120308	WO2012030821 A1 20120308; WO2012030823 A1 20120308; WO2012030822 A1 20120308; US2012078155 A1 20120329; US2012077954 A1 20120329; US2012077028 A1 20120329; US2012077887 A1 20120329	US20100380937P 20100908; US20100378235P 20100830; US20100378212P 20100830; US20100378134P 20100830	BOWMAN HOWARD	SURMODICS PHARMACEUTICALS INC	Terpolymers and pressure-sensitive adhesives.
WO2012070526 A1	20120531	US2013236723 A1 20130912; KR20130117798 A 20131028; EP2644643 A1 20131002	JP20100264415 20101126; JP20100264416 20101126; JP20100264417 20101126; JP20100264418 20101126; JP20100264419 20101126; JP20100264420 20101126; JP20100264421 20101126; JP20100264422 20101126; JP20100264423 20101126; JP20100264424 20101126; JP20100264425 20101126; JP20100264426 20101126; JP20100265578 20101129; JP20100265579 20101129; JP20100265580 20101129; JP20100265581 20101129	ISHIGURO SHIGEKI; YOSHIE SATOMI; SENDA HIROKI; AKAHIRA HITOSHI; SEKIGUCHI YUKA; HAYASHIUCHI RIE; ENDO ASUKA	NITTO DENKO CORP	Polylactic acid film or sheet.

Continued

—Cont'd

Patent Number	Publication Date	Family Members	Priority Numbers	Inventors	Applicants	Title
WO9410257 A1	19940511	JPH07502069 A 19950302; EP0618948 A1 19941012; CA2126849 A1 19940511; CA2126849 C 19990112; AU5133293 A 19940524; AU659353 B2 19950511	US19930000153 19930104; US19920968564 19921029	IOVINE CARMINE P; KAUFFMAN THOMAS F; SCHOENBERG JULES E; PULETTI PAUL P	NAT STARCH CHEM INVEST	Polylactide containing hot melt adhesive.
WO9502649 A1	19950126	US5711842 A 19980127; NO960153 A 19960112; JPH09500157 A 19970107; JP3623795 B2 20050223; FI960158 A 19960112; EP0708804 A1 19960501; EP0708804 B1 19981125; DK0708804 T3 19990809 DE69414854 T2 19990708; AU685135 B2 19980115; AT173753 T 19981215	GB19930014577 19930714	KEMMISH DAVID JOHN	ZENECA LTD	Adhesion process.
WO9510577 A1	19950420	US5753724 A 19980519; US5700344 A 19971223; US6365680 B1 20020402; JPH09505615 A 19970603; EP0723572 A1 19960731; EP0723572 B1 19991208; DE69422053 T2 20000629; CA2173753 A1 19950420; AU7604894 A 19980326; AU689130 B2 19980326; AT187477 T 19991215	US19930136670 19931015	EDGINGTON GARRY J; RYAN CHRISTOPHER M	FULLER H B LICENSING FINANC	Biodegradable/compostable hot melt adhesives comprising polyester of lactic acid.
WO9603159 A1	19960208	US5583114 A 19961210; USRE38158 E1 20030624; JPH10503102 A 19980324; JP3592718 B2 20041124; ES2186723 T3 20030516; EP0772464 A1 19970514; EP0772464 B1 20021204; DE69529075 T2 20031113; CA2194681 A1 19960208; CA2194681 C 20061010; AU2870895 A 19960222	US19940281473 19940727	BARROWS THOMAS H; LEWIS TERRY W; TRUONG MYHANH T	MINNESOTA MINING & MFG	Adhesive sealant composition.

WO9704036 A1	19970206	MX9800592 A 19981129; KR100266488 B1 20000915; JPH11510194 A 19990907; JP4113989 B2 20080709; ES2162088 T3 20011216; EP0839170 A1 19980506; EP0839170 B1 20011017; EP1132446 A2 20010912; EP1132446 A3 20030604; EP1132446 B1 20060823; DE69636485 T2 20070419; DE69616067 T2 20020711; CA2226864 A1 19970206; CA2226864 C 20030520; AU6499896 A 19970218; AT207104 T 20011115; AT337382 T 20060915	US19950001274P 19950720	NODA ISAO	PROCTER & GAMBLE	Nonwoven materials comprising biodegradable copolymers.
WO9710292 A1	19970320	US5993530 A 19991130; JPH0977910 A 19970325; JP2997995 B2 20000111; EP0850988 A1 19980701; EP0850988 A4 20010214; EP0850988 B1 20050302; DE69634410 T2 20060316; AU6890796 A 19970401; AU710136 B2 19990916; AT290047 T 20050315	JP19950235675 19950913	TANAKA HIDEYUKI; HOSOKAWA NOBUHIRO; SUGIURA NOBUYUKI; TAKAHARA MASATO	JAPAN CORN STARCH CO LTD	Aqueous dispersion of biodegradable resin composition.

REFERENCES

[1] Imam SH, Bilbao-Sainz C, Chiou B-S, Glenn GM, Orts WJ. Biobased adhesives, gums, emulsions, and binders: current trends and future prospects. J Adhes Sci Technol 2012;27:1972–97.

[2] Kumsugar NG, Inc. Water-based products – coating, paper coatings. Adhesives & sealants, inks – a multiclient study; 2000.

[3] Viljanmaa M, Södergård A, Törmälä P. Lactic acid based polymers as hot melt adhesives for packaging applications. Int J Adhes Adhes 2002;22:219–26.

[4] Ono K, Saito Y, Yura H, Ishikawa K, Kurita A, Akaike T, et al. Photocrosslinkable chitosan as a biological adhesive. J Biomed Mater Res 2000;49:289–95.

[5] Frihart CR. Adhesive groups and how they relate to the durability of bonded wood. J Adhes Sci Technol 2009;23:601–17.

[6] Fahmy Y, El-Wakil NA, El-Gendy AA, Abou-Zeid RE, Youssef MA. Plant proteins as binders in cellulosic paper composites. Int J Biol Macromol 2010;47:82–5.

[7] Khosravi S, Khabbaz F, Nordqvist P, Johansson M. Protein-based adhesives for particleboards. Ind Crops Prod 2010;32:275–83.

[8] Yu M, Hwang J, Deming TJ. Role of l-3,4-dihydroxyphenylalanine in mussel adhesive proteins. J Am Chem Soc 1999;121:5825–6.

[9] Sever MJ, Weisser JT, Monahan J, Srinivasan S, Wilker JJ. Metal-mediated crosslinking in the generation of a marine-mussel adhesive. Angew Chem 2004;116:454–6.

[10] Taylor SW, Chase DB, Emptage MH, Nelson MJ, Waite JH. Ferric ion complexes of a DOPA-containing adhesive protein from *Mytilus edulis*. Inorg Chem 1996;35:7572–7.

[11] Frank BP, Belfort G. Adhesion of *Mytilus edulis* foot protein 1 on silica: ionic effects on biofouling. Biotechnol Prog 2002;18:580–6.

[12] Loizou E, Weisser JT, Dundigalla A, Porcar L, Schmidt G, Wilker JJ. Structural effects of crosslinking a biopolymer hydrogel derived from Marine mussel adhesive protein. Macromol Biosci 2006;6:711–8.

[13] Petrie E. Biodegradable polymers in adhesive systems. Adhes Sealants Ind Mag 2007. http://www.adhesivesmag.com/articles/biodegradable-polymers-in-adhesive-systems.

[14] Stewart RJ, Ransom TC, Hladyy V. Natural underwater adhesives. J Polym Sci Part B Polym Phys 2011;49:757–71.

[15] Imam SH, Mao L, Chen L, Greene RV. Wood adhesive from crosslinked poly(vinyl alcohol) and partially gelatinized starch: preparation and properties. Starch – Stärke 1999;51:225–9.

Chapter 16

Recycling

Chapter 16 is an amended and updated version of Chapters 3, 5, and 6 of the previous book, *Biopolymers*: *Reuse*, *Recycling and Disposal*, by the same author.

16.1 REUSE

Reuse is a common practice applied to discarded or used polymer products. Rejected preforms or moldings and used articles are reprocessed as they are, without changing the chemical nature of the polymer; examples of this case include the conversion of PET bottles to fibrous material. As a result, most of the applied techniques are similar to those of physical (or mechanical) recycling described in Section 16.2: Physical recycling. However, there are certain differences. The methods of physical recycling, such as grinding, sorting, compacting, etc., are usually pretreatment processes preceding the reprocessing or recycling of the waste material. Physical recycling is expensive, in particular because the separation of the different polymers is difficult. Reusing polymers is preferable to physical recycling as it uses less energy and fewer resources. Reuse involves: (1) direct recuperation of scrap material during molding (e.g., feedback of used material); and/or (2) blending of the polymer to be used with other polymers, often in combination with compatibilizers to make new products; and/or (3) mixing with various additives such as antioxidants and/or reinforcing agents; and/or (4) modification of the polymer structure (e.g., by reactive extrusion) to recover its original properties.

16.1.1 Recuperation

This practice is widely employed for the recycling of industrial scrap, in which these industrial residues are ground and directly introduced in the processing machinery together with virgin material. Sources of industrial scrap can be melt lumps, sprues, and defective parts in injection molding; parison waste in blow molding or, for example, edge trim; cutoffs and off-spec start-up material in film and fiber production processes. The reutilization of these plastics wastes, which exist in considerable quantities in the production or processing of biopolymer products, by direct processing in an extruder, is possible only to a very limited extent because of their voluminous nature and poor flow property. Such plastics wastes must first be pretreated appropriately by comminution, and the plastics particles that have thereby become flake-like or fleece-like are then agglomerated into highly compacted, free-flowing, and abrasion-resistant granules. During the heat treatment required for the agglomeration, the biopolymers must not be thermally damaged, i.e., they must not be heated above their melting temperature (T_m) since, when this is exceeded, they decompose chemically with release of gases, which are harmful in most cases and cause the wastes to become useless for technological reutilization. The granules obtained in this way must have the same quality as the granules of virgin material, so that they can be proportionately admixed with the latter. The adjustment of the composition of recycled material in the blend and the optimization of the processing procedure are the main technological implications to be considered in order to achieve material properties similar to those of the virgin one [1].

Scrap biopolymers generated during molding operations can be viewed as potential resources for the manufacture of new products through recycling processes, with a similar status to virgin biopolymers. The prospect of reusing scrap poly(lactic acid) (PLA) as it is appears appealing from the aspect of recycling, taking into account the average cost of PLA compared to conventional plastic products. Sources of waste PLA are: (1) sprues, runners, and selvages left behind during molding and production processes; (2) offgrades of PLA formed by polymerization reaction and not meeting the standard requirements; and (3) used PLA. However, the reprocessing of biopolymer waste is not an easy task. PLA is highly susceptible to thermal deterioration, and reuse of waste PLA is liable to cause coloration, degeneration, and decrease in molecular weight. Other problems such as hygroscopicity, stickiness at high temperatures, and thermal instability of several biopolymers also have to be taken into consideration. Thus, for example, in the reprocessing of PLA it is important that the material being recycled is as dry as possible in order to prevent a hydrolytic breakdown of the molecular chains during the plasticization. However, PLA is hygroscopic, which makes efficient drying difficult. Furthermore, the low T_g at which the PLA material becomes sticky at higher temperatures, and a relatively long crystallization time, make it hard to crystallize and/or dry amorphous production wastes, especially residues of deep-drawn

Biopolymers: Processing and Products. http://dx.doi.org/10.1016/B978-0-323-26698-7.00016-7

films, with conventional crystallization systems and drying systems (2008, **WO2008058303** A1, EREMA). Therefore, unlike general-use polymers, it is difficult to reuse PLA. Similarly, plasticized starch is sensitive to hydrolysis during use and cannot normally be reprocessed for use in the same application. Like PLA, it is not compatible with mainstream plastics used in packaging and cannot be co-recycled into useful secondary products. Additional problems of reprocessing industrial scrap and virgin biopolymers include: (1) inconsistent feeding performance of the production extruder; (2) air inclusions in the melt that lead to defects of the finished products; and (3) difficulty in removing process materials like printing inks and similar.

CN101230129 A (2008, SHANGHAI NEW SHANGHUA POLYMER) discloses a recrystallization method of waste PLA comprising the following steps: recovered PLA with 30–400 ppm water content is heat treated and recrystallized for 5–100 min, preferably 30 min at 20–140 °C, more preferably 30–110 °C, by adopting different temperatures, according to two to eight ascending temperature gradients, preferably two to four, to obtain recrystallized PLA. Waste PLA refers to PLA rim leftovers and discarded products after first processing. The melting enthalpy of the melting peak of PLA crystallization (ΔH_m) is 10–30 J/g, the T_m is 140–180 °C, and the T_g of PLA is 40–70 °C. Recrystallization process of PLA has simple operation, does not need additional postprocessing, the required time is relatively short, the recrystallized PLA has satisfactory properties, and it can be reprocessed.

WO2008058303 A1 (2008, EREMA) discloses a method for the pretreatment, reprocessing, or recycling of a thermoplastic polymer, especially PLA, wherein the polymer is heated in a receiving tank or reactor (1) under constant mixing or movement and/or comminution at a temperature below T_m, preferably above T_g of the thermoplastic polymer (preferably 90–110 °C), and thereby at the same time crystallized, dried, and/or purified, especially in a single step. For the mixing and heating of the thermoplastic polymer, at least one comminuting or mixing tool (12) able to turn about a vertical axis (8) arranged possibly on several levels one above the other is used, with working edges that act on the material with a comminuting and/or mixing effect, and the heating occurs especially by applying mechanical energy (see Figure 16.1). The method is advantageously carried out either in a one-stage EREMA PC reactor or in a one- or two-stage VACUREMA reactor.

The mild, yet constant, movement of the polymer material prevents clumping or sticking of the material in the critical temperature range, until an adequate crystallization of the surface of the particles itself prevents a sticking together of the individual particles. In the treatment tank, the mild and constant movement ensures not only an abeyance of sticking but at the same time also that the temperature in the tank is or remains high enough and each particle is or remains heated gently to the proper temperature. At the same time, the movement supports a detachment of the migrating molecules from the surface of the particles.

WO2009100473 A1 (2009, EREMA) is a modification of the previous patent, wherein the pretreated thermoplastic material is transferred into a screw injection molding machine (10) having a screw (16) rotating in a housing (17) and being axially displaceable therein and/or acting as a piston, is plasticized in said screw, and molded into a molded part, for example, a preform (see Figure 16.1).

At the NPE 2009 trade show in Chicago, plastics recycling systems provider EREMA demonstrated a recycling system of turning scrap PLA film into near-margin quality pellets, using a nonvented Model 906T reclaim extruder for PE film. With a normal nonbarrier screw for PE, it processed oriented PLA scrap provided by Biax International Inc., a large producer of oriented PLA film (OPLA) sheet. Frictional heat generated in the standard cutter/compactor acts like a dryer, removing and venting moisture that makes this material difficult for some systems to reprocess. The use of a short extruder L/D ratio also helps to avoid thermal degradation. EREMA says about 9 million kg/yr of bioplastic scrap (mostly PLA) are reprocessed on EREMA reclaim extruders in the United States, and about the same amount in Europe (PLA and starch-based films for compost bags) [2,3].

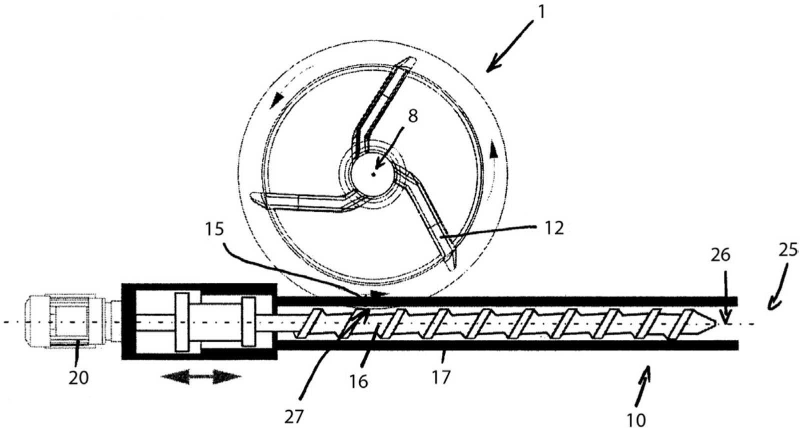


FIGURE 16.1 Device comprising a reactor or cutter-compactor (1) and a worm-gear injection molding device (10) (2009, **WO2009100473** A1 EREMA). 1, Reactor or cutter-compactor; 2, Worm-gear injection molding device; 8, Vertical axis; 10, Injection molding machine; 12, Mixing tool; 15, Removal opening; 16, Screw; 17, Housing; 20, Motor; 25, Nozzle; 26, Worm antechamber; 27, Catchment opening.

At the NPE 2012 trade show in Milan, recycling equipment maker Tecnova demonstrated the Refil/1 in-line system for reclaiming film scrap. Production rates of the system, which can handle a wide range of materials, including biopolymers, are claimed to be 40–45 kg/h. The company showed also the Mini 60 line, which is able to process bioplastic, in addition to LDPE/HDPE/PP film. The line is equipped with a special grinder, a die face cutter, and a cooling system, all specifically designed to be able to handle biopolymers as well as conventional plastics. The regenerated granules can be directly reintroduced into the extrusion process for the production of (biodegradable) film [3].

Next Generation Recyclingmaschinen GmbH (NGR) developed a new technology for bioplastics recycling. NGR's solution involves recycling machines that feed the material to the extruder with an integrated cutter-feeder, which consists of a slow rotating cutter shaft with knives that cut against fixed knives like scissors, and a feeding zone that conveys the material to the extruder without preheating it. The NGR Cutter-Feeder-Extruder can reportedly recycle most of the commonly used biopolymers, such as starch or PLA-based products. The screws, vacuum vent, and melt filter can all be tailored to the special requirements of biopolymers, for example, low heating of the material or the removing of printing inks. This method is also sensitive toward monitoring slight changes in the molecular mass distribution resulting from the inevitable heat stress in any polymer processing step [4].

PALLMANN MASCHINENFABRIK GMBH & CO. developed a special process for the recycling of waste generated during the production and processing of PLA foam and film. As is shown in Figure 16.2, the PLA waste precut into a size smaller than 1/2″ is conveyed into the storage bin of the Plast-Agglomerator with a pneumatic conveying system. From the hopper, the feed material is continuously dosed into the agglomeration chamber by a feeding screw. Through frictional heat only and mechanical pressure the material is evenly sintered, within fractions of a second, through the holes of the die. The frictional heat and the mechanical pressure can be adjusted in such a way that the sintering is performed below the T_m of each type of plastic to ensure a minimum thermal degradation of the product. During the production and processing of PLA foam and film, waste is generated. Valuable virgin material can be saved by recycling the waste. Recycled production waste can be reintroduced into the process for the production of new material.

Suitable apparatuses for the continuous regranulation of thermoplastics wastes, in particular films, fibers, filaments, foam materials and the like, are described in **DE3842072** C1 (1989) and **US2006283340** A1 (2006, PALLMANN MASCHINENFABRIK GMBH & CO. KG). These apparatuses are mainly used to transform wastes such as polyethylene, poly(vinyl chloride) (PVC), polypropylene, polystyrene, polyamide, and similar thermoplastics, and of mixtures of these and other organic or inorganic materials, into uniform, free-flowing and abrasion-resistant granules without thermal damage to the material, such as is required for technological further processing in extruders, pressers, or injection molding machines.

16.1.2 Restabilization

The reprocessing of waste polymers leads to materials with generally worse properties than those of the original materials, due to the changes in the chemical structure caused by

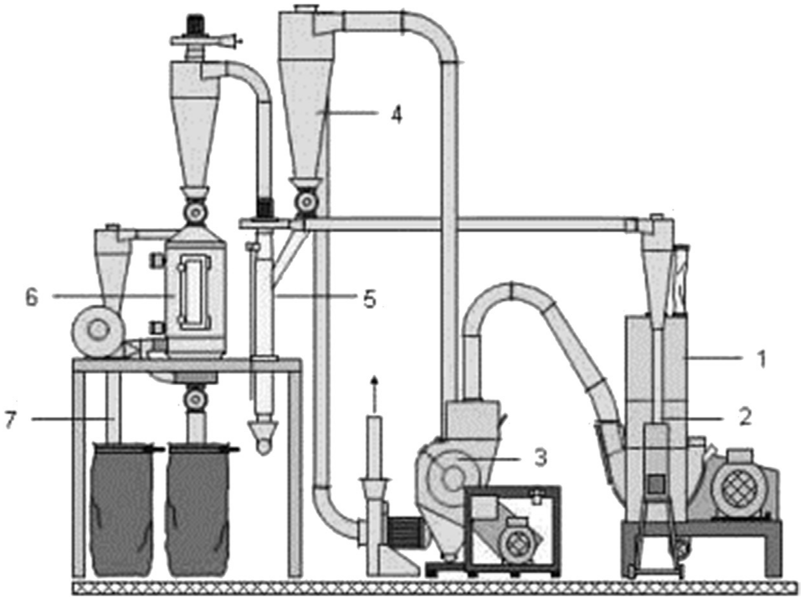


FIGURE 16.2 Plast-Agglomerator, Type PFV of PALLMANN MASCHINENFABRIK GMBH & CO. KG [5]. 1, Hopper; 2, Plast-agglomerator; 3, Hot melt granulator; 4, Cyclone; 5, Sifter; 6, Granules cooler; 7, Sacking station.

previous degradation processes. Restabilization is a well-known practice to protect recycled materials from thermo-mechanical degradation during reprocessing and enhance long-term stability throughout reuse. Restabilization does not effectively recover the degraded material but prevents further degradation processes that may be catalyzed by the oxidative moieties present in its structure or by moisture. Several processing and light stabilizers, including combinations of hindered phenols and hindered amine stabilizers, have been employed for the restabilization of recycled biopolymers, which can interfere in the auto-oxidation cycle by neutralizing peroxide radicals and decomposing hydroperoxides [1]. Some additives as catalyst deactivators have been reported to stabilize PLAs in the melt. Such additives include benzoyl peroxide [6,7], 1,4-diaminoanthraquinone [8–11], 2-hydroxy-2,4,6-cycloheptatrienone (Tropolone) [12], and natural and biodegradable acid [13]. Additives are used to retard the hydrolysis of biopolymers such as carbodiimide compounds. Compatibilizers are also added to improve the performance of waste biopolymers [14].

16.1.3 Blending Recycled Biopolymers with Other Polymers

Blending recycled polymers with virgin materials is one of the most common and well-established procedures for upgrading the properties of single-stream waste polymeric materials.

Sharp has developed recycling technology for repeatedly recovering plastic from used consumer electronics and reusing it in parts of new consumer electronics. In 2010, the volume of plastic derived from this closed-loop plastic material recycling technology that was recycled and reused in new products increased to 1300 tons. Sharp has disclosed a number of patents of related methods and apparatuses for recovering and reusing biodegradable aliphatic polyesters, such as PLA and P3HB. The methods are used for the recovery and recycling of biobased thermoplastics from discarded domestic electrical appliances such as air conditioners, televisions, refrigerators, and washing machines, and electronic office equipment and electrical-electronic components.

JP2007284495 A (2007, SHARP KK) discloses a method for separating, recovering, and reusing thermoplastic polymer (A) from a waste material comprising a thermoplastic polymer composition derived from renewable resources and a thermoplastic polymer composition derived from fossil resources. Then, a thermoplastic polymer (B) is added to the thermoplastic polymer (A), mixed, and molded. The method further involves a polymer collection process and a gravity-separation process. The polymer collection process separates and recovers thermoplastic polymer from a waste material, using water having a specific gravity difference. Similarly, the thermoplastic polymer (B) is recovered from the waste material. The gravity-separation process separates and recovers other thermoplastic polymers containing thermoplastic polymer composition from crushed material containing plastic. The thermoplastic polymer composition derived from renewable resources contained in thermoplastic polymer (A) is PLA consisting of L-lactic acid and/or D-lactic acid units. The thermoplastic polymer composition derived from fossil fuel resources contained in thermoplastic polymer (A) is polyolefin composition or polystyrene composition. During mixing, thermoplastic polymer (A) and thermoplastic polymer (B), additive (which assigns hydrolysis resistance), compatibilizing agent and/or antioxidant, and compatibilizing agent having reactive functional group(s) in side chain are added. The content of additive, compatibilizing agent, and antioxidant with respect to 100 pbw thermoplastic polymer (A) and thermoplastic polymer (B) are 0.01–10, 0.01–30, and 0.01–5 pbw, respectively. The preferred additive is carbodiimide compound. The thermoplastic polymer component contains polyolefin. The compatibilizing agent is a block copolymer containing PLA as a main component. The compatibilizing agent having reactive functional group(s) in side chain is a copolymer (a) containing an olefin-type component and styrene-type component, or modified polymer (b) having structural unit containing carboxylic acid group or its derivative(s) group in principal chain or side chain of a polyolefin. The content of copolymer (a) and modified polymer (b) are 0.1–20 and 0.1–10 pbw, respectively. Preferred antioxidant is phenolic antioxidant and/or phosphorus-type antioxidant.

JP2009161655 A (2009, SHARP KK) discloses a method for recycling a biobased thermoplastic polymer waste by mixing the biobased polymer waste with at least one polymer selected from a styrene-based polymer (a), an aliphatic polyester (b), and a vinyl-based polymer (c), and heating and melting the mixture. The biobased polymer waste material contains acrylonitrile butadiene-styrene copolymer (ABS) and PLA having L-lactic acid and/or D-lactic acid. The styrene polymer (a) is acrylonitrile butadiene-styrene copolymer (ABS). The aliphatic polyester (b) is PLA consisting of L-lactic acid and/or D-lactic acid units. The vinyl polymer (c) contains polymer of (meth)acrylic ester and has hydroxyl group and/or functional group having reactivity with carboxyl group. The thermoplastic polymer composition further contains rubber-containing copolymer (d) (0.1–50 pbw), phenolic antioxidant, and/or phosphorus-type antioxidant (e) (0.01–5 pbw) and hydrolysis-proof stabilizer (f) (0.01–10 pbw). The rubber-containing copolymer (d) is silicone acrylic type and/or core-shell-type acrylic-type copolymer.

JP2010005948 A (2010, SHARP CORP) discloses a method for reusing a biodegradable polymer waste comprising the following two processes: (1) mixing the biodegradable polymer waste, which is composed mainly of an acrylic polymer (e.g., PMMA) and at least one biopolymer selected from the group consisting of L-lactic acid and D-lactic acid units, with polymers containing a styrene-based polymer (e.g., ABS), preferably in combination with at least one antioxidant and a hydrolysis-proof stabilizer, then thermally melting this mixture to obtain a raw material as resource; and (2) manufacturing a biodegradable molded article from the recycled material. The biodegradable polymer waste is selected from domestic electrical appliances, electronic office equipment, electrical and electronic components, and the like.

JP2008100413 A (2008, SHARP CORP) discloses a method for recycling waste plastic material having a paint film formed from a biobased coating includes the following steps: (1) crushing the waste plastic material having the paint film; (2) heating/melting the crushed waste plastic material; (3) producing a plastic raw material using it; and (4) producing a plastic molding. The recycling method does not adversely affect the environment, while preventing the lowering of the physical properties of a regenerated plastic material even when the waste plastic material having a paint film, without removing the paint film, is mixed with a plastic material to be coated to be recycled.

JP2002226623 A (2002, KANEBO LTD) discloses a method of reclaiming a foam molding from a biodegradable aliphatic polyester (e.g., PLA or PBS) by grinding and molding the foam again. Furthermore, a reclaimed molded article is obtained by mixing the ground foam in unused PLA-based foamed beads (primary foam) of 70% or more and molding the mixture. The reclaimed foam is used for shock-absorbing materials and for packing.

EP1241231 A1 (2002, CANON KK) discloses, in one of its embodiments, the recycling of molded articles obtained from a biodegradable polymer composition, comprising a biodegradable biopolymer (A) and a biodegradable liquid crystalline biopolymer (B). The source material for the biodegradable biopolymer or liquid crystalline biopolymer can be waste paper. Molded articles include ink tanks of ink-jet printers, toner containers of electrophotography apparatuses, packing materials, casings of printers and cameras, transparency sheets, and so forth. In an example, a transparent sheet prepared from butyl ester of hydroxyethylcellulose (B) and PLA (A) was melted and pressed again to mold a transparency sheet. This sheet was found to be usable as a transparency sheet without causing problems in light transmissivity and other properties. In another example, the transparency sheet was melted, and pelletized, and molded by an injection machine into a casing of an ink-jet printer. The casing was formed without problem in molding (see also Section 16.3.2.3: Hydrothermal Depolymerization).

WO2011146562 A2 (2011, DU PONT) discloses a method for making a fiber containing 0.1–99.9 wt%, preferably 5–10 wt%, recycled poly(trimethylene terephthalate) (PTT), comprising the following steps: (1) providing carpet yarns containing recycled PTT (Sorona®), (2) melt-pelletizing the yarns, (3) combining the recycled PTT with virgin PTT to form a blend, and (4) spinning the blend to form a fiber. In some preferred embodiments, the PTT being reclaimed and recycled and/or virgin PTT with which the PTT is combined are bioderived; i.e., the PTT can be prepared from 1,3-propanediol that has been produced in a biological method such as fermentation; see also Chapter 1: Introduction, Section 1.4.2.3: Aromatic Polyesters (Bio-Based). The use of bioderived starting materials in virgin PTT, and preferably also in the PTT in the carpet being used for the recycled polymer, provides a sustainable and more environmentally friendly consumer product than processes using only fossil fuel–based raw materials.

CN101275009 A (2008), **US2008237910** A1 (2008), and **CN101130627** A (2008) of FUJI XEROX CO LTD disclose methods of recycling biodegradable polymer compacts used mainly as exterior members of a printer, a copying machine, a facsimile, and the like. In **CN101275009** A (2008) and **US2008237910** A1 (2008) the biodegradable polymer composition comprises 21–70 wt% of an aliphatic polyester (e.g., PLA), 35–65 wt% of a second polymer having a glass transition temperature (T_g) higher than the T_g of the aliphatic polyester (e.g., polycarbonate) and 1–20 mass% of an aluminium phosphate as flame retardant. In **CN101130627** A (2008) the composition comprises an aliphatic polyester and a lignophenol. The general recycling method comprises freeze-grinding, heating the obtained ground product at a temperature lower than the T_m of the aliphatic polyester and injection molding the ground product to obtain a biodegradable polymer compact (see also Section 16.2.2: Grinding). Examples of the aliphatic polyesters include PLA, poly(3-hydroxybutyrate) (P3HB), poly(butylene succinate) (PBS), and poly(butylene adipate) (PBA); of those, the commercially available PLA and P3HB are preferred, with PLA being particularly preferred. The use of lignophenol endows the polyester with oxidation resistance, heat resistance, surface hardness, abrasion resistance, weather resistance, and recycling efficiency [14].

16.1.4 Modification of the Chemical Structure

Chemical modification of the chemical structure of the recyclates is another way to effectively upgrade the properties of recycled products. The use of certain compounds such as radical generators, compounds with reactive functional groups, or chain extenders can be effective in inducing branching and/or crosslinking reactions, or increasing the molecular weight of the degraded polymeric chains from waste materials during melt reprocessing (reactive extrusion); this procedure increases the molecular weight of the polymer chains and improves rheological and mechanical properties [1]. Chemical modification has been successfully applied to upgrade degraded biobased aromatic polyesters.

US2011071235 A1 (2011, SABIC INNOVATIVE PLASTICS US LLC) discloses a method of making a biodegradable composition in situ containing an aliphatic-aromatic copolyester from used aromatic polyesters. In one of its embodiments the aromatic polyester is recycled polyethylene terephthalate (PET) or poly(trimethylene terephthalate) (PTT) derived from renewable resources. The biodegradable copolyester can be prepared by: (1) reacting the recycled aromatic polyester with a dihydric alcohol selected from the group consisting of ethylene glycol, propylene glycol, butylene glycol, 1,4-butane diol tetramethyl cyclobutanediol, isosorbide, cyclohexanedimethanol, bioderived alcohols, and hexylene glycol, and an aliphatic dicarboxylic acid of the formula $(CH_2)_m(COOH)_2$, wherein m is 4–10, at a temperature from 160 °C to less than 250 °C in the presence of a transition metal catalyst, e.g., a titanium alkoxide catalyst to form a first mixture; (2) subjecting the first mixture to vacuum distillation at a pressure of less than 2 Torr and a temperature of 220 °C to less than 260 °C, to form a molten aliphatic-aromatic copolyester.

Chain extenders are reactive additives that, when added during melt processing, enhance the mechanical properties of polyesters, such as PET, and polyesters derived from renewable resources such as PLA and P3HB. Chain extenders can be classified according to the polyester functional groups with which they react—either carboxyl- or hydroxyl-end chain extenders; common chain extenders are dianhydrides, bis(oxazolines), bis(hydrooxazine), carbodiimides, diepoxides, and diisocyanates. The chain extension process depends fundamentally on the chain extender concentration and the processing parameters; it is critical to adjust the concentration of chain extender to successfully achieve chain extension and avoid undesired extensive branching and crosslinking reactions.

BASF's Joncryl® ADR chain extenders are reactive polymers that can be used to upgrade the mechanical properties of degraded aliphatic polyesters such as PLA and P3HB. The usage of Joncryl® functional additives typically requires good compounding and feeding techniques to ensure that the additive is evenly dispersed into the polymer matrix and performs its function, be it chain extension or flow enhancement, effectively [15].

16.1.5 Multiple Processing

When polymer materials are subjected to elevated temperatures and pressures as are typically applied in the referenced molding processes, the polymers can be prone to molecular degradation, unwanted polymerization, and unwanted reaction with other materials that may be present in the polymer material. This is particularly true in polymer materials that have been processed once and are processed a second time at elevated temperature, i.e., subjected to a second melting and processing cycle as is typical in reusing scrap or recycled polymer preforms or bottles as the raw polymer material for new preforms and bottles. Such polymer reaction processes can cause the polymer material to acquire undesirable coloring, yellowing, blackening, haze, or other degradation of transparency. These processes may also cause a reduction in melt strength, intrinsic viscosity, or otherwise deleteriously affect their processability or layer compatibility during subsequent molding into a shaped article, or the physical or aesthetic properties of such article during use.

Multiple processing is used to assess the recyclability of polymeric materials and to study the thermomechanical degradation during processing and mechanical recycling. The analysis of the structural and morphological changes induced by consecutive processing steps offers useful information for the optimization of the processing conditions during mechanical recycling to avoid further degradation, for example, the choice of processing conditions and further addition of stabilizers and other additives. Vilaplana and Karlsson [1] reviewed the factors that affect the final properties of reprocessed polymers: condition of incoming waste material (degradation state, presence of impurities, degree of branching, residual presence of additives, constituent copolymers), and reprocessing conditions (temperature profiles, screw type, presence of residual oxygen in the extruder). The structural and macroscopic properties of polymers are therefore modified during multiple processing; chain scission is responsible for a decrease in the molecular weight of the polymeric chains, which leads to an increase in the degree of crystallinity in semicrystalline polymers, a decrease in viscosity, and a modification of the mechanical properties, thus resulting in a progressive embrittlement of the reprocessed material [1]. In the literature several research papers analyzed the effects of multiple processing on the structural, rheological, and mechanical properties of the most common biopolymer, PLA.

The effect of seven injection cycles on the rheological and mechanical properties of PLA on a pilot scale was studied by Pillin et al. [16]. The viscosity of PLA decreased strongly (from 3960 to 713 Pa s) after only one injection cycle, and after four cycles PLA's viscosity became nearly 150 Pa s. Most of the mechanical performances of PLA also rapidly became too weak for an industrial application of the polymer. This decrease could be explained by the strong degradation of PLA during processing, which yields large chain scission evidenced by rheological experiment and molecular weight measurements. Reprocessing of PLA induced an increase of crystallization during cooling with the thermomechanical cycles. This can be explained by higher chain mobility due to chain scission during injection. The addition of stabilizers suppresses this crystallization during cooling. Quinone was found to be an efficient stabilizer to trap free radicals and maintain PLA chain length with time at the processing temperatures. On the basis of these results, it was concluded that the main phenomenon of the degradation of PLA is driven by free radicals and not by hydrolysis due to moisture. The presented results indicate that PLA industrial waste can support moderate recycling, which is a significant improvement of the environmental impacts of this polymer.

The effect of multiple (up to 10 times) extrusion of PLA on its physical and mechanical properties was studied also by Żenkiewicz [17]. By raising the number of the extrusion cycles, the tensile strength slightly diminished and the impact strength clearly decreased, while the melt flow rate (MFI) and water vapor and oxygen transmission rates steadily increased. Variation of the number of extrusion cycles did not affect T_g, whereas it did cause a lowering of the cold crystallization temperature and slight diminishing of the T_m. The presented results indicate that PLA industrial waste is suitable to be reused as an additive to a virgin polymer.

The effect of multiple extrusion and injection on the rheological and mechanical properties of a 50/50 PLA/polystyrene blend (PLA/PS) was studied by Hamad et al. [18]. The viscosity of the blend decreased with increasing the processing cycle number, which was attributed to the reduction of the molecular weights with the processing cycle. The mechanical properties of the blend became worse with increasing the processing cycle number; the tensile strength and elongation at break of the blend decreased sharply after two processing cycles. The least change was observed for Young's modulus (reduction by a factor of 0.26 after four processing cycles). The presented results indicate that PLA/PS waste is suitable to be reused as an additive during compounding the PLA/PS blends or to the raw polymers (PLA, PS).

16.2 PHYSICAL RECYCLING

16.2.1 General

At first, the idea of recycling biopolymers seems odd as most biopolymers are biodegradable themselves. However, there are some good reasons for recycling.

The arguments in favor of recycling are summarized as follows:

- The disposal of biopolymer articles has the disadvantage of discarding valuable raw materials such as poly(hydroxy acids).
- The recycling of biopolymers is crucial in reducing the consumption of renewable resources needed for the synthesis of the corresponding monomers. Waste biopolymer articles may become alternative feedstocks for monomers and synthetic intermediates [19].
- The production and processing of biopolymers require a considerable amount of energy.
- Most commercial biopolymers (e.g., PLA) are not degraded under ordinary conditions even in presence of microorganisms. Large amounts of disposed PLA may create new environmental problems in the future.

The arguments against recycling are summarized as follows:

- Biodegradable biopolymers pose a serious problem when they enter either conventional plastics recycling or green-waste composting streams.
- A growing number of PET recyclers, recycling associations, and officials have expressed concerns over the potential contamination of the PET recycling stream by PLA bottles, yield loss, increased cost for sorting, and impact on recycled PET (RPET) quality and processing.
- A critical mass of biopolymers (of at least 200 million kg produced annually) is necessary for independent rigid packaging recycling to be profitable [20].

Meanwhile, the recycling of biopolymers remains a controversial issue. The debate on recycling biopolymers, specifically PLA, with mainstream PET continues to rage on, and studies on the subject seem to contradict each other. At present, physical (or mechanical) recycling of rigid biopolymers could be handled as a sideline in existing recycling facilities provided the value of the recycled product exceeds incurred costs.

Physical recycling involves reducing the size and/or separating the different polymers from a waste mixture without altering, at least to a large extent, the chemical structure of the recovered polymer(s). The physical methods work with much lower temperatures than the chemical, thermal, or enzymatic methods, so that the structure and especially the molecular chain length of the recycled plastic remain essentially intact. The physical recycling techniques are usually followed by chemical, thermal, or enzymatic depolymerization of the recovered biopolymer.

Within this category, the processing methods applied to the physical recycling of biopolymers so far are discussed in the following sections.

16.2.2 Grinding

One of the techniques of recycle sorting various plastic materials such as plastic bottles and other similar containers is to grind the materials into particulates or flakes of a flake size of about an 1/8″ to perhaps as much as a 1/2″ in width or diameter. Grinding a biodegradable polymer can be carried out according to techniques known to those skilled in the art, as, for example, shearing, impact, dry, or water grinding. Grinding a waste molding formed by a biodegradable polymer composition and remolding the ground polymer gives products with inferior properties. Most of the grinding apparatuses have inherent disadvantages that limit their usability. For instance, large-shaped articles cannot be fed as such in a grinding apparatus, and their size must be reduced before entering the grinding apparatus or they must be made brittle to facilitate the grinding. A suitable way to overcome the above problem is to use freeze-grinding in view of its capability of grinding while suppressing sufficiently the damage incurred on the biodegradable biopolymers. By cooling the shaped article with liquid nitrogen, the material can be made brittle, but it necessitates the use of special equipment that can stand such low temperatures, and also the materials will easily attract water under these conditions. Further, these grinding methods invariably lead to the formation of substantial amounts of fines (<1 mm), which are difficult to feed in polymer processing equipment such as extruders or injection molding machines. These fines should therefore be removed, which necessitates the use of a separate sieving step, and moreover, leads to loss of material. The latter particularly counts when the material is expensive such as the case with biopolymers used in medical applications. Another disadvantage of a conventional grinding apparatus such as a knife mill is the occurrence of heat when large lumps or parts of polymeric materials are ground. The heat evolved can melt or soften materials whose T_m or T_g is relatively low. When grinding such low T_m or low T_g products, the molten or tacky material may impair the functioning of the grinding apparatus. Such heat is further detrimental for those polymers that are heat labile and that can degrade upon heating. Furthermore, it is regularly observed that many knife grinding apparatuses release small metal particles from their knifes when grinding large lumps, particularly when such apparatus are not particularly designed for grinding polymers (2007, **EP1741536** A1, PURAC BIOCHEM BV).

In order to overcome the aforementioned problems, **EP1741536** A1 (2007, PURAC BIOCHEM BV) proposes a method for comminuting a polymeric-shaped article to particles having an average particle size smaller than 6 mm by using a grinding apparatus, characterized in that the shaped article prior to grinding is subjected to a milling step in a milling apparatus to substantially fully convert the shaped article into chips, after which the chips are fed into the grinding apparatus such as a knife mill for further comminuting giving at least 25 wt% less particles having a size less than 1 mm than obtained by the grinding step only. The addition of small, well-defined particles to grinding apparatuses substantially prevents the formation of fines, formation of excessive heat, and occurrence of metal particles, and usually leads to narrow particle distributions. The shaped articles are preferably aliphatic polyesters including PLA, poly(glycolic acid) (PGA), poly(lactic acid-glycolic acid), and poly(ε-caprolactone) (PCL).

CN101275009 A (2008, FUJI XEROX CO LTD; FUJIFILM CORP) discloses in one of its embodiments a method of recycling a polymer compact used mainly as exterior members of a printer, a copying machine, a facsimile, and the like. The polymer composition comprises 21–70 wt% of aliphatic polyester (e.g., PLA), 35–65 wt% of a second polymer having a T_g higher than the T_g of the aliphatic polyester (e.g., polycarbonate) and 1–20 wt% of an aluminium phosphate as flame retardant. The recycling method comprises freeze-grinding, heating the obtained ground product at a temperature lower than the T_m of the aliphatic polyester, and injection molding the ground product to obtain a polymer compact.

Grinding alone or in combination with other physical techniques such as dissolution is used by several methods as a preliminary step in order to facilitate the following depolymerization of the recovered material. For this purpose, **WO2010118954** A1 (2010), **AU2010237249** A1 (2010), and **WO2010118955** A1 (2010) of GALACTIC S.A. use one or more steps for the grinding of PLA or a polymer blend containing PLA, their number depending on the starting product but also on the cost of these operations and the targeted final granulation. The object of this step is to increase the specific surface area of the biodegradable material, so as to obtain a weight/volume ratio between 0.05 and 1.4 t/m^3, which enables to make handling steps easier and speed up the following dissolving step, making the process more easily industrially applicable. Similarly, in **JP2003128900** A (2003), **JP2004216378** A (2004), and **US2005250931** A1 (2005) of MITSUBISHI PLASTICS INC, the use of shredder dust of PLA for the recovery of lactide provides the advantage that the larger surface area of the shredder dust improves the efficiency of recovery (see also Section 16.3.1: Dry-Heat Depolymerization).

16.2.3 Sorting

There are various techniques for identifying and sorting materials by polymer type. Some of these techniques include manual sorting, density separation, electrostatic processes, and various optical systems including optical inspection using photodiodes or CCD machine vision, near infrared (NIR), ultraviolet (UV), X-ray analysis, and fluorescent light or laser radiation.

From the aforementioned techniques manual sorting is tedious, expensive, prone to error, and can be unsafe. X-ray analysis is effective only for separating poly(vinyl chloride) (PVC) from PET and has not been tested for biopolymers. Optical scanning of postconsumer plastics is useful for sorting plastics according to transparency and color but is unable to provide chemical identification of polymers. Furthermore, the optical techniques require use of costly apparatuses, such as video cameras, electronic devices, infrared detectors, and organic “markers” to provide effective segregation of like plastics. However, even sorted plastic waste can present problems in processing as a result of density and chemical differences among polymers falling in the same general class and made by different plastics manufacturers. Further, sorted plastic scrap must be subjected to batch grinding to produce flake scrap material that then must be pelletized and ground again to provide powder feedstock for blow molding, rotational molding, some extruding, spray coating, and other melt processing techniques that require powder feedstock. The high cost of sorting has greatly limited widespread use of recycling approaches that require a sorting step. In particular, collected and sorted postconsumer plastic materials are usually more expensive than the corresponding virgin plastic materials. Thus, users of plastic materials are discouraged from using sorted, recycled plastic materials.

The only area of successful physical recycling involves the sorting of rigid plastic packaging materials and in particular PET and HDPE bottles. The business of bottle recycling is sufficiently profitable since the supply of bottles is large enough and growing steadily, the technology is available to convert used bottles into a number of value-added products, and the products can be sold at a profit [20]. However, although the processes for recycling PET are very effective, they are relatively complex and sensitive. Indeed, it has been demonstrated that the presence of PLA, even at low levels in the region of 1% completely disrupts the process; the residue rate is higher (and the yield is thus not as good), and the quality of the final PET obtained is impaired (2011, **WO2011015433** A1, GALACTIC S.A.).

In the case of biopolymers, the situation is presently unfavored since these polymers have not yet reached a critical mass, the minimum amount of available material that is necessary to support freestanding recycling facilities.

16.2.3.1 Density Separation Systems

The density—also called specific gravity or float-sink—separation systems are usually used to separate components heavier than water from those lighter than water. Density separation of granulated plastics by sink/float in a water bath yields only a float product and a sink product and is not useful for a primary sort of mixed plastics. The density separation technology has been shown to be efficient for the sorting of polyolefins from a waste plastics stream of rigid packaging comprising PET, HDPE, and biopolymers, where HDPE is separated by floating in water, while the biopolymers will sink together with the PET.[1] The further separation of the biopolymers from the PET is not an easy and economically profitable task as both polymers have a density greater than 1 g/cm^3. The use of water presents some issues in that the biopolymers have to be extensively dried prior to recycling in order to prevent a hydrolytic decomposition of the molecular chains during the plasticization or upon melting (see Section 16.2.4: Drying).

The invention concerns a method for selectively separating predetermined materials contained in mixtures of materials, in particular mixtures formed by waste and containing other materials with characteristics similar to said predetermined materials. The method is characterized by the mixtures of materials being subjected, according to a known operation, to at least a process of automatic separation by density, the materials whereof the mass density is within a first range of values being separated from those within a second range of values. Before or while they are being treated, the predetermined materials are enriched with at least an additive providing them with a mass density within the first range of values. Said method enables simple and economical separation, for example, of high value or biodegradable synthetic materials contained in waste mixtures, such that they can be subsequently treated in accordance with prescribed rules or upgraded during removal.

WO0107166 A1 (2001, FRAUNHOFER GES FORSCHUNG) provides a method for the selective separation of thermoplastic polymers from material mixtures, especially mixtures formed from waste materials, by adding additives to a specific polymer to vary its specific gravity from that of the other materials. Materials of the mixture initially have similar specific gravities, and to enable specific materials to be separated from the others by an automatic density difference process additives are added during the processing, which alters the specific gravity range of the specified materials from that of the other materials. The density of the materials is increased by not less than 10% compared to the other materials. The additive is a mineral filler, especially a metal, metallic oxide, or salt, preferably dolomite, calcium carbonate, barium sulfate, or barium ferrite. Preferred thermoplastic polymers to be separated are biodegradable biopolymers (see Table 16.1). The method is used for separating thermoplastics from material mixtures, especially scrap materials from the packaging industry, automobile recycling, or electronic equipment, where the materials have similar specific gravities.

With the density separation system, there is no capability to sort the segregated polymer types into colors as different colors do not change the density of the polymer. Therefore, an end market for the mixed color polymer would have to be used or subsequent equipment would be required to color segregate each polymer type [21].

16.2.3.2 Electrostatic Separation Systems

Electrostatic separation systems are used to separate a mixture of plastics that can acquire different sign charges through triboelectrification. For this to be possible, the materials must not be aggregated—they must be separate

---

[1] Most of the commercial biopolymers have densities greater than 1.0 g/cm^3. The density of solid amorphous PLA is about 1.25 g/cm^3. The density of purely crystalline PLLA is estimated to be 1.37–1.49 g/cm^3 [51]. The densities of PS (1.05 g/cm^3) and PP (0.91 g/cm^3) are well below that of PLA. The density of PET is approximately 1.30–1.38 g/cm^3.

TABLE 16.1 Selective Separation of Biodegradable Polymers from Material Mixtures (2001, WO0107166 A1, FRAUNHOFER GES FORSCHUNG)

		Density (g/cm³) with Dolomite		
Biodegradable Biopolymer	**Density Range, Unfilled (g/cm³)**	**10%**	**20%**	**30%**
PHBHV (Biopol®, Monsanto)	1.25	1.32	1.41	1.50
PCL (Tone™, Union Carbide)	1.15	1.22	1.31	1.40
Poly(ester amide) (PEAM) (BAK®, Bayer)	1.07	1.14	1.22	1.32
PBAT (Ecoflex®, BASF)	1.25–1.27	1.32–1.34	1.41–1.43	1.50–1.52
PLA (Lacea®, Mitsui chemicals)	1.26	1.33	1.42	1.51
PBST (Biomax®, DuPont)	1.35	1.43	1.51	1.60
PES (Bionolle®, Showa HighPolymer)	1.23–1.32	1.30–1.39	1.39–1.48	1.48–1.57
Starch/PCL blend (Mater-Bi®, Novamont)	1.12	1.19	1.27	1.37
CA (Bioceta®, Rhone Poulenc)	1.27–1.32	1.34–1.39	1.43–1.48	1.52–1.57
Nonbiodegradable Polymers				
PE	0.91–0.97	0.98–1.04	1.05–1.12	1.14–1.21
PP	0.90–0.94	0.97–1.01	1.04–1.09	1.13–1.18
PS	1.05–1.08	1.12–1.15	1.20–1.23	1.30–1.33
PA	1.05–1.20	1.12–1.27	1.20–1.36	1.30–1.45
PC	1.20–1.23	1.27–1.30	1.36–1.39	1.45–1.48
PET	1.35–1.40	1.43–1.48	1.51–1.56	1.60–1.65
PVC	1.34–1.43	1.41–1.50	1.50–1.59	1.59–1.68

CA, cellulose acetate; PA, polyamide; PBAT, poly(butylene adipate-*co*-terephthalate); PBST, poly(butylene succinate-*co*-terephthalate); PC, polycarbonate; PCL, poly(ε-caprolactone); PE, polyethylene; PEAM, poly(ester amide); PES, poly(ethylene succinate); PET, poly(ethylene terephthalate); PHBHV, poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate); PLA, poly(lactic acid), polylactide; PP, polypropylene; PS, polystyrene; PVC, poly(vinyl chloride).

discrete particles, and they must be distinct from one another in their triboelectric charging behavior (or contact charging due to friction of the particles with one another). Using triboelectric charging capacity as the separation criterion, it is possible to separate even materials whose conductivities are virtually identical. Triboelectric charging can be carried out in mixers, fluidized bed dryers, or pneumatic conveying systems. The selectivity and intensity of the charge can be increased considerably by adjusting climatic conditions, such as temperature and moisture content, and by adding conditioning agents. Such particles can be so highly positively or negatively charged that in free fall through a high voltage electrical field, they can be deflected toward the appropriate counter electrode and thus separated from one another. Since triboelectric charging depends not only on the chemical constitution of the particles to be separated but also on their surface condition, the particles must be clean and dry. Different plastics additives such as pigments, flame retardants, plasticizers, etc. influence the charging characteristics. It is therefore necessary to adjust conditions to achieve the selective charging that is desired by adjusting climatic conditions or choosing a specific conditioning agent.

Hamos GmbH Recycling-und Separationstechnik, a manufacturer of electrostatic separation equipment, owns a series of patent applications for the dry electrostatic separation of metal/nonmetal and plastic/plastic-mixtures: **DE19522147** A1 (1997); **WO9828080** A1 (1998); **DE19740027** A1 (1999); **DE19739992** A1 (1999); **DE19829200** A1 (2000); **DE19901743** A1 (2000).

The most common plastics (PCV, PET, PE, PS, PA, PC, PMMA) can be electrostatically sorted from each other. As the material separation takes place in absolutely dry conditions, auxiliary equipment to handle separation liquids or conditioners are not necessary. Hamos dry plastic/plastic separators are supplied as single or double stage with throughput capacities ranging from 200 to 750 kg/h depending on the materials to be separated.

The Hamos electrostatic separation technology was tested by the Waste & Resources Action Program (WRAP) to separate mixed polymer flake. This was tested for PVC removal from PET and also PP from HDPE flake. The level of separation was not acceptable for either of the trials. This technology is primarily used as a clean-up function for removing PVC from PET flake, and the level of contamination within the trial material provided was deemed too high to be considered successful [21].

The electrostatic separation has been adapted to effectively identify and sort PLA before forwarding it to material recycling [22]. However, no reports or published experimental results are available.

The material mixture or preseparated components of the mixture of the method described by **WO0107166** A1 (2001) in Section 16.2.3.1: Density Separation Systems may additionally be subjected to a magnetic separation method by adding ferromagnetic additives (e.g., iron powder) before or during the processing stage.

16.2.3.3 Optical Systems

The optical sorting of plastics is conventionally done in a conveyor operation wherein the materials to be sorted, whether bottles or flake materials, are moved along via the conveyor or similar moving carrier to be irradiated by an electromagnetic energy source, such as at near infrared, and the electromagnetic energy passing through the various irradiated articles is detected by one or more detectors, and according to a preselected scheme of determination and evaluation of relative levels of transmitted or reflected electromagnetic energy, various of the passing articles or materials are ejected from the stream (2001, **US2001045518** A1, SOMMER E J; NATIONAL RECOVERY TECHNOLOGIES INC).

16.2.3.3.1 Near Infrared

A popular technology for sorting whole rigid plastics is based on cameras operating in the infrared radiation or visible parts of the electromagnetic spectrum to achieve polymer or color sorting. This type of unit is widely used in the UK for plastic bottle separation, and in Europe for sorting both bottles and other packaging plastics. NIR systems can effectively remove PLA and carton board from a mixed packaging stream.

NIR has many advantages. The most significant advantage is the speed of identification. Because of the great scanning speed of the spectroscopic instrument, many readings of one sample can be taken in short periods of time. This allows multiple checks to ensure proper identification. The speed also provides for increased volume of plastics sorted in smaller amounts of time. A second advantage is the lack of specimen preparation. Labels, or other obstructions like dirt, do not interfere with readings. Another advantage of this system is that color does not interfere with proper polymer identification. Except for black, the readings are independent of the color of the polymer [23]. Black is a strong absorber in the NIR region, and scanning of black plastics results in a featureless spectrum.

An apparatus that uses infrared spectroscopy and Fourier transform infrared (FTIR) to take an infrared reflection spectrum of the surface of a plastic component in mid-IR (MIR) region in a wave length region between 400 and 4000/cm and correlate it to a set of plastic materials is claimed to be able to identify black-colored plastics (1995, **GB2284477**, BRUKER ANALYTISCHE MESSTECHNIK GmbH).

A key weakness of the NIR sorting technologies is when an item contains more than one material or plastic type, e.g., label, the identification sensor may not recognize the item, or identify it based on identification of the minority material. Further misidentification can occur through placement of one item inside another or two items being stuck together—usually through compaction or baling.

NIR spectroscopy (700–2500 nm) has been applied for the identification and separation of PLA from a mixed-waste plastic stream composed mainly of PET and a minor amount of PLA. NatureWorks surveyed equipment manufacturers that had the potential to sort biopolymers from other polymers like PET, HDPE, and PVC using infrared, ultraviolet, X-ray, color identification, and laser sorting. NatureWorks identified a dozen companies and then worked closely with three of them to find out how accurate the sorting systems are (NatureWorks LLC, Using Near-Infrared Sorting to Recycle PLA Bottles) [24]. Titech's [25] NIR sorting systems removed PLA (Ingeo™) from a PET sorting stream at an accuracy of 97.5%, about as effective as removing contaminates and other items unwanted in the PET stream. MSS [26] also used an NIR system on Ingeo™, finding that the PLA emits a unique polymeric signature that the system can be programmed to identify and remove. According to NatureWorks, NIR has the most promising prospects for automated sorting of PLA from a PET recycling stream. A report published by WRAP confirmed the above findings stating that "NIR systems can effectively remove PLA and carton board from a mixed packaging stream [27]. NatureWorks attempted to establish also the level of PLA contamination that PET and HDPE could handle. The results of these studies indicated that PLA will affect the haze and color of PET, above 0.1% concentration, thus limiting its end-use markets; PLA has no effect on the color or melt index of HDPE flake at up to 2% concentration.

NatureWorks' assertions were contested by various recycling associations such as the National Association for PET Container Resources (NAPCOR) [28], the Association of Postconsumer Plastic Recyclers (APR) [29], and the Industry Council for Packaging and the Environment (INCPEN) [30], which expressed concerns that the accuracy level of the NIR systems is not high enough to remove PLA and prevent contamination problems, while too much PET could be falsely rejected along with the PLA. In addition, the cost of an NIR system could be forbidding.

Other key issues to be addressed by the NIR specialists are identification of PLA in blends, coated articles, multilayers, containers placed inside other containers, or two items being stuck together, and black moldings.

No patents dedicated to NIR sorting of biopolymers have been retrieved so far.

16.2.3.3.2 Laser

This technique offers fast (less than a microsecond) identification of plastics based on atomic emission spectroscopy in which a laser is used to release excited ions and atoms from the material surface, which can then be identified through spectral analysis to provide the elemental composition of the material (including polymer type and additives present). Commercially, laser sorting systems are available from companies such as Unisensor GmbH and Visys NV. Unisensor uses laser Raman fluorescence spectroscopy and Visys NV systems utilize the reflection of laser light to perform detection.

Unisensor GmbH (http://www.unisensor.de/) developed a flake sorting technology through laser spectroscopy named Powersort 200®, using ultra-high-speed laser spectroscopy. **DE19816881** A1 (1999) and **WO0070331** A1 (2000) of KRIEG G describe a process wherein powerful lasers expose granulate or plastics crushed into flakes to ultraviolet, visible, and infrared light (Figure 16.3). The light excites molecules in the plastic, which disperse the light. The wavelengths in the scattered light are a characteristic, physical fingerprint of the material. Sensors that capture the light and analyze it instantaneously are able to differentiate PET reliably from other polymers, color residues, and impurities such as paper or glue residues. The process even works on minute particles. Supersonic air jets remove the unwanted substances.

A laser (4) beam is guided over the measuring material (3) in a linear manner using an optical system (2). The laser beam (4) scans the entire angular range (5) for detecting the entire width of the conveyor belt (6), which is supplied with granulate material (3) via a silo (7) or with tablets or other test material via a feed device (not shown in detail). Illumination of test samples (3) is effected point by point (9) through cycling of the laser light. Linear scanning is also feasible through use of a continuously radiating laser (1). The secondary light (10) generated through scattering, fluorescence, Raman laser radiation, reflection, and other optical reemission effects is detected by the optical system (2) in a wide angular region and supplied to a spectrometer (11) whose signals are processed by an evaluation unit (12). Following classification of the test samples (3) into individual color classes, separate material classes, and contaminants, they are sorted via a conventional separation system (e.g., via cycled nozzles) into different separate portions (13), which can be transported in this form to another production process or, if contaminated, to a disposal system (1999, **DE19816881** A1; 2000, **WO0070331** A1, KRIEG G).

According to NatureWorks, Unisensor's laser technology is capable of sorting PLA (Ingeo™) flakes from desired PET flakes at efficiencies as high as 96–99%. This

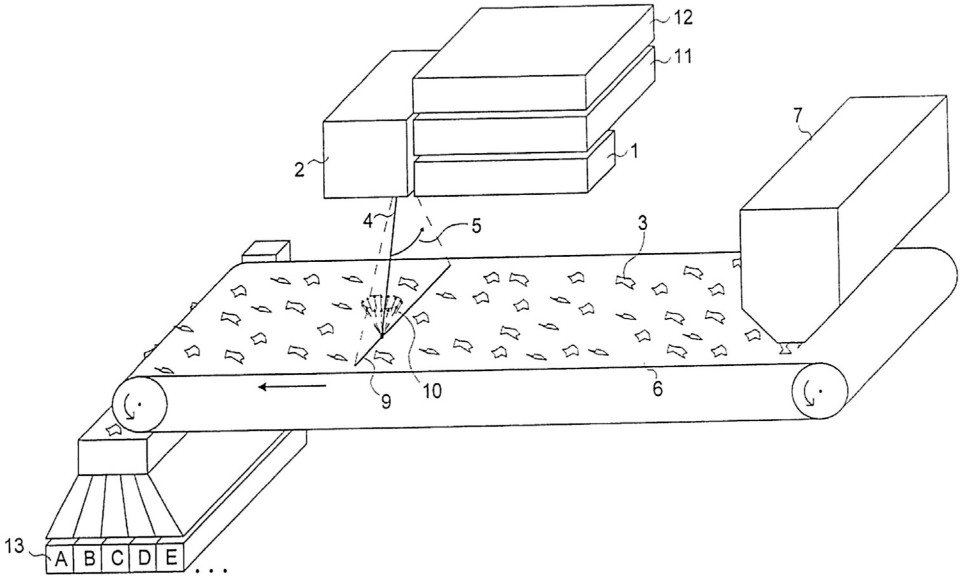


FIGURE 16.3 Basic construction of the overall system for online detection and sorting of contaminated granulates or tablets of different colors and different base materials (1999, **DE19816881** A1; 2000 **WO0070331** A1, KRIEG G).

is consistent with other plastics considered contaminants in the PET flake sorting technology. This technology allows more or less sensitivity to be adjusted for specific materials, depending on the incoming stream composition changes. According to WRAP [31] the system can sort black flakes but is not designed to handle whole packaging items such as black pots, tubs, or trays [21].

16.2.3.3.3 Marker Systems

16.2.3.3.3.1 Resin Identification Codes Most of the current plastic sorting is done manually by hand. Manual sorting is a simple process that needs very little technology, but it leaves much room for improvement. Manual sorting is a very labor intensive, costly, and an inefficient method for sorting plastics. One problem with efficiency is that the labor force involved in manual sorting has a high turnover rate. This high turnover rate creates an improperly trained or inexperienced workforce. In addition, it is difficult to differentiate between the polymer types used in packages through the visual means employed by manual sorting [32]. For this reason, the Society of the Plastics Industry (SPI) introduced the Resin Identification Code (RIC) system in 1988, a voluntary labeling system to allow consumers and recyclers to differentiate different types of plastics while providing manufacturers a consistent uniform coding system. The overwhelming majority of plastic packaging is made with one of six resins: poly(ethylene terephthalate) (PETE or PET), high density polyethylene (HDPE), PVC (or V), low density polyethylene (LDPE), polypropylene (PP) and polystyrene (PS). The RIC assigns each of these resins a number from 1 to 6, which is encircled by the recycle logo, a triangle of arrows (see Figure 16.4). The RICs are used solely to identify the plastic resin used in a manufactured article, mainly containers and bottles, and are located on the bottom of plastic moldings [33].

The RIC system includes a seventh code, identified as “7-OTHER” (Figure 16.5), which applies to a number of rather new plastics, including biopolymers, and it has limited practical value.[2]

The recycling industry has established a recycling code numbered 1–7 for plastic materials. The higher the number, the more difficult the material is to profitably deploy into useful post consumer applications other than by burning it for energy recovery or for disposal in landfills, which can create environmental problems. Polyesters, specifically PET, are afforded the no. 1 recycling code characterization as the most readily recycled plastic manufactured as a commodity. PET is the primary material used by the beverage bottle industry. PET bottles are relatively easily collected, separated, and recycled into a multitude of postconsumer applications such as fiber, carpeting, bottle, and strapping applications. The no. 2 recycling plastic is high density polyethylene (HDPE) used for manufacturing milk containers as well as for various other packaging applications. Currently, only 20–25% of all plastics manufactured are recycled into useful postconsumer products. Most plastics are landfilled, aggravating environmental problems.

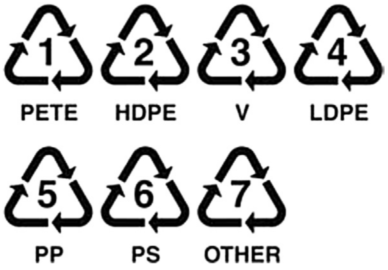


FIGURE 16.4 Resin identification codes (RIC).

The code is molded, formed, or imprinted on all containers that are large enough to accept the 1/2″ minimum-size symbol. The code is placed in an inconspicuous location on the manufactured article, such as the bottom or back, and is usually accompanied by the abbreviation symbol of the plastic.

Coding enables individuals to perform sorting before recycling, ensuring that the recycled plastic is as homogenous as possible to meet the needs of the end markets. Another potential benefit of coding is that it may facilitate the recovery of plastics not currently collected for recycling.

In 2008, SPI began work with ASTM International, a globally recognized leader in the development and delivery of international voluntary consensus standards, to develop a new standard that would expand the current RIC system. In 2010, ASTM International issued ASTM D7611—Standard Practice for Coding Plastic Manufactured Articles for Resin Identification. Other modifications to the RIC are currently being discussed and developed by ASTM’s D20.95 subcommittee on recycled plastics.

16.2.3.3.3.2 Fluorescent Additives

Alternative methods entail marking either the plastic article or the resin itself with a dye that is readily detectable. In particular, fluorescent dyes have been used for the identification and separation of plastic waste. The dye in the plastic to be sorted is excited by an irradiation source producing scattered emitted light that is intercepted by a detector and recorded. This signal is used for triggering off the classifying operation. In the case of small, granulated particles, this can involve electrostatic charging and deflection in an electric field or, in the case of larger particles, a simple process of mechanical separation. The fluorescent dyes must have high detection sensitivity, wide-ranging use fastness properties, be used in minute quantities, and be nontoxic.

---

[2] In 2007, a California State Senate bill (SB 898) proposed the marking of PLA with a new “0” code. However, this part of the bill was removed before passage (source: Wikipedia, http://en.m.wikipedia.org/wiki/Polylactide; retrieved March 21, 2012).

FIGURE 16.5 Resin identification code of biopolymers.

DE4029167 A1 (1992, BAYER AG) and **DE19530449** A1 (1997, BAYER AG) disclose a method for the identification of plastics in which a small amount of a fluorescent dye is added to the plastic during or after its manufacture. In principle, a plastic treated in this way can be irradiated with UV light and can be identified again by examining the fluorescent radiation. Suitable fluorescent dyes for a broad range of plastics, including biopolymers, comprise coumarins, perylene dyes, benzanthrones, anthrapyrimidines, and anthrapyridones; particularly preferred are complexes of rare earth metals, such as europium (Eu) or terbium (Tb) polymeric complexes that are distinguished by sharply defined red and green fluorescence emission bands, respectively, and can be identified by irradiation with a normal lamp. A further advantage of these substances is that they display considerably longer-lasting fluorescence than customary organic fluorescent dyes and therefore produce a signal that can easily be differentiated from the fluorescent emissions of other substances that may possibly be present. One difficulty with this type of identification is that the amount of suitable fluorescent dyes is limited. Moreover, in order to be able to separate different plastics labeled with different fluorescent dyes, it must be ensured that the fluorescence spectra are sufficiently clearly different from each other.

EP566948 A1 (1993, BAYER AG) relates to a method for the identification of different plastics that is characterized by providing each plastic with a plurality of fluorescent dyes that differ in terms of their emission frequencies and/or the duration of their fluorescence so that a fluorescence pattern, which is distinguished by the duration of the fluorescence and/or by the frequencies occurring, can be unambiguously assigned to each plastic; e.g., if two materials with a green fluorescence and two materials with a red fluorescence are available, as provided above, 15 different combinations can be formed therefrom, i.e., 15 different plastics can be labeled using only these four marker materials so that they can be unambiguously reidentified.

DE4231477 A1 (1994, HAN KYUNG TAE; KOELLNER M; SAUER M; SEEGER S; WOLFRUM J; SCHMITT C; SCHULZ A) discloses a method for the sorting and separation of plastic waste into its different types by marking the plastics with multiplex[3] fluorescence dyes—added during the course of their production—and measuring their fluorescence wavelength and specific fluorescence lifetime. The multiplex fluorescence dyes have the same absorption and emission wavelengths with differing quantum yields and fluorescence lifetimes. Furthermore, the addition of small quantities makes necessary the use of fluorescent dyes with high extinction coefficient at the excitation wavelength, good photostability, and reasonable quantum yields. Suitable multiplex fluorescence dyes are selected from coumarin, flavine, fluorescein, carbocyanine, phenoxazone, carbazine, oxazine, and rhodamine, formed from dyes that absorb and fluoresce in the far UV visible and/or the near IR regions (600–1000 nm). The process is rapid, requires small quantities of dye additive, and by a combined measurement of fluorescence wavelength and lifetime allows differentiation of a greater number of marked plastic types than prior art.

WO9309172 A1 (1995, EASTMAN KODAK CO) discloses the use of NIR fluorescing compounds or copolymerized residues for the identification, sorting, and recycling of thermoplastic containers made when exposed to electromagnetic radiation having a wavelength of about 670–2500 nm. The preferred NIR fluorescent compounds are selected from the classes of phthalocyanines, naphthalocyanines, and squaraines (derivatives of squaric acid).

The above plastic fluorescence identification methods do not refer necessarily to biodegradable polymers.

The following patents propose the use of florescent dyes for the identification and separation of biodegradable polymers from nonbiodegradable polymers in a recycling process.

JPH06297458 A (1994, MITSUI TOATSU CHEMICALS) discloses a method for separating biodegradable polymers from nonbiodegradable polymers by printing optically readable barcode patterns using fluorescent ink on biodegradable polymer moldings. The fluorescent substance is preferably a fluorescent whitening dye having 300–400 nm maximum absorption wavelength. In **JPH06240045** A (1994, MITSUI TOATSU CHEM INC) the same fluorescent whitening dye is added to a biodegradable polymer composition to enable differentiation of the composition from a nondegradable polymer composition.

JPH06315935 A (1994, MITSUI TOATSU CHEMICALS) discloses a method for separating packaging materials (films, bottles, and housings of electric appliances) made of biodegradable polymers, such as PLA, from nonbiodegradable polymer articles by using visual discriminative marks printed on the molded products made of biodegradable polymers. The mark is printed with a green biodegradable polymeric ink. The marked biodegradable polymer can be separated from the plastics waste at the time of recovery.

JPH06240004 A (1994, MITSUI TOATSU CHEM INC) discloses a method for separating a biodegradable polymer composition from a plastic waste by coloring the biodegradable polymer, such as PLA, during processing

---

[3] Multiplex detection refers to the process of simultaneously labeling a specimen with two or more fluorescent probes to allow correlation of multiple structural or functional features.

with an edible dye (e.g., C.I. disperse blue) to distinguish it from nondegradable polymers in appearance. The edible dye is used for food wrapping purposes.

DE19848873 A1 (2000, BASF AG) discloses a method for labeling a biodegradable polymer (e.g., an aliphatic polyester) by mixing the polymer with at least one fluorescent dye in an amount such that the prepared composition shows a strong fluorescence that can be detected by a detector when the composition is subjected to electromagnetic radiation. The fluorescence labeling facilitates sorting in a compost mill of the biodegradable polymer from the unlabeled nonbiodegradable polymer that is removed from the compost mill. Fluorescent dyes that absorb in the NIR, visible, or UV range of the electromagnetic spectrum can be used. Particularly preferred fluorescent dyes are optical brighteners, which absorb in the range 400–470 nm, are free of ionic groups, and are obtained from the class of bisstyrylbenzene, stilbene, benzoxazole, cumarin, or pyrene compounds, for example, a cyanostyryl compound.

16.2.3.4 Dissolution

Dissolution combined with separation such as filtration, precipitation, etc. is used to dissolve the biopolymer and simultaneously separate solid polymers and undissolved impurities from the polymer mixture. The dissolution uses either a single solvent at multiple temperatures or combinations of solvents. The use of organic solvents is discouraged since the need to control emissions and to recover the solvents increase the costs of such systems. There is also concern about residual solvent in the recovered polymer and its tendency to leach into products. For instance, various solvents are known to dissolve PLA such as benzene, toluene, isopropyl ether, dichloromethane, chloroform, chlorobenzene, and the like. Even though these solvents are very well able to dissolve PLA, they are nevertheless not recommended in view of the environmental concerns.

JP2004308077 A (2004), **JP2005132901** A (2005), **JP2005131856** A (2005), and **JP2007031538** A (2007) of TEIJIN FIBERS LTD disclose related methods for removing different material(s) contained in a recovered aliphatic polyester such as PLA without reducing the recovery yield of the aliphatic polyester. The recovered aliphatic polyester containing polyethylene (PE) and polypropylene (PP) and/or PVC or PET is dissolved in a dissolving solvent to obtain an aliphatic polyester solution having viscosity of 0.0001–0.1 Pa s (0.1–100 cP), and the different material of which the specific gravity is lower than that of the solution is floated to the vicinity of the surface of the aliphatic polyester solution and separated (see also Section 16.3.2: Hydrolysis/Solvolysis (Alcoholysis)).

WO2010118954 A1 (2010), **AU2010237249** A1 (2010), **WO2010118955** A1 (2010), **WO2011029648** A1 (2010), and **WO2011015433** A1 (2011) of GALACTIC S.A. use a dissolution step for separating PLA from a polymer blend by dissolving PLA in a lactic acid ester. Suitable lactic acid esters include methyl lactate, ethyl lactate, isopropyl lactate, butyl lactate, hexyl lactate, and more generally a lactic acid alkyl ester, the alkyl radical of which has 1–12 carbon atoms. The dissolution of PLA in lactic ester can be carried out at higher temperatures, ranging up to the T_m of PLA, than those reached during the solubilization in the alcohol of which this ester is derived. Indeed, the boiling temperature of the ester is generally higher than that of the alcohol, which enables dissolving more PLA. Regarding the boiling point of the recommended lactic acid esters, it is possible to eliminate water present in PLA by carrying the dissolution at a temperature of more than 100 °C and at atmospheric pressure. In the case of a PLA flow contamination by another polymer (PET, PE, PVC, PP, or any other common polymers), it is possible to remove the latter through filtration if necessary while hot or any other means known to those skilled in the art. Moreover, the dissolution process is fast enough and carried out quite rapidly.

The above set of patents of GALACTIC S.A. disclose methods for purifying a conventional polymer stream (PE, PP, PET, PVC, etc.) contaminated with a maximum of 50% PLA by suspending the polymer blend in lactic ester able to dissolve PLA. The method includes the following steps:

1. grinding the polymer blend until a weight/volume ratio between about 0.05 and about 1.4 t/m^3 is obtained;
2. suspending the polymer blend in lactic ester, in a weight ratio of the polymer to the lactic ester of 0.1–1, to dissolve PLA;
3. recovering undissolved polymers for separate and subsequent processing by filtration or any other means enabling solid/liquid separation;
4. recovering the PLA solution with a weight ratio PLA/solvent between 0.5 and about 3.

The dissolving can be carried out without prior grinding if the form of PLA (weight/volume ratio) permits it. Indeed, one of the problems of processing this type of flow is the difference in specific weight of the different reprocessed materials even after the grinding step. The suspension step (2) is preferably carried out at a temperature of 50 °C and T_m of the polymer mixture or at a temperature of 50 °C, and the boiling temperature of the lactic ester, and under a pressure of 0.05–20 bar, preferably 1–5 bar.

The PLA solution from step 4 may, for example, be subjected to catalytic hydrolysis or alcoholysis to produce a lactic ester from PLA; see Section 16.3.2: Hydrolysis/Solvolysis (Alcoholysis). The alcohol used for this transesterification depolymerization method will preferentially be that corresponding to the lactic ester used for purifying the polymer stream. The lactic ester does not block its depolymerization and, in addition, does not impose further purification steps. The proposed methods are useful for purifying the polymer, which is derived from fossil fuel resources, and are useful in the packaging field, e.g., rigid trays for fresh produce, packaging films for salad, bottles, and disposable utensils (plates, cups, and cutlery). A disadvantage of these methods is that the solvent must be removed, and the depolymerization time is very long (2013, **EP2559725** A, UHDE INVENTA FISCHER GMBH).

Some of the alternatives to organic solvents include the use of supercritical fluids. A supercritical fluid is a dense gas that is maintained above its critical temperature (the temperature above which it cannot be liquified by any pressure). Such fluids are less viscous and diffuse more readily than liquids. Examples of supercritical fluids are carbon dioxide and certain alkanes such as methane, ethane, and propane. Especially, the carbon dioxide is nontoxic, nonflammable, chemically inert, completely recoverable, abundant, and inexpensive. At room temperature and above its vapor pressure, carbon dioxide exists as a liquid with a density comparable to organic solvents but with excellent wetting properties and a very low viscosity. Above its critical temperature and pressure (31 °C and 7.4 MPa), carbon dioxide is in the supercritical state ($scCO_2$) and has gas-like viscosities and liquid-like densities. Small changes in temperature or pressure cause dramatic changes in the density, viscosity, and dielectric properties of $scCO_2$, making it an unusually tunable, versatile, and selective solvent.

WO2008045516 A1 (2008, QLT USA INC) provides methods of extracting a biodegradable polyester with a supercritical fluid effective to obtain a purified biodegradable polyester, such as a purified PLGA. The supercritical fluid can be carbon dioxide at an elevated pressure or can be carbon dioxide with one or more cosolvents. Methods for carrying out stepwise purification of the biodegradable polyester at multiple pressures or multiple temperatures, or both, are also provided. When the polyester is PLGA, a purified PLGA copolymer is obtained having a narrow molecular weight distribution with respect to the unpurified polyester. The purified PLGA copolymer can have a polydispersity index of less than about 1.7, less than about 2% monomers, and less than about 10% oligomers. The purified PLGA copolymer can exhibit a reduced initial burst effect when incorporated into a controlled release formulation such as a flowable implant adapted to be injected into body tissues.

16.2.4 Drying

In the recycling of aliphatic polyesters it is important that the material being recycled is as dry as possible, in order to prevent a hydrolytic decomposition of the molecular chains during the plasticization or upon melting. However, PLA is hygroscopic, which makes an efficient drying difficult. Furthermore, the presence of water during melt recycling creates bubbling in the recyclate due to the generation of steam.

Another issue encountered during drying is the stickiness of many biopolymers at high temperatures. The low T_g[4] at which the PLA material becomes sticky, and a relatively long crystallization time, make it hard to crystallize and/or dry amorphous production wastes, especially residues of deep-drawn films, with conventional crystallization systems and drying systems. Such conventional drying systems, known from the prior art, are dry air dryers, which operate at an air flow of around 1.85 m^3/h and kg of granulate. For example, noncrystalline PLA is dried at 45 °C, for c. 4 h, at a dew point of −40 °C, and crystallized PLA at 90 °C, for c. 2 h, at a dew point of −40 °C.

Due to the rather low drying temperatures, especially when processing noncrystallized material, the drying time is relatively long and an extremely precise temperature management is necessary. This is extremely difficult, if not impossible, for granulates and especially for all other forms, such as flakes, films, fleece, etc. For this reason, one can try to achieve a crystallization of the plastic prior to drying. Such crystallization can be achieved, for example, by moving or mechanically manipulating the particles uniformly at a temperature lower than the drying temperature, in any case at a temperature lower than the melting or plasticization temperature. The movement is advantageous for preventing a sticking together of the individual particles (2003, **WO2008058303** A1, EREMA).

WO2008058303 A1 (2003, EREMA) provides a method with which biopolymers being recycled, especially PLA, can be dried and possibly crystallized in one step at the same time, regardless of their kind, form, and composition (see also Section 16.1.1: Recuperation). The biopolymer material to be treated is heated in at least one receptacle or reactor while undergoing constant mixing or movement and/or comminuting at a temperature below the T_m of the polymer, and as a result is at the same time crystallized, dried, and/or purified, wherein at least one rotatable comminuting or mixing tool, with working edges that act on the material with a comminuting and/or mixing effect, is used for the mixing and/or heating of the biopolymer, the heating taking place in particular by applying mechanical energy.

16.3 CHEMICAL RECYCLING

From the view point of effective use of carbon resources, the ideal is that discarded products are finally restored to the raw materials by chemical recycling processes. The chemical recycling of biopolymers involves the recovery of monomers and or oligomers by depolymerization reactions

---

[4] The glass transition temperature (T_g) of PLA lies between 55 °C and 60 °C, the crystallization temperature between 100 °C and 120 °C and the melting temperature between 165 °C and 185 °C.

and includes thermal, chemical, and enzymatic processes. Chemical recycling of biopolymers is aimed mainly at saving the material resources and reusing the recovered monomers for producing new polymers and less at reducing the amount of wastes generated by slowly degrading biopolymers.

16.3.1 Dry-Heat Depolymerization (in the Melt)

Dry-heat depolymerization involves depolymerization of an aliphatic polyester, such as PLA, to its cyclic dimer or lactide at elevated temperatures, e.g., higher than the T_m.

The depolymerization of PLA by heating and reduced pressure to its cyclic dimer is an old and much studied process [10,11]. The depolymerization processes of the prior art, wherein an oligomeric or higher polymeric PLA is heated at elevated temperatures in the presence or absence of a catalyst, suffer in that depolymerization to cyclic ester tends to be slow, attributable to the difficulty of getting heat (thermal energy) rapidly and uniformly distributed throughout the PLA [34]. Side reactions occur, attributable at least in part to the formation of localized hot spots within the depolymerization mass, including decomposition of the polymer to charred and tarry products and resulting in difficult-to-handle reactor heels. The heat distribution problem is more severe with solid/higher molecular weight polymers than with liquid/lower molecular weight polymers as they tend to form more viscous melts (1994, **US5342969** A, DU PONT). The dry-heat depolymerization of PLA causes the racemization of the lactic acid ester structural unit above the T_m of PLA regardless of the molecular weight. In particular, when the temperature exceeds 320 °C, racemization of the lactic acid ester structural unit in PLA or derivative thereof proceeds readily; as a result, formation of *meso*-lactide is promoted, and the optical purity of the lactide thus obtained is degraded. On the other hand, hardly any thermal decomposition of a PLA or derivative thereof takes place at a temperature that is equal to or less than the T_m of PLA or derivative thereof.

One way to increase the depolymerization rate of high-molecular-weight PLA is by increasing the concentration of oligomers in PLA. One such method for the depolymerization of waste PLA or PGA to its corresponding dimeric cyclic ester is disclosed in **US5342969** A (1994, DU PONT). The method comprises the steps of: (1) depolymerizing PLA to its corresponding dimeric cyclic ester by heating PLA in a reaction zone at a temperature and pressure at which PLA is molten; (2) forming a vapor product stream containing the dimeric cyclic ester; (3) removing the vapor product stream from the reaction zone; and (4) recovering the dimeric cyclic ester from the product stream; the improvement comprises adding dimeric cyclic ester to step (1) in a ratio of 0.01–0.5 pbw of dimeric cyclic ester per 1 pbw of PLA. The liquid cyclic ester added in step (1) reduces the T_m and the viscosity of PLA (preferably 10–30% of the initial value) and aids distribution of catalyst and thermal energy rapidly and uniformly through the mass. Unrecovered oligomer can be recycled. The method is claimed to provide smoother and faster melting of the polymer and more rapid depolymerization than previous methods. The cyclic esters are produced in high yield, and side reactions are minimized.

In the same patent application is disclosed an alternative way to increase the depolymerization rate of high-molecular-weight PLA by adding a catalyst in combination with high temperature. Suitable catalysts for promoting the thermolysis of the polymer to cyclic esters are generally metals or compounds of metals of Group IV, Group V, and Group VIII of the Periodic Table. Preferred are metals of Group IV, notably Sn as the metal (powdered), oxide, halogenide, or carboxylate; or Group V, notably Sb, usually as the oxide Sb_2O_3. Preferred herein are Sn (II) carboxylates, especially those that are soluble in the molten polymer exemplified by stannous bis(2-ethylhexanoate), commonly referred to as stannous octoate. The catalyst is employed in catalytically effective amounts, which can vary widely depending upon the particular feed material employed and the reaction conditions. For example, with stannous octoate as the catalyst, the quantity of catalyst will generally be such that the reaction mass contains from about 0.01 wt% to 5 wt%, usually 0.3–3 wt%, and for best results, at least about 1%. High catalyst loadings are desirable because polymer residence time decreases with increase in the initial catalyst concentration, thereby improving the cyclic ester production rate.

DE19637404 A1 (1997, SHIMADZU CORP; TOYOTA MOTOR CO LTD) discloses a method for the recovery of lactide from PLA, comprising the steps of: (1) heat treating a high-molecular-weight PLA to a temperature equal to or higher than its T_m (170–300 °C) in the presence of a catalyst comprising one or more metals selected from elements of Group IA, Group IVA, Group IVB, and Group VA of the Periodic Table, or compounds thereof; and (2) reducing the pressure to equal to or less than the vapor pressure of lactide (<200 mmHg) at said temperature, to thereby distill and recover the produced lactide.

All the above catalysts are conventionally used in the polymerization to give PLA. Among them, catalysts of group IVA, especially catalysts comprising tin or a compound thereof, are preferably used in terms of catalyst activity. The catalyst is preferably used in an amount of 0.05–15 wt%, preferably 3–7 wt% of PLA. A disadvantage of this method is the high amount of used catalyst and the high temperature (up to 300 °C). The method uses trimmings that remain after the molding is cut to a fixed length as a starting material.

The thermal decomposition temperature of PLA depends greatly on the level of trace amounts remaining of a polymerization initiator, e.g., tin compounds [10]. When the tin content is 169 ppm or greater, the decomposition temperature of PLA is very low, and lactide having high optical purity is selectively formed as a decomposition product. On the other hand, when the tin content is 60 ppm or less, the decomposition temperature of PLA becomes high, the optical purity of the decomposition product is degraded, and contamination with oligomer becomes noticeable. Such a function of tin is effective in chemical recycling, but since decomposition easily occurs during melt molding of PLA, in general as much as possible of the residual tin compound is extracted prior to melt molding. This is one cause of the high cost of PLA (2007, **WO2005105775** A1, 2007, KYUSHU INST OF TECHNOLOGY; KITAKYUSHU FOUNDATION; KINKI UNI).

WO03091238 A1 (2003, NISHIDA H; FAN Y; SHIRAI Y) discloses a catalyst and depolymerization conditions for efficiently converting waste poly(L-lactic acid) (PLLA) into a lactide having a high optical purity. The method is characterized by adding a compound of an alkaline earth metal to PLLA and heating the mixture to 320 °C or lower.

WO2005105775 A1 and its family member **EP1741707** A1 (2007, KYUSHU INST OF TECHNOLOGY; KITAKYUSHU FOUNDATION; KINKI UNI) disclose a method for efficiently recovering lactide of high optical purity by thermally decomposing a mixture of a PLLA or derivative thereof and aluminum hydroxide at a temperature in the range from at least the T_m of PLLA or derivative thereof to no greater than 320 °C, and preferably 200–300 °C. In general, the lower the molecular weight of a polymer, the lower the temperature range in which decomposition proceeds. In addition to the above components, the mixture may contain a polymer such as polystyrene, a reinforcing fiber, a filler, an additive, etc. The amount of this polymer added may be selected as appropriate according to physical properties required for the product, but in general, it is 200 pbw or less relative to 100 pbw of PLLA or derivative thereof, preferably 100 pbw or less, and more preferably 50 pbw or less. The polymer is normally melted during the chemical recycling of PLLA or derivative thereof and subjected to material recycling by repelletizing.

When aluminum hydroxide is added to PLLA, in the case where the PLLA contains a large amount of residual tin compound, the thermal decomposition temperature tends to increase in response to an increase in the amount of aluminum hydroxide added (contributing to stability during melt molding). On the other hand, in the case of a purified PLLA from which most of the residual tin compound has been extracted, the thermal decomposition temperature tends to decrease in response to an increase in the amount of aluminum hydroxide added. That is, the addition of aluminum hydroxide has the effect of making thermal decomposition of the PLLA polymer converge to a specific temperature range, and also an effect in counteracting the outstanding decomposition promotion effect of the tin compound and contributing to stabilization of PLLA containing residual tin. Therefore, PLLA containing a tin compound can easily be melt molded as a mixture with aluminum hydroxide even without specially removing the tin compound.

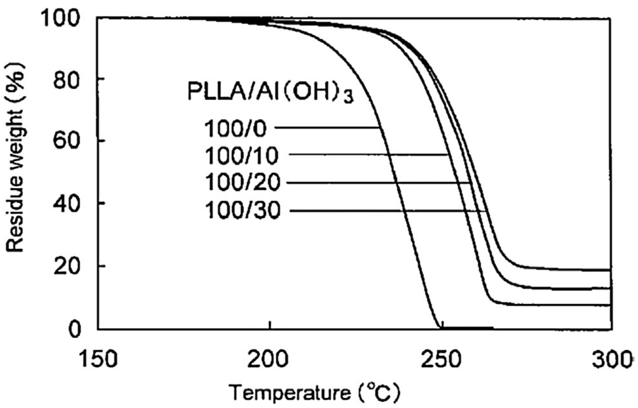


FIGURE 16.6 Thermogravimetric/differential thermal analysis (TG/DTA) curves of tin-containing poly(L-lactic acid) (PLLA)/aluminum hydroxide $Al(OH)_3$ compositions obtained using a TGA/DTA6200 under a nitrogen atmosphere at a heating rate of 5 °C/min (2007, **EP1741707** A1, KYUSHU INST OF TECHNOLOGY; KITAKYUSHU FOUNDATION; KINKI UNI).

As is demonstrated in Figure 16.6 and Table 16.2 tin-containing PLLA on its own, which did not contain aluminum hydroxide, weight reduction due to decomposition of PLA started beyond 180 °C and the decomposition is almost complete at about 250 °C. In contrast thereto, compositions containing 10–30 pbw of aluminum hydroxide start thermally decomposing at around 200 °C, and decomposition is almost complete at about 270 °C with an amount of residue remaining corresponding to the amount of aluminum hydroxide added. The aluminum hydroxide used undergoes a dehydration reaction at a temperature of 200 °C or higher, releases 34.6 wt% of water (in theory), and changes into alumina. The conversion of aluminum hydroxide into alumina in this temperature range is 32–59%. From these results, it is clear that the tin-containing PLA/aluminum hydroxide composition gives an increase in the thermal depolymerization temperature of about 20 °C compared with the tin-containing PLA alone, the PLA is almost completely depolymerized and vaporized, and aluminum hydroxide partly changes into alumina, which is stable (2007, **WO2005105775** A1, KYUSHU INST OF TECHNOLOGY; KITAKYUSHU FOUNDATION; KINKI UNI).

JP2008231048 A (2008, KYUSHU INST OF TECHNOLOGY; KITAKYUSHU FOUNDATION) discloses a method for efficiently recovering a highly pure lactide from PLA in a manner capable of enhancing the catalytic function of magnesium oxide as a catalyst for depolymerizing

TABLE 16.2 Thermal Decomposition Products of Tin-Containing Poly(L-Lactide) (PLLA)/Aluminum Hydroxide $Al(OH)_3$ Compositions Using a TGA/DTA6200 under a Nitrogen Atmosphere at a Heating Rate of 5 °C/min (2007, **EP1741707** A1, KYUSHU INST OF TECHNOLOGY; KITAKYUSHU FOUNDATION; KINKI UNI)

PLLA/$Al(OH)_3$			
Ratio by Weight	$Al(OH)_3$ (wt%)	Final Residue (wt%)	$Al(OH)_3 \rightarrow Al_2O_3$ Conversion Factor (%)
100/0	~0		
100/10	9.1	8.1	32
100/20	16.7	13.3	59
100/30	23.1	19.0	51

the polymer. The method for the lactide recovery involves adding 0.1–10 pbw, per 100 pbw PLA, magnesium oxide having a specific surface area of 5 m^2/g or larger to the polymer and heating the mixture to 200–300 °C. A high optical purity lactide can be more efficiently recovered when the magnesium oxide is heat treated in the temperature range of 300–600 °C or when the surface hydroxyl groups of the magnesium oxide are replaced by carbonate groups.

JP2011162480 A (2011, KITAKYUSHU FOUNDATION) discloses a method of efficiently recovering L-lactide as a raw material from a polymer composition comprising PLLA and aromatic polycarbonate by selectively decomposing PLLA. The method of recovering lactide comprises adding an ester exchange catalyst such as tin oxide and/or an organoaluminum compound into the polymer composition, heating the mixture preferably in the temperature range of 200–330 °C to selectively decompose PLLA, and recovering the resulting L-lactide as a raw material.

JP2008201679 A (2008) and **JP2008201680** A (2008) of TEIJIN FIBERS LTD provide a method for thermally degrading PLA, wherein the thermal decomposition temperature of PLA is lowered to produce a lactide of good quality. The method is characterized in that PLA is degraded in the coexistence of an acid compound, preferably a lactic acid oligomer, and a catalyst in the temperature of 170–240 °C, at a pressure equal to or lower than the vapor pressure of the lactide (<200 mmHg), while distilling away the produced lactide. The lactic acid oligomer compound is a mixture of a dimer and/or polymer compound. The catalyst is a tin compound.

JP2003128900 A (2003), **JP2004216378** A (2004), and **US2005250931** A1 (2005) of MITSUBISHI PLASTICS INC provide a method for recycling shredder dust that includes pulverisates of automobile parts and home electric appliances that consist mainly of PLA. The PLA-based composition includes 30–100 wt% of PLA, and 0–50 wt% of an aliphatic polyester, such as PBS, and/or an aliphatic-aromatic polyester, such as poly(tetramethylene adipate-*co*-terephthalate) (PTeMAT). In the basic procedure (see Figure 16.7) shredder dust that could contain metals and/or glass as contaminants is filled in a sealed vessel and heated with purging by an inert gas such as dehumidified air or air to decompose PLA and recover the formed vapor. Setting the heating vessel and recovery passages under a reduced pressure of 13.3 KPa (100 Torr) or less, preferably 2.6 KPa (20 Torr) or less, facilitates recovering lactide vapor. The heating temperature is preferably within the range of 150–280 °C, preferably 170–250 °C. Addition of 0.1–3 wt% of tin, titanium, and zirconium compounds to the shredder dust upon heating accelerates the decomposition rate of PLA. However, this is not always necessary. It is considered that shredder dust contains more or less catalyst component such as metals that exhibit a similar effect of acceleration. The thus recovered lactide can be repolymerized by any known method. Recovering lactide by using the shredder dust provides the advantage that the larger surface area of the shredder dust improves the efficiency of recovery.

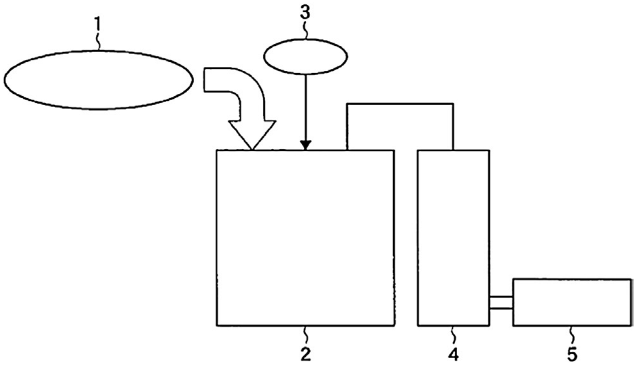


FIGURE 16.7 Schematic diagram depicting the method for recovering lactide (2005, **US2005250931** A1, MITSUBISHI PLASTICS INC).

Shredder dust (1) for recycling is charged in a heating vessel (2), which is heated by a heating means (not shown) while purging by an inert gas (3) to generate a vapor component. The generated vapor component is cooled in a cooling vessel for recovering lactide (4). The cooling is preferably performed under the conditions where a reduced pressure is established by removing inert gas and the like by pressure reduction unit (5).

The shredder dust has a particle size of preferably 20 mm or less, more preferably 10 mm or less. Automobile parts include besides parts related to automobiles, parts casings, etc. that constitute an automobile. Home electric appliances include, for example, besides ordinary parts such as a shade of a lamp, those parts casings, etc. of home electric appliances.

16.3.2 Hydrolysis/Solvolysis (Alcoholysis)

16.3.2.1 Hydrolysis

The hydrolysis rates of aliphatic polyesters appear to be too slow to permit recovery from other insoluble ingredients and reuse of the valuable hydroxycarboxylic acid moieties within a time frame. For monomer recovery, hydrolytic degradation of aliphatic biodegradable polyesters in the solid state is not recommended because highly hydrolysis-resistant crystalline residues (or extended chain crystallites) are formed and their very slow degradation will give a low monomer yield in a limited short period or will take a long time to give a high yield [35].

Another disadvantage of hydrolysis involves the partial racemization of PLA. This means that the hydrolysis of a PLA, consisting, for example, of 98% L-lactic acid and 2% D-lactic acid, results in a lactic acid mixture with a D-content larger than 2%. Other biodegradable polymers, such as PCL, depolymerize slowly or to a limited degree when treated with alkaline solutions. Some of these biodegradable polymers undergo alkaline depolymerization at a convenient rate only at temperatures greater than about 170 °C. Such high temperatures may not be reached by some simple steam systems, such as steam autoclaves (2002, **WO0236675** A2, PROCTER & GAMBLE COMPANY).

US5268507 A (1993, DU PONT) discloses a method for depolymerizing waste aliphatic polyesters by reacting the polyester with an amine to form monomeric amide. The amine is ammonia, methylamine, or dimethylamine. The molar ratio of amine to polyester is in the range 1/1–2/1.

US5229528 A (1993, DU PONT) discloses a process of depolymerizing waste aliphatic hydroxycarboxylic acid-derived polyester, preferably PLA, to monomeric hydroxyl acid monomer and low-molecular-weight oligomers comprising mixing said polyester in water at sufficient temperature (100–200 °C) and pressure (0.35–1.40 MPa) for a sufficient time to significantly depolymerize the polymer, said temperature and pressure being insufficient to form undesirable degradation products. The amount of water used affects the time required to carry out the depolymerization and the percent conversion. Normally, a molar ratio of water to aliphatic polyester (on an acid unit basis) in the range of 1/1–5/1, preferably 1.5/1–2/1, is used. An important economical aspect of the present method is the speed of the depolymerization. By selecting optimal reaction conditions, particularly pressure and temperature, significant quantities of aliphatic polyester can be batch depolymerized often in 1 h and even in as little as 15 min. Reactor design, i.e., agitation, etc., also plays an important role in reaction rate. Where speed is less a factor than other economies, batch times as long as 16 h may be appropriate. Continuous process depolymerization is also possible, such as with the feed materials being continuously introduced into the first depolymerization stage of a multistage system, and the monomer and oligomer product being recovered from the last stage.

US5264626 A (1993, DU PONT) is a modified version of the method described in **US5229528** A involving depolymerization of the waste aliphatic polyester in acidic water and subjecting the resulting mixture to a temperature and pressure sufficient to at least partially depolymerize the aliphatic hydroxycarboxylic acid–derived polyester. In general, strong organic or inorganic acids that do not react with the polyester to form depolymerization products or form undesirable by-products can be used. Liquid or water-soluble solid catalysts are preferred for ease of use and concentration. Sulfuric acid and *p*-toluene sulfonic acid (solid) are suitable inexpensive acid catalysts. Methane sulfonic acid is also acceptable. Hydrochloric acid, although effective, is generally undesirable because of its excessive corrosiveness to equipment. Very small quantities of acid are required, preferably in the range of 0.1–1.0 wt% of said polyester to be catalytically effective. The depolymerization proceeds even if large quantities of water are introduced with the acid (dilute acid). The depolymerization product is a low-molecular-weight oligomer, the average molecular weight depending on the depolymerization conditions of time, temperature, and pressure of heating and the water/acid content of the dissolving liquid. Preferably, depolymerization is continued long enough to yield a depolymerization product at a concentration of at least 10%, preferably greater than 70%, in the acidic water that can be handled as a liquid.

EP0573042 A1 (1993) and **JPH0649266** A (1994, MITSUI CHEM INC; MITSUI TOATSU CHEM INC) disclose a method for decomposing an aliphatic hydroxycarboxylic acid-derived polyester homopolymer or copolymer in an alkaline solution such as calcium hydroxide of pH ≥ 10, while maintaining the configuration intact. The alkaline solution used for the decomposition of the aliphatic polyester can be prepared by adding an inorganic base, such as sodium and potassium hydroxide, to an aqueous solvent. The hydroxycarboxylic acid is recovered by electrodialysis or acid precipitation and can be used as a raw material of a polymer. Suitable aliphatic polyesters are PLA and poly (D,L-lactide) (PDLLA). Suitable copolyesters include poly(D,L-lactide-*co*-glycolide) (PDLGA) and poly(L-lactide-*co*-ε-caprolactone). Other comonomers that can be used include, for example, 3-hydroxybutyric acid, 4-hydroxybutyric acid, 4-hydroxyvaleric acid, 5-hydroxyvaleric acid, and 6-hydroxycaproic acid (6-hydroxyhexanoate).

JPH1036553 A (1998, SHIMADZU CORP) provides a method for treating an aliphatic polyester waste involving hydrolysis of the aliphatic polyester, such as PLA, in a tank equipped with a rotating moving body using a motor. Waste PLA (20) is charged from a charging port (22), finely crushed with a crusher (24) and subsequently charged into a tank (4). The tank (4) is equipped with a stirrer (28) driven with a motor (26) to always stir and mix the crushed waste polymer with an alkali aqueous solution. The rotation of the moving body causes alkali hydrolysis of the aliphatic polyester waste. When the PLA is hydrolyzed, precipitates are generated and accumulated on the bottom of the tank (4). Thereby, a recovery tube (30) reaching the bottom of the tank (4) is disposed, and the precipitates (34) accumulated on the bottom of the tank (4) are recovered from the bottom into a recovery tank (36) with a pump (32) (see Figure 16.8).

JP2006274231 A (2006, CHIBA PREFECTURE) provides a method and an apparatus suitable for depolymerizing and solubilizing PLA and recovering the treated PLA as a monomer lactic acid in order to carry out recycle treatment of PLA. A monomer lactic acid can be obtained by treating one part L-type or D-type PLA or PLA containing L-type and D-type in an arbitrary ratio at a temperature of less than 200 °C in the presence of at least 0.2–20 parts water in the solution state. The monomer lactic acid having an arbitrary ratio of L-type and D-type in which the ratio of L-type to D-type retains the ratio of L-type and D-type of PLA or the ratio of L-type to D-type is 1:1 can be obtained by controlling mutual transfer of L-type and D-type of PLA. The treatment of PLA at a temperature of less than 200 °C inhibits reactions other than lactic acid formation.

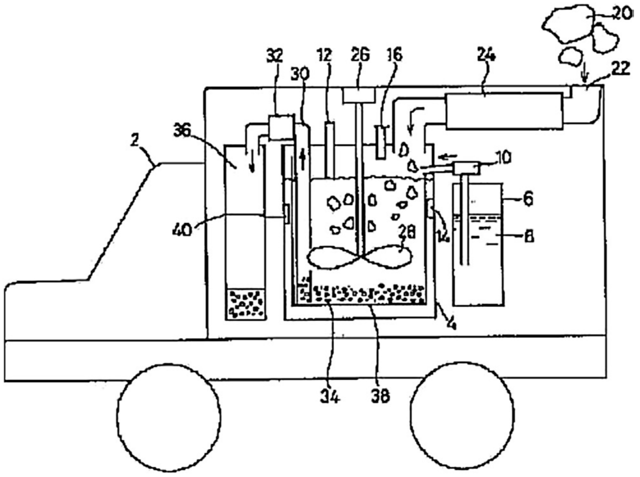


FIGURE 16.8 Outline cross-sectional view showing an example of the recovery vehicle that was adapted in the present invention (1998, **JPH1036553** A, SHIMADZU CORP). 2, Recovery vehicle; 4, Decomposition tank; 6, Tank of calcium hydroxide aqueous solution; 20, Waste PLA; 22, Charging port; 24, Crusher; 26, Motor; 28, Stirrer; 30, Recovery tube; 32, Pump; 34, Precipitates; 36, Recovery tank; 38, Heater.

JP2007224113 A (2007, TEIJIN FIBERS LTD) discloses a method for recovering the effective components from waste biodegradable polyester by depolymerizing the polyester with water at a temperature of 80–300 °C, and then recovering a monomer/oligomer mixture as the depolymerization product. The preferred biodegradable polyester is PLA, the monomer of depolymerization product is lactic acid, and other depolymerization products are lactide and lactic acid oligomer. The waste material originates from agricultural, forestry, fishery, civil engineering and construction articles, and food packaging containers made from biodegradable polyesters.

JP2005132901 A (2005), **JP2005131856** A (2005), and **JP2007031538** A (2005) of TEIJIN FIBERS LTD disclose related methods for removing different material(s) contained in a recovered aliphatic polyester such as PLA without reducing the recovery yield of the aliphatic polyester. The recovered aliphatic polyester containing polyethylene and polypropylene and/or PVC is depolymerized in aqueous ammonia at 80 °C to obtain a depolymerized reaction liquid with a viscosity of 0.0001–0.1 Pa s (0.1–100 cP) and the different material(s) of which the specific gravity is lower than that of the solution is floated to the vicinity of the surface of the depolymerized reaction liquid and separated. Alternatively, the recovered aliphatic polyester is dissolved in a dissolving solvent (see also Section: 16.2.3.4 Dissolution).

JP2007277389 A (2007, AKAMATSU K; KONISHI N; NAKAMURA K) discloses a method for separation and recovery of plastic wastes comprising a mixture of biodegradable polymers derived from renewable (plant-based) and fossil fuel–based resources, and nonbiodegradable polymers derived from fossil fuel-based resources. The method allows the recovery of groups of polymers by batch processing of plastic wastes without beforehand classification. The recovery method comprises the following steps: (1) crushing the plastic wastes into a controlled size; (2) hydrolyzing the crushed plastics; (3) extracting a crude acid aqueous solution of a monomer (e.g., lactic acid) formed from the plant-based biodegradable polymer (e.g., PLA); (4) sorting the biodegradable fossil fuel-based polymer in powder form from the remaining solid component; and (5) sorting the nonbiodegradable fossil-based polymer by removing the impurities from the residual solid component. The plastic wastes are generated from industries of perishable foodstuffs, preservation-processed products and cooked products, and from restaurants, supermarkets, and convenience stores.

JP2008050351 A (2008, VICROR COMPANY OF JAPAN) discloses a method for hydrolyzing waste PLA by mixing PLA with water and a depolymerization catalyst slightly soluble or insoluble in water, heating the resultant mixture, degrading PLA, and thereby recovering lactic acid.

PLA can be degraded at a relatively low temperature in a short time and the produced lactic acid can be recovered and used as raw material for PLA. The depolymerization catalyst is an oxide, a carbonate, or a hydroxide of at least one kind of element selected from group 2A, group 4A, group 5A, group 6A, group 7A, group 8, group 1B, group 2B, group 3B, and group 4B of the Periodic Table; preferably oxide of beryllium, magnesium, titanium, zirconium, vanadium, chromium, manganese, rhenium, iron, ruthenium, cobalt, nickel, copper, silver, zinc, cadmium, aluminum, indium, tin, lead, and/or silicon; more preferably magnesium carbonate, calcium carbonate, barium carbonate, manganese carbonate, cobalt carbonate, nickel carbonate, copper carbonate, silver carbonate, zinc carbonate, cadmium carbonate, lead carbonate, magnesium hydroxide, calcium hydroxide, chromium hydroxide, iron hydroxide, nickel hydroxide, gold hydroxide, zinc hydroxide, aluminum hydroxide and/or lead hydroxide.

WO2010118954 A1 (2010), **AU2010237249** A1 (2010), **WO2010118955** A1 (2010), and **WO2011015433** A1 (2011) of GALACTIC S.A. disclose methods for the catalytic hydrolysis or alcoholysis of PLA, which has been dissolved in a lactic ester solvent (see Section 16.2.3.4: Dissolution). In particular, the PLA solution is subjected to a catalytic hydrolysis or alcoholysis reaction, at a temperature of 80°–180 °C and a pressure of 0.05–10 bar in order to transform PLA into lactic ester or a derivative thereof.

The PLA hydrolysis or alcoholysis step enables the recovery of a lactic acid ester by breaking down an ester linkage of PLA followed by a protonation of the carbonyl group and a nucleophilic attack. The protonation of the carbonyl group is carried out through the use of a transesterification catalyst, which may be solid or liquid and of Lewis acid type such as, for example, tin octoate, tin lactate, antimony octoate, zinc octoate, APTS (*p*-toluene sulfonic acid), etc. or preferably basic, a member of the guanidine family, such as, for example, triazabicyclodecene (TBD) and derivatives thereof. Since the amount of water or alcohol influences reaction kinetics, it is nevertheless important to hold a compromise enabling to avoid removing a too high amount of alcohol during the following purification steps. In **WO2010118954** (2010) the nucleophilic attack is carried out using water or an alkaline solution such as NaOH, KOH, and the like. In **WO2010118955** A1 (2010) the nucleophilic attack is carried out using an alcohol. Suitable alcohols contain 1–12 carbons, ideally corresponding to the ester used for dissolving, such as methanol, ethanol, *n*-butanol, isobutanol, *sec*-butanol, *tert*-butanol, *n*-propanol, iso-propanol, 2-ethylhexanol, 2-ethylbutanol, hexanol, and the like.

A problem common to all these methods is that they do not make it possible to eliminate the D-enantiomers that may be generated firstly by the whole of the PLA production process and secondly by the various chemical recycling. This means that D-enantiomers are formed when working with PLLA (the form mainly present on the market). Similarly, there will be the formation of L-enantiomers when working with PDLA. This progressive enrichment in undesired enantiomer with regard to the lactic acid or derivatives thereof will have a significant impact on the yield and the costs of production of a new PLA.

WO2011029648 A1 (2010, GALACTIC S.A.) addresses this problem by disclosing a method for chemical stereospecific recycling of a mixture of polymers containing PLA, characterized in that the method comprises the steps of: (1) combining the mixture of polymers and a lactic ester into a solution, wherein the lactic ester is capable of dissolving in the PLA fraction; and (2) depolymerizing the PLA fraction of step (1) by transesterification, wherein the depolymerization is stopped subsequent to forming an oligoester mixture with an average molecular weight between about 400 and 5000 Da, preferably between 400 and 3000 Da.

The reaction can be stopped by eliminating the alcohol function (coming from the lactic ester or the alcohol), which makes it possible to keep control of the molecular weight of the oligoester. In this context, any technology allowing rapid extraction of the alcohol or lactic ester will be favored, such as thin film technology. Once formed, the oligoester mixture may be subjected to a catalytic cyclization step, wherein a vapor phase rich in lactide and a liquid phase rich in oligoesters is produced. The use of a catalyst is essential in order to reduce the thermocracking temperature and thus to prevent chemical and optical deterioration of the synthesized lactide. The catalysts are the same as those that were used in the depolymerization by transesterification step; see also **WO2010118955** A1 (2010). The vapor phase rich in lactide is condensed to raw lactide, wherein volatile components are removed. The raw lactide is subjected to stereospecific purification into a purified lactide fraction, wherein the purified lactide fraction has a *meso*-lactide content of 0.1–40 wt%, preferably between 0.1 and 20 wt%, which makes it possible to control and, therefore prevent, the enrichment in D-enantiomer in the whole of the process.

As with many processes, the manufacturing process of cellulose acetate results in some waste products that are not utilized in the final, desired products, as well as considerable waste post consumer. In the past, much of these waste products from the manufacture of products or postconsumer used materials that incorporate cellulose acetate were simply shipped off to the landfill. **US2010175691** A1 (2010, CELANESE ACETATE LLC) discloses a process for recycling cellulose acetate ester waste resulting from the production of materials (e.g., tobacco products) through the use of carboxylic acids. The process for recycling cellulose acetate ester waste (10), outlined in Figure 16.9, comprises the following steps:

1. providing a reactor (20);
2. adding cellulose acetate ester waste to the reactor;

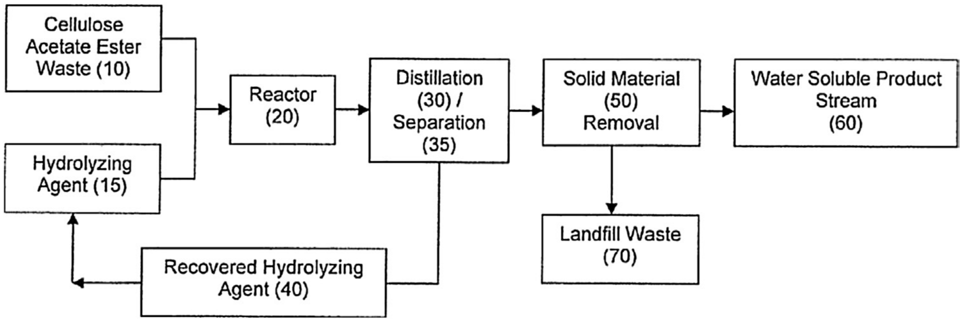


FIGURE 16.9 Recycling of cellulose acetate ester waste by hydrolysis (2010, **US2010175691** A1, CELANESE ACETATE LLC).

3. adding a hydrolyzing agent (15) to the reactor to create an agent/waste mixture;
4. hydrolyzing the cellulose acetate ester waste by agitating and heating the agent/waste mixture for a period of time to create a hydrolyzed mixture;
5. distilling (30) and/or separating out (35) the hydrolyzing agent from the hydrolyzed mixture;
6. separating and removing solid material (50) (which may end up as landfill waste 70), from the hydrolyzed mixture to create a water-soluble product stream (60), which includes monosaccharides, polysaccharides, partially hydrolyzed cellulose, acetic acid, or combinations thereof;
7. collecting the water-soluble product stream.

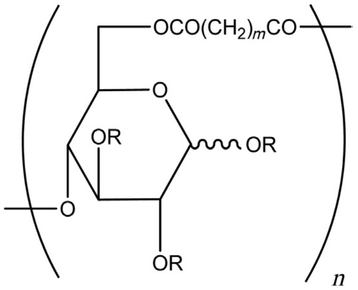
The hydrolyzing agent is a carboxylic acid selected from the group consisting of acetic acid, formic acid, or combinations thereof.

In one of its embodiments **JP2001040078** A (2001, CANON KK) discloses a process for recycling a thermoformed product produced from a sugar chain polymer compound in which the thermoformed body is ground and hydrolyzed to produce D-glucopyranose (see Scheme 16.1) and an aliphatic dicarboxylic acid, which are used again to produce the sugar chain polymer compound.

The sugar chain polymer compound is useful for the production of a thermoformed article such as packaging container, toy, and sheet by alternately ester-copolymerizing a specific D-glucopyranose derivative and an aliphatic dicarboxylic acid. The hydroxyl group bonded to the 4- and 6-carbon atoms of the D-glucopyranose is alternately ester-copolymerized with an aliphatic dicarboxylic acid.

16.3.2.2 *Alcoholysis*

US5264614 A (1993, DU PONT) discloses a method for the recovery of waste aliphatic hydroxycarboxylic acid–derived polyester by (1) heating the waste under pressure in the presence of a lower alkyl alcohol (C_1–C_6 alcohol), and optionally also water so as to solubilize the polyester, the heating being such that significant degradation of the polyester is avoided; and (2) cooling the solution and recovering the polymer.



SCHEME 16.1 D-Glucopyranose. R, Hydrogen atom, acetyl, propionyl, butyryl, methyl, ethyl, or benzyl; *m*, Integer between 2 and 16; *n*, Integer between 1 and 35,000 representing the degree of polymerization.

US5264617 A (1993, DU PONT) discloses a method for depolymerizing waste aliphatic polyester through alcoholysis by (1) heating the waste in the presence of a lower alcohol (C_1–C_6 alcohol), so as to solubilize the polymer; (2) removing the undissolved trash material optionally by filtering; (3) adding acid catalyst and heating to produce an alkyl ester.

CA2098220 A1 (1994, DU PONT) discloses a method for the recovery and recycling of hydroxycarboxylic acid from waste aliphatic polyester such as fast food container by (1) contacting the waste with a solubilizing fluid selected from the group consisting of water, lower alkyl alcohol (C_1–C_6 alcohol)s, mixtures of water and said alcohols, amines, diamines, and mixtures of said amines and/or diamines with water and/or said alcohols; (2) maintain the resultant mixture at a temperature and time sufficient to at least solubilize the aliphatic polyester and form a liquid phase of increased monomer and oligomer hydroxyl acid value; and (3) isolating the liquid phase. Regardless of the nature of the solubilizing fluid, it is important to use temperatures and pressures adequate to cause rapid solubilization of the aliphatic polyesters, but not severe enough to form undesirable degradation products. Higher temperature increases the rate of depolymerization and solubilization. By selecting optimal reaction conditions, particularly pressure and temperature, significant quantities of the aliphatic polyester can be adequately solubilized by a batch method, often in 1 h and even in as little as 0.25 h. In many cases, overall economics and reaction kinetics dictate running the method at atmospheric pressure although elevated pressure sometimes is needed to reach the necessary temperatures for rapid and complete solubilization. Normally, autogenous pressure is adequate. The method can be used for the depolymerization of PLA and the recovery of lactic acid. Once the PLA is depolymerized back to lactic acid, the resulting lactic acid must be synthesized into lactide before carrying out polymerization to form PLA. This method is considered to be complicated and not economically advantageous.

All three patents of DU PONT use waste originating mainly from discarded food-containing containers made from hydroxycarboxylic acid–derived polyesters; the hydroxycarboxylic acid–derived polyesters are selected from PLA, PGA, or a copolymer containing a major portion of PLA and PGA copolymerized with up to 30% ε-caprolactone, δ-valerolactone, 1,5-dioxepen-2-one, 1,4-dioxan-2-one, β-butyrolactone or -propiolactone, and/or 6-methyl-2,5-morpholinedione and mixtures thereof. Typically, the temperature of the process is in the range 100–200 °C and the time is in the range of 15 min–16 h. The alcohol is preferably *n*-butanol.

JPH09241417 A (1997, DAINIPPON INK & CHEM INC) discloses a method for recovering lactide from lactic acid–based polymer wastes, by adding specific alcohols and a heat-decomposing catalyst to the lactic acid–based polymer and carrying out alcoholysis. The method involves adding alcohols, which have a boiling point of 170 °C or higher, at 1 kPa (7.5 Torr) and a heat-decomposing catalyst to a lactic acid–based polymer, such as PLA or a copolymer of a polyester comprising a diol and a dicarboxylic acid and a lactide, heating the mixture under reduced pressure or in an inert gas atmosphere to carry out the alcoholysis. Thereby, a backbite reaction is conducted for recovering the produced lactide. Preferred alcohols are monohydric alcohols with ≥6C, diols with ≥5C, triols, or tetrols. The preferred catalyst is a compound containing tin as element.

JPH08253619 A (1997, MATSUSHITA DENKI SANGYO KK) discloses a method of decomposing molded products containing biodegradable polyester(s) by contacting the molded products (1) with a solution containing (2) at least an alkali metal compound or an alkaline-earth metal compound, and an alcohol (3) such as methanol. Among the aliphatic polyesters are poly(3-hydroxyvalerate) (P3HV) and its copolymers, P3HB, PCL, poly(ethylene succinate) (PES), poly(ethylene glutarate), poly(ethylene adipate) (PEA), PBA, and PBS. The addition of an alcohol to the treating solution accelerates the decomposition of the polyester to monomers by promoting the solvolysis of ester bonds without the application of heat or pressure. It is preferable that the component (1) to be treated is immersed in a solution containing both the components (2) and added with (3) inorganic compound particles (e.g., alumina particles with a size of 10 μm to several mm) followed by agitation (4). The method is claimed to be effective for the recovery of the monomers of the decomposed polymer. The outline of the method of adding, stirring, and processing an inorganic compound particle in a solution is shown in Figure 16.10.

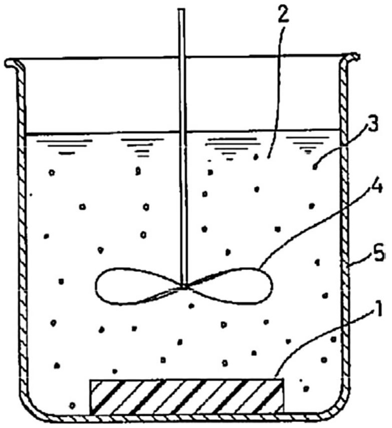


FIGURE 16.10 Schematic diagram showing the disposal method of the biodegradable polymer molding in one working example (1997, **JPH08253619** A, MATSUSHITA DENKI SANGYO KK). 1, Biodegradable polymer sample; 2, Treating solution; 3, Inorganic compound particle; 4, Agitating blades; 5, Container.

Working example: A polymer sample (1) of size 10 × 20 × 1 mm made of poly(ethylene adipate) (PEA) was used. As the inorganic compound particle (3) 2.5 g calcium carbonate particles (particle diameter of 350–500 μm) were added in a solution (2) comprising 1.1 g sodium hydroxide, 21.0 g ethanol, and 6.0 g water. The aforementioned polymer sample (1) was immersed in this solution at room temperature (20 °C), and the agitating blades (4) stirred the mixture at a revolving speed of 100 rpm. The weight of the sample was measured at a fixed time interval and the degradation rate was 260 mg/h. When the same experiment was conducted using the treating solution without adding the calcium carbonate particles, the degradation rate was 180 mg/h; i.e., the degradation rate was promoted by the addition of the inorganic compound particle.

WO2005105908 A1 (2005 UNIV KEIO) discloses a method for the depolymerization of an aliphatic polyester by reacting the polyester with a solid acid catalyst, thereby obtaining a repolymerizable monomer and/or oligomer as a depolymerization product; and a method for producing an aliphatic polyester by polymerizing the repolymerizable monomer and/or oligomer obtained by the depolymerization. The aliphatic polyesters are PLA, PCL, poly(alkylene alkanoate), or PHA. The depolymerization reaction is generally carried out by dispersing the solid acid catalyst in a solvent (toluene or ethanol) in which the polymer is dissolved, and regulating the temperature to an appropriate temperature, for a predetermined time. Known representative solid acid catalysts include Nafion®-H, sulfated zirconia (VI), and Montmorillonite K11. As the solid acid catalyst, in addition to those cited above, there can also be utilized, for example, Dowex® 50W-X8 or 50W-X2 or Duolite® C20. It is also possible to utilize vermiculite or heteropolyacid, or further a Zeolite catalyst such as MCM-22.

Among the solid acids above, Montmorillonite K10 and Nafion®-H have a high activity, and particularly Montmorillonite K10 is preferable as the solid acid catalyst for use in the present invention, as it is a clay mineral, which is safe, easy to handle, and a substance with a low environmental load, and it is available inexpensively in large quantities (at a cost of from 0.5 to 2 times compared to that of 95% sulfuric acid). Nafion®-H is a cation exchange resin (perfluorosulfonic acid ion-exchange powder) developed by Du Pont, and has a side chain with a terminal sulfonic group on a linear chain of a fluorinated resin, and exhibits an acidity stronger than that of 100% sulfuric acid.

JP2009072759 A (2009, UNIV KEIO; KUROSAKI H; KOGYO KK; MIZUSAWA IND CHEM LTD) discloses a method for the depolymerization of PLA by heating PLA in the presence of a solid catalyst consisting of acid-treated dioctahedral smectite clay. The acid-treated dioctahedral smectite clay has 0.28–0.63 mmol/g solid acid content when measured in an absolutely dried state, 0.25–0.40 cc/g pore volume of pores having 17–3000 Å pore size when measured by a nitrogen adsorption method and 150–400 m^2/g BET specific surface area. The solid acid catalyst allows oligomers having predetermined polymerization degrees to be obtained in a short time by depolymerization, and is separated easily from oligomers to be obtained by depolymerization, so that oligomers of PLA can be recovered at a high recovery.

The proposed solid acid catalysts by the last two patents are insoluble in a solvent and have the following advantages in comparison with soluble catalysts (2005, **WO2005105908** A1, UNIV KEIO):

1. Conventional alkali processes generally are usually incapable of obtaining an oligomer mixture having repolymerization properties and reactivity; for example, an alkali depolymerization of PLA decomposes it to a lactic acid monomer. When the decomposition product is intended for repolymerization, it is preferred that the depolymerization product is in the form of an oligomer, which is also a polymerization intermediate, rather than a monomer. In this respect, the depolymerization by a solid acid allows the easy obtaining of an oligomer mixture having repolymerization properties and reactivity.
2. An oligomer mixture, having repolymerization properties and reactivity, can be obtained directly, at a relatively low temperature. In prior technologies, for example, decomposition with an alkali, the product is an alkali salt, which requires a neutralizing operation with an acid in order to be used as a polymerization raw material or a chemical raw material. This operation requires a strong acid, in addition to the alkali as the catalyst, and also generates a salt. A purifying operation is also required in order to remove salts, excessive acid, or unreacted salts. Also the alkali decomposition requires a considerably high temperature, is accompanied by generation of by-products and decomposition products other than the desired ones, and is accompanied by a color deterioration associated therewith. The chemical recycling utilizing the solid acid is expected to achieve energy savings and have a low environmental load.
3. The use of solid acid catalyst enables a separation of the product by filtration alone. On the other hand, in a decomposition of an aliphatic polyester such as PLA, with an alkali such as ammonia, the generated lactic acid forms a salt, which has to be neutralized (thus generating an unnecessary salt), and a dehydration process and a purification of hydrated lactic acid also become necessary. In contrast, in the case of utilizing a solid acid catalyst, lactic acid is obtained as a free carboxylic acid, thus not requiring neutralization and providing free lactic acid oligomers that are directly repolymerizable as they are.
4. The solid acid catalyst is reusable repeatedly by simple postprocessing such as rinsing with water and drying.
5. The solid acid catalyst is not deactivated even at a high temperature, and is applicable to the decomposition of a broad range of polymers.
6. The solid acid catalyst is easy to handle as it lacks an irritant odor or corrosive properties, and is not very hazardous.

JP2009029757 A (2009, TEIJIN FIBERS LTD) discloses a depolymerization method of PLA by using an easily handleable catalyst. The depolymerization method comprises alcoholyzing PLA (e.g., Lacty® 9010, Shimadzu) using methanol at 60–100 °C in the presence of a zinc compound catalyst composed of zinc carboxylate (e.g., zinc acetate) and/or zinc carbonate. Methyl lactate is obtained in adequate quantity. PLA originates from agricultural material, fishery material, food packaging containers, and civil engineering and construction material.

16.3.2.3 Foam Hydrolysis

JP2009242545 A (2009, KANEKA CORP) discloses a pretreatment method preceding the chemical recycling of a PLA-based foam, of which the volume is difficult to be reduced by crushing. The PLA-based foam is treated at 80–100 °C in a relative humidity of 80% or more and then crushed and injected to a reaction extruder, without using a large size crusher.

16.3.3 Hydrothermal Depolymerization

Hydrothermal depolymerization involves hydrolysis of biodegradable polymers at high temperature and often high pressure water. The reaction can be performed under sub- and supercritical conditions, and in the presence or absence of oxidants.

High-temperature hydrolysis is effective in hydrolyzing aliphatic polyesters, such as PLLA [36]. PLLA is readily depolymerized by hydrolysis under hydrothermal conditions in the absence of catalysts [37]. The optimum condition for depolymerization of PLLA was found to be 220 °C and 20 min. Under this condition, the recovery of L-lactic acid was more than 95% without loss of optical purity. At a higher temperature (260–300 °C), the optical purity decreased with increasing temperature, and a racemic mixture was formed at 300 °C [36].

When the hydrolysis is carried out at a temperature lower than the T_m of PLLA, crystalline residues are formed as a result of selective hydrolysis of the chains in the amorphous regions. The crystalline residues prolong the time required for the complete hydrolysis of PLLA or decrease the yield of L-lactic acid when the hydrolysis is short [38]. The reported yield of water-soluble monomers and oligomers from PLLA was as low as 56% even when the hydrolysis temperature was increased to 97 °C and the hydrolysis was continued as long as 40 h [38]. Hydrolysis carried out at a temperature above the T_m of PLLA causes racemization and decomposition of the formed lactic acids due to the high temperature [39].

The hydrolytic degradation of aliphatic polyesters in the melt in high temperature and high pressure water overcomes the problem of slow degradation encountered during the hydrolysis in the solid state. On the other hand, hydrothermal depolymerization and dry-heat depolymerization require high temperatures, normally above 200 °C.

JPH05178977 A (1993, TOYO INK MFG CO) discloses a hydrolysis method by contacting moldings mainly comprising PLA with steam of high temperature (>100 °C) and high pressure (>1 atm). Preferably, the hydrolysis takes place in tightly closed vessels preventing oxidation with air. The hydrolyzed polymers become powder or pasty. The method permits the simple and easy recovery and reuse of PLA.

JPH07309863 A (1995, JAPAN STEEL WORKS LTD) discloses a method for recovering lactide from a PLA product in a short time, in high yield at low cost by heating and blending the PLA product in a screw type extruder in the presence of water and a catalyst at a specific temperature. A PLA product (1) such as a film sheet or hollow article is heated and blended by a screw type extruder in the presence of (2) water and (3) a catalyst such as an alkylaluminum, zinc oxide, or manganese acetate at 200–400 °C hydrolyzed and depolymerized to recover the objective lactide from the component (1). The amounts of the components (2) and (3) used are preferably 0.1–5.0 wt% of the component (2) and 0.1–1.0 wt% of the component (3) based on the amount of the component (1).

JP2007002160 A (2007) and **JP2007023176** A (2007) of TEIJIN FIBERS LTD provide related methods for the depolymerization of a biodegradable polyester such as PLA by mixing the polyester—at least a part of which is in a molten state—with water at a reaction temperature of 150–300 °C and pressure of 0.1–1 MPa (1–10 atm) and removing the depolymerized product from the gaseous phase portion with water vapor. In an example, 100 parts of PLA is put in a reaction tank heated to 220 °C and stirred at 100 rpm for 4 h at an atmospheric pressure. Water vapor is extracted by superheating. The depolymerization product is a mixture containing lactic acid, lactide, and/or lactic acid oligomers. The ratio converted into lactic acid is 28% (optical purity: 98% of L-forms) with respect to the PLA. The process enables the recovery of the depolymerized product of a biodegradable polyester without containing foreign materials or unreacted products being included in the biodegradable polyester polymer reaction product.

EP1241231 A1 (2002, CANON KK) discloses the recycling of molded articles obtained from a biodegradable polymer composition, comprising a biodegradable polymer (a) and a biodegradable liquid crystalline polymer (b). Molded articles include ink tanks of ink-jet printers, toner containers of electrophotography apparatuses, packing materials, casings of printers and cameras, transparency sheets, and so forth. In an example, a transparent sheet prepared from butyl ester of hydroxyethylcellulose (b) with PLA (a) was shredded into chips by a shredder. The sheet chips were decomposed by action of high temperature and high pressure water (at a pressure of 35 MPa and a temperature of 400 °C), or fuming hydrochloric acid (at a temperature of 25 °C). The glucose chemically separated from the decomposition product was used as a source material for synthesis of glucose-sebacic acid copolymer.

JP2007210889 A (2007, TEIJIN FIBER KK; UNIV TOYOHASHI) provides a method for monomerizing a stereocomplex type–PLA (scPLA), by processing the biodegradable polymer at 170–330 °C, for 5–240 min, at pressure of 0.8–16 MPa (8–160 atm) in an atmosphere of inert gas in the presence of water. The preferred composition of scPLA contains PLLA and PDLA mixed in the weight ratio of 4/6–6/4. A lactic acid mixture of L-lactic acid and D-lactic acid is obtained.

JP2007051202 A (2007, NAKAMURA K; AKATSU S; NAGAHAMA M; YOKOSUKA M) discloses a method for the regeneration of PLA used for containers and bags comprising hydrolysis treatment and supercritical extraction treatment. PLA and water in an amount of 20% with respect to total amount of to-be-processed material are reacted at 140 °C under saturated water vapor pressure to hydrolyze PLA and to produce an aqueous lactic acid solution. The aqueous lactic acid solution is introduced in a supercritical environment of carbon dioxide ($scCO_2$) at a temperature of 60 °C and pressure of 8 MPa (80 atm) and made to dissolve in $scCO_2$. The generated refined lactic acid is separated from carbon dioxide at normal temperature and pressure. The method enables efficient regeneration of lactic acid of high purity from PLA, without impairing the quality.

In actual recycling of PLA products, however, there are many kinds of mixing substances such as ink and paint attached to the products of substances mixed in the products, and fillers. Therefore, practical application of the above technology has the problem of separating them and of how to extract sole lactic acid (**WO2007102488** A1, 2007, NAKAMURA K).

WO2007102488 A1 (2007), **JP2007238691** A (2007), and **JP4118313** B1 (2008) of NAKAMURA K and **JP2008179713** A (2008, REAL PLASTIC KK) disclose related methods for the decomposition and reclamation of discarded PLA articles by conducting hydrolysis and separate recovery successively. The discarded PLA articles are exposed to a water vapor atmosphere into a treatment chamber filled at or below the saturated water vapor pressure and heated at a temperature at or below the T_m of the polymer, preferably in the range 130–150 °C (see Figure 16.11). It was found that the hydrolysis completion time is between 4.5 h and about 1.5 h from the start of the treatment for PLA samples (molding, pellet) of Terramac® (Unitika); in particular, the 1.5 h lower limit was reached at 150 °C of hydrolysis temperature. The waste biodegradable polyester can be hydrolyzed without establishing the supercritical state, and the reaction products are separated into gas or liquid component and solid component, and collected separately.

In one of its embodiments, the decomposition method includes a pretreatment step, preceding the hydrolysis treatment, to crystallize PLA by heating the PLA articles to a temperature in a range from the crystallization point to the T_m of PLA for at least 30 min. As a result of the pretreatment, the hydrolysis of the crystallized PLA can be shortened. In addition, the pretreatment considerably increases the brittleness of PLA so the polymer can be easily pulverized.

The collected components of the decomposition can be used as raw materials for the regeneration of PLA. A practical application of the proposed technology is the problem of separation substances, such as ink and paint attached to PLA products, filler, and extraction of sole lactic acid. The present invention is not limited to the hydrolysis of PLA and can also be applied in a very similar manner to the hydrolysis of other polyesters including biodegradable polymers such as PBS, PCL, polyhydroxyalkanoate (PHA), and nonbiodegradable polymers such as PET and polyamide 6 (PA 6 or Nylon 6).

JP2007001940 A (2007, MITSUBISHI HEAVY IND LTD) provides a method for the recycling of a poly(alkylene succinate) and monomer recovery. The method involves adding water (1–20 pbw) to poly(alkylene succinate) (1 pbw), decomposing and monomerizing by heating at 200–400 °C under 1–30 MPa (10–300 atm) pressure, and purifying monomer. The poly(alkylene succinate) is PES, PBS, poly(butylene succinate-*co*-adipate) (PBSA), poly(butylene succinate-*co*-carbonate), and/or poly(ethylene succinate-*co*-terephthalate) (PEST).

Tsuji et al. [35] studied the hydrolytic degradation of aliphatic dicarboxylic acid/aliphatic diol-derived biodegradable polyesters such as PBS and PBSA in the melt.

JP2009249508 A (2009, KYUSHU INSTITUTE OF TECHNOLOGY; MUSASHINO KAGAKU KENKYUSHO KK) discloses a method for the recycling of PLA and/or its derivative(s) that combines partial hydrolysis of PLA with depolymerization of the obtained oligomers to lactide. The method comprises the following steps of: (1) putting a PLA having a weight-average molecular weight (M_w) of 50,000–2,000,000 and/or its derivative(s) in a reactor and introducing steam into the reactor by decompressing the reactor and/or replacing a gas phase of the reactor with steam; (2) hydrolyzing the PLA and/or its derivative(s) in a heated steam atmosphere; (3) discharging the steam by decompressing the reactor and introducing dry air and/or an inert gas; and (4) recovering the lactic acid oligomer having a M_w of 1000–50,000 and/or its derivative(s) that are obtained at step (3).

The hydrolysis of PLA and/or its derivative(s) is performed under coexistence of heat steam atmosphere and basic atmosphere by using alkali. The alkali is chosen from $Ca(OH)_2$, $Mg(OH)_2$, CaO, MgO, and/or NaOH. The water vapor is introduced under reduced pressure of 0.02 MPa (0.2 atm) or less. The heating process is performed at 100–150 °C under pressure of 0.05–0.56 MPa (0.5–5.6 atm). The water vapor is discharged under reduced pressure of 0.02 MPa (0.2 atm) or less. The method is claimed to recover lactide without loss of its optical purity. A disadvantage of this recycling method is that the hydrolysis occurs batchwise by adding steam to solid PLA. This adds further cost to the process of recycling PLA, making it economically less viable on a large scale (2013, **EP2559725** A, UHDE INVENTA FISCHER GMBH).

EP2559725 A (2013, UHDE INVENTA FISCHER GMBH) discloses a method for recovery of lactide from PLA or glycolide from PGA, comprising the steps of: (1) reacting PLA or PGA with a hydrolyzing medium into a melt, and hydrolytically reducing the melt into PLA-oligomers having a M_n of 162–10,000 g/mol., or hydrolytically reducing the melt into PGA-oligomers having a M_n of 134–10,000 g/mol.; and (2) subjecting the PLA- or PGA-oligomers to a cyclizing depolymerization to obtain lactide or glycolide. The disclosed method is claimed to achieve large-scale production of the lactide and glycolide, with less expense of energy and the apparatus, and reduce the partial racemization of the products.

Example: PLA (30 g) was dissolved in water (0.7 g) in a laboratory pressure vessel and sealed. The vessel was placed

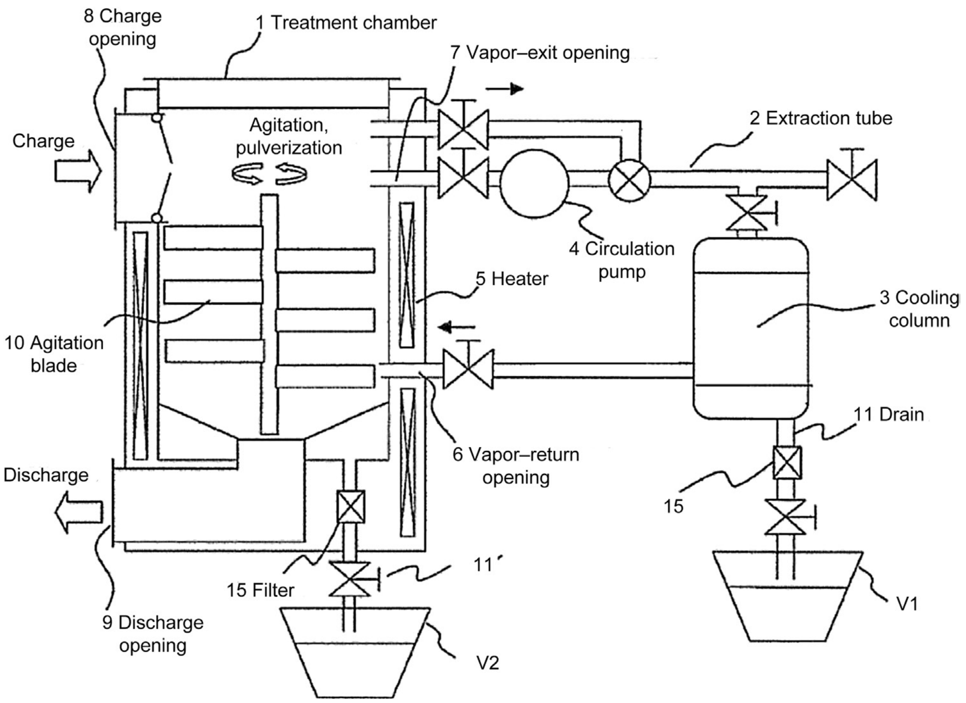


FIGURE 16.11 Schematic diagram of the hydrolysis apparatus (2007, **WO2007102488** A1, NAKAMURA K).

in a circulating air-drying cabinet at 190 °C; after 6 h, the vessel was removed from the drying cabinet and cooled to obtain a viscous mass, which was further worked up to obtain L-lactide and *meso*-lactide.

JP2003300927 A (2003, INST NAGOYA IND SCIENCE RES), **JP2005330211** A (2005, UNIV TOYOHASHI; TEIJIN FIBERS LTD), **JP2005298401** A (2005, UNIV TOYOHASHI TECHNOLOGY), **JP2006137892** A (2006, UNIV TOYOHASHI TECHNOLOGY; TEIJIN FIBERS LTD), and **JP2007099663** A (2007, UNIV TOYOHASHI TECHNOLOGY; TEIJIN FIBERS LTD) provide a series of related methods and apparatuses for decomposing biodegradable polyesters, such as PLA, P3HB, and PCL, and recovering the generated monomers. A representative example of these patents is **JP2003300927** A (2003), which discloses a method and an apparatus (see Figure 16.12) for depolymerizing PLLA and recovering L-lactic acid for recycling the PLLA. The monomerization of PLLA is performed by treating one part PLLA in approximately 20 parts water at a high temperature of 200–350 °C (preferably 200–300 °C) for approximately 5–60 min (preferably 5–30 min). As an especially favorable condition, the L-lactic acid is recovered by at least 90% yield at 250 °C reaction temperature for approximately 10 min reaction time. The depolymerization maintains the optical activity of PLLA.

JP2005330211 A (2005) discloses a method and an apparatus (see Figure 16.12) for separating and recovering PLA from a polymer mixture waste by hydrolysis. The method comprises treating a mixture of PLA and a general-purpose polymer (for example, PET or PS) with water at a high temperature of about 160 °C to about 200 °C for about 30 min or more and then separating and recovering the lactic acid. According to the method, the lactic acid can be separated and recovered in a high yield, and the optical activity of the lactic acid is held in the original optical activity state. The mixture of PLA, general-purpose polymer, and water in a liquid state are reacted in a continuous-type or a batch-type high temperature processing machine, the pressure of which is kept higher than 1 MPa.

JP2005298401 A (2005) provides a method with which a biodegradable polyester such as P3HB and PCL is reacted with high temperature and pressure water and thereby converted into a monomer. In particular, P3HB is reacted with water under a temperature of 250–300 °C for 5–20 min, preferably 100–240 °C for 120–360 min; PLC is reacted with water under a temperature of 350–400 °C for 5–30 min. The monomers 3-hydroxybutanoic acid and 6-hydroxycaproic acid can be obtained from P3HB and PCL, respectively, in a short time in high yield. The processing apparatus (see Figure 16.12) is a continuous-type or batch-type apparatus. The processing apparatus is set at high pressure more than 0.1 MPa (1 atm), such that water and biodegradable polyester of a liquid state are mixed by high temperature processing machine.

JP2006137892 A (2006) discloses a method and apparatus for recovering lactic acid from waste PLA in high yield and purifying the lactic acid to a prescribed optical purity. The method for the regeneration of waste PLA comprises (1) a step to monomerize PLA by heating a composition containing PLA in the presence of water at a high reaction temperature, i.e., about 110 °C to about 300 °C for about 5 min to about 96 h; (2) a step to determine the optical purity of the lactic acid obtained by the monomerization step, and (3) a purity adjusting step to heat the lactic acid having determined optical purity in the presence of water at a high reaction temperature, i.e., about 180 °C to about 300 °C for about 5 min to about 96 h to adjust the optical purity to a prescribed level. When the optical purity of the lactic acid is lower than the prescribed level, the acid is subjected to a mixing step to mix the recovered lactic acid with a lactic acid having an optical purity of ≥90% to prepare the lactic acid having prescribed optical purity.

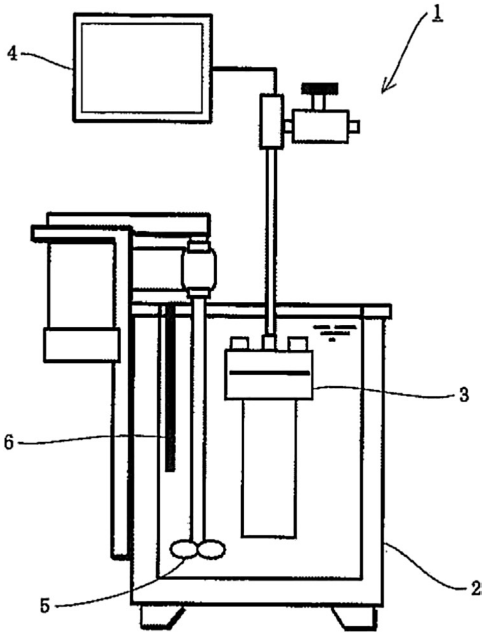


FIGURE 16.12 Schematic diagram of a high temperature, high pressure water-processing apparatus of the biodegradable polyester (2003, **JP2003300927** A, INST NAGOYA IND SCIENCE RES; 2005, **JP2005330211** A, UNIV TOYOHASHI; TEIJIN FIBERS LTD; 2005, **JP2005298401** A, UNIV TOYOHASHI TECHNOLOGY); 2006, **JP2006137892** A, UNIV TOYOHASHI TECHNOLOGY; TEIJIN FIBERS LTD; 2007, **JP2007099663** A, UNIV TOYOHASHI TECHNOLOGY, TEIJIN FIBERS LTD). 1, Processing apparatus; 2, Thermostat; 3, Reaction container; 4, Pressure indicator; 5, Rotary blade; 6, Heater.

An apparatus (20) for separating and recovering lactic acid is described in Figure 16.13, which has a high temperature processing machine (21) for performing initial stage processing of waste material, and a reaction liquid extraction hole (29) for removing reaction liquid in the processing machine. The lactic acid is efficiently recovered with high optical purity from the waste material.

JP2007099663 A (2007) discloses a method for recovering lactic acid from a mixed waste material (16) containing two or more PLAs having different melting temperatures that is heated at 110–200 °C with water (W) for 1 h or more in a high temperature treatment apparatus (see Figure 16.13). The reaction liquid is recovered at predetermined time intervals of from 10 min to 24 h. Lactic acid is separated and recovered, and its optical purity is checked. The optical purity is adjusted to a prescribed level (90% or more) by heating the lactic acid in the presence of water at a high reaction temperature, i.e., about 180 °C to about 300 °C for about 5 min to about 96 h. When the optical purity of the lactic acid is lower than the prescribed level, the acid is subjected to a mixing step to mix the lactic acid with a lactic acid having an optical purity of ≥90% to prepare the lactic acid having prescribed optical purity. The recycling of PLA can be effectively performed by this method.

JP2008007611 A (2008, KUMAMOTO TECH & IND FOUND) discloses a method for recovering lactic acid and/or water-soluble oligomer by decomposing PLA for food packaging film without impairing the optical specificity of lactic acid. The method involves soaking the PLA in an aqueous solution of lactic acid, which contains 10% or more lactic, and then heating at 120–135 °C under pressurization to recover lactic acid and/or water-soluble oligomer from PLA. The preferred weight ratio of PLA and lactic acid is 1/1–1/100. The water-soluble oligomer of lactic acid is a dimer or trimer of lactic acid.

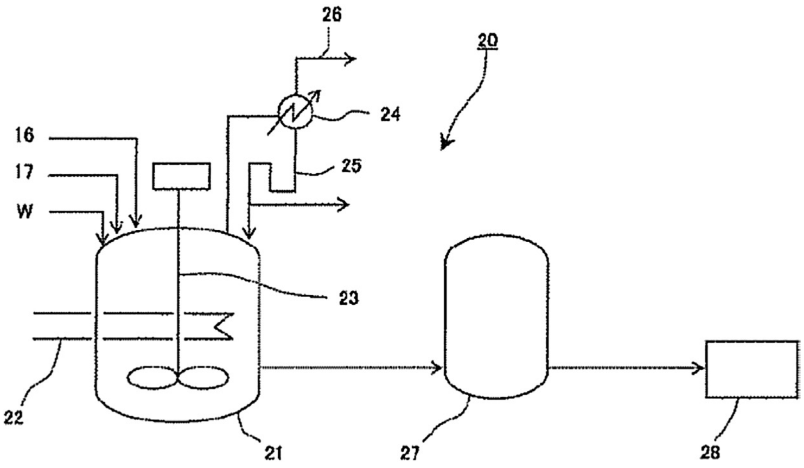


FIGURE 16.13 Outline diagram of a processing apparatus for recovering and separating lactic acid (2006, **JP2006137892** A; 2007, **JP2007099663** A, UNIV TOYOHASHI TECHNOLOGY; TEIJIN FIBERS LTD). 16, PLA waste material; 17, Circulation liquid; 20, Separation recovery apparatus; 21, Reaction tank; 22, Thermal treatment equipment; 23, Agitator; 24, Cooler; 25, Return path; 26, Vent path; 27, Hold tank; 28, Purification; 29, Reaction liquid extraction hole; W, Water.

16.3.4 Enzymatic Depolymerization

Most of the aforementioned chemical recycling processes (1) consume much energy; (2) have a low yield of monomers in a short period; and (3) require the removal of catalysts and additives that were used for depolymerization, hydrolysis, or solvolysis [39]. Furthermore, if the depolymerization of PLA is conducted by thermal degradation or chemical degradation, both ends of a generated low-molecular-weight compound are irregular and such compound cannot be repolymerized into a polymer.

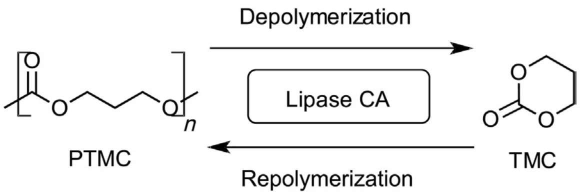
Enzymatic depolymerization is a rather new technique of chemical recycling. This technique is distinguished from the enzymatic hydrolysis applied to the disposal of biodegradable polymers by the fact that the main aim is to reuse the products generated after the enzymatic degradation.

One of the advantages of using an enzyme (especially hydrolase) is the reversible reaction between polymerization and depolymerization. Biodegradable polymers containing enzymatically hydrolyzable moieties such as esters are first cleaved by the action of a hydrolase enzyme. The degradation products containing low-molecular-weight fragments are repolymerized by the enzyme under water-limited conditions.

The enzymatic depolymerization and repolymerization were carried out with the objectives of developing the enzymatic recycling of aliphatic polyesters, such as PCL, P3HB, PBA, PBS, poly(butylene adipate-*co*-succinate) (PBAS), and PLA, which are typical biodegradable polymers. They were degraded by lipase in an organic solvent solution containing a small amount of water to produce cyclic oligomers. The produced (cyclic) oligomers were readily repolymerized in bulk by the same catalyst to produce a polyester having an equal or higher molecular weight compared to the parent polymer [19,40–43].

Most of the research so far on the enzymatic recycling of biopolymers has been carried out at Keio University, Japan (http://www.keio.ac.jp/), and all patent applications have been filed by the same university.

JP2002017384 A (2002, UNIV KEIO) discloses a method for producing trimethylene carbonate (TMC) by selectively converting a poly(trimethylene carbonate) (PTMC) to a repolymerizable monomer in the presence of a hydrolase. The hydrolase used for depolymerizing is recovered and used repeatedly without reducing its activity. The preferred hydrolase is lipase derived from *Candida antarctica* (CA) (Novozym® 435, Novozymes Japan Ltd.). The CA lipase was added to chloroform and separated by filtration, using citrite. Solvent was concentrated from a filtrate using an evaporator. Trimethylene carbonate was obtained at 75% of yield by a silica gel column chromatography. PTMC transformed into monomer can be repolymerized selectively.



SCHEME 16.2 Enzymatic recycling of poly(trimethylene carbonate) (PTMC) [43].

Matsumura et al. [43–46] reported the recycling of PTMC using an enzyme. The enzymatic transformation of PTMC having a M_n of 3000–48,000 using CA lipase in acetonitrile at 70 °C afforded the corresponding cyclic monomer TMC, in a yield of up to 80% [46]. The obtained TMC readily polymerized again using lipase (see Scheme 16.2).

JP2002017385 A (2002, UNIV KEIO) discloses a depolymerizing method for producing dicaprolactone by selectively converting PCL to a repolymerizable monomer using a hydrolase. By this depolymerization method, dicaprolactone is produced in a high yield, and the dicaprolactone can be repolymerized in the presence of hydrolase such as lipase derived from *C. antarctica*. The hydrolase used for depolymerization can be recovered and used repeatedly, since activity reduction of the enzyme seldom occurs. The recovered dicaprolactone can be used as a monomer for the same polymer and also as a comonomer for improving the polymer properties [45].

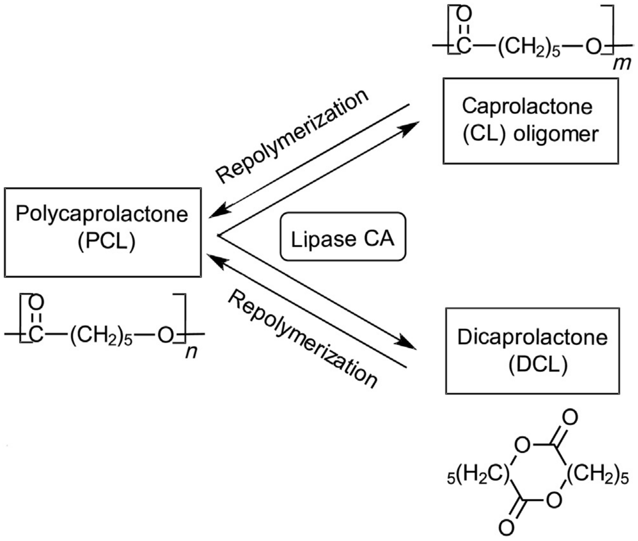
The enzymatic depolymerization of PCL into dicaprolactone generally requires large amounts of organic solvents, such as 0.2% toluene solutions, in order to facilitate intramolecular cyclization [47]. Organic solvents, such as toluene and volatile chloroform, may cause pollution and harm when released into the environment.

Besides the selective ring-closing depolymerization of PCL into the cyclic dimer, dicaprolactone, there is another route for the enzymatic recycling of PCL [47] (see Scheme 16.3). This second method involves the enzymatic conversion of PCL into repolymerizable 6-hydroxyhexanoate oligomers [40,45]. This oligomer can be used for the reproduction of PCL. In a particular example, PCL with a $M_n = 110{,}000$ was degraded into the corresponding oligomer using immobilized lipase CA in toluene and water. The obtained viscous caprolactone (CL) oligomer with a molecular weight of about 500 could be repolymerized by lipase for 6 h at 70 °C under a slightly reduced pressure to yield a high-molecular-weight PCL having a $M_n > 80{,}000$.

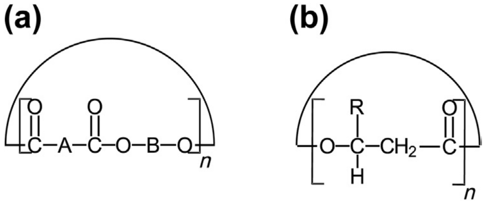
JP2002320499 A (2002, UNIV KEIO) discloses a depolymerizing method for converting poly(alkylene alkanoate) or PHA to cyclic oligomers, mainly composed of cyclic compounds of formula (a), particularly formula (b) of Scheme 16.4, using a hydrolase, particularly lipase. The original polymers can be produced by repolymerizing the cyclic oligomers in the presence of a hydrolase or a polymerization catalyst.

There are two routes for the enzymatic recycling of PHAs. One is the enzymatic degradation using the specific hydrolase enzyme related to P3HB, which is secreted by the P3HB-degrading microbes as extracellular P3HB-depolymerase (PHBDP). The other is the enzymatic degradation using conventional lipase, which shows a broad substrate specificity in an organic solvent. Scheme 16.5 depicts the two routes for the enzymatic recycling of P3HB.

Takahashi et al. [19] reported the transformation of PLA into a cyclic oligomer by lipase in an organic solvent. Kobayashi et al. used proteinase K in a buffer solution for the enzymatic degradation of PLA [40–42].



SCHEME 16.3 Lipase-catalyzed chemical recycling of poly(ε-caprolactone) (PCL); *Adapted from Ref. [43].*



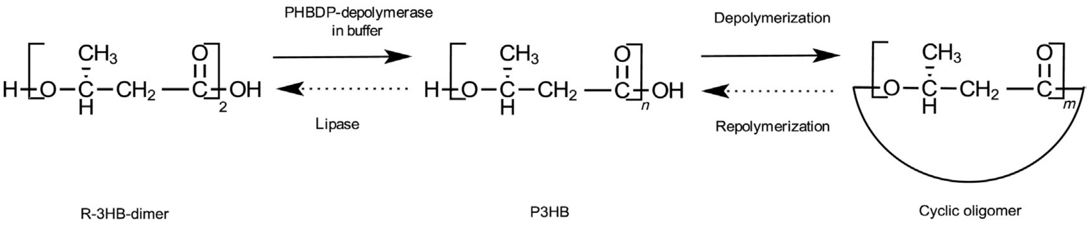
SCHEME 16.4 Oligomer consisting essentially of the ring compound represented by chemical formulas (a) or (b) (2002, **JP2002320499** A, UNIV KEIO); A, 2–8C alkylene group; B, 2–6C alkylene group; *n*, Integer of 1–6; R, Hydrogen atom or a 1–12C alkyl group; *N*, Integer of 2–10.

The depolymerization methods in the aforementioned patent applications is of a low energy consumption because of the use of an enzyme, and the products obtained by the depolymerization can be repolymerized into polymers by an enzyme, so that these methods can effectively utilize the carbon resources without waste, and can be considered as a polymer reutilization of complete recycling type. Therefore, from the viewpoint of sustainable material utilization, the aforementioned methods are practical chemical recycling methods. Also, the enzyme catalyst methods are optimal for obtaining cyclic monomer or oligomer that is repolymerizable.

On the other hand, as a detriment resulting from the substrate specificity of enzyme, these methods are limited to polymers susceptible to an enzyme reaction. Also, the enzyme catalyst, being a protein catalyst, involves limitations inherent thereto, such as that the reaction temperature cannot be made very high and that it requires a long time to the completion of reaction for a polymer having a high crystallinity and a high intermolecular force.

In order to be able to make an enzyme act on a solid polymer as it is and also to dissolve the polymer, organic solvents, such as acetonitrile, tetrahydrofuran, toluene, and benzene, are made necessary. However, many of the organic solvents will normally cause pollution when they are discharged to the environment. An alternative approach involves the use of supercritical fluids instead of organic solvents (see Section 16.2.3.4: Dissolution). The supercritical fluids used are carbon dioxide ($scCO_2$) and fluoroform ($scCHF_3$). Carbon dioxide and fluoroform are suitable for handling relatively hydrophobic and hydrophilic molecules, respectively. Carbon dioxide is harmless, inexpensive, and noninflammable, with a critical point of about 31 °C at 7.4 MPa. The carbon dioxide easily reaches its critical point and is suitable as a medium for the depolymerization and the repolymerization of aliphatic polyesters or polycarbonates.

JP2003079388 A (2003, UNIV KEIO) discloses a method of depolymerizing an aliphatic polyester or polycarbonate in a supercritical fluid ($scCO_2$ or $scCHF_3$) in the presence of a hydrolase. The recovered cyclic oligomer(s) can be repolymerized in a supercritical fluid in the presence of an enzyme or a polymerization catalyst. Polyesters



SCHEME 16.5 The two routes for the enzymatic recycling of poly(3-hydroxybutyrate) (P3HB). *Adapted from Ref. [48].*

that can be used for depolymerization include PCL, PBS, PBA, and PBSA. The preferred hydrolase is CA lipase (Novozym® 435 Novozymes Japan, Ltd.).

Takamoto et al. [41] reported that the lipase-catalyzed degradation of PCL in $scCO_2$ in the presence of acetone produced an oligomer of lower molecular weight (less than 500), which can be polymerized by the same catalyst [41]. Similar results were obtained such that PCL beads were transformed in $scCO_2$ in the presence of a small amount of water and lipase to produce repolymerizable oligomers having a M_n of about 500 [44]. The produced caprolactone oligomer was again polymerized with CA lipase by a dehydration process to yield a PCL having a M_n greater than 80,000. $scCO_2$ was also an adequate reaction medium for the lipase-catalyzed depolymerization of a PCL of $M_n = 110{,}000$ into a cyclic dicaprolactone (DCL) using immobilized CA lipase in $scCO_2$ fluid containing a small amount of water within 6 h at 40 °C and 18 MPa $scCO_2$ with a yield of 91%. The DCL was readily polymerized by CA lipase in $scCO_2$ to yield PCL with $M_n = 33{,}000$ after 6 h [47].

Osanai et al. [49] used lipase in both an organic solvent and supercritical carbon dioxide for the selective degradative transformation into polymerizable oligomers and repolymerization of PCL, P3HB, and PBA.

WO2004013217 A (2004, UNIV KEIO) discloses a method for the enzymatic depolymerization of PLA that comprises depolymerizing PLA in an organic solvent or supercritical fluid in the presence of a hydrolase to yield a repolymerizable oligomer, as well as a process for producing PLA in which the repolymerizable oligomer obtained by the depolymerization method is polymerized in the presence of a hydrolase or polymerization catalyst. The hydrolase used to conduct the depolymerization or the polymerization can be collected and repeatedly used.

Any solvent in which PLA can be dissolved at least partly and further in which the enzyme is not inactivated, such as *o*-xylene, toluene, acetonitrile, 1,4-dioxane, tetrahydrofuran, hexane, or the like, may be used without any limitation. It has been confirmed that xylene and toluene are particularly useful for the depolymerization. Combinations of various solvents at a specific composition ratio make it possible to make the conversion ratio higher than the use of any one of the organic solvents alone. For example, although it is not much preferred to use chloroform alone (the enzyme is inactivated), the conversion ratio is made better in the case of mixing a small amount of chloroform with hexane than in the case of 100% hexane. The addition of hexane to *o*-xylene or toluene makes the conversion ratio better than the use of *o*-xylene or toluene only.

The depolymerization of PLA in a supercritical fluid is conducted by putting the PLA and a hydrolase into a pressure-resistant reaction tube, pouring liquefied carbon dioxide into it, while pressuring the carbon dioxide with a liquid-feeding pump, so as to make the carbon dioxide into a supercritical state, and then causing the PLA to undergo depolymerization reaction for a suitable time while keeping the $csCO_2$ at a suitable temperature and preferably stirring the solution. The temperature of $csCO_2$ at the time of the depolymerization is preferably about 40–90 °C, and the pressure is preferably 7.2–30 MPa. The reaction time for the depolymerization is preferably at least 3 h. The upper limit of the reaction time is not particularly limited.

The PLA is a PLLA or PLA copolymer. The preferred hydrolase is lipase. An example of CA lipase is Novozym® 435 (Novozymes Japan Ltd.), and an example of lipase derived from *Rhizomucor miehei* is Lipozyme RM IM™ (Novozymes Japan Ltd.). Besides this, Bioprase™, which is a protease derived from *Bacillus subtilis* (Nagase ChemteX Corp) may also be used as the hydrolase in the same manner.

WO2005026245 A1 (2005, UNIV KEIO) discloses a method for the continuous depolymerization of an aliphatic polyester (e.g., PLA, P3HB, PCL, PBA) or polycarbonate, which comprises continuously passing both a supercritical fluid (preferably $scCO_2$) and an organic solvent solution of the polymer through a column packed with a hydrolase (e.g., Novozym® 435, Novozymes Japan, Ltd.) to depolymerize the aliphatic polyester or polycarbonate by the action of the hydrolase and separating the depolymerization product from the reaction mixture, which contains the depolymerization product and flows out from the hydrolase-packed column. The apparatus for use in the continuous depolymerization method is shown in Figure 16.14 and comprises a device for producing a supercritical fluid, a column packed with a

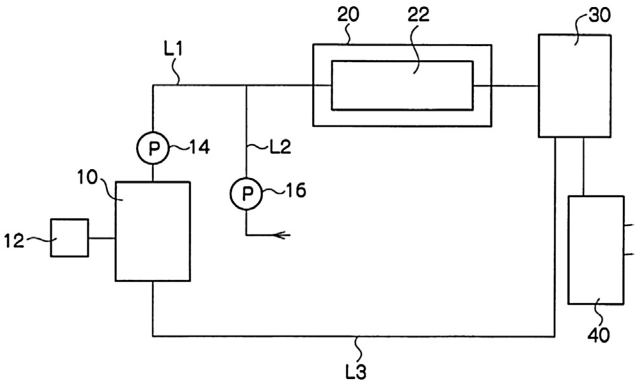


FIGURE 16.14 Continuous depolymerization apparatus (2005, **WO2005026245** A1, UNIV KEIO). 10, Supercritical carbon dioxide ($csCO_2$) generation apparatus; 12, Supply means of a carbon dioxide (CO_2); 20, Equipped with the heating apparatus and temperature control apparatus that are not illustrated so that column temperature may be kept constant by the thermostat; 22, Hydrolase-packed column; 30, Back-pressure regulator; 40, Means to isolate/separate the organic-solvent solution of a depolymerization product to an organic solvent and a depolymerization product; L1, Pipe that sends the supercritical fluid generated by the supercritical fluid production generation apparatus with the pump 14 to the packed column; L2, Pipe that sends the polymer dissolved in an organic solvent to the packed column with the pump 16; L3, Pipe that collects the carbon dioxide gas released from a back-pressure regulator and is returned to a supercritical fluid generation apparatus.

hydrolase, a back pressure regulator, a means for separating a depolymerization product from a reaction mixture containing the depolymerization product, a means for sending the supercritical fluid produced by the device for supercritical-fluid production to the column, and a means for sending an organic solvent solution of the aliphatic polyester or polycarbonate to the column. Since the enzyme in the column used in this invention is stable for a long period of time (several months) and does not deteriorate, the same column can be used continuously for a long period of time, and a lot of processing can be implemented with high efficiency.

Compared with degradation results using pure organic solvents (e.g., toluene), by the addition of $scCO_2$ as a mobile phase, the polymer transformation into cyclic oligomers through the enzyme column was significantly promoted with respect to the reaction time, temperature, and polymer concentration [49].

The continuous enzymatic degradation of aliphatic polyesters into cyclic oligomers was carried out using an immobilized lipase column in an organic solvent and supercritical carbon dioxide ($scCO_2$). P3HB, PCL, and PBA were readily depolymerized into the corresponding cyclic oligomers by passage through the enzyme column packed with immobilized CA lipase using a toluene solution or $scCO_2$ at 40 °C. The enzyme column packed with immobilized lipase CA using toluene was active at least 3 months at 40 °C.

WO2010050482 A (2010, TOYO SEIKAN KAISHA LTD) discloses a method for producing an oligomer and/or a monomer by biodegrading an aliphatic polyester (e.g., PLA or PBS) in a degradation liquid containing an enzyme (e.g., hydrolase), a buffer agent, an organic solvent (e.g., ethanol), and water. The SP value (Hildebrand solubility parameter) of the organic solvent is less than 8.5 or more than 11.5, and the percentage volume content of the organic solvent in the degradation liquid is higher than 1 vol.% and lower than 15 vol.%. The biodegradable polymer also contains a decomposition promotion agent such as poly(ethylene oxalate) (PEOx). The decomposition promotion agent discharges an acid by hydrolysis and has a higher degradation rate than that of the aliphatic polyester. The hydrolase is protease, lipase, cellulase, or cutinase. In the method for producing an oligomer or a monomer, the degradation percentage of the biodegradable polymer is low, and deposits of aggregates of the oligomer and/or the monomer are few, so that the recovery percentage is high [14].

The advantages and disadvantages of enzymatic depolymerization can be summarized as follows:

- The products obtained by the depolymerization can be again polymerized into polymers by an enzyme, so that the carbon resources can be effectively utilized without waste and can be considered as a polymer reutilization of complete recycling type. The enzymatic depolymerization is of low energy consumption.
- The enzymatic depolymerization is an optimal method for obtaining cyclic monomers or oligomers that are repolymerizable.
- The enzymatic depolymerization is limited to polymers susceptible to an enzyme reaction.
- The enzyme catalyst, being a protein catalyst, involves limitations thereto, such as that the reaction temperature cannot be made very high.
- The enzymatic depolymerization requires a long time to complete the reaction for a polymer having a high crystallinity and a high intermolecular force.

JP2004290130 A (2004, MITSUBISHI CHEM CORP) discloses a method for recovering monomers from a polyester by carrying out contact reaction of the polyester with an esterase in a solution to hydrolyze the polyester and recovering these monomers constituting the polyester or their salts from the resultant solubilized hydrolyzate. The invention claims to depolymerize aromatic and aliphatic polyesters. The aliphatic polyesters are selected from the group that consists of PES, PBS, PBSA, poly(butylene succinate-*co*-lactide) PBSL, PLA, PCL, and a copolymer that has them as a main component. The esterase is an esterase having thermal stability, preferably carboxylate-ester hydratase, more preferably cutinase or lipase.

The enzymatic recycling of biopolymers is a promising method of establishing a sustainable polymer recycling system of biodegradable polymers, such as aliphatic polyesters, polycarbonates, and poly(amino acid)s [19,43]. The biopolymer can be depolymerized into low-molecular-weight compounds without using high energy, such as fossil fuel; the low-molecular-weight compounds can be effectively utilized; and, if desired, the original polymer can be obtained from the low-molecular-weight compounds without similarly consuming any high energy (**WO2004013217** A, 2004, UNIV KEIO). In spite of its obvious benefits, there are no reports so far for the practical application of this method to the recycling of biopolymers. More research is needed in terms of a more efficient use of enzymes, improved polymer polymerizability of the cyclic oligomers, etc. The repetitive production and chemical recycling of polymeric materials using an enzyme may become an effective method.

During tobacco manufacture, substantial amounts of waste filter material and cigarette paper are generated. Such waste materials generally have no utility in cigarette manufacture, but rather are typically disposed of by burning after separation from tobacco components. Disposal of these waste products and the economic losses incident thereto could be avoided by converting the waste materials to a product useful in the manufacture of tobacco products.

US4298013 A (1981) and **GB2107320** A (1983) of PHILIP MORRIS INC disclose a method for recycling cellulose waste material generated during tobacco manufacturing by (1) subjecting the waste to enzymatic saccharification to hydrolyze cellulose to simple sugars, especially glucose, (2) recovering the sugars, and (3) using the recovered sugar in a tobacco treatment process. The cellulose waste material is preferably first comminuted and dispersed in water. Cellulose acetate is then deesterified by treatment with an alkali, e.g., NaOH or KOH. The obtained material is washed free of excess alkali. A *Trichoderma viride cellulase* is employed to effect enzymatic saccharification.

16.3.5 Miscellaneous Processes

Ariffin et al. [50] investigated the chemical recycling of PHAs by thermal degradation from the viewpoint of biorefinery, which resulted in successful transformation of PHAs into vinyl monomers using alkali earth compound catalysts. Poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate) (PHBHV) was smoothly and selectively depolymerized into crotonic and 2-pentenoic acids at lower degradation temperatures in the presence of CaO and $Mg(OH)_2$ as catalysts. Obtained crotonic acid from 3-hydroxybutyrate sequences in PHBHV was copolymerized with acrylic acid to produce useful water-soluble copolymers poly(crotonic acid-*co*-acrylic acid) that have high T_gs. The copolymerization of crotonic acid derived from PHA pyrolysis is an example of cascade utilization of PHAs, which meets the idea of sustainable development.

A special case of chemical recycling is the method disclosed by **WO2009081362** A1 (2008, TORINO POLITECNICO) for the recycling of waste polymers, including aliphatic polyesters by pyrolysis. In this method, waste materials are subjected to pyrolysis, and the gaseous products are converted into carbon nanotubes via vapor-phase chemical deposition in an inert gas; this is done with the help of an unsupported organometallic catalyst. The method makes it possible to convert pyrolysis products into a raw material of high value (nanotubes). Although said patent application does not conform strictly with the definition and aim of chemical recycling, which is the recovery of raw materials such as monomers and/or oligomers with the purpose of making new polymers, it was found expedient to classify it also under the general heading of chemical recycling.

PATENTS

Patent Number	Publication Date	Family Members	Priority Numbers	Inventors	Applicants	Title
AU2010237249 A1	20110818	KR20120015440 A 20120221	WO2009BE00231 20090414; WO2010EP54280 20100331	COSZACH P; BOGAERT J-CH; WILLOCQ J	GALACTIC S.A	Chemical recycling of PLA by alcoholysis.
CA2098220 A1	19941211	EP0628533 A1 19941214; JPH0711044 A 19950113	JP19930143107 19930615; CA19932098220 19930611; EP19930109098 19930607	ROOREN D B; NARAAYANAN S S; NEBIRU E D; BRAKE L D; DRYSDALE N E; SUBRAMANIAN N S	DU PONT	Recovery of hydroxy acid from waste.
CN101130627 A	20080227	US2008048365 A1 20080228; US7598305 B2 20091006; JP2008050446 A 20080306; JP5045030 B2 20121010 CN101130627 B 20120502	JP20060226967 20060823	YAO K	FUJI XEROX CO LTD	Resin composition, resin molding, package, production method of resin molding and recycling method of resin molding.
CN101230129 A	20080730		CN20071173495 20071228	PENG T; XIAO M; XU Y	SHANGHAI NEW SHANGHUA POLYMER	Recrystallization method of polylactic acid and polylactic acid acquired thereby.
CN101275009 A	20081001	JP2008274222 A 20081113; CN101275009 B 20120222	JP20070092711 20070330; JP20070321186 20071212	YAO K; MORIYAMA M; SUZUKI F; MOCHIZUKI T; KAWASAKI H	FUJI XEROX CO LTD; FUJIFILM CORP	Resin composition, resin compact, production method of resin compact and recycling method of resin compact.
DE19522147 A1	19970102	DE19522147 C2 19970507	DE19951022147 19950619	KOEHNLECHNER R	HAMOS ELEKTRONIK GMBH	Vorrichtung zum elektrostatischen Sortieren von Gemischen aus Teilchen unterschiedlicher Kunststoffe. “Electrostatic sorter for comminuted particles of differing types, esp. Plastics.”
DE19530449 A1	19970220	JPH0959337 A 19970304; EP0759451 A2 19970226	DE19951030449 19950818	EIER H-M; SENG F; BECKER A; KUCKERT E; BOECKER T; LUTTERMANN K	BAYER AG	Polymere Fluoreszenzmarker. “Polymeric fluorescence markers.”

Continued

—Cont'd

Patent Number	Publication Date	Family Members	Priority Numbers	Inventors	Applicants	Title
DE19637404 A1	19970320	US5728847 A 19980317; JPH0977904 A 19970325; JP3503127 B2 20040302; DE19637404 B4 20060511	JP19950236278 19950914	OKAMOTO T; OHARA H	SHIMADZU CORP; TOYOTA MOTOR CO LTD	Verfahren zur Rückgewinnung von lactid aus Polymilchsäure mit hohem Molekulargewicht. "Method for recovering lactide from high-molecular weight polylactic acid."
DE19739992 A1	19990826		DE19971039992 19970911	KOEHNLECHNER R	HAMOS GMBH RECYCLING UND SEPARATIONSTECHNIK	Verfahren, Anlage, Vorrichtungen und Vorrichtungsanordnung zur triboelektrischen Trennung von unterschiedlich Stoffgemischen aus Nichtleitern, insbesonder ausKunststoffen. "Triboelectric separation of differently composed material mixtures of non-conducting materials, especially plastics."
DE19740027 A1	19990318		DE19971040027 19970911	KOEHNLECHNER R	HAMOS GMBH RECYCLING UND SEPARATIONSTECHNIK	Verfahren und Vorrichtung zur Bestimmung triboelektrischer Eigenschaften von Nichtleitern. "Electrostatic separation of mixture of different nonconductive materials."
DE19816881 A1	19991021	DE19816881 B4 20120105	DE19981016881 19980417	FEY D; BOHLEBERJ; DAUSELN M; KRIEG G	KRIEG G	Verfahren und Vorrichtung zur Detektion und Unterscheidung zwischen Kontaminationen und Gutstoffen sowie zwischen verschiedenen Farben in Feststoffpartikeln. "Method and device for detecting and differentiating between contaminations and accepts as well as between different colors in solid particles."
DE19829200 A1	20000105		DE19981029200 19980630	KOEHNLECHNER R	HAMOS GMBH RECYCLING-UND SEPARATIONSTECHNIK	Verfahren, Anlagen und Vorrichtungen zur elektrostatischen separation von unterschiedlich zusammengesetzten Nichtleitergemischen, insbesondere von Kunststoffgemischen. "Automatic electrostatic separation of nonconductive material mixtures, use of process, process plant and electrostatic separating unit."

DE19848873 A1	20000427	WO0024819 A1 20000504; NO20011910 A 20010418; JP2002528585 T 20020903; EP1129131 A1 20010905	DE19981048873 19981023; WO1999EP07677 19991013	WITT U; SKUPIN G; DELAVIER P	BASF AG	Zusammensetzungen aus biologisch abbaubare Polymeren und Fluoreszenzfarbstoffen. “Compositions consisting of biodegradable polymers and fluorescent dyes.”
DE19901743 A1	20000720		DE19991001743 19990118		HAMOS GMBH RECYCLING UND SEPARATIONSTECHNIK	Verfahren, Anlage, Vorrichtungen und Vorrichtungsanordnung zur triboelektrischen Aufladung und anschliessenden elektrostatischen Trennung von unterschiedlich chemisch zusammengesetzten Stoffgemischen aus Nichtleitern, insbesondere unterschiedlich chemisch zusammengesetzten Kunststoffen. “Triboelectric charging and electrostatic separation of diverse, non-conductive mixed waste, especially plastic, employs enclosed vibro-conveyor followed by in-flight separation influenced by non-linear electrostatic field.”
DE3842072C1	19891228	EP0373372 A2 19900620; JPH02202403 A 19900810; JPH0613176 B 19940223; US5009586 A 19910423; EP0373372 A3 19910502; EP0373372 B1 19930908	DE19883842072 19881214	PALLMANN W	PALLMANN MASCHINENFABRIK GMBH & CO. KG	Vorrichtung zum kontinuierlichen Regranulieren von thermoplastischen Kunststoffabfällen, insbesondere von Folien, Fäden und dgl. “Agglomerating apparatus for the continuous regranulation of thermoplastic wastes. Especially, films, filaments and the like.”
DE4029167 A	19920319	US5201921 A 19930413; JPH04246425 A 19920902; EP0476416 A2 19920325; EP0476416 A3 19930217	DE19904029167 19900914	LUTTERMANN K; CLAUSSEN U; SAYED AZIZ EL; RIESS R	BAYER AG	Verfahren zur Kennzeichnung von Kunststoffen. “Method for the masking of plastics.”
DE4231477 A1	19940324		DE19924231477 19920919	HAN KYUNG TAE; KOELLNER M; SAUER M; SEEGER S; WOLFRUM J; SCHMITT C; SCHULZ A	HAN KYUNG TAE; KOELLNER M; SAUER M; SEEGER S; WOLFRUM J; SCHMITT C; SCHULZ A	Verfahren zur optischen Sortierung von Kunststoffen mittels zeitaufgelöster Laserspektroskopie. “Sorting of plastic by y time-resolved laser spectroscopy.”
EP0566948 A1	19931027	US5329127 A 19940712; JPH0673191 A 19940315; JP3203355 B2 20010827; EP0566948 B1 19960911; DE4213323 A1 19931028	DE19924213323 19920423	BECKER A; LUTTERMANN K; CLAUSSEN U; ORTH P; HEILIGER L; EL SAYED AZIZ	BAYER AG	Verbessertes Verfahren zur Kennzeichnung von Kunstoff. “Improved method for marking plastics.”

Continued

—Cont'd

Patent Number	Publication Date	Family Members	Priority Numbers	Inventors	Applicants	Title
EP0573042 A1	19931208	EP0573042 B1 19961204; DE69306308 T2 19970619; US5780704 A 19980714	JP19920143940 19920604	AIJOKA M; ENOMOTO K; ENOMOTO T; SUZUKI K; YAMAGUCHI A; YAMAGUCHI T	MITSUI TOATSU CHEM INC	Process for treating plastic product.
EP1241231 A1	20020918	US2002130436 A1 20020919; US7608593 B2 20091027; US2006035860 A1 20060216; US7064113 B2 20060620; JP2002275379 A 20020925; JP3902916 B2 20070411	JP20010076559 20010316; US20020096016 20020313; US20050251790 20051018	MAEHARA H	CANON KK	Method for forming monomer of biodegradable polyester.
EP1741536 A1	20070110	WO2007003659 A1 20070111; US2008315020 A1 20081225; US7762482 B2 20100727; ES2394653 T3 20130204; EP1907182 A1 20080409; EP1907182 B1 20120912; BRPI0612775 A2 20101130	EP20050106142 20050706; WO2006EP63965 20060706		PURAC BIOCHEM BV	Method for comminuting polymeric shaped articles by milling.
EP2559725 A	20130220	WO2013026784 A1 20130228; CA2844149 A1 20130228	EP20110006825 20110819	HAGEN RAINER	UHDE INVENTA FISCHER GMBH	Verfahren und Vorrichtung zur Rückgewinnung von lactid aus Polylactid bzw. Glycolid aus Polyglycolid. "Method and device for recovery of lactide from polylactide and glycolide from polyglycolide."
GB2107320 A	19830427		GB19810029314 19810929	SEMP B AT; MING-YI T D; KERITSIS D	PHILIP MORRIS INC	Method for recycling cellulosic waste materials from tobacco product manufacture.
GB2284477 A	19950607	DE4340914 A1 19950608; GB2284477 B 19971210; US5510619 A 19960423	DE19934340505 19931127; DE19934340914 19931201	ZACHMANN G; GAST J; SIMON A; SCHUEBEL R	BRUKER ANALYTISCHE MESSTECHNIK	Identification of plastics by infra-red spectroscopy.
JP2001040078 A	20010213		JP19990219688 19990803	MINAMI M	CANON KK	Sugar chain polymer compound and its thermoformed product.
JP2002017384 A	20020122		JP20000198867 20000630	MATSUMURA S	UNIV KEIO	Method for producing trimethylene carbonate.
JP2002017385 A	20020122	JP4140804 B2 20080827	JP20000198866 20000630	MATSUMURA S	UNIV KEIO	Method for producing dicaprolactone and caprolactone polymer.

JP2002226623 A	20020814		JP20010028034 20010205	YAMAMOTO M; KUBO T; YAMA S; NAKAE T; HASHIMURA T	KANEBO LTD	Reclaimed foam and regenerating method of foam.
JP2002320499 A	20021105		JP20010131768 20010427	MATSUMURA S	UNIV KEIO	Depolymerization method to oligomer consisting essentially of ring compound of polyalkylene alkanoate or poly(3-hydroxyalkanoate), and method for polymerizing the cyclic oligomer.
JP2003079388 A	20030318	JP4171823 B2 20081029	JP20020193114 20020702; JP20010204999 20010705	MATSUMURA S	UNIV KEIO	Method for depolymerizing polyester or polycarbonate by using super critical fluid and method for producing polyester or polycarbonate.
JP2003128900 A	20030508	JP3583097 B2 20041027	JP20010324849 20011023	TAKAGI J	MITSUBISHI PLASTICS IND LTD	Lactic acid resin articles and its recycling process.
JP2003300927 A	20031021	JP4177992 B2 20081105	JP20020109918	FUJIE K; TSUJI H; DAIMON H	INST NAGOYA IND SCI RES	Method for forming monomer of biodegradable polyester.
JP2004216378 A	20040805		JP20040111029 20040405	TAKAGI J	MITSUBISHI PLASTICS IND	Shredder dust for recycling, lactic acid resin molding using the same, and method for its recycling.
JP2004290130 A	20041021		JP20030089915 20030328	ABE S; KATO S; DEGUCHI J	MITSUBISHI CHEM CORP	Method for recovering monomer constituting polyester.
JP2004308077 A	20041104		JP20030106187 20030410	HONNA H; MITA T; MOTOMIYA T	TEIJIN FIBERS LTD	Polyester fiber product meeting the demands of recycling society and recycling method.
JP2005131856 A	20050526		JP20030368541 20031029	ISHIHARA K; HORIUCHI H	TEIJIN FIBERS LTD	Method for removing different material from aliphatic polyester.
JP2005132901 A	20050526		JP20030368542 20031029	ISHIHARA K; HORIUCHI H	TEIJIN FIBERS LTD	Method for removing foreign material from aliphatic polyester.
JP2005298401 A	20051027		JP20040116653 20040412	TSUJI H; FUJIE K; DAIMON H	UNIV TOYOHASHI TECHNOLOGY	Method for converting biodegradable polyester into monomer.
JP2005330211 A	20051202		JP20040149151 20040519	FUJIE K; HORIUCHI H; ISHIHARA K; OKADO H; SAEKI T; TSUJI H	UNIV TOYOHASHI TECHNOLOGY; TEIJIN FIBERS LTD	Method for hydrolyzing biodegradable polyester into monomer, and apparatus for treating biodegradable polyester.

Continued

—Cont'd

Patent Number	Publication Date	Family Members	Priority Numbers	Inventors	Applicants	Title
JP2006137892 A	20060601	JP4665073 B2 20110406	JP20040330154 20041115	SAEKI T; DAIMON H; TSUJI H; FUJIE K; NAKAJIMA M; ISHIHARA K	UNIV TOYOHASHI TECHNOLOGY; TEIJIN FIBERS LTD	Method for regeneration waste polylactic acid.
JP2006274231 A	20061012		JP20050127057 20050330	TANAKA MASAO; NABESHIMA KOJI; MORI FUMIHIKO; EBIHARA NOBORU; UEHARA TAKESHI	CHIBA PREFECTURE	Method for obtaining monomer of polylactic acid.
JP2007001940 A	20070111		JP20050184757 20050624	MATSUBARA W; OMOTO S; YAMAMOTO I	MITSUBISHI HEAVY IND LTD	Method for recycling polyalkylene succinate, and method for recycling.
JP2007002160 A	20070111	JP4647413 B2 20110309	JP20050186223 20050627	ISHIHARA K; NAKAJIMA M	TEIJIN FIBERS LTD	Depolymerization process for biodegradable polyester.
JP2007023176 A	20070201		JP20050208434 20050719	ISHIHARA K; NAKAJIMA M	TEIJIN FIBERS LTD	Method for depolymerizing biodegradable polyester.
JP2007031538 A	20070208	JP4486561 B2 20100623	JP20050215630 20050726	ISHIHARA K; NAKAJIMA M	TEIJIN FIBERS LTD	Method for removing foreign material from polylactic acid stereo-complex polymer.
JP2007051202 A	20070301		JP20050236656 20050817	NAKAMURA K; AKATSU S; NAGAHAMA M; YOKOSUKA M	NAKAMURA K; AKATSU S; NAGAHAMA M; YOKOSUKA M	Method for regenerating lactic acid-based biodegradable plastic.
JP2007099663 A	20070419		JP20050290614 20051004	SAEKI T; DAIMON H; TSUJI H; FUJIE K; NAKAJIMA M; ISHIHARA K	UNIV TOYOHASHI TECHNOLOGY; TEIJIN FIBERS LTD	Separating and recovering method of waste of polylactic acid.
JP2007210889 A	20070823		JP20060029128 20060207	FUJIE K; ISHIHARA K; NAKAJIMA M; OKADO H; SHIMBO T; TSUJI H	UNIV TOYOHASHI TECHNOLOGY; TEIJIN FIBERS LTD	Method for monomerizing stereocomplex type polylactic acid.

JP2007224113 A	20070906		JP20060045058 20060222	ISHIHARA KI; NAKAJIMA M	TEIJIN FIBERS LTD	Method for recovering effective components from recovered biodegradable polyester.
JP2007238691 A	20070920	JP4006457 B2 20071114	JP20060060529 20060307	NAKAMURA K	NAKAMURA K	Process of regenerating lactic acid based biodegradable plastic.
JP2007277389 A	20071025	JP4747366 B2 20110817	JP20060105070 20060406	AKAMATSU K; KONISHI N; NAKAMURA K	AKAMATSU K; KONISHI N; NAKAMURA K	Recovery process of plastic waste by type.
JP2007284495 A	20071101		JP20060111038 20060413	KAWAGUCHI Y; SUMIDA N; FUKUSHIMA Y; OTA T; ISHIGAMI Y	SHARP CORP	Recycling method of thermoplastic resin, and, raw material of thermoplastic resin, thermoplastic resin member and manufacturing method thereof.
JP2008007611 A	20080117		JP20060178853 20060629	SASHI A; SHINOHARA R	KUMAMOTO TECH & IND FOUND	Method for collecting lactic acid and/or water-soluble oligomer from polylactic acid.
JP2008050351 A	20080306		JP20060204174 20060727; JP20070194291 20070726	KAWAI N	VICTOR COMPANY OF JAPAN	Method of recovering lactic acid.
JP2008100413 A	20080501		JP20060283988 20061018	FUKUSHIMA Y; SUMIDA N; UCHIUMI Y; KOSAKA H; MATSUMOTO K	SHARP CORP	Method for recycling waste plastic material, method for producing plastic raw material, method for producing plastic member, plastic raw material, and plastic member.
JP2008179713 A	20080807		JP20070014951 20070125	NAKAMURA K	REAL PLASTIC KK	Method for recycling polylactic resin.
JP2008201679 A	20080904	JP5193475 B2 20130508	JP20070036034 20070216	ISHIHARA K; NAKAJIMA M	TEIJIN FIBERS LTD	Method for producing lactide from polylactic acid.
JP2008201680 A	20080904	JP5161466 B2 20130313	JP20070036035 20070216	ISHIHARA K; NAKAJIMA M	TEIJIN FIBERS LTD	Method for producing lactide from polylactic acid.
JP2008231048 A	20081002	JP5136880 B2 20130206	JP20070074639 20070322	NISHIDA HARUO; MOTOYAMA TORU; SHIRAI YOSHITO	KYUSHU INST OF TECHNOLOGY; KITAKYUSHU FOUNDATION	Method for recovering lactide.
JP2009029757 A	20090212	JP5280656 B2 20130904	JP20070197628 20070730	ISHIHARA K; NAKAJIMA M	TEIJIN FIBERS LTD	Depolymerization method of polylactic acid.
JP2009072759 A	20090409	JP4948440 B2 20120606	JP20070224542 20070830; JP20080026060 20080206	MATSUMURA S; TSUNEIZUMI Y; OKAMOTO K; KUROSAKI H	UNIV KEIO; KUROSAKI H; KOGYO KK; MIZUSAWA IND CHEM LTD	Catalyst for depolymerizing polylactic acid and depolymerization method.

Continued

—Cont'd

Patent Number	Publication Date	Family Members	Priority Numbers	Inventors	Applicants	Title
JP2009161655 A	20090723		JP20080000609 20080107	NIIZAKI M; SUMIDA N; FUKUSHIMA Y; KAWAGUCHI Y	SHARP CORP	Method for recycling biomass-based thermoplastic resin waste, method for producing biomass-based thermoplastic resin molded article and biomass-based thermoplastic resin molded article.
JP2009242545 A	20091022		JP20080090256 20080331	FURUKAWA T; FUKUNAGA S	KANEKA CORP	Treatment method for polylactic acid based foam before recycling.
JP2009249508 A	20091029		JP20080099486 20080407	ADNAN A F M; NISHIDA H; SHIRAI Y; TANIGUCHI M	KYUSHU INST OF TECHNOLOGY; MUSASHINO KAGAKU KENKYUSHO	Method for oligomerzing polylactic acid product efficiently.
JP2010005948 A	20100114		JP20080168671 20080627	NIIZAKI MI; SUMIDA N; FUKUSHIMA Y; KAWAGUCHI Y	SHARP CORP	Method for manufacturing biomass-based plastic molded form and biomass-based plastic molded form.
JP2011162480 A	20110825	JP5376373 B2 20131225	JP20100027084 20100210	NISHIDA; SHIRAI Y	KITAKYUSHU FOUNDATION	Method of recovering lactide.
JP4118313 B1	20080716	JP2008208258 A 20080911	JP20070047535 20070227	NAKAMURA K	NAKAMURA K	Decomposition recycling method of synthetic resin having constitution structure of ester bond.
JPH05178977 A	19930720		JP19910361580 19911227	ITO K; MURATA M; MOROHASHI N; OKABAYASHI A	TOYO INK MFG CO	Method for treating molded polymer article.
JPH06240004 A	19940830	JP3267369 B2 20020318	JP19930031657 19930222	AJIOKA M; KAWASHIMA N; YAMAGUCHI T	MITSUI TOATSU CHEM INC	Method for fractionating degradable polymer composition.
JPH06240045 A	19940830	JP3512208B B2 20040329		AJIOKA MASANOBU; YAMAGUCHI TERUHIRO	MITSUI TOATSU CHEM INC	Method for separating degradable polymer composition.
JPH06297458 A	19941025	JP3487608 B2 20040119	JP19930089678 19930416	AJIOKA M; YAMAGUCHI T; AJIOKA M	MITSUI TOATSU CHEM INC	Separating method for decomposable polymer composition.
JPH06315935 A	19941115		JP19930105557 19930506	AJIOKA M; YAMAGUCHI T	MITSUI TOATSU CHEM INC	Method for separating degradable polymer composition.

JPH0649266 A	19940222	JP3356825 B2 20021216	JP19930131852 19930602; JP19920143940 19920604	AIJOKA M; ENOMOTO K; ENOMOTO T; SUZUKI K; YAMAGUCHI A; YAMAGUCHI T	MITSUI CHEM INC; MITSUI TOATSU CHEM INC	Treatment of plastic article.
JPH07309863 A	19951128	JP2821986 B2 19981105	JP19940103091 19940517		JAPAN STEEL WORKS LTD	Method for recovering lactide from polylactic acid product.
JPH08253619 A	19961001		JP19950058948 19950317	ONISHI H; TERADA T; YAMAGATA Y	MATSUSHITA DENKI SANGYO KK	Method for treating plastic molded form.
JPH09241417 A	19970916		JP19960057586 19960314	TAKAHASHI A	DAINIPPON INK & CHEM INC	Recovery of raw material for lactic acid -based polymer.
JPH1036553 A	19980210		JP19960215061 19960726	OTA M	SHIMADZU CORP	Treatment of waste aliphatic polyester.
US2001045518 A1	20011129	US6610981 B2 20030826	US20010841519 20010424; US20000200720P 20000427	SOMMER E. J	SOMMER E. J; NATIONAL RECOVERY TECHNOLOGIES INC	Method and apparatus for near-infrared sorting of recycled plastic waste.
US2005250931 A1	20051110	US2007100051 A1 20070503	US20040838223 20040505	TAKAGI J	MITSUBISHI PLASTICS INC	Shredder dust for recycling, molding for shredder dust and a method for recovering lactide from the shredder dust as well as molding formed from the lactide.
US2006283340 A1	20061221	US7467585 B2 20081223; DE102005027861 A1 20061228; DE102005027861 B4 20120802	DE200510027861 20050616	PALLMANN H	PALLMANN MASCHINENFABRIK GMBH & CO. KG	Apparatus for converting free-flowing feed material into granules, agglomerates, pellets, compacts, and the like.
US2008237910 A1	20081002	US7767744 B2 20100803	JP20070092711 20070330; JP20070321186 20071212	YAO K; MORIYAMA M; SUZUKI F; MOCHIZUKI T; KAWASAKI H	FUJI XEROX CO LTD; FUJIFILM CORP	Resin composition, resin compact, production method of resin compact and recycling method of resin compact.
US2011071235 A1	20110324	WO2011038071 A1 20110331; KR20120099384 A 20120910; EP2480589 A1 20120801; CN102498151 A 20120613; CN102498151 B 20131106	US20100823629 20100625; US20090245073P 20090923	KANNAN G; ALIDEDEOGLU H A; GALLUCCI R R	SABIC INNOVATIVE PLASTICS US LLC	Biodegradable aliphatic-aromatic copolyesters, methods of manufacture, and articles thereof.

Continued

—Cont'd

Patent Number	Publication Date	Family Members	Priority Numbers	Inventors	Applicants	Title
US4298013 A	19811103	FR2481081 A 19811030; DE3116655 A 19820401; CA1133686 A 19821019	US19800144227 19800428	SEMP B AT; MING-YI T D; KERITSIS D	PHILIP MORRIS INC	Method for recycling cellulosic waste materials from tobacco product manufacture.
US5229528 A	19930720		US19910796273 19911122	BRAKE L D; SUBRAMANIAN N S	DU PONT	Rapid depolymerization of polyhydroxy acids.
US5264614 A	19931123		US19910796274 19911122	BRAKE L D	DU PONT	Recovery of polyhydroxy acids.
US5264617 A	19931123		US19910797502 19911122	BRAKE L D	DU PONT	Preparation of alkyl esters by depolymerization.
US5264626 A	19931123		US19910797503 19911122	BRAKE L D	DU PONT	Rapid depolymerization of polyhydroxy acids .
US5268507 A	19931207		US19910796272 19911122	BRAKE L D	DU PONT	Preparation of amide derivatives of hydroxy acids.
US5342969 A	19940830		US19930025923 19930303	FORD T M; HOCKESSIN J V	DU PONT	Recovery of hydroxycarboxylic acid values from poly(hydroxycarboxylic acids).
WO0070331 A1	20001123	US6509537 B1 20030121; EP1105715 A1 20010613	WO1999EP03325 19990514	KRIEG G; FEY D BOHLEBER J; DAUSCH M	KRIEG G	Verfahren und Vorrichtung zur Detektion und Unterscheidung zwischen Kontaminationen und Gutstoffen sowie zwischen verschiedenen Farben in Feststoffpartikeln. "Method and device for detecting and differentiating between contaminations and accepts as well as between different colors in solid particles."
WO0107166 A1	20010208	SK962002 A3 20020604; PL354035 A1 20031215; HU0201525 A2 20020828; DE19934259 A1 20010208; CZ20020269 A3 20020717	DE1999134259 19990727	HOLLEY WOLFGANG; HUBER KONRAD; KATZSCHNER GREGOR; PFEIFFER THOMAS; SCHOENWEITZ CLAUDIA	FRAUNHOFER GES FORSCHUNG	Verfahren zur selektiven Abtrennung von vorgebbaren Stoffen aus Stoffgemischen. "Method for selectively separating predetermined materials in mixtures of materials."

WO0236675 A2	20020510	WO0236675 A8 20031030; WO0236675 A3 20020906; US2003208034 A1 20031106; KR20030068147 A 20030819; KR100566707 B1 20060403; JP2004513200 A 20040430; EP1332173 A2 20030806; CN1473171 A 20040204; CA2423601 C 20070522; BR0115158 A 20031021; AU2571302 A 20020515; AU2002225713 A8 20050915	US20000246158P 20001106; WO2001US43853 20011106; US20030430793 20030506	NODA I	PROCTER & GAMBLE	Plastic articles digestible by hot alkaline treatment.
WO03091238 A1	20031106	AU2003231482 A1 20031110; JP4458422 B2 20100428	JP20020124375 20020425	NISHIDA H; FAN Y; SHIRAI Y	NISHIDA H; FAN Y; SHIRAI Y	Process for producing lactide.
WO2004013217 A1	20040212	US2005233425 A1 20051020; US7396667 B2 20080708; JP4359718 B2 20091104; EP1548053 A1 20050629; AU2003252345 A1 20040223	JP20020227644 20020805	MATSUMURA S	UNIV KEIO	Method of enzymatic depolymerization of polylactic acid and process for producing polylactic acid from depolymerization product.
WO2005026245 A1	20050324	JP2005082710 A 20050331	JP20030316611 20030909	MATSUMURA S; OSANAI Y	UNIV KEIO	Method of continuously depolymerizing polyester, polycarbonate, or polylactic acid with supercritical fluid and apparatus for continuous depolymerization.
WO2005105775 A1	20071001	US2008004454 A1 20080103; US7557224 B2 20090707; KR20070009625 A 20070118; KR100830022 B1 20080515; JP4517069 B2 20100804; EP1741707 A1 20070110; CN1926126 A 20070307; EP1741707 A4 20090225; CN100475808 C 20090408	WO2005JP07813 20050425; JP20040135476 20040430	NISHIDA H; FAN Y; SHIRAI Y	KYUSHU INST OF TECHNOLOGY; KITAKYUSHU FOUNDATION; UNIV KINKI	Method of recovering lactide from polylactic acid or derivative thereof.
WO2005105908 A1	20051110	US2007293591 A1 20071220; US8513379 B2 20130820; JP4817321 B2 20111116; DE112005000965 T5 20070322	JP20040133594 20040428; WO2005JP08241 20050428	MATSUMURA S	UNIV KEIO	Depolymerization method for polymer containing ester bond in main chain and method for producing polymer containing ester bond in main chain from depolymerization product.

Continued

—Cont'd

Patent Number	Publication Date	Family Members	Priority Numbers	Inventors	Applicants	Title
WO2007102488 A1	20070913	US2009099270 A1 20090416; US7985778 A1 20090416; KR20080109010 A 20081216; EP2022818 A1 20090211; EP2022818 A4 20111005; EP2022818 B1 20130102	JP20060060529 20060307; JP20070014951 20070125	NAKAMURA K	NAKAMURA K	Process for the decomposition and reclamation of synthetic resins having ester-linkage structures.
WO2008045516 A1	20080417	JP2010506965 A 20100304; EP2079767 A1 20090722; EP2079767 A4 20100127; CA2666341 A1 20080417; CA2666341 C 20120103	US20060850744P 20061011	MOORE L; NORTON R	QLT USA INC	Preparation of biodegradable polyesters with low-burst properties by supercritical fluid extraction.
WO2008058303 A1	20080522	US2010216902 A1 20100826; SI2101974 T1 20120831; SI2295218 T1 20130329; RU2009122359 A 20101220; RU2010150609 A 20120620; RU2412804 C1 20110227; MX2009004892 A 20090521; KR20090092806 A 20090901; KR20110007259 A 20110121; JP2012066588 A 20120405; JP2010509413 A 20100325; ES2385105 T3 20120718; EP2295218 A1 20110316; EP2101974 A1 20090923; DK2101974 T3 20120723 CN101535018 A 20090916; CN102357943 A 20120222; CA2668902 A1 20080522; AU2007321746 B2 20110818; AU2007321746 A1 20080522; AT505462 A1 20090115; AT552958 T 20120415	AT20060001880 20061113; WO2007AT00515 20071113	WENDELIN G; HACKL M; FEICHTINGER K	EREMA ENGINEERING RECYCLING MASCHINEN UND ANLAGEN GESELLSCHAFT M.B.H	Method for the pretreatment, reprocessing or recycling of thermoplastic material.
WO2009081362 A1	20090702	IT1380839 B 20100913	IT2007TO00923 20071220	MUSSO SI; ZANETTI M; TAGLIAFERRO A; LUDA M P	TORINO POLITECNICO; UNIV DEGLI STUDI TORINO	Process for recycling organic materials with the production of carbon nanotubes.

WO2009100473 A1	20090820	US2011049763 A1 20110303; US8419997 B2 20130416; MX2010008248 A 20100823; RU2010137909 A 20120320; KR20100120212 A 20101112; JP2011514850 A 20110512; EP2252440 A1 20101124; EP2252440 B1 20121128; DK2252440 T3 20130318; CN101945743 A 20110112; CA2715048 A1 20090820; AU2009214810 A1 20090820; AT506489 A1 20090915; AT506489 B1 20101215	AT20080000245 20080214	HACKL M; FEICHTINGER K; WENDELIN G	EREMA ENGINEERING RECYCLING MASCHINEN UND ANLAGEN GESELLSCHAFT M.B.H	Method and to a device for injection molding plastic material.
WO2010050482 A1	20100506	US2011201069 A1 20110818; US2013288322 A1 20131031; US8501445 B2 20130806; JP2010132886 A 20100617; JP2010138389 A 20100624; JP2010138390 A 20100624 EP2348122 A1 20110727; EP2348122 A4 20120704; CN102264912 A 20111130	WO2009JP68433 20091027; JP20080275738 20081027; JP20080290320 20081112; JP20080290321 20081112	YOSHIKAWA S; KATAYAMA T; KOGURE M	TOYO SEIKAN KAISHA LTD	Method for producing oligomer and/or monomer by degrading biodegradable resin.
WO2010118954 A1	20101021	US2012142958 A1 20120607; US8431683 B2 20130430; MXPA11010716 A 20111031; JP2012523442 A 20121004; CN102348673 A 20120208; EP2419395 A1 20120222; EP2419395 B1 20130710; EP2419395 B8 20130828; BE1018716 A3 20110705; AU2010237248 A1 20101021	BE20090000232 20090414; WO2010EP54274 20100331	COSZACH P; BOGAERT J-CH; WILLOCQ J	GALACTIC S.A	Chemical recycling of PLA by hydrolysis.
WO2010118955 A1	20101021	US2012029228 A1 20120202; US8481675 B2 20130709; JP2012523443 A 20121004; EP2419396 A1 20120222; EP2419396 B1 20130501; CN102348672 A 20120208; BE1019608 A3 20120904	BE20090000231 20090414	COSZACH P; BOGAERT J-CH; WILLOCQ J	GALACTIC S.A	Chemical recycling of PLA by alcoholysis.
WO2011015433 A1	20110210	WO2011015433 A9 20110721; US2012116049 A1 20120510; US8431677 B2 20130430; MX2012001088 A 20120314; JP2013501111 A 20130110; EP2462189 A1 20120613; EP2462189 B1 20140326; CN102482447 A 20120530; BE1018850 A3 20111004; AU2010280940 A1 20111215	BE20090000475 20090806; WO2010EP60142 20100714	COSZACH P; WILLOCQ J.	GALACTIC S.A	Purification of a conventional of a polymer flow contaminated with PLA.

Continued

—Cont'd

Patent Number	Publication Date	Family Members	Priority Numbers	Inventors	Applicants	Title
WO2011029648 A1	20110317	US2012165554 A1 20120628; MX2012002137 A 20120314; JP2013504634 A 20130207; EP2475689 A1 20120718; EP2475689 B1 20140326; CN102482369 A 20120530; BE1018882 A3 20111004; AU2010294423 A1 20120119	BE20090000554 20090910	COSZACH P.; WILLOCQ J.	GALACTIC S.A	Procédé de recyclage stéréospécifique d'un mélange de polymères à base de PLA; "Method for stereospecifically recycling a PLA polymer mixture."
WO2011146562 A2	20111124	WO2011146562 A3 20120518; US2012128924 A1 20120524; KR20130109972 A 20131008; JP2013527338 A 20130627; EP2572020 A2 20130327; CN102892936 A 20130123; AU2011256163 A1 20121101	US20100345698P 20100518	LENGES G M; MADELEINE D G; SAMANT K	DU PONT	Recycled poly(trimethylene) terephthalate and processes thereof.
WO9309172 A1	19930513	US5553714 A 19960910; US5461136 A 19951024; US5397819 A 19950314; TW211035 A 19930811; SG47881 A1 19980417; MX184254 B 19970325; JP2003176289 A 20030624; JPH07507074 A 19950803; ES2095494 T3 19970216; EP0616621 A1 19940928; EP0700961 A2 19960313; EP0700961 A3 19960410; EP0616621 B1 19961218; EP0875505 A2 19981104; EP0700961 B1 19981223; DE69216114 E 19970130; DE69228010 E 19990204; CA2121507 C 19980616	US19910789570 19911108; WO1992US08676 19921013; US19930156746 19931124	CUSHMAN M R; KRUTAK J J SR; PARHAM W W; COATES C A JR; WEAVER M A; PATONAY G	EASTMAN CHEM CO	Method for tagging thermoplastic materials with near infrared fluorophores.
WO9828080 A1	19980702		WO1996DE02510 19961223	KOEHNLECHNER R	HAMOS GMBH RECYCLING UND SEPARATION-STECHNIK	Vorrichtung zum elektrostatischen sortieren von Gemischen aus Teilchen unterschiedlicher Kunststoffe. "Device for electrostatically sorting mixtures of particles of different plastic materials."

REFERENCES

[1] Vilaplana F, Karlsson S. Quality concepts for the improved use of recycled polymeric materials: a review. Macromol Mater Eng 2008;293:274–97.

[2] bio-plasticsorg. http://www.bio-plastics.org/en/news–news-a-events/news-archive/1447.

[3] Laird K. PlasticsTodaycom; May 21, 2012. http://www.plasticstoday.com/articles/recycling-made-simple-erema-ngr-052220125.

[4] eppm – NEWS. NGR develops effective solution for bioplastic recycling (6 14); 2012. http://www.eppm.com/x/guideArchiveArticle.html?gname=&&browse=p&bid=21&id=35453.

[5] PALLMANN MASCHINENFABRIK GMBH & CO KG. Recycling of PLA (Polylactic acid) foam and film waste with the Plast-Agglomerator, type PFV. http://www.pallmannindustries.com/pla_foam_waste_recycling.htm.

[6] Södergård A, Näsman J. Stabilization of poly(L-lactide) in the melt. Polym Degrad Stab 1994;46:25–30.

[7] Södergård A, Näsman JH. Melt stability study of various types of poly(L-lactide). Ind Eng Chem Res 1996;35:732–5.

[8] McNeill I, Leiper H. Degradation studies of some polyesters and polycarbonates—1. Polylactide: general features of the degradation under programmed heating conditions. Polym Degrad Stab 1985;11:267–85.

[9] McNeill I, Leiper H. Degradation studies of some polyesters and polycarbonates—2. Polylactide: degradation under isothermal conditions, thermal degradation mechanism and photolysis of the polymer. Polym Degrad Stab 1985;11:309–26.

[10] Nishida H, Mori T, Hoshihara S, Fan Y, Shirai Y, Endo T. Effect of tin on poly(-lactic acid) pyrolysis. Polym Degrad Stab 2003;81:515–23.

[11] Fan Y, Nishida H, Mori T, Shirai Y, Endo T. Thermal degradation of poly(L-lactide): effect of alkali earth metal oxides for selective, L-lactide formation. Polymer 2004;45:1197–205.

[12] Wachsen O, Platkowski K, Reichert KH. Thermal degradation of poly-L-lactide—studies on kinetics, modelling and melt stabilisation. Polym Degrad Stab 1997;57:87–94.

[13] Hartmann M. Advance in the commercialization of poly(lactic acid). Polym Prepr 1999;40:570–1.

[14] Niaounakis M. Biopolymers reuse, recycling, and disposal, chapter 7: degradation on demand. 1st ed Plastics Design Library (PDL); 2013. Access Online via Elsevier; p. 432.

[15] BASF-News Release. New life for recycled plastics and bioplastics in packaging applications; March 19, 2009. http://www2.basf.us/corporate/news_2009/news_release_2009_00073.htm.

[16] Pillin I, Montrelay N, Bourmaud A, Grohens Y. Effect of thermo-mechanical cycles on the physico-chemical properties of poly(lactic acid). Polym Degrad Stab 2008;93:321–8.

[17] Żenkiewicz M, Richert J, Rytlewski P, Moraczewski K, Stepczyńska M, Karasiewicz T. Characterisation of multi-extruded poly(lactic acid). Polym Test 2009;28:412–8.

[18] Hamad K, Kaseem M, Deri F. Effect of recycling on rheological and mechanical properties of poly(lactic acid)/polystyrene polymer blend. J Mater Sci 2011;46:3013–9.

[19] Takahashi Y, Okajima S, Toshima K, Matsumura S. Lipase catalyzed transformation of poly(lactic acid) into cyclic oligomers. Macromol Biosci 2004;4:346–53.

[20] Cornell D. Biopolymers in the existing postconsumer plastics recycling stream. J Polym Environ 2007;15:295–9.

[21] Project code. MDP024-004. WRAP final report. Development of NIR detectable black plastic packaging; September 2011. http://www.wrap.org.uk/sites/files/wrap/Recyclability%20of%20black%20plastic%20packaging.pdf.

[22] Bioplastics European. Fact sheet. Mechanical recycling; December 2010. http://en.european-bioplastics.org/wp-content/uploads/2011/04/fs/FactSheet_Mechanical_Recycling.pdf.

[23] Huth-Fehre Th, Feldhoff R, Kantimm Th, Quick L, Winter F, Cammann K, et al. NIR – remote sensing and artificial neural networks for rapid identification of post consumer plastics. J Mol Struct 1995;348:143–6.

[24] NatureWorksLLC, Using near-infrared sorting to recycle PLA bottles. http://www.natureworksllc.com/the-ingeo-journey/end-of-life-options/recycling/recycling-sortation.aspx.

[25] http://www.titech.com.

[26] http://www.magsep.com.

[27] Project code:MDP017. WRAP final report: domestic mixed plastics packaging waste options; June 2008. http://www.wrap.org.uk/sites/files/wrap/Mixed%20Plastic%20Final%20Report.pdf.

[28] http://www.napcor.com/pdf/NAPCOR_PLA.pdf.

[29] http://www.plasticsrecycling.org.

[30] http://www.incpen.org.

[31] http://www.wrap.org.uk/downloads/Recyclability_of_black_plastic_packaging1.dffe0c83.11203.pdf.

[32] Bruno EA. Automated sorting of plastics for recycling; 2000. http://infohouse.p2ric.org/ref/09/08620.pdf.

[33] SPI: The Plastics Industry Trade Association. http://www.plasticsindustry.org/AboutPlastics/content.cfm?ItemNumber¼4823; 2012.

[34] Niaounakis M. Biopolymers reuse, recycling, and disposal, chapter 2: definition and assessment of (bio)degradation. 1st ed Plastics Design Library (PDL); 2013. Access Online via Elsevier; p. 432.

[35] Tsuji H, Yamamura Y, Ono T, Saeki T, Daimon H, Fujie K. Hydrolytic degradation and monomer recovery of poly(butylene succinate) and poly(butylene succinate/adipate) in the melt. Macromol React Eng 2008;2:522–8.

[36] Saeki T, Tsukegi T, Tsuji H, Daimon H, Fujie K. Depolymerization of poly(L-lactic acid) under hydrothermal conditions. Jpn J Polym Sci Technol 2004;61:561–6.

[37] Tsuji H, Nakahara K, Ikarashi K. Poly(L-lactide), 8. High-temperature hydrolysis of poly(L-lactide) films with different crystallinities and crystalline thicknesses in phosphate-buffered solution. Macromol Mater Eng 2001;286:398–406.

[38] Ikarashi K, Tsuji H. Hydrolytic behavior of poly(L-lactide) crystalline residues. Polym Prepr, Japan-English Edn 2000;49:480.

[39] Tsuji H, Daimon H, Fujie K. A new strategy for recycling and preparation of poly(L-lactic acid): hydrolysis in the melt. Biomacromolecules 2003;4:835–40.

[40] Kobayashi S, Uyama H, Takamoto T. Lipase-catalyzed degradation of polyesters in organic solvents. A new methodology of polymer recycling using enzyme as catalyst. Biomacromolecules 2000;1:3–5.

[41] Takamoto T, Uyama H, Kobayashi S. Lipase-catalyzed degradation of polyester in supercritical carbon dioxide. Macromol Biosci 2001;1:215–8.

[42] Takamoto T, Uyama H, Kobayashi S. Lipase-catalyzed synthesis of aliphatic polyesters in supercritical carbon dioxide. e-Polym 2001:1–6.

[43] Matsumura S. Enzyme-catalyzed synthesis and chemical recycling of polyesters. Macromol Biosci 2002;2:105–26.

[44] Matsumura S, Ebata H, Kondo R, Toshima K. Organic solvent-free enzymatic transformation of poly(ε-caprolactone) into repolymerizable oligomers in supercritical carbon dioxide. Macromol Rapid Commun 2001;22:1325–9.

[45] Ebata H, Toshima K, Matsumura S. Lipase-catalyzed transformation of poly(ε-caprolactone) into cyclic dicaprolactone. Biomacromolecules 2000;1:511–4.

[46] Matsumura S, Harai S, Toshima K. Lipase-catalyzed transformation of poly(trimethylene carbonate) into cyclic monomer, trimethylene carbonate: a new strategy for sustainable polymer recycling using an enzyme. Macromol Rapid Commun 2001;22:215–8.

[47] Kondo R, Toshima K, Matsumura S. Lipase-catalyzed selective transformation of polycaprolactone into cyclic dicaprolactone and its repolymerization in supercritical carbon dioxide. Macromol Biosci 2002;2:267–71.

[48] Kaihara S, Osanai Y, Nishikawa K, Toshima K, Doi Y, Matsumura S. Enzymatic transformation of bacterial polyhydroxyalkanoates into repolymerizable oligomers directed towards chemical recycling. Macromol Biosci 2005;5:644–52.

[49] Osanai Y, Toshima K, Matsumura S. Enzymatic transformation of aliphatic polyesters into cyclic oligomers using enzyme packed column under continuous flow of supercritical carbon dioxide with toluene. Sci Technol Adv Mater 2006;7:202–8.

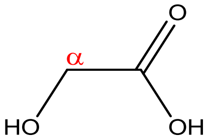
[50] Ariffin H, Nishida H, Hassan MA, Shirai Y. Chemical recycling of polyhydroxyalkanoates as a method towards sustainable development. Biotechnol J 2010;5:484–92.

[51] Witzke DR. Introduction to Properties, Engineering, and Prospects of Polylactide Polymer. State University [Ph.D. thesis]. Chemical Engineering, Michigan. http://www.jimluntllc.com/pdfs/polylactic_acid_technology.pdf; 1997.

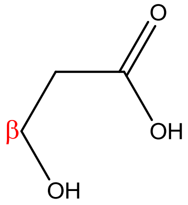
Glossary

α-Amino acid Amino acid substituted on the α-carbon atoms by the substituent R, i.e., $H_2N–C(R)H–COOH$. The monomer from which proteins and other polypeptides may be considered to be derived by the loss of water.

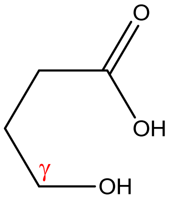
α-Hydroxy acid or 2-hydroxy acid Organic compound that consists of a carboxylic functional acid substituted with a hydroxyl functional group on the adjacent carbon. Common and simple α-hydroxy acids are lactic acid and glycolic acid.



β-Hydroxy acid or 3-hydroxy acid Organic compound that contains a carboxylic acid functional group and hydroxy functional group separated by two carbon atoms. It is closely related to α-hydroxy acid in which the two functional groups are separated by one carbon atom. Known examples of β-hydroxy acids are β-hydroxypropionic acid (3-hydroxypropionic acid) and β-hydroxybutyric acid (3-hydroxybutyric acid).

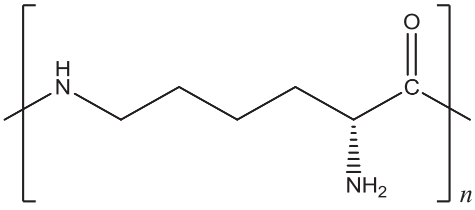


γ-Hydroxy acid or 4-hydroxy acid Organic compound that contains a carboxylic acid functional group and hydroxy functional group separated by three carbon atoms. A known example of a γ-hydroxy acid is γ-hydroxybutyric acid (4-hydroxybutyric acid or 4-hydroxybutanoic acid).



γ-PGA See poly(γ-glutamic acid).

ε-Poly(L-lysine) (ε-PL) Biodegradable water-soluble natural homopolymer of the essential amino acid L-lysine that is produced by bacterial fermentation. ε-PL is represented by the chemical formula:



Additive Substance added to a material or product in order to, for example, generate certain properties.

Aerobic It means "requiring oxygen." Aerobic processes can only function in the presence of molecular oxygen (O_2).

Aesthetic properties Properties that determine the reactions (perceptions) of the senses: the eye (color, luster, covering power, appearance), and the tactile sense, viz., the tactile corpuscles of the skin (handle).

Algae (micro-) Large and diverse group of unicellular photo- and heterotrophic organisms that have attracted much attention in recent years due to their potential value as a renewable energy source. Focus has been on storage lipids in the form of triacylglycerols, which can be used to synthesize biodiesel via transesterification. The remaining carbohydrate content can also be converted to bioethanol via fermentation. Biopolymers derived from algae evolved as a byproduct of algae biofuel production.

Amino acid Organic acid containing both an amino group and a carboxylic group, i.e., in general, $H_2N–R–COOH$. The monomer from which polyamides may be considered to be formed by loss of water.

Amylose A linear polysaccharide made up of D-glucose units. It is one of the two components of starch, making up approximately 20–30% of the structure. The other component is amylopectin, which makes up 70–80% of the structure.

Anaerobic It means deficient in oxygen and describes environments where there is no molecular oxygen (O_2).

ASTM International Formerly known as the American Society for Testing and Materials (ASTM), it is an international standards organization that develops and publishes voluntary consensus technical standards for a wide range of materials, products, systems, and services.

Bacterial cellulose Cellulose produced from certain types of bacteria such as genera *Acetobacter*, *Sarcina ventriculi*, and *Agrobacterium*. Bacterial cellulose has the same molecular formula as plant cellulose, but it has significantly different macromolecular properties and characteristics. In general, microbial cellulose is more chemically pure, containing no hemicellulose or lignin.

Bagasse Fibrous material that remains after sugarcane or stalks are crushed to extract their juice. It is currently used as a biofuel and in the manufacture of pulp and paper products, building materials, and, lately, biopolymers.

Bioabsorbable Material that is capable of being degraded or absorbed when exposed to bodily fluids such as blood, and components thereof such as enzymes, and that can be gradually resorbed, absorbed, and/or eliminated by the body.

Bio-based The term refers to a material or product that is (partly) derived from biomass (plants).

Biocompatible polymer Polymer that does not cause substantial adverse health effects upon oral ingestion, topical or transdermal application, subcutaneous injection, intramuscular injection, inhalation, implantation, or intravenous injection. A biocompatible polymer in its intact, as-synthesized state and in its decomposed state, i.e., its degradation products, is not, or at least is minimally, toxic to living tissue; does not, or at least minimally and reparably, injure(s) living tissue; and/or does not, or at least minimally and/or controllably, cause(s) an immunological reaction in living tissue.

Biocomposite Biopolymers or synthetic polymers reinforced with natural fibers, such as sisal, flax, hemp, jute, banana, wood, and various grasses, and/or fillers and additives. Novel biocomposites are based on a biodegradable matrix resin reinforced with natural fibers.

Biodegradable polymer Polymer that can be broken down chemically by natural biological processes, such as being digested by bacteria or fungi into smaller components not harmful to the environment.

Biofuel Any fuel or oil that is industrially applicable and originates from a biological and/or renewable resource. Biological and/or renewable resources include waste materials from industry and farming, but do not include fossil fuels such as coal or oil. The biofuel may be a raw biofuel, in the sense that it may need further processing before reaching an end user, for example, it may contain components that needs to be removed prior to use in, e.g., a vehicle, via, for example, further distillation and/or chemical processes (refining). Various definitions are used in defining classes of fuel or petroleum products. For example, a diesel fuel may be defined by a boiling point range or by the length of its hydrocarbon chains. In addition to this, certain minimum requirements may have to be met in order to market a fuel or biofuel as, for example, a "diesel" (e.g., European standard EN 590) or a "biodiesel" (e.g., International standard EN 14214).

Biomass The weight of all organisms in a given population.

Biomax® PTT Poly(trimethylene terephthalate) (PTT) marketed by DuPont. It is a biosourced polyester made from propanediol and terephthalic acid containing up to 37 wt% renewably sourced content for packaging applications. Biomax® PTT is an unfilled polyester and is especially suitable for cosmetic applications and other demanding packaging applications where chemical resistance and durability are essential.

Bionolle™ Poly(butylene succinate)-based aliphatic (co)polyesters marketed by Showa High Polymer Company. Two different grades of Bionolle™ are commercially available: poly(butylene succinate) (PBS), known as the 1000 series; and poly(butylene succinate-*co*-adipate) (PBSA), the 3000 series.

Bioplastic Substance that contains the biopolymer as an essential component.

Biopolymer Polymer that is based on renewable raw materials, as well as biological and fossil fuel–based, biodegradable polymers. Biopolymers can be produced by biological systems such as microorganisms, plants, or animals, or obtained by chemical synthesis.

Biorefinery Facility that convert biomass—biological materials from living or recently living organisms—into fuels, energy, chemicals, and materials (and feed).

Blend, polymer Physical mixture of two or more polymers. Polymer blends can be broadly divided into three categories:

1. Immiscible polymer blend. This is a blend of two polymers exhibiting two glass transition temperatures (T_g).
2. Compatible polymer blend. This is an immiscible polymer blend that exhibits macroscopically uniform physical properties. The macroscopically uniform properties are usually caused by sufficiently strong interactions between the component polymers.
3. Miscible polymer blend. This is a polymer blend that is a single-phase structure. In this case, a single T_g is observed.

Burst effect Term used to refer to the burst effects in which a higher than optimal rate of diffusion of a bioactive agent out of a controlled release formulation occurs during the solidification of a liquid delivery system and/or during the initial period following implantation of a preformed solid implant such as a monolithic or a microparticulate implant; also called "initial burst effect" (**WO2008045516,** 2008, QLT USA INC).

CA See cellulose acetate.

CAB See cellulose acetate butyrate.

CAP See cellulose acetate propionate.

Carbon-14, ^{14}C, or radiocarbon Radioactive isotope of carbon with a half-life time of 5730 years. It is used in various techniques called carbon dating and carbon labeling. Cosmic rays colliding with the atmosphere create secondary cosmic rays in the form of energetic neutrons. When these energetic neutrons collide with a ^{14}N atom, it turns into ^{14}C atom and a hydrogen atom. Since nitrogen gas makes up about 78% of the Earth's air, by volume, a considerable amount of ^{14}C is produced. The ^{14}C atoms combine with oxygen to form carbon dioxide, which is used by plants in photosynthesis, so new plant material will contain both ^{14}C and ^{12}C. A product made from renewable resources (biomass) will have a relatively high level of ^{14}C, while a product made from fossil fuel–based resources will have no ^{14}C. The percentage of renewable carbon in a material (solid or liquid) can be measured with an accelerator mass spectrometer.

Casein Natural polymer extracted from skim milk proteins.

Castor oil Triacylglycerol that is composed of 85–90% 12-hydroxyoleic acid, also known as ricinoleic acid. Castor oil is a unique natural material and is obtained from the *Ricinus Communis* plant, which grows in tropical regions. Castor oil is the only commercially available natural oil that is produced directly from a natural source. It is used in the production of polyamides such as polyamide 11 (PA 11), polyamide 610 (PA 610), and polyamide 1010 (PA 1010).

Cellulose Crystalline polysaccharide of noncrosslinked long chain $(C_6H_{10}C_5)_n$ whose monomeric units, glucose, are interlinked by β-1-4 bonds. These bonds are harder to hydrolyze than the α-1-4 bonds present between the glucose molecules that constitute the polymeric chain of the starch. Cellulose is the most common organic compound on Earth, and it is the structural component of the primary cell wall of green plants and many forms of algae. About 33% of all plant matter is cellulose (the cellulose content of cotton is 90% and that of wood is 40–50%).

Cellulose acetate (CA) The acetate ester of cellulose prepared by reacting cellulose with acetic acid and acetic anhydride in the presence of sulfuric acid.

Cellulose acetate butyrate (CAB) A mixed cellulose ester prepared by treating fibrous cellulose with butyric acid, butyric anhydride, acetic acid and acetic anhydride in the presence of sulfuric acid.

Cellulose acetate propionate (CAP) A mixed cellulose ester prepared by treating fibrous cellulose with propionic acid, acetic acid, and anhydrides in the presence of sulfuric acid.

Cellulose nitrate (CN) The nitrate ester of cellulose prepared by treating fibrous cellulosic materials with a mixture of nitric and sulfuric acids.

CEN See European Committee for Standardization.

CN See cellulose nitrate.

$scCO_2$ See supercritical carbon dioxide.

Coefficient of friction (μ) The ratio of the tangential force F to the normal load W when the surface is moved relative to another surface.

$$\mu = F/W$$

The coefficient of friction depends on the load, contact area, surface structure, velocity of sliding, temperature, and presence of lubricants.

Compatibilizer Polymer or copolymer that, when added to an immiscible polymer blend, modifies its interfacial character and stabilizes its morphology. Compatibilizers usually stabilize morphologies over distances of the order of micrometers or less (UAPC).

Composite Multicomponent material comprising multiple different (nongaseous) phase domains in which at least one type of phase domain is a continuous phase (IUPAC).

Composite laminate Laminate consisting of one or more layers of a substrate, often fibrous, impregnated with a curable polymer, or liquid reactants (IUPAC).

Composting Process of degrading waste materials under conditions no higher than 70 °C, and averaging more nearly 55–60 °C, at or near 100% relative humidity, and for durations ranging from 2 weeks to more than several months. The materials continue to degrade into low-molecular-weight fragments and/or monomers that can ultimately be biodegraded, that is, metabolized by microorganisms, completely into biomass, biogas, and liquid leachate.

Conjugate fiber Extrudate of two polymers from the same spinneret with both polymers contained within the same filament. The term is often used, particularly in Asia, as synonymous with bicomponent fiber.

Crimp Degree of deviation from linearity of a non-straight fiber. Fiber crimp is the waviness of a fiber expressed as waves or crimps per unit length or as the difference between the lengths of the straightened and crimped fiber (expressed as a percentage of the straightened length). Crimp in a textile strand is defined as undulations or succession of waves or curls in a strand induced either naturally during fiber growth, mechanically or chemically.

Crotonic acid Unsaturated organic acid, CH_3–CH=CH–COOH, found in croton oil and having many industrial uses.

Degradation The process of polymer chain scission by the cleavage of bonds in the polymer backbone. This leads to a reduction of length of the polymer chains. Erosion is the mass loss of a polymer matrix, which can be due to the loss of monomers, oligomers, polymer chains, or parts thereof. Erosion can be the result of biological, chemical, or physical effects. Accordingly, it can be understood that polymer degradation is part of the polymer erosion process.

Degra-novon® Biodegradable additive of Novon (JP). It comprises starch powder whose surface is treated with a silane coupling agent, unsaturated fatty acid and aliphatic esters, and transition metal catalysts. Degra-novon® is usually used as an additive in a polyolefin to promote its decomposition by sunlight, heat, and microorganisms in soil or water.

Destructured starch Starch that has lost most of its crystalline order and so no longer has its natural structure. Since natural starch generally has a granular form, it needs to be destructed before it can be melted.

DEXON™ S Braided and monofilament synthetic absorbable surgical sutures composed of the homopolymer of glycolic acid. The sutures are sterile, inert, noncollagenous, and nonantigenic. DEXON™ S sutures are available in the undyed natural beige color and also green dyed to enhance visibility in tissue. DEXON™ S sutures meet all requirements established by the United States Pharmacopoeia (USP) and European Pharmacopoeia (EP) for synthetic absorbable surgical sutures. Braided DEXON™ S sutures are indicated for use as absorbable sutures in general soft tissue approximation and/or ligation, including use in ophthalmic procedures, but not for use in cardiovascular or neural tissue.

dtex See tex.

Eastar Bio® Poly(butylene adipate-*co*-terephthalate) copolyester (PBAT) produced by Eastman Chemicals. Novamont (IT) bought Eastar Bio technology in 2004.

Ecoflex® Poly(butylene adipate-*co*-terephthalate) copolyester (PBAT) produced by BASF. It is a biodegradable polymer based on nonrenewable (fossil) resources and is synthesized from butane diol, adipic acid, and dimethyl terephthalate. Introduced in 1998, Ecoflex® has properties that mimic those of low density polyethylene (LDPE).

Ecovio® Blend of Ecoflex® and PLA. Introduced in 2004 by BASF, Ecovio® has improved stiffness.

Emulsion Mixture of two or more immiscible liquids held in suspension. Typically, one liquid of the two (termed "the dispersed phase") is dispersed in the second liquid (the "continuous phase"). Emulsions typically have a cloudy appearance due to the many phase interfaces (the boundary between the phases) that scatter light that passes through the emulsion.

EnPol® Series of biodegradable aliphatic and aliphatic-aromatic copolyesters, produced through the polycondensation reaction of glycols and dicarboxylic acids produced by Ire Chemical Ltd. (KR). The EnPol series contains the major grades EnPol® G4560, EnPol® G4560J (>MFI), and Enpol® G8060.

Enzymatic hydrolysis Hydrolysis mediated by hydrolytic enzymes. It includes the breaking of ester and amide linkages from the polymer backbone by the addition of water mediated by hydrolytic enzymes to result in the parent carboxylic acid group and the respective functional group, that is, the hydroxyl functional group for esters (i.e., alcohols such as methanol) and the appropriate amine for amides. This is also known as hydrolytic degradation of the polymer backbone.

Enzymes Catalytic proteins that decrease the level of activation energy of molecules favoring chemical reactions. Enzymes are named and numbered (EC numbers) according to rules adopted by the Enzyme Commission of the International Union of a Pure and Applied Chemistry. The enzymes are grouped in six different classes according to the reaction catalyzed. The first number identifies the class of enzymes catalyzing a given chemical reaction: (1) oxidoreductases for catalyzing redox reactions; (2) transferases for catalyzing transfer of functional group reactions; (3) hydrolases for catalyzing hydrolysis; (4) lyases for catalyzing addition to double bond reactions; (5) isomerases for catalyzing isomerization; (6) ligases for catalyzing formation of new bonds using ATP.

Esterase Enzyme that catalyzes the hydrolysis of an ester. The term is used interchangeably with polyesterase.

European Committee for Standardization (CEN) CEN (Comité Européen de Normalisation) contributes voluntary technical standards that promote free trade, the safety of workers and consumers, environmental protection, exploitation of research and development programs, and public procurement.

Exfoliation Delaminating process by which a polymer material is inserted into the adjacent thin layers of a layered clay compound to widen the interlayer distance there between (sometimes referred to as "gallery") from its normal size of 1 nm to about 20 nm or higher. Thus, there is a clear disruption of the layers which get spatially separated apart bringing about nanoscale dispersion in the polymer matrix.

Fabric A three-dimensional assembly of filaments that may be woven, knitted, felted, or otherwise formed into a flexible sheet having two-layer dimensions and a thinner thickness dimension. A fabric may be cut to a desired size before or at the time of use.

Feedstock Raw material fed into an industrial process for conversion into something different.

Filament A single, long, thin flexible structure. It may be continuous or staple.

Flame retardancy Property of not continuing combustion or not generating afterglow after removing an ignition source. A flame retardant is a component, which when added to a polymer contributes to improvement of flame retardancy of the polymer.

Gel A three-dimensional network organization swelling in a solvent. When water is the solvent, the gel may be defined as "hydrogel." Further, the three-dimensional network is due to polymer chain entanglements for a physical gel, whereas it is due to chemical bonds for a chemical gel.

Gelatinized starch Processed starch obtained by treating starch by any known gelatinization method such as by heating in the presence of water at a temperature of about 40 °C or more. Gelatinization may also be effected by kneading starch granules in the presence of 1–45 wt% of water for a period of time sufficient to disrupt the granules.

Genetically modified organisms (GMOs) Organisms in which the genetic material (DNA) has been altered in a way that does not occur naturally.

Glycosidic bond Type of covalent bond that joins a carbohydrate (sugar) molecule to another group, which may or may not be another carbohydrate.

GreenPla® The generic term for biodegradable polymers or plastics, raw materials, and products that contain biodegradable polymers or plastics and that conform to the identification standards prescribed by the Japan Bioplastics Association (JBPA).

Gypsum Very soft mineral composed of calcium sulfate dehydrate. It has the chemical formula of $CaSO_4{\cdot}2H_2O$. It is mainly deposited from lake and seawater, as well as in hot springs, from volcanic vapors, and sulfate solutions in veins in sedimentary rocks.

Highly attenuated fiber A fiber having a high drawdown ratio.

HLB See Hydrophile–Lipophile Balance.

Hot-melt adhesive Thermoplastic polymer or copolymer that is heated to obtain a liquid of flowable viscosity, and, after application, cooled to obtain a solid. Generally, the molecular weight of the adhesive is tailored to provide good rheology as a melt and sufficient strength as a solid to resist shearing forces experienced in the application.

Hydrogel Crosslinked polymeric material that exhibits the ability to swell in water or aqueous solution without dissolution and to retain a significant portion of water or aqueous solution within its structure.

Hydrolysis Process in which a molecule is cleaved in two by the addition of a molecule of water. This process can occur both chemically and enzymatically. In a hydrolysis reaction that involves breaking an ester bond, one hydrolysis product contains a hydroxyl functional group and the other a carboxylic acid functional group. Amides hydrolyze to the parent carboxylic acid and the corresponding amine.

Hydrolytic enzymes Class of hydrolases that include, but are not limited to, proteases, lipases, cutinases, and esterases. These enzymes have been proven useful for a variety of industrial applications, including the enzymatic hydrolysis of aliphatic polyesters.

Hydrophile–lipophile balance (HLB) The HLB is an expression of the relative amounts of the hydrophilic (water-loving or polar) and lipophilic (oil-loving or nonpolar) groups in a disposable biopolymer without weighting their polarity strengths. A disposable material that is lipophilic (i.e., hydrophobic) in nature is assigned a low HLB (below 9.0, on a scale of 0–20 units). HLB measurements are useful in estimating whether a candidate additive will help to speed or retard water permeation. For example, the HLB value of PLA is approximately 10 and that of PGA is about 15. Lactide has an HLB of about 12, and glycolide has an HLB of about 15. A typical good plasticizer for PLA is dimethyl adipate (HLB about 10); however, this plasticizer does not function well with poly(glycolic acid) (from: 2002, **US2002123546** A1, ECOPOL LLC; CARGILL DOW POLYMERS LLC).

Immiscible Property of two or more substances, most typically liquids, that prevents them from mixing together and forming a single homogeneous phase.

Ingeo™ Trademark name for a range of poly(lactic acid)s (PLAs) owned by NatureWorks LLC (USA).

Interpenetrating polymer network (IPN) Combination of two or more polymers in which each polymer forms a network. There are entanglements and interactions between the networks. When swollen in a solvent, none of the polymers will dissolve in the solvent.

Invention New product, process, or apparatus or any new use thereof. To be patentable, an invention must be novel, involve an inventive step (i.e., not be obvious to those having ordinary skill in the particular art of the invention), and be susceptible of industrial application (European Patent Office, EPO).

Ionic liquid Liquid containing substantially only anions and cations. The cations associated with an ionic liquid are structurally diverse but generally contain one or more nitrogens that are part of a ring structure and can be converted to a quaternary ammonium. Examples of these cations include pyridinum, pyridazinium, pyrimidinium, pyrazinium, imidazolium, pyrazolium, oxazolium, triazolium, thiazolium, piperidinium, pyrrolidinium, quinolinium, and isoquinolinium. The anions associated with an ionic liquid can also be structurally diverse and can have a significant impact on the solubility of the ionic liquid in different media. For example, an ionic liquid containing hydrophobic anions such as hexafluorophosphates or triflimides has very low solubility in water, while an ionic liquid containing hydrophilic anions such as chloride or acetate is completely miscible in water.

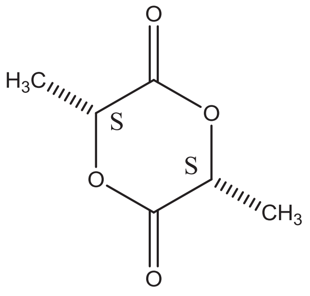
IPN See interpenetrating polymer network.

Isosorbide The diol 1,4:3,6-dianhydro-D-sorbitol. Isosorbide is readily made from renewable resources, such as sugars and starches. For example, isosorbide can be made from D-glucose by hydrogenation followed by acid-catalyzed dehydration (Fleche G., et al., Starch/Starke, 38(1), 26–30, 1986).

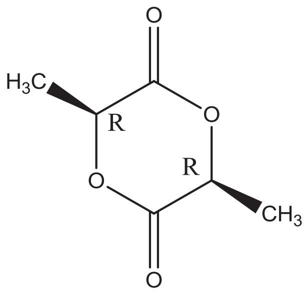
Kenaf Annual plant belonging to the mallow family classified into the same category as hibiscus, which grows rapidly, reaching as high as 4–5 m and as wide a stem diameter as 4–5 cm; in the fastest cases, its growth is about 10 cm per day. In this way, kenaf has a fast photosynthetic rate and thus can absorb a large amount of carbon dioxide; therefore, it is attracting attention as one of the means to simultaneously solve the global problems of global warming caused by carbon dioxide and deforestation. The stem of kenaf consists of bast, which is a fiber of stem bark and xylem existing at the center of the stem, each of which has different features. The bast accounts for 30% (mass ratio) of the kenaf stem and has a feature that it is long and excellent in strength similar to fiber of coniferous trees. This bast fiber is used for ropes, cloths, bags, and papers. The xylem comprises 70% (mass ratio) of the kenaf stem and is used as reinforcing material of houses or material of canoes, and has a feature that the fiber is shorter than the fiber of broad-leaf trees. The whole stem composed of bast and xylem resembles broad-leaf tree fiber, which can be formed into paper-like high quality Japanese washi (2004, WO2004063282 A1, NEC CORP).

"L*, a*, b" color space (or CIELAB) Method for describing colors developed by the CIE (Commission Internationale de l'Eclairage). The CIE provides recommendations for colorimetry by specifying the illuminants, the observer, and the methodology used to derive values for describing color. Three coordinates are utilized to locate a color in a color space, which is represented by L*, a*, and b*. When a color is expressed in CIELAB, L* defines lightness; if a value is closer to 0, it means total absorption or how dark a color is. If the L* value is closer to 100, it means total reflection or how light a color is. a* represents red and green hues, whereas b* represents blue and yellow hues. A material being described as "white" exhibits an L* value that can range from 70, 80, or 85 to 100, with a corresponding set of "a" and "b" values that are substantially close to 0 (less than 5 units on the CIE color scale).

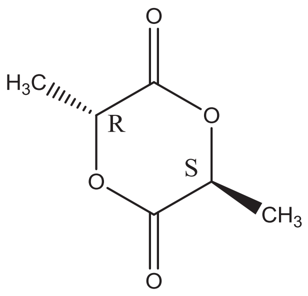
Lactide Ring closure of two lactic acid molecules. Three different stereoisomers of lactide are known depending on whether they consist of: (1) two L-lactic acid molecules: L-lactide; (2) two D-lactic acid molecules: D-lactide, (3) one L-lactic acid molecule and one D-lactic acid molecule: meso-lactide. Meso-lactide is characterized by a melting temperature of around 50 °C, whereas the melting temperature of L- and D-lactide isomers is 97 °C. An equimolar mixture of L- and D-lactide results in LD-lactide (rac-lactide):



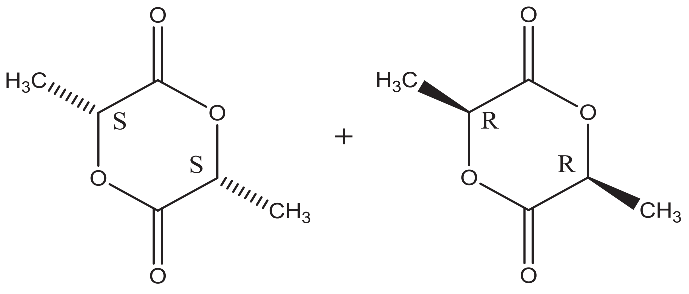
L-Lactide



D-Lactide



meso-Lactide



L-Lactide D-Lactide

LD-Lactide (*rac*-lactide) : equimolar mixture of L-lactide and D-lactide

Lacty® Poly(lactic acid) (or polylactide) produced by Shimadzu Corp. The series of Lacty® contains three major grades, namely #5000, 9000, and 9800. Crystallinity of the aliphatic polyester decreases gradually in this order. Lacty® #5000 and 9000 have crystallinity, while #9800 has noncrystallinity. Melt flow rate, that indicates the mold property, increases in this order. The series of Lacty® are fitted for injection molding, fiber, film, and sheet.

Laminate Material consisting of more than one layer, the layers being distinct in composition, composition profile, or anisotropy of properties. Laminates may be formed by two or more layers of different polymers (IUPAC).

Landfill Specially structured solid waste pit, lined with plastic and/or clay into which solid waste is dumped, isolated from ground water and air, and kept dry, thereby preventing microbial action from breaking down the waste, which, as a result, degrades slowly. A landfill is a solid waste context, generally in an anaerobic environment at the temperature of the ambient air or adjacent soil in relatively low humidity.

Lignin Crosslinked macromolecule, highly hydrophobic, comprised of aromatic elements derived from phenol. Lignin is a complex organic substance binding the cells, fibers, and vessels that constitute wood and the lignified elements of plants. After cellulose, it is the most abundant renewable carbon source on Earth.

Lignosulfonate Water-soluble anionic polyelectrolyte polymer. It is the byproduct of pulp and paper; also called sulfonated lignin.

Lipase Enzyme that catalyzes the hydrolysis of fats into glycerol and fatty acids by hydrolyzing ester bonds.

Macrophyte Macroscopic fresh or brackish water aquatic plant that is comprised of multicellular specialized tissues with highly differentiated forms. Macrophytes include aquatic angiosperms (flowering plants), pteridophytes (ferns), and bryophytes (mosses, homworts, and liverworts).

Masterbatch Composition comprising a carrier polymer and one or more ingredients (e.g., colorants) in higher concentration than occurring in the final mixture, and which composition is subsequently diluted with the remainder of the ingredients.

Mechanical recycling See physical recycling.

Microalgae See algae.

Mineralization Conversion of a biodegradable polymer to CH_4 or CO_2 and H_2O, inorganic compounds and biomass.

Miscible Property of two or more substances, most typically liquids, that allows them to be mixed together and form a single homogeneous phase.

Modulus The ratio of a component of stress or force per unit area applied to a material divided by the strain along an axis of applied force that results from the applied force.

Multicomponent fibers Fibers formed from at least two polymers (e.g., biocomponent fibers) that are extruded from separate extruders.

Multiconstituent fibers Fibers formed from at least two polymers (e.g., biconstituent fibers) that are extruded from the same extruder.

Natural fibers Fibers found in nature and utilized "in natura" (as found in nature) or after its beneficiation. The natural fibers are divided, in relation to their origin, into mineral, animal, and vegetable fibers.

Nonwoven Web having a structure of individual fibers or threads that are interlaid, but not in an identifiable manner as in a knitted web. A nonwoven contains more than 15% of a plurality of fibers that are continuous or noncontinuous and physically and/or chemically attached to one another. Nonwoven webs have been formed from many processes, such as, for example, melt blowing processes, spunbonding processes, air laying processes, coforming processes, and bonded carded web processes.

Norrisch mechanism The mechanism of fragmentation of organic carbonyl-containing compounds, when subjected to ultraviolet radiation (UV). Both Norrisch type I and type II mechanisms result in carbon–carbon bond dissociation of the excited state, producing chain scission in polymers.

Norrisch type I reaction A reaction step of carbonyl compounds according to the Norrisch mechanism, in which two free radicals are produced that can continue degradation reactions.

Norrisch type II reaction A reaction step of carbonyl compounds according to the Norrisch mechanism, in which chain scission occurs but no free radicals are produced, unlike the Norrisch type I reaction.

Nucleating agent Compound, such as talc or other filler particles, added to a polymer (e.g., thermoplastic in a dissolved or melted state) to promote formation of nucleation sites for crystallization from a single-phase or homogeneous solution; also called nucleant.

P3HB See poly(3-hydroxybutyrate).

P3HB4HB See poly(3-hydroxybutyrate-*co*-4-hydroxybutyrate).

PA 11 See polyamide 11.

PA 12 See polyamide 12.

Patent Legal title that gives inventors the right, for a limited period (usually 20 years), to prevent others from making, using, or selling their invention without their permission in the countries for which the patent has been granted (EPO).

Patent application Request for patent protection for an invention filed with a patent office (EPO).

Patent family Set of interrelated patent applications filed in one or more countries to protect the same or a similar invention by a common inventor and linked by a common priority (or priorities). It is used by those who wish, for example, to establish the geographical coverage of a particular patent (EPO).

Pebax® Rnew Bio-based thermoplastic elastomer of Arkema (FR). Pebax® Rnew is a poly(ether-*b*-amide) made up of polyamide 11 block copolymers.

Percent crimp elongation The term is defined by the equation:

$$(L1 - L0)\,/L0 \times 100$$

Each term of the equation is measured according to the following procedure: A specimen textured yarn is left for longer than 24 h at a temperature of about 20 °C and a relative humidity of about 65% and, subsequently, is treated in a boiling water bath for about 20 min. After drying, the yarn of 20 cm free length is subjected to a loading of 2 mg/denier for 30 s, and the length ($L0$) thereof is recorded. Further, the yarn is subjected to a loading of 100 mg/denier for 30 s, and the length ($L1$) is recorded.

Percent crimp potentialization Defined by the equation:

$$(B - A)\,/B \times 100$$

Provided that the measurement applied to the calculation of the percent crimp elongation is performed as to the specimen yarn in the condition before treatment with the boiling water, percent crimp elongation before the boiling water treatment is designated as A and that after the treatment is designated as B.

PHA See polyhydroxyalkanoate.

Phyllosilicate Swellable lamellar clay mineral, and examples thereof, include smectite, vermiculite, and swellable fluoromica. Examples of the smectite include montmorillonite, beidellite, hectorite, and saponite. Examples of the swellable fluoromica include Na-type tetrasilicic fluoromica, Na-type taeniolite, and Li-type taeniolite.

Physical or mechanical recycling Recycling processes involving the reduction in size (e.g., by grinding) and/or separation (e.g., by sorting) of the different polymers from a waste mixture without altering, at least to a large extent, the chemical structure of the recovered polymer(s).

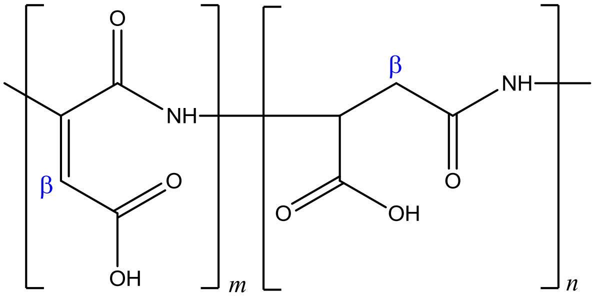
Pigment Substance usually in the form of a dry powder that imparts color to a polymer or article made from the polymer. Pigments can be inorganic or organic and natural or synthetic. Generally, pigments are inert (i.e., electronically neutral and do not react with the polymer and are substantially insoluble in the medium to which they are added).

scPLA See stereocomplex PLA.

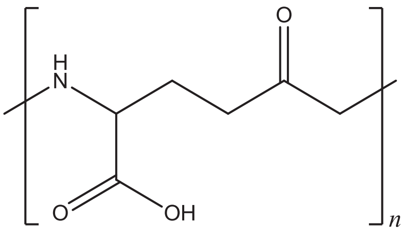
Plasma (in physics) A state of partially or completely ionized gas. A plasma consists of charged ions (positive or negative), negatively charged electrons, and neutral species, radicals, and excited species. The term “plasma treatment” as used herein means a treatment of exposing the surface of a substrate to an environment under plasma state, thereby subjecting the surface to the chemical, physical, and mechanical (bombardment) actions of the plasma. As known in the art, a plasma may be generated, for example, by a power source such as an alternating current (AC), a direct current (DC), low frequency (LF), audio frequency (AF), radio frequency (RF), and microwave power source, preferably a microwave or an RF power source.

Plastic Substance that contains the polymer as an essential component.

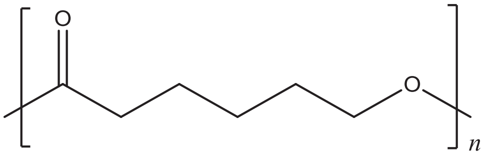
Poly(α-aspartic acid) (PASP) Poly(amino acid) having free carboxylic acid groups. PASP, belonging to the family of synthetic polypeptides, is a biodegradable water-soluble polymer; also called polyaspartate.



Poly(γ-glutamic acid) (γ-PGA) Poly(γ-glutamic acid) (also known as polyglutamate and γ-PGA) is a water-soluble, anionic, biodegradable polyamide consisting of D- and L-glutamic acid monomers connected by amide linkages between α-amino and γ-carboxyl groups (see Scheme 1.28). γ-PGA is synthesized by several bacteria and its molecular weight can vary from 20,000 to over 2 million Da depending on the method of production.

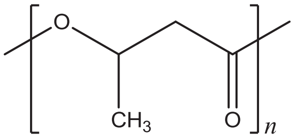


Poly(ε-caprolactone) or polycaprolactone (PCL) A poly(6-hydroxyhexanoic acid) of the chemical formula:



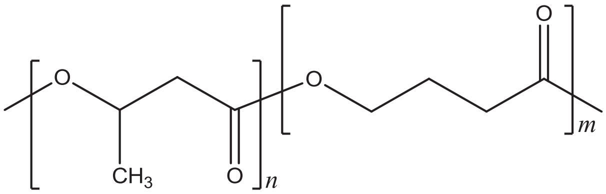
It is a biodegradable synthetic partially crystalline polyester with low melting temperature (60 °C) and a glass transition temperature (T_g) of −60 °C. Poly(ε-caprolactone) is an important polymer due to its mechanical properties, miscibility with a large range of other polymers, and biodegradability. Two main pathways to produce polycaprolactone have been described in the literature: the polycondensation of a hydroxycarboxylic acid, 6-hydroxyhexanoic acid; and the ring-opening polymerization (ROP) of a lactone, ε-caprolactone.

Poly(3-hydroxybutyrate) (P3HB, PHB) Polyhydroxyalkanoate of the chemical formula:



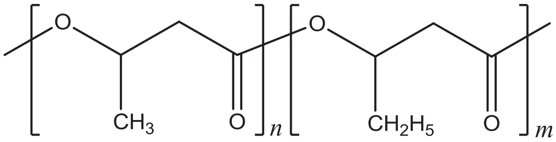
It is the most commonly occurring form of polyhydroxybutyrate with a chiral site in each molecular unit, all of which are in the D- (or R) configuration. It is a natural polymer produced by many bacteria as a means to store carbon and energy. The polymer is also called poly(3-hydroxybutanoic acid) or poly(hydroxybutyric acid). The abbreviation P3HB is used interchangeably with PHB.

Poly(3-hydroxybutyrate-*co*-4-hydroxybutyrate) (P3HB4HB) Polyhydroxyalkanoate obtained by the incorporation of 4-hydroxybutyrate (4HB) units into poly(3-hydroxybutyrate) (P3HB or PHB). P3HB4HB is represented by the chemical formula:



Poly(3-hydroxybutyrate-*co*-3-hydroxyoctanoate) (PHBO or P3HB/3HO) Polyhydroxyalkanoate copolyester of 3-hydroxybutyrate (3HB) and 3-hydroxyhexanoate (3HO).

Poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate) (PHBHV) Polyhydroxyalkanoate copolymer in which 3-hydroxyvalerate (3HV) units are incorporated in the poly(3-hydroxybutyrate) (P3HB) backbone during the fermentation process.



Poly(6-hydroxyhexanoic acid) See poly(ε-caprolactone).

Poly(alkylene alkanoate) Polyester prepared from a dicarboxylic acid containing 4–10 carbon atoms and a diol containing 2–6 carbon atoms, and two or more kinds of each of dicarboxylic acid and diol may be employed.

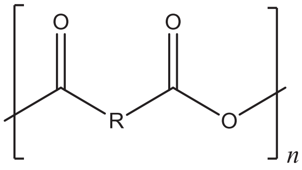
Poly(alkylene dicarboxylate) Polyester derived from a dicarboxylic acid and dihydroxy compound; see also poly(alkylene alkanoate).

Polyamide 11 or Nylon 11 (PA 11) Nonbiodegradable polyamide derived from vegetable oil. It is produced by Arkema under the commercial name Rilsan® from castor beans.

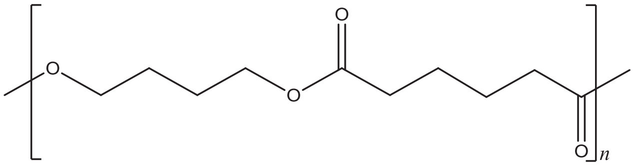
Polyamide 12 or Nylon 12 (PA 12) Nonbiodegradable polyamide derived from laurolactam, which itself is obtained from the trimerization of butadiene.

Poly(amino acid) Synthetic biopolymer made from α-amino acid repeating units, i.e., $–[NH–CHR–CO]_x–$. A poly(amino acid) is sometimes called a polypeptide.

Polyanhydride Biodegradable polymer characterized by anhydride bonds that connect repeating units of the polymer backbone chain. It is represented by the chemical formula:

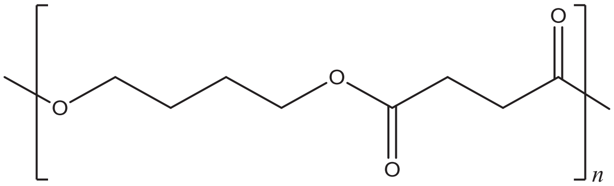


Poly(butylene adipate) (PBA) Poly(alkylene dicarboxylate) of the chemical formula:



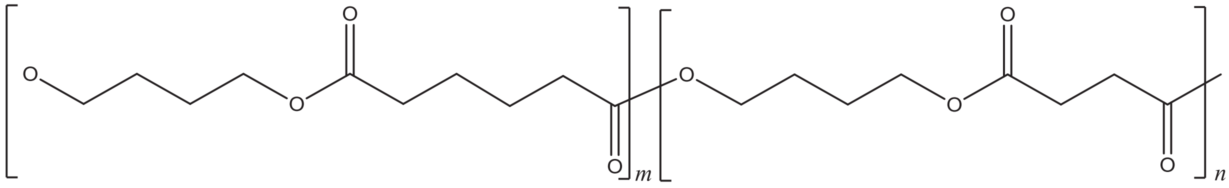
PBA is synthesized from adipic acid and 1,4-butanediol.

Poly(butylene succinate) (PBS) Poly(alkylene dicarboxylate) of the chemical formula:



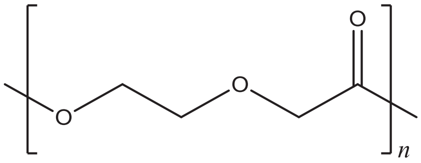
with a melting temperature of 112–114 °C. PBS is synthesized from succinic acid and 1,4-butanediol. Its mechanical properties are comparable to polypropylene and low density polyethylene (LDPE).

Poly(butylene succinate-*co*-adipate) (PBSA) Poly(alkylene dicarboxylate) of the chemical formula:



PBSA is synthesized from succinic acid, adipic acid, and 1,4-butanediol. It is a biodegradable aliphatic polyester based on nonrenewable (fossil) resources.

Polydioxanone or poly-*p*-dioxanone (PDO) Biodegradable poly(ether-ester) polymer represented by the chemical formula:

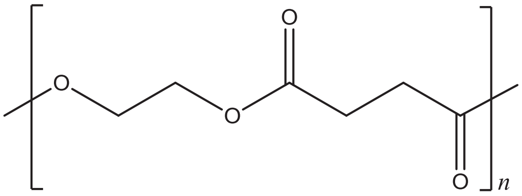


It is obtained by ring-opening polymerization of *p*-dioxanone. Polydioxanone is used for biomedical applications, particularly in the preparation of surgical sutures.

Poly(ethylene adipate) (PEA) Poly(alkylene dicarboxylate) of the chemical formula: $[–O–(CH_2)–O–CO–(CH_2)_4–CO–]_n$. It is synthesized from adipic acid and ethanol. It is a biodegradable aliphatic polyester based on nonrenewable (fossil) resources. It is often blended with other polyesters to get specific desirable properties such as soft segments.

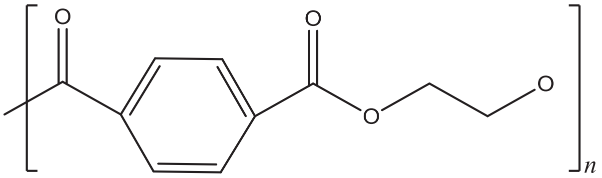
Poly(ethylene furanoate) (PEF) Bio-based polyester made from ethylene glycol and 2,5-furan dicarboxylic acid (FDCA). Avantium (NL) developed a process using catalytic reactions to create FDCA, which reacts with ethylene glycol to make PEF.

Poly(ethylene succinate) (PES) Poly(alkylene dicarboxylate) of the chemical formula:



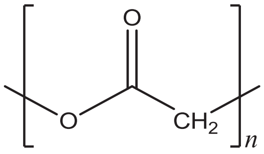
with a melting temperature of 103–106 °C. It is a biodegradable aliphatic polyester based on nonrenewable (fossil) resources and is synthesized from adipic acid and ethylene glycol. Its mechanical properties are comparable to polypropylene and low density polyethylene (LDPE).

Poly(ethylene terephthalate), bio-based (PET) Bio-based polyester made from ethylene glycol and terephthalic acid or its ester-forming derivative, wherein at least one of the diol component and/or terephthalate component are derived from at least one bio-based material.



Polyesterase See esterase.

Poly(glycolic acid) or polyglycolide (PGA) Aliphatic polyester having a recurring unit represented by the chemical formula:

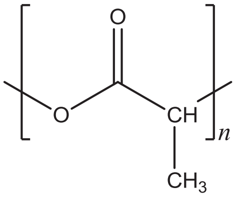


Polyglycolide See poly(glycolic acid).

Polyhydroxyalkanoate or poly(hydroxylalkanoic acid) (PHA) Biodegradable aliphatic polyester whose monomers contain both a carboxylic acid group and a hydroxyl group, commercially produced by several bacteria as intercellular carbon and energy storage materials in their cell. Examples of known commercially available forms of polyhydroxyalkanoates include poly(3-hydroxybutyrate) (P3HB) and poly (3-hydroxybutyrate-*co*-3-hydroxyvalerate) (PHBHV).

Poly(hydroxylalkanoic acid) See polyhydroxyalkanoate.

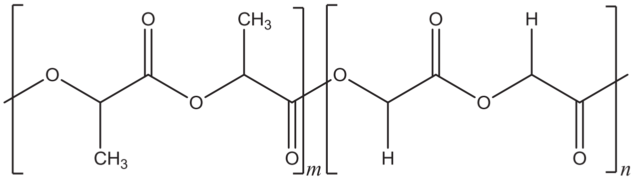
Poly(lactic acid) or polylactide (PLA) Aliphatic polyester of the chemical formula:



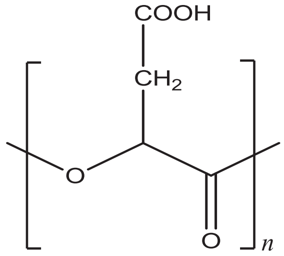
The polymer can be produced by fermentation from renewable resources. It can also be synthesized either by condensation polymerization of lactic acid or by ring opening polymerization of lactide in the presence of a catalyst. This polymer exists in the form of three stereoisomers: poly(L-lactide) (L-PLA), poly(D-lactide) (D-PLA) and poly(DL-lactide) (DL-PLA). The term poly(lactic acid) is misleading and does not comply with standard nomenclatures (such as IUPAC), potentially leading to ambiguity; PLA is not a polyacid but rather a polyester.

Polylactide See poly(lactic acid).

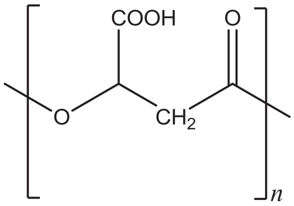
Poly(lactide-*co*- polyglycolide) (PLGA) Copolymer of hydrophobic PLA and hydrophilic PGA of the chemical formula:



Poly(malic acid) (PMA) Biodegradable and bioabsorbable water-soluble polyester. PMA is known as polyhydroxyalkanoate having a carboxyl group in a side chain. A polymer of polymalic acid is known, by a manner of polymerization, in an α-type represented by the chemical formula:



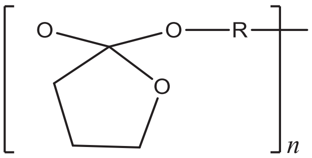
and a β-type represented by the chemical formula:



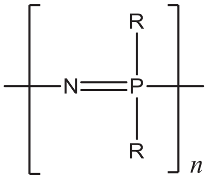
Polymer blend Macroscopically homogeneous mixture of two or more different species of polymer (IUPAC).

Polymer composite Composite in which at least one component is a polymer (IUPAC).

Poly(ortho ester)s (POE)s Hydrophobic biocompatible and bioerodible polymers potentially useful as a sustained drug delivery system. Four distinct families have been developed so far, designated as POE I (see chemical formula), POE II, POE III, and POE IV. These polymers can be prepared by a transesterification reaction or by the addition of polyols to diketene acetals, and it is the latter method that has proven to be preferred one.

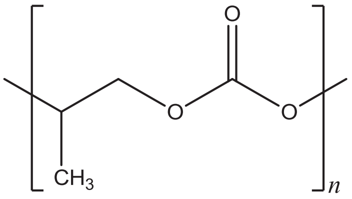


Polyphosphazene (PPHOS) Biodegradable polymer with alternating nitrogen and phosphorus atoms in the backbone of the chemical formula:

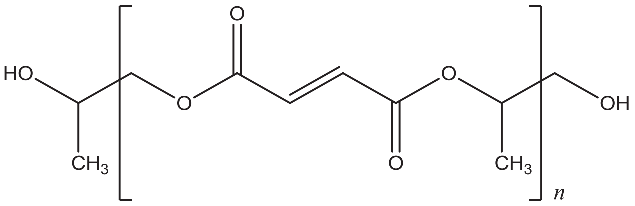


where R can be either an alkoxy, or aryloxy, or amino group.

Poly(propylene carbonate) (PPC) Aliphatic polycarbonate obtained by the alternating copolymerization of ethylene oxide and carbon dioxide. It is represented by the chemical formula:

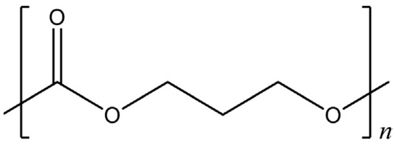


Poly(propylene fumarate) (PPF) Biodegradable unsaturated linear polyester that can be modified or crosslinked through its fumarate double bonds of the chemical formula:

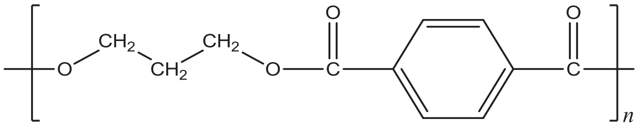


Poly(propylene terephthalate), bio-based (PPT) See poly(trimethylene terephthalate).

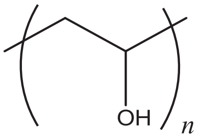
Poly(trimethylene carbonate) (PTMC) Biodegradable polycarbonate with rubber-like properties. PTMC is obtained by ring-opening polymerization of trimethylene carbonate, catalyzed with diethyl zinc. PTMC is represented by the chemical formula:



Poly(trimethylene terephthalate), bio-based (PTT) Also called poly(propylene terephthalate) (PPT). Bio-based PTT is made by polycondensation of 1,3-propane diol derived from renewable sources and either terephthalic acid or dimethyl terephthalate. Bio-based PTT is marketed by DuPont Company as Sorona® fibers.



Poly(vinyl alcohol) (PVOH) Water-soluble, polymer prepared via the hydrolysis of poly(vinyl acetate). PVOH is represented by the chemical formula:



Polyurethane (PU) Polymer incorporating urethane groups (–NH–CO–O–) in the polymer backbone. Polyurethanes are commonly formed by the polyaddition reaction of a polyisocyanate such as a diisocyanate with a polyol such as a diol, resulting in the formation of linear, branched, or crosslinked polymers.

PPC See poly(propylene carbonate).

PPF See poly(propylene fumarate).

PPT See poly(propylene terephthalate); also called poly(timethylene terephthalate).

Proteins Natural chains of α-amino acids joined by amide linkage.

PTMC See poly(trimethylene carbonate).

PTT See poly(trimethylene terephthalate).

Pyrolysis Form of thermal treatment that chemically decomposes organic materials by heat in the absence of oxygen.

Rilsan® Polyamide 11 (PA 11) or Nylon 11 derived from vegetable oil. It is produced by Arkema from castor beans. PA 11 is a bio-based nonbiodegradable biopolymer.

Scaffold (in medicine) Artificial, biocompatible malleable structure that can be used to deliver therapeutic compositions, e.g., proteins, peptides, nucleic acids, viruses, etc., into the body, to support and direct the growth of new cells of an organ or tissue. In addition, scaffold can be used to support cells that are implanted or "seeded," and that can support three-dimensional cell growth, such as tissue or organ growth or regeneration (**US2007014752,** 2007, UNIV TEXAS SYSTEM).

Short Rotation Coppice (SRC) Coppice grown mainly as an energy crop. This woody solid biomass is used as biofuel; it has also been proposed as a second generation crop for bio-based biopolymers.

Skygreen® Series of poly(butylene succinate) (PBS), poly(butylene succinate-*co*-adipate) (PBSA), and poly(butylene adipate-*co*-terephthalate) (PBAT) produced by SK Chemicals (KR). The series of Skygreen® contains three major grades: SG100 (PBS), SG200 (PBSA), and SG300 (PBAT).

Solubility parameter The force of attraction existing between the molecules of the solvent and of the polymer, and more particularly, the variation in density of the cohesion energy of the solvent, i.e., the energy required to vaporize it. The solubility parameter units are thus expressed at 25 °C and in $(MPa)^{1/2}$ or $(J/cm^3)^{0.5}$ in which $1\ (J/cm^3)^{0.5} = 1\ (MPa)^{1/2}$; also called Hildebrand parameter.

Spunbond web or layer Nonwoven web containing small-diameter substantially continuous filaments. The filaments are formed by extruding a molten thermoplastic material from a plurality of fine, usually circular, capillaries of a spinnerette, with the diameter of the extruded filaments then being rapidly reduced as by, for example, eductive drawing and/or other well-known spunbonding mechanisms. Spunbond filaments may sometimes have diameters less than about 40 μm, and are often 5–20 μm.

Spunlacing (hydroentanglement) A nonwoven manufacturing process that employs jets of high pressure water to entangle a web of loose fibers and, thereby, provide fabric integrity; also called "jet entangled," "water entangled", and "hydroentangled" or "hydraulically needled."

Standard Official publications used in industry and trade to describe specifications and procedures. Standards provide rules and recommendations for quality, safety, performance, and construction, codes of practice, methods of testing, symbols, and terminology.

Staple fibers Term used to designate a group of shorter filaments that are usually twisted together to form a longer continuous thread. The term was originally applied to fibers of natural origin long enough to be processed on textile machinery, but excluding endless filaments, e.g., silk. Staple fibers are of relatively uniform length, c. 1.3–10.2 cm.

Starch Natural polymer composed of two types of α-D-glucose polymers: amylose, a substantially linear polymer with molecular weight of about 1×10^5; and amylopectin, a highly branched polymer with very high molecular weight of the order 1×. Depending on the origin of the starch, the ratio of amylose to amylopectin can vary significantly. Most starches contain 20–30% amylose and 70–80% amylopectin. Starch typically exists in small granules having a crystallinity ranging from about 15% to 45%.

Stereocomplex PLA (scPLA) A crystal in which a segment of a poly(L-lactic acid) (PLLA) and a segment of a poly(D-lactic acid) (PDLA) are packed in a one-to-one ratio; this can increase the melting temperature of PLLA alone or PDLA alone by about 50 °C.

Stereocomplexation A nonbonded interaction between polymers that leads to crystalline form having a higher melting temperature than the nonstereocomplexed form.

Strand A plurality of filaments or threads twisted, plaited, braided, or laid parallel to form a unit for further construction into a fabric, or used per se, or a monofilament of such size as to be woven or used independently.

Supercritical CO_2 ($scCO_2$) Fluid state of carbon dioxide where it is held at or above its critical temperature and critical pressure. Carbon dioxide usually behaves as a gas in air at standard temperature and pressure (STP), or as a solid called dry ice when frozen. If the temperature and pressure are both increased from STP to at or above the critical point for carbon dioxide, it can adopt properties midway between a gas and a liquid. More specifically, it behaves as a supercritical fluid above its critical temperature (31.1 °C) and critical pressure (72.9 atm/7.39 MPa), expanding to fill its container like a gas but with a density like that of a liquid (from Wikipedia).

Surface roughness Surface irregularities that result from the various surface preconditioning methods used such as mechanical abrasion and etching to create suitable anchoring structures. These surface irregularities/anchoring structures combine to form the "surface texture," which directly influences the bond strength achieved between the polymer article and the material bonded onto it; also called "surface texture" and "surface topography."

The parameter most frequently used for surface roughness is Ra. It measures the average roughness by comparing all the peaks and valleys to the mean line, and then averaging them all over the entire length that a stylus is dragged across the surface. It is also referred to as CLA (center line average) and AA (area average).

Tear resistance Force needed to propagate the tear of a notched film sample, also known as Elmendorf tear, as measured by the procedures of ASTM D-1922.

Tex Unit of measure for the linear weight density of fibers defined as the weight in grams per 1000 m of fiber; for example 1 tex means that a fiber filament having a length of 1000 m has a weight of 1 g; and 10 tex means that a fiber of 1000 m has a weight of 10 g. Tex is more likely to be used in Canada and Continental Europe, while denier remains more common in the United States and United Kingdom. The most commonly used unit is actually the decitex, abbreviated dtex, which is the mass in grams per 10,000 m. When measuring objects that consist of multiple fibers, the term "filament tex" is sometimes used, referring to the mass in grams per 1000 m of a single filament.

Thermoplastic Polymer that softens or melts when heated and solidifies when cooled.

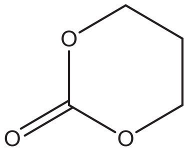
Thermoplastic elastomer Melt processable polymer blend or copolymer in which a continuous elastomeric phase domain is reinforced by dispersed hard (glassy or crystalline) phase domains that act as junction points over a limited range of temperature. The behavior of the hard phase domains as junction points is thermally reversible (IUPAC).

Thermoset Polymer that is irreversibly hardened by forming a three-dimensional, crosslinked structure between the chains when heated.

Thread A plurality of filaments, either continuous or staple, twisted together.

Toughness The amount of energy absorbed prior to fracture, or equivalently, the amount of work required to fracture a material. One measure of toughness is the area under a stress–strain curve from zero strain to the strain at fracture. The stress is proportional to the tensile force on the material, and the strain is proportional to its length. The area under the curve then is proportional to the integral of the force over the distance the polymer stretches before breaking. This integral is the work (energy) required to break the sample.

Trimethylene carbonate (TMC) or 1,3-dioxan-2-one of chemical formula:



Used as monomer for the production of poly(trimethylene carbonate) (PTMC); it can also be used as comonomer for the production of poly(ester-carbonate) using both enzyme and chemical catalysts.

Volume resistivity The resistance to leakage current through the body of an insulating material. The volume resistivity is expressed in ohms—cm.

Index

Note: Page numbers followed by "b", "f" and "t" indicate boxes, figures and tables respectively

A

Acetyl trialkyl citrate plasticizer, 230f
Acrylonitrile-butadiene-styrene (ABS), 89, 484
Additives, 215, 223. *See also* Compounding
  patents, 242–261
  performance boosters
    antioxidants, 237
    antistatic additives, 239–241
    colorants, 239, 239t
    compatibilizers, 238
    coupling agents, 238
    fillers, 238
    flame retardants, 235–237, 238t
    heat deflection temperature modifiers, 237–238
    heat stabilizers, 238
    impact modifiers, 234–235
    light and UV stabilizers, 237
    miscellaneous additives, 241
    phosphorus compound, 237f
    plasticizers, 228–233, 230t
  processability boosters
    drying/desiccant agents, 226–227
    heat stabilizers, 223
    hydrolysis-suppressing agents, 226–227
    lubricants, 225
    melt strength enhancers, 223
    nucleating agents, 225–226, 227t
    plasticizers, 225
Adhesive compositions
  bio-based adhesives
    chitin, 468
    chitosan, 468
    natural resins, 468
    proteins, 467
    starch, 468
  classification, 459
  nonreactive adhesives
    drying adhesives, 459–460
    HMAs, 464–466
    PSAs, 461–464
  patents, 469–479
  reactive adhesives, 466
    multi-component reactive adhesives, 467
    one-component reactive adhesives, 466–467
Adhesive lamination, 372
Aesthetic properties, 92–93
  color, 93
  color stability, 93–94
  decoration, 93
  gloss, 93
  surface effects, 93
After treatment of foams
  coating, 343
  heat treatment, 342–343
  liquid, solid or phase elimination, 343
Alcoholysis, 503–505. *See also* Dry-heat depolymerization; Hydrolysis
Aliphatic carbonates, 368
Aliphatic polycarbonates, 24
  biopolymer blends, 138, 147
  blending with aliphatic polyesters, 126–127
  PBC, 25
  PEC, 24
  PPC, 24–25
  PTMC, 25
Aliphatic polyesters, 327–328, 391, 396, 484
  blending, 118, 120t–121t
    PGA, 123
    PHAs, 124–125
    PLA, 118–123
  chemical formulae, 450f
  solvents suitable for, 84t–85t
Aliphatic-aromatic (co)polyesters, 20, 21t, 368
  blending with aliphatic (co)polyesters, 125–126, 126t
  components, 20
  PBAT, 21
  PBST, 328
  PTeMAT
Alkylene oxide sulfonate salt-type plasticizer, 231f
Alloys, 117
α-hydroxyalkanoic acids, 4–5, 5t
t-amyl-2-ethylhexyl peroxycarbonate (TAEC), 286
Ananas lucidus. *See* Curaua
Anionic surfactant, 130
Antimicrobials, 241
Antioxidants, 237
Antistatic
  additives, 239–241
  fibers, 399–400
  properties, 92
APG. *See* Atmospheric pressure glow
APR. *See* Association of Postconsumer Plastic Recyclers
APTS. *See* *p*-toluene sulfonic acid
Aqueous emulsions, 187
Arboform®, 38
Aspect ratio, 387
Association of Postconsumer Plastic Recyclers (APR), 491–492
Atmospheric pressure glow (APG), 306
attactic PDLLA. *See* Attactic poly(D,L-lactide)
Attactic poly(D,L-lactide) (attactic PDLLA), 6
Az-CH-LA. *See* Chitosan containing both azide and lactose moieties

B

b* value, 398
BAK®
Barus effect, 117
BDI. *See* Butane diisocyanate
3-(S)-[benzoyloxycarbonyl]-methyl-1,4-dioxane-2,5-dione (BMD), 277–278
Bio-based adhesives. *See also* Nonreactive adhesives; Reactive adhesives
  chitin, 468
  chitosan, 468
  natural resins, 468
  proteins, 467
  starch, 468
Bio-based aromatic polyesters, 21, 22t, 391
  PEF, 22–23, 23f
  PET, 21–22
  PTT, 23
Bio-based poly(ether ester)s, 23
  PDO, 23–24
Bio-based polymer, 1, 3t
Bio-based polyethylenes (Bio-PE), 39
Bio-based raw materials, 468
Bio-PE. See Biopolyethylene
Bio-PP. See Biopolypropylene
bio-PVC. *See* Biopolyvinylchloride
(Bio)composites, 411. *See also* Prepregs
  patents, 423–429
  reinforcing biopolymers with coherent fibrous material, 411
    with carbon fibers, 411–412
    with glass fibers, 412–413
    with pretreated fibers, 417
    vegetable or animal fibers, 413–416
  reinforcing biopolymers with fillers
    with inorganic fillers, 417
    nanocomposites, 417–421
    with organic fillers, 417
BioAdimide™ 100, 227
BioAdimide™ 500 XT, 223

Biocomposites, 4
Biodegradability, 1
Biodegradable polymers, 1, 3t, 132–133
    coating compositions, 436t–438t
    enzymatically hydrolyzable moieties, 510
    low-molecular-weight, 412
    particles uses, 263
    POEs, 39–41, 41f
    polyanhydrides, 41
    PPHOSs, 41–42
    selection, 447
    separation of, 490t
    starch blends with, 131t–132t
    thermoplastic polymer, 387
  copolyester, 486
  fibers, 395
  foams, 341
  gels, 197
  polyester
    blends, 125
    molding, disposal method, 504f
    water-processing apparatus, 509f
(Bio)degradation, 94, 98–99
  aerobic and anaerobic, 99f
  hydrolysis, 98
  mechanical degradation, 98
  thermal degradation, 95, 96f
  types and mechanisms, 94–99
Biolloy™, 150–151
Biomax® PTT, 23
Biomax® Strong 120, 235
Biomax® Thermal 300, 238
Bionolle® series, 123
  Bionolle® 3001, 125
  Bionolle® 1010, 146–147
  Bionolle® 1040, 192–193
Bionolle™, 19
Biopole®, 81t, 131
Biopolyethylene (bio-PE), 2
Biopolymer, 2, 117
  aliphatic polycarbonates, 24
    PBC, 25
    PEC, 24
    PPC, 24–25
    PTMC, 25
  bio-based content, 2
  bio-based poly(ether ester)s, 23
    PDO, 23–24
  blending in majority, 133–143
    aliphatic polycarbonates, 138
    cellulose derivatives, 138
    PHAs, 137–138
    PLAs, 133–137
    starch, 138–143
  blending in minority, 143
    aliphatic polycarbonates, 147
    cellulose derivatives, 147
    PCL, 146
    PHAs, 145–146
    PLAs, 143–145
    poly(alkylene alkanoate)s, 146–147
    polypropylene/starch blend composition, 149t
    starch, 147–150
  classification, 2–4, 3t
  diene polymers, 39
  feedstocks for production, 42t
  films, 314
  lignin, 35–37
    production methods, 37–38
    sources, 37
    structure, 36f
  miscibilities, 119t–120t
  poly(ester amides), 30
  polyamides, 25
    bio-polyamides, 26t–27t
    poly(α-amino acids), 25–28
    polycondensation, 25
  polyesters, 4–23
    PADCs, 17–23
    poly(hydroxy acid)s, 4–17
  polyols, 31t
  polysaccharides, 31–35
    cellulose, 32–34, 33t–34t
    chitin, 35
    chitosan, 35
    starch, 34–35
  polyurethane, 30–31
  sources, 42–43
  types and chemistry, 4
  vinyl polymers
    bio-LDPE, 2
    bio-HDPE, 2
    biopolyethylene
    biopolyolefins, 39t
    biopolypropylene (bio-PP), 2
    polyolefins, 38–39
    PVC, 39
    PVOH, 39, 40t
Biopolymer foams, 327. *See also* Foaming agents
  polyesters, 327
    aliphatic, 327–328
    aliphatic-aromatic, 328
  starch, 328–329
  types, 327
Biopolymer-based microparticles, 265
Biopolyolefins, 39t
Biopolypropylene (bio-PP), 2
Biopolyvinylchloride (bio-PVC), 2
l,l-bis(*t*-butylperoxy)-3,3,5-trimethylcyclohexane (CPK), 286
Blending, 117–118
  fibers, 411
  recycled polymers, 484–485
Blending biopolymer, 117–118
  aliphatic polycarbonates with aliphatic polyesters, 126–127
  aliphatic polyesters, 118, 120t–121t
    PGA, 123
    PHAs, 124–125
    PLA, 118–123
  aliphatic–aromatic copolyesters, 125–126, 126t
  cellulose derivatives with biodegradable polymers, 127–128
  commercial blends, 150t–151t
  commercial products, 150–151
  lignin with biodegradable polymers, 131–132
  patents, 152–182
  starch with biodegradable polymers, 128–131
  with synthetic nonbiodegradable polymers, 133, 142t–143t
    biopolymer in majority, 133–143
    biopolymer in minority, 143–150
    miscibilities, 134t
    P3HB blends, 133
    starch blends, 133
Blowing agents. *See* Foaming agents
Blown film, 361
BMD. *See* 3-(S)-[benzoyloxycarbonyl]-methyl-1,4-dioxane-2,5-dione
Bonding preformed biopolymers, 421–422
  using adhesives, 421–422
  using heat, 422
  using surface treatment, 422
Butane diisocyanate (BDI), 30
t-butylperoxybenzoate (TBPB), 286

C
CA. *See Candida antarctica*; Cellulose acetate
CAB. *See* Cellulose acetate butyrate
Candida antarctica (CA), 510
CAP. *See* Cellulose acetate propionate
Capa™, 18t
Caprolactone (CL), 510
Carbon dioxide (CO_2), 330
Carbon fibers, 411–412
Carrier resin, 452
CD. *See* Cross direction
Cellulose, 32, 33t–34t, 99
  cellulosic derivatives, 32–34, 434–435
    biopolymer blends, 138, 147
    blending with biodegradable polymers, 127–128
    CA, 32
    CAB, 34
    CAP, 34
  esters, 127
Cellulose acetate (CA), 32, 127, 147
Cellulose acetate butyrate (CAB), 32, 34, 127, 222–223
Cellulose acetate propionate (CAP), 32, 34, 127, 222–223
Cellulose nitrate (CN), 34
CERENOL™, 31
Cereplast Compostable® 3000 film, 150
CESA®-dry MB 1, 226
CESA®-extend chain extender, 223
Chemical foaming agents, 329, 332, 333t
Chemical modification. *See* Chemical treatment
Chemical treatment, 277, 304–305
  controlled degradation, 283–284
  functional groups, 277
    block grafting/copolymerization, 280–281
    incorporation of functional monomers, 277–278
    methods for introduction, 277
    phosphonium sulfoisophthalate structure, 282f
    PLA, 281–282

    reactive extrusion process, 281f
    starch chemical modification, 282
    terminal functional group modification, 278–280
  functional groups incorporation, 305–307
  grafting, 307–308
  hydrolysis/aminolysis, 305
  increasing molecular weight, 284
  interreacting polymers, 285
    crosslinking, 286–289
    IPN, 289
    polymer branching/bridging, 285–286
  patents, 290–299
  PLA oligomer
    and glycidyl methacrylate isocyanate reaction, 279f
    TMI® unsaturated aliphatic isocyanate reaction, 280f
  radiation, 284–285
Chemical vapor deposition (CVD), 311
Chitin, 35, 468
Chitosan, 35, 468
Chitosan containing both azide and lactose moieties (Az-CH-LA), 466–467
cis-1,4-polyisoprene, 39
CL. *See* Caprolactone
CN. *See* Cellulose nitrate
Co-extruded polyester, 373
Coagulating dispersions, 268
Coated paperboard, 434f
Coating, 343. *See also* Printing
  with inorganic materials, 308–310
  with low-molecular-weight organic materials, 310–311
  multiple, 313
  single polymer, 311–313
Coating compositions, 431
  biodegradable polymer coating compositions, 436t–438t
  patents, 439–445
  powder coatings, 435
  strippable coatings, 435
  thermoplastic coating compositions
    cellulose derivatives, 434–435
    PHAs, 431–432
    PLA, 432–434
    starch, 434
Color, 93
  changing inks, 452
  stability, 93–94
Colorants, 239
  dye, 240t
  pigment, 239t
Compatibility, 215
Compatibilizers, 238
Composite foams, 340–341
Compostable polymer, 2
Compounding
  ingredients, 332
    inorganic compounds, 332–333, 334t
    mixtures of, 335–336
    organic compounds, 333–335, 334t
    polymer components, 335, 336t
  in liquid or solution
    with inorganic compounds, 218
    with organic compounds, 218
  patents, 242–261
  process in twin screw extruder, 137f
  by shear and heat, 215
    with inorganic compounds, 215–217
    with organic compounds, 217–218
  techniques and formulations of biopolymers, 219t
Controlled degradation, 283–284
Conventional flexographic ink compositions, 449
Copolymerization, 277–278
Corona treatment, 306–307
Corrosion inhibitors, 241
Coupling agents, 238, 411
CPK. *See* l,l-bis(t-butylperoxy)-3,3,5-trimethyl-cyclohexane
Cross direction (CD), 394
Crosslinking, 286–289, 341–342
  agent, 286
Crystallinity, 79–80, 90–91
Curaua (*Ananas lucidus*), 415
Cutter-Feeder-Extruder, 483
CVD. *See* Chemical vapor deposition

D

DaniMer processing, 223
DCL. *See* Dicaprolactone
DCP. *See* Dicumyl peroxide
"De-nest" characteristics, 223
Decoration, 93
Degradable polymer, 1
DegraPol®, 31
Degree of substitution (DS), 32, 99, 282
Density, 79, 80t
Density separation systems, 489, 490t. *See also* Electrostatic separation systems
Depolymerization
  enzymatic, 510–514
  hydrothermal, 505–509
Dialdehydes, 288
Dicaprolactone (DCL), 512
Dicumyl peroxide (DCP), 286
Differential scanning calorimetry (DSC), 117
L-3,4-dihydroxyphenylalanine (DOPA), 467
N,N-dimethylacetamide (DMAc), 420
Dimethyl ether, 330
Dispersion, 187
  nonsolvent destructuring methods, 194–195
  patents, 199–213
  solvent-based methods, 187
    emulsification-diffusion technique, 191–192
    emulsification-evaporation technique, 187–190
    (nano)precipitation technique, 190–191
    salting-out technique, 191
  thermomechanical methods, 192–194
Dissolution, 495–496. *See also* Electrostatic separation systems; Optical sorting systems
Dissolution-deposition method, 265–266
DMA. *See* Dynamic mechanical analysis
DMAc. *See* N, N-dimethylacetamide
DOPA, 4-dihydroxyphenylalanine. *See* L-3
Double-tube micro-nozzle apparatus, 397f
Dowex® 50W-X8 or 50W-X2, 504–505
Dry spinning, 387
Dry-heat depolymerization, 497–500. *See also* Alcoholysis; Hydrolysis
  method for recovering lactide, 499f
  TG/DTA curve, 498f
  thermal decomposition products, 499t
Drying, 496. *See also* Grinding
Drying adhesives, 459. *See also* Hot melt adhesive (HMA); Pressure-sensitive adhesive (PSA)
  solvent-based adhesives, 460
  water-based adhesives, 459–460
Drying/desiccant agents, 226–227
DS. *See* Degree of substitution
DSC. *See* Differential scanning calorimetry
Duolite® C20, 504–505
Dye, 447
Dynamic mechanical analysis (DMA), 117

E

E1cB. *See* Elimination Unimolecular conjugate Base
EAA. *See* Ethylene-acrylic acid
Eastar Bio, 372. *See also* Origo-Bi®
Ecoflex, 372
Ecomer®, 468
EcoPure®, 148
Ecostar™, 148
Ecovio® FS Paper, 151
Ecovio® FS Shrink Film, 151
Ecovio®, 4, 151
EcoWorks®, 150
Electromagnetic properties, 87
Electrophotographic toners, 451–452
Electrostatic separation systems, 489–491. *See also* Optical sorting systems
Elimination Unimolecular conjugate Base (E1cB), 283–284
EMforce® Bio additive, 235
Emulsification-diffusion technique, 191–192
Emulsification-evaporation technique, 187–190
Emulsion-precipitation method, 266–268
Emulsions, 187. *See also* Hydrogels; Solutions
  nonsolvent destructuring methods, 194–195
  patents, 199–213
  solvent-based methods, 187
    emulsification-diffusion technique, 191–192
    emulsification-evaporation technique, 187–190
    (nano)precipitation technique, 190–191
    salting-out technique, 191
  thermomechanical methods, 192–194
Engagement-type twin screw extruder, 216–217
Environmental behavior, 94–99
Enzymatic depolymerization, 510–514
Epoxy-functionalized polyolefins, 144
ε-Poly(L-lysine) (ε-PL), 25, 28

Ethylene vinyl acetate (EVA), 129
Ethylene-acrylic acid (EAA), 129
Ethylene-vinyl alcohol copolymer (EVOH), 83–85, 373–374
EVA. *See* Ethylene vinyl acetate
EVOH. *See* Ethylene-vinyl alcohol copolymer
Exemplary commercial biocomposite products, 414
Expancel®, 341
Expandable particles, 336
  biodegradable foamed product manufacture, 340f
  production methods, 336–338
    by extrusion foaming process, 339f
  sintering, 339–340
Expanding agents. *See* Foaming agents
Extrudate swelling. *See* Barus effect

F

Farm Security and Rural Investment Act of 2002 (FSRIA), 1
FDM. *See* Fused deposition modeling
Fiber. *See also* Nonwoven; Woven/Knitted
  antistatic fibers, 399–400
  formation, 387–391
    aliphatic-aromatic polyesters, 391
    aromatic polyesters (bio-based), 391
    PHAs, 390–391
    PLA, 387–390
    starch, 391
  patents, 401–410
  spinning machine, 390f
  wearing resistance of fibers, 398–399
Fillers, 132–133, 215, 238
Films, 361–371. *See also* Laminates
  by chemical type
    aliphatic carbonates, 368
    aliphatic-aromatic copolyesters, 368
    PCL, 367–368
    PHA, 366–367
    PLA, 362–364
    poly(alkylene alkanoates), 368
    starch, 361–362
  patents, 375–386
  porous, 371
  shrinkable, 369–371
Flame
  retardancy, 92
  retardants, 235–237, 238t
  treatment, 305
Flammability, 92
Flexographic inks, 449–451
Fluorescent additives, 493–495
Foam hydrolysis, 505
Foamed starch, 329
Foaming
  biopolymer foams, 327
  composite foams, 340–341
  compounding ingredients, 332–336
  crosslinking, 341–342
  expandable particles, 336–340
  patents, 345–359
  after treatment of foams, 342–344
Foaming agents, 329–332. *See also* Biopolymer foams
  chemical, 332, 333t
  physical, 330–332, 331t
Friction, 89–90
FSRIA. *See* Farm Security and Rural Investment Act of 2002
Functional group-capping agents. *See* Hydrolysis-suppressing agents
Functional groups incorporation, 305
  corona treatment, 306–307
  plasma treatment, 306
  radiation, 305–306
Functionalization, 281
Fused deposition modeling (FDM), 316

G

γ-PGA. *See* Poly(γ-glutamic acid)
Gas antisolvent process (GAS process). *See* Supercritical antisolvent process (SAS process)
Gas barrier properties, 83–86
Gas plasma treatment, 306
Gel, 197–198
Gelatinization, 195
General purpose polystyrene (GPPS), 148
Glass fibers, 412–413
Global warming potential (GWP), 330
Gloss, 93
D-Glucopyranose, 503f
Glycerol fatty acid esters, 240
Glycidyl methacrylate (GMA), 278–280
Gordon–Taylor equation, 117
GPPS. *See* General purpose polystyrene
Grafting
  polymerizable compounds, 307
  preformed polymers, 308
Gravure inks, 449–451
Green polyethylene. *See also* Biopolyethylene
Grinding, 487–488. *See also* Sorting
GWP. *See* Global warming potential

H

Halogenated hydrocarbons, 330
Hamos electrostatic separation technology, 491
Hazardous air pollutants (HAPs), 330
4HB. *See* 4-hydroxybutyrate
HDI. *See* Hexamethylene diisocyanate
HDPE. *See* High density polyethylene
HDT. *See* Heat deflection temperature
Heat
  deflection temperature modifiers, 237–238
  resistance, 90–92
  stabilizers, 223, 238
  treatment, 304, 342–343
Heat deflection temperature (HDT), 215–216
HEMA. *See* 2-hydroxyethyl methacrylate
Hexamethylene diisocyanate (HDI), 30
HFCs. *See* Hydrochlorofluorocarbons
HFO-1234yf. *See* 2,3,3,3-tetrafluoropropene
HFO-1243zf. *See* 3,3,3-trifluoropropene
High density polyethylene (HDPE), 493
High impact polystyrene (HIPS), 148
Hildegardia populifolia fiber, 416
HLB value. *See* Hydrophilic–lipophilic balance value
HMA. *See* Hot melt adhesive
Hot melt inks, 448
Hot melt adhesive (HMA), 459, 464–466. *See also* Drying adhesives; Pressure-sensitive adhesive (PSA)
3HV. *See* 3-hydroxyvalerate
Hydrocarbons, 330
Hydrochlorofluorocarbons (HFCs), 330
Hydrogels, 197–198. *See also* Emulsions; Solutions
Hydrolysis, 98, 500–503. *See also* Alcoholysis; Dry-heat depolymerization
  apparatus, 508f
  foam, 505
  high-temperature, 506
Hydrolysis-suppressing agents, 226–227
Hydrophilic–lipophilic balance value (HLB value), 310
Hydrothermal depolymerization, 505–509
4-hydroxybutyrate (4HB), 16
2-hydroxyethyl methacrylate (HEMA), 280–281, 285
3-hydroxyvalerate (3HV), 80

I

IFDs. *See* Internal fixation devices
Impact modifiers, 234–235
Impact resistance, 90
Industry Council for Packaging and the Environment (INCPEN), 491–492
Ingeo™, 492–493
Inks, 447
  color changing, 452
  electrophotographic toners, 451–452
  flexographic, 449–451
  in general, 447
  gravure, 449–451
  hot melt, 448
  jet printing, 447–448
  patents, 454–458
  screen, 449–451
  writing, 452–453
Inorganic compounds, 332–333, 334t. *See also* Organic compounds; Polymer components
Inorganic fillers, 417
Inorganic foaming agents, 329
Inorganic materials, coating with, 308–310
Inorganic nanofillers/nanofibers, 417–420
Internal fixation devices (IFDs), 289
International Organization for Standardization (ISO), 1
Interpenetrating network (IPN), 289
Interreacting polymers, 285
  crosslinking, 286–289
  IPN, 289
  polymer branching/bridging, 285–286
Intrinsic properties, 79. *See also* Processing properties; Product properties
  crystallinity, 79–80
  density, 79, 80t

  electromagnetic properties, 87
  gas barrier properties, 83–86
  mechanical properties, 81–83, 86t, 89t
  solubility, 81
  transition temperatures, 79–80, 82t–83t
  transparency, 86–87
Ionic liquids, 196
IPN. *See* Interpenetrating network
ISO. *See* International Organization for Standardization
Isotactic stereocomplex PLA (scPLA), 6–8

J

Japan Bioplastics Association (JBPA), 1
Jet printing inks, 447–448
Joncryl® ADR chain extenders, 486

K

Kneading-type antistatic agents, 240

L

L-lactide, 6f
D-lactide, 6f
Lacea®, 4, 145
Laminates, 371–374. *See also* Films
Laser, 492–493
Latex, 187
LCP. *See* Liquid crystal polymer
LDPE. *See* Low density polyethylene
LiCl. *See* Lithium chloride
Light and UV stabilizers, 237
Lignin, 35–37, 413, 468
  blending with biodegradable polymers, 131–132
  production methods, 37–38
  sources, 37
  structure, 36f
Lignocellulose, 42–43
Linear low density polyethylene (LLDPE), 148
Linking moiety (LM), 467
Lipase-catalyzed chemical recycling, 511f
Liquid crystal polymer (LCP), 416
Lithium chloride (LiCl), 420
LLDPE. *See* Linear low density polyethylene
LM. *See* Linking moiety
Low density polyethylene (LDPE), 493
Low-molecular-weight organic materials, coating with, 310–311
Lubricants, 225

M

Machine direction (MD), 394
Marker systems
  fluorescent additives, 493–495
  RIC system, 493
Masterbatch technique, 219. *See also* Compounding
  biodegradable nanocomposite preparation method, 222
  for biodegradable polymer, 220
  dispersing agent, 219–220
  formulation of corrosive inhibitor composition, 221t
  masterbatches of biopolymers, 224t–225t
  melt mixing, 222–223
  PBSA, 221–223
  PLA masterbatch, 221
  trimesic acid amide compound, 220
Mater-Bi®, 4, 150t–151t
MD. *See* Machine direction
MDI. *See* Methylene diisocyanate
Mechanical degradation, 98
Mechanical properties, 81–83, 86t, 89t
Melt blowing process, 387, 388f–389f
Melt flow index (MFI), 412, 487
Melt spinning, 387
Melt strength enhancers, 223
Melt-coating process, 432f
Meso-lactide, 6f
Metal sulfonate groups, 450f
Methyl formate, 330
Methyl methacrylate (MMA), 280–281, 285
Methylene diisocyanate (MDI), 238
MFI. *See* Melt flow index
Miscellaneous additives, 241
MMA. *See* Methyl methacrylate
Modifiers, 223. *See also* Additives
  heat deflection temperature, 237–238
  impact, 234–235
Molar ratio, 449
Montmorillonite K10, 505
Multi-component reactive adhesives, 467. *See also* One-component reactive adhesives
Multiple coatings, 313
Multiple processing, 486–487
Mussels (*Mytilus edulis*), 467

N

Nafion®-H, 505
(Nano)precipitation technique, 190–191
Nanobiocomposites, 417
  inorganic nanofillers/nanofibers, 417–420
  organic nanofillers/nanofibers, 420–421
Nanofibers, 397–398
NAPCOR. *See* National Association for PET Container Resources
National Association for PET Container Resources (NAPCOR), 491–492
Natural resins, 468
NatureFlex®, 313
NatureWorks' assertions, 491–492
Near infrared (NIR), 488
  for optical sorting systems, 491–492
Neck-in, 432
NIR. *See* Near infrared
Nonreactive adhesives. *See also* Bio-based adhesives; Reactive adhesives
  drying adhesives, 459–460
  HMAs, 464–466
  PSAs, 461–464
Nonsolvent destructuring methods, 194–195. *See also* Solvent-based methods; Thermomechanical methods
Nonwoven, 391–396. *See also* Woven/Knitted
  carpets, 394–396
  method for forming melt blown fibers, 394f
NPE 2009 trade show in Chicago, 482
Nucleating agents, 225–226, 227t

O

O/W emulsion. *See* Oil-in-water emulsion
ODP. *See* Ozone depletion potential
Oil-in-water emulsion (O/W emulsion), 187, 191, 267–268
OnCap™ BIO, 241
OnCap™ BIO Impact T, 235
OnColor™ BIO Colorants, 239
One-component reactive adhesives, 466–467. *See also* Multi-component reactive adhesives
OPLA film. *See* Oriented poly(lactic acid) film
Optical sorting systems, 491
  laser, 492–493
  marker systems, 493–495
  NIR systems, 491–492
Organic compounds; Inorganic compounds; Polymer components, 333–335, 334t
Organic fillers, 417
Organic foaming agents, 329
Organic nanofillers/nanofibers, 420–421
Oriented poly(lactic acid) film (OPLA film), 482
Origo-Bi®, 21, 126. *See also* Eastar Bio®
Ozone depletion potential (ODP), 330

P

P3HB. *See* Poly(3-hydroxybutyrate)
P3HB-depolymerase (PHBDP), 511
P3HB4HB. *See* Poly(3-hydroxybutyrate-*co*-4-hydroxybutyrate)
P3HO. *See* Poly(3-hydroxyoctanoate)
P4HB. *See* Poly(4-hydroxybutyrate)
PAAs. *See* Poly(alkylene alkanoate)s
PADCs. *See* Poly(alkylene dicarboxylate)s
Paraloid™ BPM-500, 235
Patents
  adhesives, 469–479
  (bio)composites, 423–429
  blending biopolymer, 152–182
  chemical treatment, 290–299
  coating compositions, 439–445
  compounding and additives, 242–261
  emulsions, dispersion, solutions and gels, 199–213
  for fiber formation, 401–410
  films and laminates, 375–386
  foaming, 345–359
  inks, 454–458
  polymer properties, 100–114
  polymer recycling, 515–528
  powdering, 270–275
  surface treatment, 317–325
PBA. *See* Poly(butylene adipate)
PBAT. *See* Poly(butylene adipate-co-terephthalate)
PBC. *See* Poly(butylene carbonate)

PBS. *See* Poly(butylene succinate)
PBSA. *See* Poly(butylene succinate-co-adipate)
PBST. *See* Poly(butylene succinate-*co*-terephthalate)
PBT. *See* Poly(butylene terephthalate)
PCL. *See* Poly(ε-caprolactone); Polycaprolactone
PDLA. *See* Poly(d-lactic acid)
PDLGA. *See* Poly(D,L-lactide-co-glycolide)
PDLLA. *See* Poly(D,L-lactide)
PDO. *See* Polydioxanone
PE. *See* Polyethylene
PEA. *See* Poly(ethylene adipate)
PEC. *See* Poly(ethylene carbonate)
PEF. *See* Poly(ethylene furanoate)
PEG. *See* Polyethylene glycol
PEG-MA. *See* Poly(ethylene glycol) methacrylate
Pelletization, 263–264
Pellets. *See* Polymer beads
1,5-pentanediamine (1,5-PD), 28
PEOx. *See* Poly(ethylene oxalate)
Performance boosters. *See also* Processability boosters
  antioxidants, 237
  antistatic additives, 239–241
  colorants, 239, 239t
  compatibilizers, 238
  coupling agents, 238
  fillers, 238
  flame retardants, 235–237, 238t
  heat deflection temperature modifiers, 237–238
  heat stabilizers, 238
  impact modifiers, 234–235
  light and UV stabilizers, 237
  miscellaneous additives, 241
  phosphorus compound, 237f
  plasticizers, 228–233, 230t
PES. *See* Poly(ethylene succinate)
PESA. *See* Poly(ethylene succinate-co-adipate)
PET. *See* Poly(ethylene terephthalate)
PETG. *See* Poly(ethylene terephthalate glycol modified)
PGA. *See* Poly(glycolic acid)
PHA. *See* Polyhydroxyalkanoate
Phase change agent, 448
PHB. *See* Poly(3-hydroxybutyrate) (P3HB)
PHBO. *See* Poly(3-hydroxybutyrate-*co*-3-hydroxyoctanoate)
PHBDP. *See* P3HB-depolymerase
PHBHHx. *See* Poly(3-hydroxybutyrate-*co*-3-hydroxyhexanoate)
PHBHO. *See* Poly(3-hydroxybutyrate-*co*-3-hydroxyoctanoate)
PHBHP. *See* Poly(3-hydroxybutyrate-3-*co*-hydroxypentanoate)
PHBHV. *See* Poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate)
PHBHx. *See* Poly(3-hydroxybutyrate-*co*-3-hydroxyhexanoate)
PHBO. *See* Poly(3-hydroxybutyrate-octanoate)
PHO. *See* Poly(hydroxy octanoate)
Phosphorus compound, 237f
Photodegradation, 95–98
PHV. *See* Poly(3-hydroxyvalerate)
Physical foaming agents, 329–332, 331t
Physical recycling, 481
Physical treatment
  heat treatment, 304
  roughening, 304
  with solvents/swelling agents, 303–304
Pigment, 447
PLA. *See* Poly(lactic acid)
PLA/carbon fiber composite, 412
PLA/polystyrene blend (PLA/PS), 487
PLA/PS. *See* PLA/polystyrene blend
Plamate® PD-150, 235
Plant–Bottle™, 22
Plasma treatment, 306
Plast-Agglomerator, 483f
Plasticizers, 225, 228–233, 230t
  acetyl trialkyl citrate plasticizer, 230f
  alkylene oxide sulfonate salt-type plasticizer, 231f
  biopolymer/plasticizer systems, 233t–234t
  destructurized starch, 232
  high-molecular-weight plasticizers, 232
  for PLA, 228–231
Plastics, 490–491
  wastes, 481
PLCL. *See* Poly(lactide-*co*-caprolactone)
PLGA. *See* Poly(lactide-*co*-glycolide)
PLLA. *See* Poly(l-lactic acid)
PLLCL. *See* Poly(L-lactide-*co*-ε-caprolactone)
PM. *See* Polymandelide
PMLA. *See* Poly(β-malic acid)
POEs. *See* Poly(ortho esters)
Poly (D, L-lactide) (PDLLA), 500–501
Poly(3-hydroxybutyrate-3-*co*-hydroxypentanoate) (PHBHP), 217
Poly(3-hydroxybutyrate-*co*-3-hydroxyhexanoate) (PHBHHx), 13, 16, 80, 188
  properties, 81t
Poly(3-hydroxybutyrate-*co*-3-hydroxyhexanoate) (PHBHx), 194–195
Poly(3-hydroxybutyrate-*co*-3-hydroxyoctanoate) (PHBO), 80, 188
Poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate) (PHBHV), 13, 15–16, 15f, 80, 265, 303, 390, 431, 459–460, 514
  properties, 81t
Poly(3-hydroxybutyrate-*co*-4-hydroxybutyrate) (P3HB4HB), 13, 16, 188
Poly(3-hydroxybutyrate-octanoate) (PHBO), 459
Poly(3-hydroxybutyrate) (P3HB), 13–15, 15f, 80, 217, 390, 431, 485
  routes for enzymatic recycling, 511f
Poly(3-hydroxyoctanoate) (P3HO), 16–17, 17f, 188
Poly(3-hydroxyvalerate) (PHV), 504
Poly(4-hydroxybutyrate) (P4HB), 15, 80
Poly(alkylene alkanoate)s (PAAs), 18, 19t, 368
  biopolymer blends, 146–147
  PBA, 19–20, 20f
  PBS, 18–19, 19f
  PBSA, 20
  PES, 18, 19f
  Polyoxalates, 20
  PPF, 20, 21f
Poly(alkylene dicarboxylate)s (PADCs), 17–18
  aliphatic-aromatic copolyesters, 20, 21t
    components, 20
    PBAT, 21, 22f
  bio-based aromatic polyesters, 21, 22t
    PEF, 22–23, 23f
    PET, 21–22
    PTT, 23
  PAAs, 18, 19t
    PBA, 19–20, 20f
    PBS, 18–19, 19f
    PBSA, 20
    PES, 18, 19f
    Polyoxalates, 20
    PPF, 20, 21f
Poly(butylene adipate-*co*-terephthalate) (PBAT), 4, 20–21, 22f, 97–98, 283, 313, 327, 364, 372, 415
Poly(butylene adipate) (PBA), 19–20, 20f, 222–223, 485
Poly(butylene carbonate) (PBC), 25
Poly(butylene succinate-*co*-adipate) (PBSA), 20, 219–220, 364, 411–412, 507
Poly(butylene succinate-*co*-terephthalate) (PBST), 20–21, 220
Poly(butylene succinate) (PBS), 2, 18–19, 19f, 87, 219–220, 265, 327–328, 485
  pellets, 192–194
Poly(butylene terephthalate) (PBT), 23
Poly(butylene-adipate-*co*-terephthalate) (PBAT), 191, 222–223
Poly(D, L-lactide-co-glycolide) (PDLGA), 500–501
Poly(D-lactic acid) (PDLA), 6, 79, 218
  weight ratio, 432
Poly(D-lactide). *See* Poly(d-lactic acid) (PDLA)
Poly(ester amides), 30
Poly(ester-urethane)s, 30
Poly(ethylene adipate) (PEA), 504
Poly(ethylene carbonate) (PEC), 24, 368
Poly(ethylene furanoate) (PEF), 22–23
Poly(ethylene glycol) methacrylate (PEG-MA), 281
Poly(ethylene oxalate) (PEOx), 21f, 513
Poly(ethylene succinate-co-adipate) (PESA), 287
Poly(ethylene succinate) (PES), 219–220, 287, 504
Poly(ethylene terephthalate glycol modified) (PETG), 148
Poly(ethylene terephthalate) (PET), 21–22, 387–388, 486, 493
Poly(glycolic acid) (PGA), 11–12, 79, 263, 277, 305, 327, 364, 488
  blends, 123
  crystallinity, 80
  in film formation, 364–366
  heat stability improvement, 217
  processing properties, 88

- Poly(hydroxy acid)s, 4
  - poly(α-hydroxyalkanoic acid)s, 4–12
  - poly(ω-hydroxyalkanoate)s, 17
  - polyhydroxyalkanoates, 12–17
- Poly(hydroxy octanoate) (PHO), 460
- Poly(L-lactic acid) (PLLA), 6, 79, 498
  - photodegradation mechanisms, 97f
  - weight ratio, 432
- Poly(L-lactide-*co*-ε-caprolactone) (PLLCL), 305–306
- Poly(lactic acid) (PLA), 2, 79, 277, 327–328, 481–482, 512
  - α-hydroxycarboxylic acid-derived polyesters, 9t–11t
  - adhesive for forming cigarette filter, 460
  - blends, 118
    - blending optical isomers, 118–122
    - in majority, 133–137
    - in minority, 143–145
    - with other aliphatic (co)polyesters, 122–123
  - for coating compositions, 432–434
  - crystallinity, 79
  - depolymerization, 497
  - in fiber formation, 387–390
  - in film formation, 362–364
  - hydrolysis, 98, 99f
  - mechanical properties, 81–83
  - pellets, 263
  - processing properties, 87–88
  - properties comparison, 92t
  - solubility, 81
  - stereoisomeric forms, 7f–8f
  - stereoisomers, 6
  - three-and four-branched, 461f
  - transition temperature, 7t, 79
  - types, 6
- Poly(lactide-*co*-caprolactone) (PLCL), 267
- Poly(lactide-*co*-glycolide) (PLGA), 12, 277, 306
- Poly(ortho esters) (POEs), 39–41, 41f
- Poly(propylene carbonate) (PPC), 24–25, 416
  - miscibilities, 139t
- Poly(propylene fumarate) (PPF), 20, 21f, 289
- Poly(propylene glycol) (PPG), 280–281
- Poly(propylene terephthalate) (PPT), 23
- Poly(tetramethylene adipate-*co*-terephthalate) (PTeMAT), 20–21, 499
- Poly(tetramethylene carbonate) (PTeMC), 25
- Poly(tetramethylene succinate) (PTMS), 25
- Poly(trimethylene carbonate) (PTMC), 25, 510
  - enzymatic recycling, 510f
- Poly(trimethylene terephthalate) (PTT), 23, 391, 485–486
- Poly(vinyl acetate) (PVAc), 198
  - hydrogels, 198
- Poly(vinyl alcohol) (PVOH), 39, 40t, 280–281, 420
- Poly(vinyl chloride) (PVC), 39, 483
- Poly(α-amino acids), 25, 27
  - ε-PL, 28
  - poly(α-aspartic acid), 28
  - poly(γ-glutamic acid), 27–28
- Poly(α-aspartic acid), 28
- Poly(α-hydroxyalkanoic acid)s, 4
  - α-hydroxyalkanoic acids, 4–5, 5t
  - PGA, 11–12
  - PLA, 5–8
    - α-hydroxycarboxylic acid-derived polyesters, 9t–11t
    - stereoisomeric forms, 7f–8f
    - transition temperature, 7t
    - types, 6
  - PLGA, 12
  - PM, 8–11, 11f
- Poly(β-malic acid) (PMLA), 17
- Poly(γ-glutamic acid) (γ-PGA), 25, 27–28
- Poly(ε-caprolactone) (PCL), 2, 17, 80, 277
  - crystallinity, 80
  - in film formation, 367–368
  - lipase-catalyzed chemical recycling, 511f
  - polymer blends, 146
  - processing properties, 89
  - transition temperatures, 80
- Poly(ω-hydroxyalkanoate)s, 17
  - commercial polyactones, 18t
  - PCL, 17
- Poly[oligo(tetramethylene succinate)-*co*-(tetramethylene carbonate)] (PTMS/PTeMC), 25
- Polyaldehydes, 288
- Polyamides, 25
  - bio-polyamides, 26t–27t
  - poly(α-amino acids), 25–28
  - polycondensation
    - of ω-amino carboxylic acids or lactams, 25
    - of diamines and dicarboxylic acids, 25
- Polyanhydrides, 41
- Polyaspartate. *See* Poly(α-aspartic acid)
- Polydioxanone (PDO), 23–24
- Polyesters, 4, 327, 493. *See also* Aliphatic polycarbonates; Lignin; Vinyl polymers
  - aliphatic, 327–328
  - aliphatic-aromatic, 328
  - PADCs, 17–18
    - aliphatic-aromatic copolyesters, 20–21
    - PAAs, 18–20
  - poly(hydroxy acid)s, 4
    - poly(α-hydroxyalkanoic acid)s, 4–12
    - poly(ω-hydroxyalkanoate)s, 17
    - polyhydroxyalkanoates, 12–17
- Polyethylene (PE), 495
- Polyethylene glycol (PEG), 467
- Polyethylene succinate (PES), 18, 19f
- Polyglutamate. *See* Poly(γ-glutamic acid)
- Polyglycolide. *See* Poly(glycolic acid) (PGA)
- Polyhydroxyalkanoate (PHA), 1–2, 4, 12, 217–218, 265, 327, 431–432, 459, 507
  - aqueous dispersions, 188
  - β-, γ-, and δ-hydroxyalkanoic acids, 13t
  - β-hydroxyalkanoic acid, 13f
  - blends, 124–125
    - in majority, 137–138
    - in minority, 145–146
  - commercial, 14t
  - crystallinity, 80
  - in fiber formation, 390–391
  - in film formation, 366–367
  - γ-hydroxyalkanoic acid, 13f
  - general formula, 12f
  - mechanical properties, 83
  - P3HB, 13–15, 15f
  - P3HB4HB, 16
  - P3HOs, 16–17, 17f
  - P4HB, 15
  - PHBHHx, 16
  - PHBHV, 15–16, 15f
  - PMLA, 17
  - processing properties, 88–89
  - routes for enzymatic recycling, 511
  - solubility, 81
- Polylactide. *See* Poly(lactic acid) (PLA)
- Polymandelide (PM), 8–11
- Polymer
  - beads, 329
  - branching/bridging, 285–286
  - fibers, 387
  - foams, 327, 329
- Polymer blends, 117. *See also* Blending biopolymer
  - miscibility, 117–118
  - starch with biodegradable polymers, 128
- Polymer components, 335, 336t. *See also* Inorganic compounds; Organic compounds
- Polymer properties, 79
  - intrinsic properties, 79
    - crystallinity, 79–80
    - density, 79, 80t
    - electromagnetic properties, 87
    - gas barrier properties, 83–86
    - mechanical properties, 81–83, 86t, 89t
    - solubility, 81
    - transition temperatures, 79–80, 82t–83t
    - transparency, 86–87
  - patents, 100–114
  - processing properties, 87
    - PCL, 89
    - PGA, 88
    - PHA, 88–89
    - PLA, 87–88
  - product properties, 89
    - aesthetic properties, 92–94
    - antistatic properties, 92
    - environmental behavior, 94–99
    - flammability/flame retardancy, 92
    - heat resistance, 90–92
    - mechanical behavior, 89–90
    - water resistance, 92
- Polyolefins, 38–39
- Polyols, 31t
- Polyoxalates, 20
- Polyoxyethylene, 467
- Polyphosphazenes (PPHOSs), 41–42
- Polypropylene (PP), 493, 495
- Polysaccharides, 31–35. *See also* Aliphatic polycarbonates; Lignin; Vinyl polymers
  - cellulose, 32–34, 33t–34t
  - chitin, 35
  - chitosan, 35
  - starch, 34–35

Polystyrene (PS), 89, 493
Polyurethane (PU), 30–31
Porous films, 371
Powder coatings, 435. *See also* Thermoplastic coating compositions
Powdering
  coagulating dispersions, 268
  dissolution-deposition method, 265–266
  emulsion-precipitation method, 266–268
  patents, 270–275
  pelletization, 263–264
  pulverization, 264–265
  SCF technology, 268–269
PP. *See* Polypropylene
PPC. *See* Poly(propylene carbonate)
PPF. *See* Poly(propylene fumarate)
PPG. *See* Poly(propylene glycol)
PPHOSs. *See* Polyphosphazenes
PPT. *See* Poly(propylene terephthalate)
Prepregs, 421. *See also* (Bio)composites
Pressure-sensitive adhesive (PSA), 459, 461–464. *See also* Drying adhesives; Hot melt adhesive (HMA)
  tapes, 462–464
Pretreated fibers, 417
Printing, 313, 447. *See also* Coating
  antiforgery paper sheet, 314f
  biopolymer films for, 314
  3D printing, 315–316
Processability boosters. *See also* Performance boosters
  drying/desiccant agents, 226–227
  heat stabilizers, 223
  hydrolysis-suppressing agents, 226–227
  lubricants, 225
  melt strength enhancers, 223
  nucleating agents, 225–226, 227t
  plasticizers, 225
Processing properties, 87. *See also* Intrinsic properties
  PCL, 89
  PGA, 88
  PHA, 88–89
  PLA, 87–88
Product properties, 89. *See also* Intrinsic properties
  aesthetic properties, 92–94
  antistatic properties, 92
  environmental behavior, 94–99
  flammability/flame retardancy, 92
  heat resistance, 90–92
  mechanical behavior, 89–90
  water resistance, 92
Proteins, 467
Proximity coating, 433
PS. *See* Polystyrene
PSA. *See* Pressure-sensitive adhesive
PTeMAT. *See* Poly(tetramethylene adipate-co-terephthalate)
PTeMC. *See* Poly(tetramethylene carbonate)
PTMC. *See* Poly(trimethylene carbonate)
PTMS. *See* Poly(tetramethylene succinate)
PTMS/PTeMC. *See* Poly[oligo(tetramethylene succinate)-co-(tetramethylene carbonate)]
PTT. *See* Poly(trimethylene terephthalate)
PU. *See* Polyurethane
Pulverization, 264–265
PVAc. *See* Poly(vinyl acetate)
PVC. *See* Poly(vinyl chloride)
PVOH. *See* Poly(vinyl alcohol)

Q

Quasi-crosslinking, 146

R

Radiation, 284–285, 305–306
Rapid expansion of supercritical solutions (RESS), 268
Reactive adhesives, 466. *See also* Bio-based adhesives; Nonreactive adhesives
  multi-component reactive adhesives, 467
  one-component reactive adhesives, 466–467
Recuperation, 481–483
Recycled PET (RPET), 487
Recycling
  of cellulose acetate ester waste, 503f
  chemical, 496–497
    alcoholysis, 503–505
    dry-heat depolymerization, 497–500
    foam hydrolysis, 505
    hydrolysis, 500–503
  enzymatic depolymerization, 510–514
  hydrothermal depolymerization, 505–509
  miscellaneous processes, 514
  patents, 515–528
  physical
    drying, 496
    general, 487
    grinding, 487–488
    sorting, 488–496
  reuse, 481
    blending recycled polymers, 484–485
    chemical structure modification, 485–486
    multiple processing, 486–487
    recuperation, 481–483
    restabilization, 483–484
Reinforcing biopolymers
  with coherent fibrous material, 411
    with carbon fibers, 411–412
    with glass fibers, 412–413
    with pretreated fibers, 417
    with vegetable or animal fibers, 413–416
  with fillers
    with inorganic fillers, 417
    nanobiocomposites, 417–421
    with organic fillers, 417
Resin Identification Codes system (RIC system), 493–494
RESS. *See* Rapid expansion of supercritical solutions
Restabilization, 483–484
Reuse, 481
  blending recycled polymers, 484–485
  chemical structure modification, 485–486
  multiple processing, 486–487
  recuperation, 481–483
  restabilization, 483–484
Reversible crosslinkers, 288
RIC system. *See* Resin Identification Codes system
Rikemal®, 240–241
Rikemaster®, 240–241
Ring-opening polymerization (ROP), 277–278
Rotogravure ink, 450–451
Roughening, 304
RPET. *See* Recycled PET

S

Salting-out technique, 191. *See also* Solvent-based methods
SAS process. *See* Supercritical antisolvent process
sbcPLA. *See* Stereoblock copolymer PLA
scCO$_2$. *See* Supercritical carbon dioxide
SCF. *See* Supercritical fluid
scPLA. *See* Isotactic stereocomplex PLA; Stereocomplex PLA
Scrap biopolymers, 481–482
Screen inks, 449–451
Screen printing, 451
"7-OTHER" code, 493
Shredder dust, 499–500
Shrinkable films, 369–371
Single polymer coating, 311–313
Sintering expandable particles, 339–340
Sn (II) carboxylates, 497
Society of the Plastics Industry (SPI), 493
Solubility, 81
Solutions, 195–197. *See also* Emulsions; Hydrogels
Solvent-based adhesives, 460
Solvent-based methods, 187. *See also* Nonsolvent destructuring methods; Thermomechanical methods
  emulsification-diffusion technique, 191–192
  emulsification-evaporation technique, 187–190
  (nano)precipitation technique, 190–191
  salting-out technique, 191
Solvents, 84t–85t, 303–304
Sorona®, 485
Sorting, 488–496
  density separation systems, 489, 490t
  dissolution, 495–496
  electrostatic separation systems, 489–491
  optical systems, 491–495
Soy-based polyols, 327
Spherulites, 90–91
SPI. *See* Society of the Plastics Industry
Spun bonding process, 387, 388f
Stannous octoate, 497
Starch, 34–35
  for adhesive compositions, 468
  biopolymer blends, 138–143, 147–150
  biopolymer foams, 328–329
  blending with biodegradable polymers, 128–131, 131t–132t
  for coating compositions, 434

  in fiber formation, 391
  in film formation, 361–362
  pellets, 339
  starch-based products, 35t
Stereoblock copolymer PLA (sbcPLA), 6
Stereocomplex PLA (scPLA), 79, 388
Strippable coatings, 435
Sucrose fatty acid ester, 310
Supercritical antisolvent process (SAS process), 268
Supercritical carbon dioxide (scCO$_2$), 81, 513
Supercritical fluid (SCF), 496
  technology, 268–269
Surface active substances, 187
Surface effects, 93
Surface treatment, 303
  chemical treatment, 304–305
    functional groups incorporation, 305–307
    grafting, 307–308
    hydrolysis/aminolysis, 305
  coating
    with inorganic materials, 308–310
    with low-molecular-weight organic materials, 310–311
    multiple coatings, 313
    single polymer, 311–313
  patents, 317–325
  physical treatment
    heat treatment, 304
    roughening, 304
    with solvents/swelling agents, 303–304
  printing, 313
    antiforgery paper sheet, 314f
    biopolymer films for, 314
    package for disposable bodily discharge absorbent article, 315f
    3D printing, 315–316
Swelling agents, 303–304
Syndiotactic PLA, 6
Syndiotactic poly(D,L-lactide) (syndiotactic PDLLA), 6

T
TAEC. *See* t-amyl-2-ethylhexyl peroxycarbonate
TBD. *See* Triazabicyclodecene
TBPB. *See* *t*-butylperoxybenzoate
Temporary coatings. *See* Strippable coatings
TephaFLEX®, 15
Terraloy™ 20000 series, 150
2,3,3,3-tetrafluoropropene (HFO-1234yf), 332
Tetrahydrofuran (THF), 81
TG/DTA. *See* Thermogravimetric/differential thermal analysis
Thermal decomposable foaming agents. *See* Chemical foaming agents
Thermal decomposition products, 499t
Thermal degradation, 95, 96f
Thermochromic inks, 452
Thermogravimetric/differential thermal analysis (TG/DTA), 498f
Thermomechanical methods, 192–194. *See also* Nonsolvent destructuring methods; Solvent-based methods
Thermoplastic coating compositions. *See also* Powder coatings
  cellulose derivatives, 434–435
  PHAs, 431–432
  PLA, 432–434
  starch, 434
Thermoplastic methylol polyester, 465f
Thermoplastic polymers, 330
Thermoplastic starch (TPS), 128
THF. *See* Tetrahydrofuran
3D printing, 315–316
TMC. *See* Trimethylene carbonate
TMDI. *See* Trimethylhexamethylene diisocyanate
p-toluene sulfonic acid (APTS), 502
Tone®, 17
TPS. *See* Thermoplastic starch
Trans-1,3,3,3-tetrafluoropropene (trans-HFO-1234ze), 332
Transition temperatures, 79–80, 82t–83t
Transparency, 86–87
Triazabicyclodecene (TBD), 502
3,3,3-trifluoropropene (HFO-1243zf), 332
Trimethylene carbonate (TMC), 25, 510
Trimethylhexamethylene diisocyanate (TMDI), 31
Two-step molding process, 342–343

U
Ultraviolet (UV), 488

V
Vegetable or animal fibers, 413–416
Vinyl polymers
  bio-LDPE, 2
  bio-HDPE, 2
  biopolyethylene, 2. *See also* Bio-based polyethylene
  biopolyolefins, 39t
  biopolypropylene (bio-PP), 2
  polyolefins, 38–39
  PVC, 39
  PVOH, 39, 40t
Volatile organic compounds (VOCs), 330

W
Waste PLA, 482
Water resistance, 92
Water-based adhesives, 459–460
Water-based flexographic ink composition, 449
Water-in-oil emulsion (W/O emulsion), 187, 267–268
Wide-angle X-ray diffraction (WAXS), 190
Wood dust, 413
Wearing resistance, 89–90, 398–399
Wet spinning, 387
Wood flour, 413
Wood residues, 413
Woven/Knitted, 396–397.
Writing inks, 452–453

Index of Companies

Note: Page numbers with "f" and "t" denote figures and tables, respectively.

0–9

3M INNOVATIVE PROPERTIES CO, 228, 230, 363

A

ABBOTT CARDIOVASCULAR SYSTEMS INC, 8–11
ABE SHUNSUKE, 100–114, 270–275, 375–386
ACHILLES CORP, 337–338
ADEKA CORP, 334t, 345–359
ADVANCED TECHNOLOGIES AND REGENERATIVE MEDICINE LLC, 304, 306
AGENCY IND SCIENCE TECHN, 124, 128, 143, 149
AGRI TECH IND INC, 148
AGROFERM A G, 81, 84t–85t, 100–114
AIR PROD & CHEM, 138, 139t, 147
AKAD WISSENSCHAFTEN DDR, 196
AKZO GMBH, 265
AKZO NOBEL NV, 286
ALBANY INT CORP, 333t, 345–359
ALGIX LLC, 415
ALLIED CORP, 229
ALLIED SIGNAL INC, 149
ALMA MATER STUDIORIUM UNI DI B, 283
ALZA CORP, 39–41
AMCOR FLEXIBLES TRANSPAC N V, 313
AMERICAN CYANAMID CO, 93–94
AMPAC HOLDINGS LLC, 363–364
ANEBO LTD, 401–410
ARAKAWA CHEM IND, 189, 433
ARCHER DANIELS MIDLAND CO, 217–218, 278–280
ARCO CHEM TECH, 466
ARKEMA FRANCE, 135–136, 265
ARKEMA INC, 330, 332
ARTUR FISCHER TIP GMBH & CO KG, 434
ASAHI CHEMICAL CORP, 264, 339–340
ASAHI CHEMICAL IND, 145
ASAHI DENKA KOGYO KK, 7–8, 225–226
ASAHI KASEI CHEMICALS CORP, 371
ASAHI KASEI CORP, 345–359
ASAHI KASEI LIFE & LIVING CORP, 93, 328, 335
ASTRA MEDITEC AB, 16
ASTRAZENECA AB, 303–304
ASTRAZENECA UK LTD, 303–304
ATO BV, 195, 264, 288

B

BASF AG, 495, 4, 20, 85, 122, 125–126, 147–148, 191, 308, 336, 339, 372
BASF SE, 30, 137, 312, 335–337, 368
BATTELLE MEMORIAL INSTITUTE, 133–135, 231
BAYER AG, 494, 29, 138, 312
BAYER MATERIALSCIENCE AG, 30
BERNACCHIA IDA, 434
BIJENKORF ZETMEEL, 329
BINDSCHAEDLER CHRISTIAN, 191
BIO DEG MOULDINGS PTY LTD, 414
BIO MATERIAL UNIVERS, 6–7
BIO PROD INT, 333t, 345–359
BIO SCAFFOLD INTERNAT PTE LTD, 316
BIO TEC ENVIRONMENTAL LLC, 145, 148
BIOAPPLY SARL, 334t, 345–359
BIOGRADE HONG KONG PTY LTD, 222–223
BIOMATERA INC, 449
BIOMATERIALS UNIVERSE INC, 266
BIOMET DEUTSCHLAND GMBH, 466
BIOP BIOPOLYMER GMBH, 149
BIOPAK TECHNOLOGY LTD, 231
BIOPOLYMER NETWORK LTD, 338
BIOSPHERE IND LLC, 434–435
BIOTEC BIOLOG NATURVERPACK, 118, 129, 140, 312, 460
BIOVATION LLC, 375–386
BLUE MARBLE POLYMERS LTD, 328, 340
BOEHRINGER INGELHEIM INT, 5
BOEHRINGER INGELHEIM KG, 5, 91, 229
BONSET AMERICA CORP, 370–371
BOSTIK SA, 465–466
BRASKEM SA, 38, 42–43
BRUKER ANALYTISCHE MESSTECHNIK, 491
BUCK CHEM TECH WERK, 372
BUNA SOW LEUNA OLEFINVERB GMBH, 268
BUTTERFLY SRL, 149

C

C I KASEI CO LTD, 369–370
CAMBRIDGE SCIENT INC, 289
CANON KK, 447, 485, 503, 506
CARGILL DOW LLC, 90–91
CARGILL INC, 4, 88, 93, 136, 285, 388f, 432–433
CASIO COMPUTER CO LTD, 452
CASIO ELECTRONICS CO LTD, 452
CBPAK EMBALAGENS ECO SUBSTANTA, 313
CELANESE ACETATE LLC, 32, 502
CENTRE NAT RECH SCIENT, 190, 266
CEREPLAST INC, 148
CERESTAR HOLDING BV, 34
CHANGCHUN APPLIED CHEMISTRY, 24, 127, 222, 419
CHANGSHA LEYUAN CHEMICAL TECHNOLOGY CO LTD, 460
CHEIL IND INC, 136
CHEM IND BASEL, 196
CHI MEI CORP, 263, 264f
CHIBA INST TECHNOLOGY, 414
CHIBA PREFECTURE, 501
CHIKYU KANKYO SANGYO GIJUTSU, 128
CHISSO CORP, 396
CHISSO POLYPRO FIBER COMPANY L, 393, 396
CHRONOPOL INC, 231
CHUKOH CHEM IND, 390
CHUO KAGAKU KK, 239–241
CLATTY JAN L, 327, 345–359
CLEANING AND PAPER DISPOSABLES PLC, 123
COCA COLA CO, 22, 304
COGNIS BRASIL LTDA, 232
COGNIS DEUTSCHLAND GMBH, 232
COLLINS & AIKMAN FLOORCOVERING, 401–410
COLOROLL LTD, 147
COMISSAO NAC ENERGIA NUCLEAR, 313
COMTECH CHEMICAL CO LTD, 335
CONNAUGHT LAB, 27
CONSEJO SUPERIOR INVESTIGACION, 420
COOKSON PLC, 431
CORN PRODUCTS CO, 468
CORNELL RES FOUNDATION INC, 29, 278–280
CORTEC CORP, 221
COUNCIL OF SCIENTIFIC & INDUSTRIAL RESEARCH, 17
CRESCENT INNOVATIONS INC, 27–28
CRYOLIFE, INC, 342
CRYOVAC INC, 342–343
CT VALORISATION IND AGRO RESSO, 131, 281

D
DAESANG CORP, 329
DAI ICHI KOGYO SEIYAKU CO LTD, 189, 229
DAICEL CHEM, 6–7, 130, 267, 285, 342
DAINICHISEIKA COLOR CHEM, 219–220, 451
DAINIPPON INK & CHEM INC, 504
DAINIPPON PRINTING CO LTD, 373, 462
DANUBIA PETROCHEM DEUTSCHLAND, 431
DANUBIA PETROCHEM POLYMERE, 267
DARLING & CO, 37
DEBIO RECH PHARMA SAA, 19
DEPARTMENT OF AGRICULTURE AND INSPECTION, 375–386
DING SHAOZHONG, 222
DONLAR CORP, 28
DOW CHEMICAL CO, 146, 193
DOW GLOBAL TECHNOLOGIES LLC, 146–147
DS TEXTILE PLATFORM NV, 396
DSM IP ASSETS BV, 30
DU PONT, 4–7, 94, 145, 228–229, 231, 308, 362, 364, 388, 391, 485, 497, 500, 503

E
EASTMAN CHEM CO, 117, 196
EASTMAN KODAK CO, 494f, 32, 127, 138, 147
ECOSYNTHETIX INC, 264, 460, 468
EKISUI CHEMICAL CO LTD, 130
ELECTRONICS FOR IMAGING INC, 448
ELLIS FOSTER CO, 20
ENFORECO CO LTD, 362
ENSO OYJ, 422, 433
EREMA ENGINEERING RECYCLING MASCHINEN UND ANLAGEN GESELLSCHAFT MBH, 515–528
ETHICON INC, 23–24, 228–229
EVERCORN INC, 117, 129

F
FAR EASTERN NEW CENTURY CORPORATION, 122, 125–126, 136, 138, 145
FAR EASTERN TEXTILE LTD, 90, 100–114
FIBERWEB SODOCA SARL, 392–393
FIDIA SPA, 197
FINA TECHNOLOGY, 144, 278–280, 279f–280f, 364
FLAHERTY MICHAEL JOHN, 336
FLAMEL TECH SA, 28
FOLLRI SCIEN TEC CO LTD, 371
FRAUNHOFER GES FORSCHUNG, 35–38, 421
FUJI XEROX CO LTD, 92, 485, 488
FUJIFILM CORP, 488
FUJITSU LTD, 92, 312, 412
FULLER H B LICENSING FINANC, 465

G
GALACTIC SA, 488–489, 495, 502
GENENCOR INT, 23
GLOTECH CO LTD, 419
GRACE W R & CO, 366
GUANGZHOU ZHUOYANG NEW MATERIAL TECHNOLOGY CO LTD, 416
GULF OIL CORP, 5, 362
GUNZE KK, 367

H
HAMOS ELEKTRONIK GMBH, 515–528
HAMOS GMBH RECYCLING UND SEPARATIONSTECHNIK, 490, 515–528
HEFEI GENIUS NEW MAT CO LTD, 412
HENKEL KGAA, 140
HITACHI CHEMICAL CO LTD, 138, 144
HITACHI PLANT TECHNOLOGIES LTD, 18–19
HITACHI SHIPBUILDING ENG CO, 8
HUECK FOLIEN GMBH, 448
HUETTERMANN A, 37
HUHTAMAEKI OYJ, 226
HUHTAMAKI FORCHHEIM, 374
HYCAIL B V, 465–466, 469–479
HYUNDAI MOTOR CO LTD, 118, 136

I
IBB KK, 416
ICI LTD, 196
IDEMITSU KOSAN CO, 145
IDEMITSU PETROCHEMICAL CO, 135
IJENKORF ZETMEEL, 343
IMP INNOVATIONS LTD, 27
IND TECH RES INST, 231
INNOVATIVE TECH CENTER, 268
INNOVIA FILMS LTD, 435
INST FIZIOL IM I S BERITASHVIL, 30
INST GETREIDEVERARBEITUNG, 152–182
INST NAGOYA IND SCI RES, 508, 509f
INST OF POLYMERS AND CARBON MA, 283
INST VOOR AGROTECH ONDERZOEK, 194, 267
INT PAPER CO, 372
INTERNATIONAL PAPER COMPANY, 373
IRE CHEMICAL LTD, 20–21
ISHIDA SEISAKUSHO, 309
ISHIKAWA PREFECTURE, 390

J
JAPAN ATOMIC ENERGY RES INST, 284–286, 288, 342
JAPAN CORN STARCH CO LTD, 187, 459
JAPAN POLYPROPYLENE CORP, 220
JAPAN PULP & PAPER CO LTD, 309
JAPAN SCIENCE & TECH AGENCY, 269
JAPAN SCIENCE & TECH CORP, 401–410
JAPAN STEEL WORKS LTD, 506
JSP CORP, 124, 338–340, 342
JUJO CENTRAL KK, 374

K
KANAZAWA INST OF TECHNOLOGY, 307, 311
KANEBO LTD, 19–20, 88, 91, 135–136, 264, 337, 339, 393, 396, 398–399, 485
KANEBO SYNTHETIC FIBERS LTD, 91, 136, 337, 339, 396
KANEGAFUCHI CHEMICAL IND, 16, 311–312, 328
KANEKA CORP, 16, 81t, 146, 194–195, 267–268, 328, 335, 339, 368, 390, 431
KANSAI PAINT CO LTD, 435
KAO CORP, 144, 216, 236, 371
KASEI CO C I, 364, 369
KEHL IND E COM LTDA, 100–114
KEMIRA OYJ, 196
KHASHOGGI E IND, 118, 329
KIMBERLY CLARK CO, 127–128, 140, 140f, 147, 278–281, 283, 306, 362, 391–392, 394
KIMBERLY–CLARK WORLDWIDE INC, 43, 387–388
KIMOTO KK, 304
KINGFA SCI & TECH CO LTD, 220
KITAKYUSHU FOUNDATION, 498–499
KITOZYME S A, 466–468
KOLON INC, 313
KONISHI CO LTD, 460
KOREA ENERGY RESEARCH INST, 413, 415
KOREA INST OF FOOTWEAR & LEATHER TECHNOLOGY, 335
KOREA INST SCI & TECH, 218, 419
KOTOBUKI SEIHAN PRINTING CO, 452
KRIEG G, 492
KUMAMOTO TECH & IND FOUND, 509
KUMOH NAT INST TECH ACAD COOP, 398
KUNSHAN XIANGHUAJING BIOTECHNOLOGY CO LTD, 452
KUREHA CHEM IND CO LTD, 11–12, 83–85, 88, 93–94, 361, 364–365, 422
KUREHA CORP, 11, 85, 88, 92, 123, 217, 263–266, 364–366
KUREHA GOSEN KK, 313
KYODO PRINTING CO LTD, 422
KYOTO INST OF TECHNOLOGY, 436t–438t, 439–445
KYOWA HAKKO CHEMICAL CO LTD, 136–137, 232
KYOWA YUKA KK, 232
KYUSHU INST OF TECHNOLOGY, 498–499

L
LG HAUSYS LTD, 230–231
LIFOAM IND, 338–339
LITTLE INC A, 28
LOGO TAPE GES FUER SELBSTKLEBE, 463
LOGOS QUIMICA LTDA, 100–114, 242–261

M
MAFO SYSTEMTECH GMBH & CO KG, 329
MAHISHI LATA HANAMANTRAO, 17

MARKEM IMAJE, 447
MASARU O, 416
MASSACHUSETTS INST TECHNOLOGY, 41, 277–278, 289
MATSUSHITA DENKI SANGYO KK, 504
MAYO FOUNDATION, 20
MEIDENSHA ELECTRIC MFG CO LTD, 435
METABOLIX INC, 12–13, 15–16, 126, 191–192, 226, 278–280, 286, 332–333, 335, 460, 462
MICRO POWDERS INC, 265
MINIMA TECHNOLOGY CO LTD, 287–288
MINNESOTA MINING & MFG, 467
MITSUBISHI CHEM CORP, 18–20, 225–226, 513
MITSUBISHI CHEM IND, 100–114
MITSUBISHI CHEM MKV CO, 375–386
MITSUBISHI GAS CHEM CO INC, 125
MITSUBISHI HEAVY IND LTD, 507
MITSUBISHI KAGAKU FOODS KK, 375–386
MITSUBISHI PLASTICS INC, 92, 369–370, 488, 499
MITSUBISHI PLASTICS IND, 91–92, 123, 236, 240, 308, 313, 369–371, 421–422
MITSUBISHI RAYON CO, 145–146
MITSUI CHEM INC, 500–501
MITSUI CHEMICALS POLYURETHANES, 30
MITSUI PETROCHEMICAL IND, 239–240
MITSUI TOATSU CHEM INC, 491, 361, 500–501
MIYOSHI YUSHI KK, 188, 340
MOBIL OIL CORP, 43, 366
MONSANTO CO, 88–89, 188, 196, 285–286, 431–432, 432f
MONSANTO TECHNOLOGY LLC, 265
MUSASHINO KAGAKU KENKYUSHO, 91–92, 122, 189, 433, 507
MUTUAL CORP, 91–92, 122, 189, 433

N

NAGASE CHEMTEX CORP, 412–413
NAGOYA CITY, 136
NAKAMOTO PAKKUSU KK, 309
NAT INST FOR MATERIALS SCIENCE, 17
NAT INST RES INORGANIC MAT, 332–333, 344, 419
NAT STARCH CHEM CORP, 329
NATIONAL RECOVERY TECHNOLOGIES INC, 491
NATUREWORKS LLC, 8, 90–91
NEC CORP, 87, 236–237, 374, 412, 416
NESTE OY, 37, 285
NEVALAINEN KIMMO, 434
NEW JAPAN CHEM CO LTD, 220, 225–226
NIDEK KK, 436t–438t, 439–445
NIPPON A & L KK, 395
NIPPON CATALYTIC CHEM IND, 18–19, 128–130, 415
NIPPON FOIL MFG, 374
NIPPON KOONSUTAAC KK, 195
NIPPON SYNTHETIC CHEM IND, 367–368
NISHIKAWA RUBBER CO LTD, 132–133
NISSAN CHEMICAL IND LTD, 90–91, 226
NISSEI KK, 307
NITTO BOSEKI CO LTD, 412–413
NITTO DENKO CORP, 461–464
NORNER AS, 147
NOVAMONT SPA, 89, 123, 125, 128, 130–131, 339
NOVOMER INC, 25
NTNU TECHNOLOGY TRANSFER AS, 420

O

OCV INTELLECTUAL CAPITAL LLC, 193–194
OFAA SEKKEI JIMUSHO KK, 341
OKURA INDUSTRIAL CO LTD, 367, 416
ORIX INTERIOR CORP, 395–396
OSAKA IND PROMOTION ORG, 304
OSAKA MUNICIPAL TECHNICAL RES INST, 460
OTTAWA HEALTH RESEARCH INST, 289

P

PAC POLYMERS INC, 368
PACTIV CORP, 329–330, 336–337
PALLMANN MASCHINENFABRIK GMBH & CO KG, 483
PANASONIC CORP, 89, 237
PCD PETROCHEMIE DANUBIA DEUTSCHLAND, 194
PELLINGRA SALVATORE, 375–386
PENN STATE RES FOUND, 12, 42
PENTEL KK, 452
PG RES FOUNDATION INC, 199–213
PHB IND SA, 125, 228, 232, 413, 415
PHILIP MORRIS INC, 513–514
PLASTIC SUPPLIERS INC, 362–363, 370–371
POLYMER COREX KUOPIO LTD OY, 193
POLYNEW INC, 411
POLYNOVO BIOMATERIALS PTY LTD, 30
POLYONE CORP, 93–94, 219, 232, 237, 239
PROCTER & GAMBLE, 124–125, 188, 197, 367, 390–391, 459, 466, 500
PULP PAPER RES INST, 194, 367, 431
PURAC BIOCHEM BV, 122, 226, 488

Q

QINGDAO INST OF BIOMASS ENERGY, 18
QLT USA INC, 496

R

REAL PLASTIC KK, 507
REGEN BIOTECH INC, 267
REGURUSU KK, 30
RES CORP TECHNOLOGIES INC, 42
RES INST INNOVATIVE TECH EARTH, 128, 136, 149, 337, 339
RES TRIANGLE INST, 344
RESEARCH CORP, 44t–74t
RICE UNIVERSITY, 20
RIKEN TECHNOS CORP, 220–221
RIKEN VITAMIN CO, 143–144, 221, 226, 229, 235, 239–240
RISU PACK CO LTD, 310
RODENBURG VEEVOEDERS BV, 138–139
ROHM & HAAS, 435
ROQUETTE FRERES, 189, 193–194, 196

S

SABANCI UNIVERSITES, 419–420, 423–429
SABIC INNOVATIVE PLASTICS IP, 100–114
SABIC INNOVATIVE PLASTICS US LLC, 486
SAFTA SPA, 367
SAKAMOTO YAKUHIN KOGYO CO LTD, 229
SAKATA INKS, 450–451, 454–458
SAMYANG CORP, 135, 267
SAN DIA POLYMER LTD, 198
SANITARIA SCALIGERA SPA, 305–306
SANOL ARZNEI SCHWARZ GMBH, 280–281
SANWA KAKO CO, 342
SANYO CHEMICAL IND LTD, 231
SATO TATSUO, 317–325
SCHOLTEN HONIG RESEARCH BFV, 290–299
SCHWEMMER MARTIN, 412, 423–429
SEED COMPANY LTD, 133
SEKISUI CHEMICAL CO LTD, 414
SEKISUI PLASTICS, 136, 327–328, 335
SEQUA CHEMICALS INC, 195
SERICOL LTD, 448
SETENTA E TRES MIL E CEM LDA, 31–32
SHANDONG ECOMANN TECHNOLOGY CO LTD, 138
SHANGHAI GENIUS ADVANCED MAT, 421
SHANGHAI KINGFA SCI & TECH CO, 220
SHANGHAI NEW SHANGHUA POLYMER, 482
SHARP CORP, 484–485
SHARP KK, 452
SHELL OIL CO, 147
SHENZHEN ECOMANN BIOTECHNOLOGY, 124, 222, 418
SHIFRIN SHARI, 451
SHIMADZU CORP, 88, 91, 122, 136, 229, 232, 240, 363, 393, 398–399, 412, 417, 452, 497, 501
SHINETSU CHEMICAL CO, 236–237, 369–370
SHINETSU POLYMER CO, 463
SHOWA CHEM, 143, 242–261
SHOWA DENKO KK, 18–19, 219–220, 341–342
SHOWA HIGHPOLYMER, 18–19, 30, 129–130, 192, 196, 219–220, 284, 314, 342
SHOWA RUBBER, 132
SIOX MACHINES AB, 331t, 345–359
SK NETWORKS CO LTD, 418
SOJASUN TECHNOLOGIES, 453
SOLE GEAR DESIGN INC, 242–261
SOLVAY, 146, 196
SONY CORP, 236, 304

STANFORD RES INST INT, 39–41
STEIN HALL MFG CO, 468
STICHTING ONDERZOEK EN ONTWIKKELING NOORD NEDERLAND, 194, 431
STORA ENSO OYJ, 434
STOWE PHARR MILLS INC D B A PH, 396
SUKANO MAN & SERVICES AG, 90, 221, 234–235
SUMINOE TEXTILE, 395
SUMITOMO ELEC FINE POLYMER INC, 86, 286–287, 289, 363
SUN CHEMICAL LTD, 434, 451
SUNSTAR INC, 463
SURMODICS INC, 342
SURMODICS PHARMACEUTICALS INC, 466
SUZUKI MOTOR CO, 215–216
SYNBRA TECH B.V., 339, 343
SYNTHOMER LTD, 194–195

T

TAIYO KAGAKU KK, 229–230
TAKI CHEMICAL, 343
TANABE SEIYAKU CO, 190
TECHNO POLYMER CO LTD, 133
TECNARO GES ZUR IND ANWENDUNG, 35–38
TEIJIN FIBERS LTD, 495, 499, 501f, 505, 506, 508, 509f, 396–397
TEIJIN LTD, 91–92, 122, 189, 388–391, 396–397, 399–400, 412, 433
TEKNOLOGIAN TUTKIMUSKESKUS VTT, 449
TEPHA INC, 15
TESA SE, 464
TIANJIN GREENBIO MATERIAL CO LTD, 16
TNO, 419–420, 423–429
TOABO MATERIAL CO LTD, 393
TOHCELLO CO LTD, 85, 230, 309–310, 373
TOHO CHEM IND CO LTD, 266, 313, 363
TOHOKU ELECTRIC POWER CO, 8
TOKUYAMA CORP, 303
TOKYO ELECTRIC POWER CO, 132
TOMOEGAWA PAPER CO LTD, 392–393
TOPPAN FORMS CO LTD, 189
TOPPAN PRINTING CO LTD, 281–282, 307, 312, 314–315, 340, 449–450
TORAY INDUSTRIES, 89–90, 117, 121, 127–128, 135–136, 144–145, 222, 236, 278–280, 312, 328, 335, 341–342, 364, 371, 373, 388–389, 393, 395–396, 398–400, 411
TORAY PLASTICS AMERICA INC, 308–309, 374
TORAY SAEHAN INC, 418
TORINO POLITECNICO, 514–528
TOSOH CORP, 135, 137
TOTAL PETROCHEMICALS RES FELUY, 222
TOWA ORIMONO CO LTD, 395
TOYO BOSEKI, 118, 122, 191, 196, 220, 222, 281–282, 303, 308–309, 314–315, 363, 365, 392, 449–450, 462–463
TOYO FOOD COLOR & CHEMICAL CO, 451
TOYO INK MFG CO, 220, 281–282, 309, 315, 411–412, 450, 506
TOYO METALIZING, 309
TOYO PURASUTO KK, 343
TOYO SEIKAN GROUP HOLDINGS LTD, 311
TOYO SEIKAN KAISHA LTD, 20, 90–91, 123, 216, 304, 310–311, 513
TOYODA GOSEI KK, 278–280, 417
TOYOTA CENTRAL RES & DEV, 91
TOYOTA MOTOR CO LTD, 452, 497
TOYOTA MOTOR CORP, 7–8, 133, 225–226, 422
TRESPAPHAN GMBH, 240, 363, 373
TRIAL CORP, 266
TRISTANO PTY LTD, 128–129, 148, 222–223
TSUTSUNAKA PLASTIC KOGYO, 130

U

UCB SA, 150, 288–289
UHDE GMBH, 5, 6t
UHDE INVENTA FISCHER GMBH, 5, 6t
ULICE SA, 131
UNI CHARM CORP, 314, 315f
UNI STAR IND LTD, 345–359
UNION CARBIDE CORP, 146
UNITIKA FIBERS LTD, 393, 395, 400
UNITIKA LTD, 18–20, 87, 90–91, 190, 216, 236, 239–240, 308, 312, 336, 364–365, 371, 392–394, 396, 413–414, 416, 418, 422
UNITIKA TEXTILES LTD, 389
UNIV ALABAMA, 196–197
UNIV ALBERTA, 198, 268–269
UNIV BOLOGNA ALMA MATER, 283
UNIV CHUNG YAN CHRISTIAN, 84t–85t, 100–114
UNIV CONCEPCION, 436t–438t, 439–445
UNIV DEGLI STUDI TORINO, 515–528
UNIV GENEVE LABORATOIRE DE PHA, 187–188, 190–192
UNIV GENEVE, 187–188, 190–192
UNIV GUELPH, 132
UNIV HEBEI TECHNOLOGY, 419
UNIV HENAN NORMAL, 310
UNIV IOWA STATE RES FOUND INC, 327
UNIV JIANGNAN, 398
UNIV KEIO, 504–505, 510–512
UNIV KINKI, 515–528
UNIV KOREA IND UNIV COOP FOUND, 84t–85t, 100–114
UNIV LELAND STANFORD JUNIOR, 423–429
UNIV LIEGE, 332–333, 340
UNIV MASSACHUSETTS, 123, 125
UNIV MCGILL, 194, 431
UNIV MICHIGAN STATE, 278–280, 414, 418
UNIV MONTREAL, 41
UNIV NAGOYA NAT UNIV CORP, 8
UNIV NEBRASKA, 98
UNIV OKAYAMA NAT UNIV CORP, 397–398
UNIV OSAKA, 229–230, 304
UNIV OTTAWA, 289
UNIV PITTSBURGH, 42
UNIV RYUKOKU, 337
UNIV SHANGHAI JIAOTONG, 126, 222, 414
UNIV SICHUAN, 305–306
UNIV TEXAS, 197–198, 306
UNIV TOTTORI, 466–467
UNIV TOYOHASHI TECHNOLOGY, 508, 509f
UNIV UTRECHT, 197–198
UNIV WM MARSH RICE, 20
UNIV ZHEJIANG, 412
UPM KYMMENE OYJ, 372
URETHANE SOY SYSTEMS CO, 327
US AGRICULTURE, 147–149, 361–362, 434
USTAV POLYMEROV SAV, 15, 124

V

VALAGRO CARBONE RENOUVELABLE POITOU CHARENTES, 242–261
VICTOR COMPANY OF JAPAN, 501–502
VIDEOJET TECHNOLOGIES INC, 448
VIRIDIAN CHEMICAL PTY LTD, 196

W

WACKER CHEMIE AG, 141
WACKER POLYMER SYSTEMS GMBH, 152–182
WARNER LAMBERT CO, 34, 138, 140
WIBMER GMBH U. CO. KG PAPIER-FORMTECHNIK, 37
WONBIOGEN CO LTD, 398

X

XEROX CORP, 448, 451

Y

YAMAGATA UNIV RES INST, 216
YAMATO ESURON KK, 373–374
YHTYNEET PAPERITEHTAAT OY, 432
YONGYU APPLIED TECHNOLOGY MATERIAL CO LTD, 412
YOSHINO KOGYOSHO CO LTD, 91–92, 217, 304

Z

ZENECA LTD, 124–125, 188, 190, 192, 194, 268, 366–367, 367f, 431–432, 459–460
ZHANGJIAGANG CHAINENG BIOLOG SCIENCE CO LTD, 17
ZHANGJIAGANG CHAINENG BIOLOG TECHNOLOGY CO LTD, 370–371
ZHUHAI WANTONG CHEMICAL CO LTD, 220

Index of Inventors

Note: Page numbers with “f” and “t” denote figures and tables, respectively.

A

ABE SHINGO, 317–325, 515–528
ABE SHUNSUKE, 100–114, 270–275, 375–386
ADACHI MINORU, 242–261
ADAMS SAMUEL DAVID, 152–182
ADAMUS GRAZYNA, 290–299
ADEBAYO ADELAIDE TITILAYO OLUR, 439–445
ADHIKARI R, 44t–74t
ADNAN A F M, 515–528
AGARI Y, 469–479
AGNELLI JOSE AUGUSTO MARCONDES, 100–114, 152–182, 242–261, 423–429
AHLBRECHT ARTHUR H, 242–261
AHMED SHARF U, 242–261
AIDA HIRONORI, 401–410
AIHARA HISASHI, 152–182, 242–261, 345–359
AJIOKA MASANOBU, 100–114, 152–182, 199–213, 242–261, 317–325, 345–359, 375–386, 439–445, 469–479, 515–528
AKAHASHI KEI, 345–359
AKAHIRA HITOSHI, 469–479
AKAMATSU K, 515–528
AKAMATSU YOSHIMI, 345–359, 375–386
AKASHI KAZUSHIROU, 317–325
AKASHINA NAOKO, 454–458
AKATSU S, 506–507, 515–528
AKIMARU FUSAYOSHI, 345–359
AKIMOTO MIKIO, 270–275, 317–325, 375–386
AKSELA REIJO, 199–213
AKUTSU FUMIO, 242–261, 270–275
ALBERT POLISTINA ROCCO, 100–114
ALDERSON BARRY, 100–114, 199–213
ALEXY PAVOL, 152–182, 242–261
ALIDEDEOGLU HUSNU ALP, 100–114, 515–528
ALLCOCK H, 44t–74t
ALLEMANN ERIC, 199–213
ALLEN C GEOFFREY, 454–458
ALLENZA PAUL, 152–182
ALTIERI PAUL A, 345–359
AMANO YOSHIKAZU, 423–429
AMATA YUKIRO, 199–213
AMBROSIO A, 44t–74t
AMRUTIYA NILESH, 345–359
ANAMI SHINICHI, 345–359
ANDERSEN PER JUST, 152–182
ANDERSON KELLY S, 242–261, 375–386
ANDO MASAHIKO, 469–479
ANDO SADAMASA, 317–325
ANDO YOJI, 290–299, 423–429
ANDRADE DE FREITAS MARIA FILOMENA, 44t–74t
ANNAN NIKOI, 439–445
AOYAMA TAIZO, 152–182
AOYAMA TOMOHIRO, 375–386, 401–410, 454–458
ARA PAOLO, 231, 242–261
ARAI HIROSHI, 317–325
ARANISHI YOSHITAKA, 290–299, 375–386, 401–410
ARENA DAWSON BUIM, 100–114, 242–261
ARIGA NAGARO, 199–213
ARIGA TOSHIROU, 152–182
ARIME MORITATSU, 375–386
ARISAWA S, 469–479
ARITA TSUNEO, 317–325
ARITAKE TOSHIYUKI, 317–325
ARIYOSHI SATORU, 454–458
ARR LAURA GONCALVES, 317–325
ASEBE TADASHI, 242–261
ASHBAUGH JOHN, 290–299
ASRAR JAWED, 100–114, 199–213, 290–299, 439–445
ASZEMSKI M J, 44t–74t
ATENCIO A M, 44t–74t
ATSUMI YOSHIKO, 152–182
ATSUO NISHIMURA, 100–114
AUFFERMANN JOERG, 375–386
AUSEN RONALD W, 242–261, 375–386
AUSTIN P E, 44t–74t
AUTRAN JEAN-PHILIPPE MARIE, 152–182, 401–410
AUWETER HELMUT, 100–114
AVAKIAN ROGER W, 242–261
AWATA T, 317–325
AYAUCHI MASATO, 375–386

B

BABROWICZ ROBERT, 345–359
BAGRODIA SHRIRAM, 152–182
BAHR KARK-HEINZ, 44t–74t
BAILEY PETER BRADBY SPIROS, 152–182
BAILEY W, 100–114
BAKIS GEORGE, 345–359
BAKKEN ALEXANDER CHARLES, 434, 439–445
BAKOS DUSAN, 152–182, 242–261
BARBIER JACQUES, 152–182, 242–261, 290–299
BARHAM PETER JOHN, 375–386
BARRERA DENISE, 290–299
BARROWS THOMAS H, 469–479
BARTL HERBERT, 152–182
BASH THOMAS F, 152–182
BASTIOLI CATIA, 100–114, 152–182, 345–359, 439–445
BASTOS CLAUDIO ROCHA, 317–325
BATES SUSAN H, 100–114
BAUER JORDAN V, 469–479
BAUER PETER, 152–182
BAUER S, 44t–74t
BECK CHARLES, 454–458
BECKER A, 515–528
BECKER G, 152–182
BEELEN BRIGIT, 469–479
BEIMBORN DIETER BERNHARD, 199–213
BELLIN INGO, 345–359
BELLOTTI VITTORIO, 100–114, 152–182
BENOVIC FRANTISEK, 152–182, 242–261
BERGER WERNER, 152–182
BERGNER RAINER, 152–182
BERNAERTS JOEL, 199–213
BEROFF HOWARD, 44t–74t
BERTRAND ERIC, 401–410
BESCOND GWENAELLE, 199–213
BEYER DOUGLAS E, 152–182
BIAN ZHONGHUA, 375–386
BIELZER RAFFAEL, 100–114, 242–261
BIENKOWSKI IRENA, 439–445
BILLINGTON SARAH L, 417, 423–429
BIN YANG, 152–182
BINDSCHAEDLER CHRISTIAN, 191, 199–213
BIPPERT D A, 44t–74t
BIRD ANA T, 345–359
BLACK KIRBY S, 345–359
BLAUHUT WILFRIED, 100–114, 270–275
BLOEMBERGEN STEVEN, 152–182, 270–275, 469–479
BLONDIN JEAN-MARIE, 152–182
BLUHM TERRY L, 454–458
BOECKER T, 515–528
BOECKH DIETER, 44t–74t

BOERSMA ARJEN, 199–213, 270–275, 290–299
BOGAERT J-CH, 515–528
BOGAN RICHARD T, 152–182
BOHLEBER J, 515–528
BOHN HERIBERT, 100–114
BOND ERIC BRYAN, 401–410
BONDESON DANIEL, 423–429
BONTINCK DIRK, 152–182, 290–299
BOPP RICHARD C, 100–114
BORSCH ANDREA LEE, 242–261, 290–299
BOSNYAK CLIVE P, 345–359
BOTOSOVA MONIKA, 152–182, 242–261
BOUVIER FREDERIC, 199–213
BOWALD S F, 44t–74t
BOWMAN HOWARD, 469–479
BRADY FRANCIS X, 469–479
BRAKE L D, 515–528
BRANDON MATTHEW VINCENT, 375–386
BRAUN BIRGIT, 423–429
BRAUN FRANK, 345–359
BRAUN-LUELLEMANN A, 44t–74t
BRISON N, 44t–74t
BRITTON ROBIN NICHOLAS, 345–359
BROOKER ANJU DEEPALI MASSEY, 199–213
BROSCH ANDREA LEE, 401–410
BRUCHMANN BERND, 152–182
BRUENING KAI, 152–182
BRYM ANNA KATHARINA, 345–359
BUCHANAN CHARLES MICHAEL, 100–114, 152–182, 199–213
BUCHANAN NORMA LINDSEY, 199–213
BUEHLER NANCY UZELA, 401–410
BUENO DE ALMEIDA WANDERSON, 242–261
BUESCHL RAINER, 44t–74t
BUGAJ PETER, 152–182, 242–261
BUISMAN GODEFRIDUS JOHANNES HE, 199–213, 439–445
BUN SEINICHI, 423–429
BURCH R R, 44t–74t
BURNAY JEAN-PAUL, 152–182
BUSCH DETLEF, 242–261, 375–386

C

CAIYING SHAO, 401–410
CANNARSA MICHAEL J, 469–479
CAPUZZI LUIGI, 439–445
CARDENAS TRIVINO GALO, 439–445
CARLETON E, 44t–74t
CARVALHO FERNANDES DE MIRANDA REIS MARIA D ASCENSA, 44t–74t
CASANELLO DIEGO LOPEZ, 100–114
CASEY DONALD JAMES, 100–114
CELLA GIAN DOMENICO, 317–325
CERNOHOUS JEFFREY J, 345–359
CHANDLER CHRISTOPHE, 242–261
CHANG JING C, 401–410
CHANG KEUNSUK P, 317–325, 375–386
CHANG LI-LING, 100–114, 152–182
CHANGPING CHEN, 152–182, 242–261
CHAOQUN LI, 242–261, 423–429
CHAOYANG OU, 152–182
CHAPALAIN FLORIAN, 439–445
CHAPMAN TIMOTHY JAMES, 345–359
CHAPOTOT AGNES, 152–182
CHATTERJEE ANANDA M, 152–182
CHEN CHENG, 242–261
CHEN CHIN-FU, 341, 345–359
CHEN G-Q, 44t–74t
CHEN JONG-WU, 341, 345–359
CHEN MING-TUNG, 141, 152–182
CHEN XIAOMAO, 242–261
CHEONG MYUNG SU, 375–386
CHIANG HENG-BO, 270–275
CHIAPPINI EMANUELA, 317–325
CHIBA JUNICHI, 242–261, 317–325
CHIDAMBARAKUMAR MARIAPPAN, 423–429
CHIGA KOJI, 401–410
CHIKI KOICHI, 375–386
CHIU TIN-HO C O ALLIED CORPORA, 242–261
CHO JIN-KYUNG, 152–182
CHO JUNG HWAN, 152–182
CHODAK IVAN, 152–182, 242–261
CHOE IN CHEOL, 345–359
CHOI KYUNG MAN, 345–359
CHOI NAM SOK, 44t–74t
CHOI SEUNG RYUL, 152–182
CHONG P, 44t–74t
CHOU MING-TSE, 100–114
CHRIS SCHWIER, 345–359
CHRISTIANSEN FREYA, 469–479
CHU CHIH-CHANG, 290–299
CHUNBAI ZHENG, 242–261, 423–429
CHUNE ZHAO, 317–325
CHUNG GUN SOO, 345–359
CHUNG H S, 44t–74t
CHUNG YOUNG-MI, 152–182
CLABAUX PIERRE PHILIPPE, 199–213
CLANCHIN OLIVIER, 454–458
CLATTY JAN L, 327, 345–359
CLAUSS JOACHIM, 199–213
CLAUSSEN U, 515–528
CLENDINNING ROBERT A, 152–182
CLEVELAND CHRISTOPHER S, 375–386
CLOUTIER JOSHUA R, 317–325
COATES C A JR, 515–528
COELHO ANA CRISTINA, 100–114, 242–261
COFFY TIM J, 152–182, 375–386
COLLINS STEPHEN HUGH, 44t–74t
COLPAERT MARC, 152–182, 290–299
COMBS KATHERINE HELEN, 199–213
COMBS M T, 44t–74t
COMBS ROBERT L, 152–182
COOPER KEVIN L, 317–325
COOPER TERENCE A, 469–479
CORNELL STEPHEN W, 152–182
COSZACH P, 515–528
COTY VERNON F, 100–114, 375–386
CRACCO FRANCIS JEAN, 375–386
CRETU ADINA M, 199–213
CUPERUS FOLKERT PETRUS, 199–213, 439–445
CURRIER B L, 44t–74t
CURRIER JUDE, 242–261
CUSHMAN M R, 515–528

D

DADDEY ERNEST OHENE KORANTENG, 242–261
DAIMON H, 515–528
DALMAWAN DALWISS, 345–359
DALY DANIEL T, 199–213
DAN HUANG, 401–410
DARMAWAN DARWIS, 290–299
DARWIS DARMAWAN, 290–299
DAUGHTRY SEAN, 290–299, 469–479
DAUM LUDWIG, 469–479
DAUMERIE MICHEL, 152–182, 375–386
DAUSCH M, 515–528
DE JONG JOSEPHUS PETRUS MARIA, 345–359
DE MICHELI CLAUDIO, 375–386
DE SAEDELEIR DIRK, 401–410
DE SAINT-ROMAIN PIERRE, 447, 454–458
DE VOS SIEBE CORNELIS, 152–182
DEBRAS GUY, 242–261
DEGUCHI J, 515–528
DEL GIUDICE LUCIANO, 152–182
DEL TREDICI GIANFRANCO, 100–114, 152–182
DELAVIER P, 515–528
DELGADO ALVES VITOR MANUEL, 44t–74t
DELLA VALLE FRANCESCO, 199–213
DELLINGER DAVID A, 439–445
DEMING XIE, 423–429
DENNIS DOUGLAS E, 270–275
DENT PHILIP ANDREW, 317–325
DESAI NEIL P, 199–213
DESAI SHROJAL M, 290–299, 423–429
DEVER CEDRIC, 152–182, 242–261, 290–299
DEVISSAGUET JEAN-PHILIPPE, 199–213, 270–275
DEWAEL PASCAL, 152–182
D'HAENE POL, 439–445
DING SHAOZHONG, 222, 242–261
DIXON DALE D, 152–182
DO NASCIMENTI JEFTER FERNANDES, 242–261
DOBLER BEAT, 44t–74t
DOELKER ERIC, 191, 199–213
DOI MIKIO, 242–261
DOI TSUNEO, 345–359
DOI YOSHIHARU, 100–114
DOI YUKIO, 199–213, 469–479
DOMB AB, 44t–74t
DOMBO PETER, 100–114
DONG LISONG, 242–261
DOORMALEN FRANCISCUS ADRIANUS HENDRIKUS CORNELIS VAN, 345–359
DORGAN JOHN R, 423–429
DORSCH R R, 44t–74t
DOTTER ROBERT, 290–299
DOU SHICHEN, 317–325, 375–386
DRAGNER LOUIS R, 199–213
DRYSDALE N E, 515–528

DRZAL LAWRENCE T, 290–299, 423–429
DUJARDIN R, 44t–74t

E

EAGLES DANA BURTON, 345–359
EBATO HIROSHI, 345–359
EBIHARA NOBORU, 515–528
ECKERT ARMIN, 44t–74t
ECKL W, 44t–74t
EDFORD JR RICHARD A, 375–386
EDGINGTON GARRY J, 469–479
EFSTATHIOU THEO, 454–458
EGGINK GERRIT, 199–213, 439–445
EHRET PHILIPPE, 401–410
EICHEN CONN ROBIN SUE, 439–445
EIER H-M, 515–528
EISENREICH N, 44t–74t
EL AASSER MOHAMED S, 187–188, 199–213
EL SAYED AZIZ, 515–528
ELING B, 44t–74t
ELSNER P, 44t–74t
EMIL SCHMITT EDWARD, 100–114
EMIRU ANDUALEM W, 242–261
EMPTAGE M, 44t–74t
ENDO ASUKA, 469–479
ENDO KOHEI, 152–182
ENDO TERUYA, 317–325
ENDO YOSHIKAZU, 375–386
ENGELMANN GUNNAR, 423–429
ENOMOTO KATASHI, 317–325, 375–386, 515–528
ENOMOTO TSUYOSHI, 242–261, 345–359, 515–528
ENTENMANN GUENTHER, 100–114, 242–261
ERRINGTON JOHN GOUGH, 345–359
ESTERMANN ROBERT, 199–213, 439–445
ETTRIDGE PETER, 317–325
EVANS PAUL D JR, 401–410
EYERER P, 44t–74t

F

FAN Y, 498, 515–528
FANTA GEORGE F, 439–445
FEI BIN, 242–261
FEICHTINGER K, 515–528
FEIL HERMAN, 199–213, 270–275, 290–299
FELKER FREDERICK C, 439–445
FERGUSON RICHARD C, 469–479
FESSI HATEM, 199–213, 270–275
FEY D, 515–528
FINE THOMAS, 152–182
FIORI STEFANO, 242–261
FISCHER ARTUR, 439–445
FISCHER AUGUST C JR, 469–479
FISCHER HARTMUT RUDOLF, 423–429
FISCHER SABINE, 423–429
FISK DONALD, 345–359
FITCH JOHN J, 317–325
FITTON MICHAEL G, 44t–74t
FLAHERTY MICHAEL JOHN, 336, 345–359
FLAT JEAN-JACQUES, 270–275
FLEXMAN EDMUND ARTHUR, 152–182
FLORIDI GIOVANNI, 152–182
FLOYD WILLIAM C, 199–213
FOCARETE MARIA LETIZIA, 290–299
FOLTRAN ISMAELA, 290–299
FORD MICHAEL E, 152–182
FORD T M, 515–528
FORSHEY PAUL ARLEN, 199–213
FORSYTH STEWART A, 199–213
FORSYTHE NEIL, 317–325
FRANK JOHN W, 242–261, 375–386
FREDRIKSEN SIW BODIL, 152–182
FREESE FRANZISKA, 375–386
FREITAS OLIVEIRA RUI MANUEL, 44t–74t
FRIJLINK WILHELM KLAAS, 290–299
FRINGANT CHRISTOPHE, 152–182
FRITZ HANS-GERHARD, 152–182
FUESL ANDREAS, 345–359
FUJIE K, 515–528
FUJIHIRA HIROKO, 242–261, 317–325
FUJII KIYOTOSHI, 242–261
FUJII TORU, 423–429
FUJII YASUHIRO, 100–114, 401–410
FUJIMAKI TAKASHI, 152–182, 317–325
FUJIMOTO KATSUHIRO, 270–275
FUJIWARA TAKAYUKI, 423–429
FUKASAWA YOSHIHITO, 345–359
FUKAWA NORIO, 100–114
FUKAWA SOJI, 242–261
FUKUHIRA YUKAKO, 401–410
FUKUKITA TAKESHI, 345–359
FUKUNAGA SHINICHI, 345–359, 515–528
FUKUNAGA SHOICHI, 242–261
FUKUNAGA SUKEFUMI, 401–410
FUKUSHIMA Y, 515–528
FUKUZAKI HIRONOBU, 345–359
FULLER TIMOTHY J, 454–458
FUNAE AKIHIRO, 401–410
FUNAOKA DAIKI, 469–479
FUNATSU KENICHI, 401–410
FURUKAWA T, 515–528
FURUSAWA SACHIKO, 152–182
FURUTA TATSUHIKO, 317–325
FUTAMURA NAOYUKI, 345–359

G

GAEHR FRANK, 199–213
GALLAGHER F G, 44t–74t
GALLUCCI R R, 515–528
GANG YANG, 317–325
GANSTER JOHANNES, 423–429
GAO FENGXIANG, 152–182
GARDI STEFANO, 317–325
GARDNER ROBERT M, 100–114, 152–182
GAST J, 515–528
GAYET JEAN-CHARLES JACQUES, 454–458
GEN JOKYU, 44t–74t
GENTILINI C, 44t–74t
GEORGE NEIL, 199–213, 270–275, 439–445
GERNGROSS TILLMAN U, 199–213
GESSNER SCOTT LOUIS, 401–410
GEYER OTTO-CHRISTIAN, 152–182
GIERLINGER WOLFGANG, 100–114, 270–275
GIEZEN FRANCISCUS EGENIUS, 199–213, 270–275, 290–299
GILAIN JACQUES, 100–114, 199–213
GITTLEMAN DAVID, 270–275
GLENN GREGORY M, 345–359
GLUECK GUISCARD, 345–359
GODWIN RICHARD E, 401–410
GOEHLER KLAUS-DIETER, 44t–74t
GOES C, 44t–74t
GOMI A, 469–479
GONDA TAKASHI, 469–479
GOSNEY H W, 401–410
GOTLIEB KORNELIS FESTER, 199–213, 270–275, 290–299
GOTO JUN, 345–359
GOTO KENICHI, 270–275
GOTO TAKESHI, 317–325
GOTOH KATSUHIKO, 100–114
GOTTLIEB KORNELIS FESTER, 270–275
GOUIN S, 44t–74t
GOULD CLAIRE LOUISE, 317–325
GRABLOWITZ HANS, 290–299
GRAEFE JUERGEN ERNST, 345–359
GRAENACHER CHARLES, 199–213
GRAY D S, 44t–74t
GRESSER JOSEPH D, 290–299
GRIFFIN GERALD JOSEPH LOUIS, 152–182
GRIFFITH MAY, 290–299
GRIGAT ERNST, 317–325, 469–479
GRIMES THOMAS FRANCIS, 434, 439–445
GROSS RICHARD A, 152–182
GRUBER PATRICK RICHARD, 242–261, 290–299, 439–445
GUANELLA ITALO, 152–182
GUILLAUME DOUARD, 100–114, 242–261
GUIPOUY PHILIPPE, 401–410
GUNATILLAKE P A, 30
GUNN DONALD MURRAY, 454–458
GUO KAI, 44t–74t
GUO Y-Y, 44t–74t
GUOLIANG XU, 317–325
GUOQIANG CHEN, 199–213
GURAU GABRIELA, 199–213
GURNY ROBERT, 191, 199–213

H

HAASMAA KRISTIINA, 199–213
HACHIFUSA KAZUYA, 317–325
HACKL M, 515–528
HAEDE PETRA, 242–261, 375–386
HAEUBL GEORG, 199–213, 439–445
HAGBERG ERIK, 242–261
HAGEN RAINER, 515–528
HAGER ST L, 44t–74t
HAGOORT THOMAS HENR, 345–359
HAHN KLAUS, 345–359
HAIBING HONG, 317–325
HAIDER K W, 44t–74t
HALE PETER, 375–386
HALE WESLEY R, 152–182
HALL ALAN, 199–213
HALL ERIC STANLEY, 100–114, 152–182, 439–445
HAMILTON C J, 44t–74t

HAMMEL WALLACE J, 401–410
HAMMERL STEFANIE, 454–458
HAMMOND TIMOTHY, 152–182, 199–213, 439–445
HAMREFORS JAN, 345–359
HAN DO SUCK, 100–114, 152–182
HAN DONG HUN, 345–359
HAN KYUNG TAE, 494, 515–528
HAN SEONG OK, 423–429
HANDA Y PAUL, 345–359
HANEL P, 152–182
HANSEN S M, 44t–74t
HAO XUEEN GEORGE, 152–182
HAO ZHU, 401–410
HARA YOSHIO, 152–182
HARADA SHOICHIRO, 345–359
HARADA TADASHI, 152–182
HARAGUCHI KENJI, 345–359
HARLAN ROBERT D, 290–299
HARRIS NICOLE, 439–445
HARRISON WILLIAM H, 327, 345–359, 401–410
HARTE BRUCE R, 423–429
HARTMANN MARK HENRY, 100–114, 152–182, 242–261, 290–299, 439–445
HASE A, 44t–74t
HASEBE TADASHI, 242–261
HASEGAWA AKIRA, 152–182
HASEGAWA KENJI, 401–410
HASEGAWA SHIN, 290–299
HASEGAWA TAKASHI, 44t–74t
HASEGAWA TORU, 152–182
HASHIMOTO KOJI, 401–410
HASHIMOTO MAKOTO, 44t–74t
HASHIMOTO MASANORI, 100–114
HASHIMURA T, 515–528
HASHIZUME YUICHIRO, 345–359
HASSAN RAMANATH SATHYANARAYANA, 317–325
HASTINGS MARIA LOUISE, 345–359
HATANO Y, 152–182, 290–299
HATAYA TAKAFUMI, 100–114
HATFIELD STEPHEN F, 290–299
HAUNERT A, 44t–74t
HAYAKAWA MAKOTO, 317–325
HAYASAKA KENJI, 469–479
HAYASE SHIGERU, 423–429
HAYASHI HISATAKA, 317–325
HAYASHI NAOKI, 242–261
HAYASHI YOSHIKI, 401–410
HAYASHIBARA HITOSHI, 345–359
HAYASHIBARA KAZUNORI, 345–359
HAYASHIUCHI RIE, 469–479
HAYATA YUSUKE, 152–182
HAYES SIMON ANTHONY, 152–182
HAYNIE S, 44t–74t
HE AIMIN, 290–299, 401–410
HE S, 44t–74t
HECHT STACIE ELLEN, 199–213
HEIKKILAE MAIJA ELINA, 199–213
HEILIGER L, 515–528
HEIMGARTNER F, 44t–74t
HEINZLE ELMAR, 100–114
HELLAND IRENE, 152–182
HELLER JORGE, 44t–74t
HELOU ELIE, 439–445
HELWING R, 44t–74t
HENDRIX JAMES E, 401–410
HENNINK WILHELMUS EVERHARDUS, 199–213
HEO SU HAK, 423–429
HERMANUTZ FRANK, 199–213
HIDA ETSUO, 242–261
HIDA KAZUNORI, 375–386
HIDEMITSU TAKINISHI, 100–114
HIGGINS NORTON A, 375–386
HIGO YUKIKO, 454–458
HIGUCHI CHOJIRO, 242–261, 469–479
HIKOSAKA WAKA, 469–479
HILBURGER JOHANN, 454–458
HILL ALLAN LEON SYDNEY, 423–429
HILL JENNIFER L, 199–213
HILMER KLAUS, 152–182
HILTUNEN ELINA, 242–261
HINAKO HIDEKI, 152–182
HINO TOMOHARU, 317–325
HINOHARA MITSURU, 345–359
HIOKI MASANOBU, 100–114, 375–386
HIRAI TAKAAKI, 345–359
HIRAI YOSHIAKI, 100–114, 401–410
HIRANO H, 469–479
HIRAYAMA NORIO, 423–429
HIROKAWA TAKASHI, 199–213
HIROKAZU, 44t–74t
HIROMI NIITSU, 100–114
HIROSE FUMINOBU, 345–359
HIROSE TADASHI, 454–458
HIROTA MASAYUKI, 375–386
HIRUMA TAKASHI, 375–386
HITOSHI TAKAHIRA, 469–479
HO MING-HUA, 100–114
HOCHI MOTONORI, 375–386
HOCKESSIN J V, 515–528
HODSON SIMON K, 152–182, 345–359
HODZIC ALMA, 152–182
HOEKSTRA AAD, 242–261
HOEPPNER M, 44t–74t
HOFMANN MAXIMILIAN, 345–359
HOGT ANDREAS HERMAN, 290–299
HOKARI YUKI, 242–261
HOLBREY JOHN DAVID, 199–213
HOLLEY WOLFGANG, 515–528
HOLMES PAUL ARTHUR, 100–114, 152–182, 199–213, 375–386, 401–410
HOLZER T, 37
HONDA KEISUKE, 375–386
HONDA SUSUMU, 401–410
HONG LUHUA, 469–479
HONG SUNG MIN, 152–182
HONGFEI ZHOU, 317–325
HONMA TSUTOMU, 454–458
HONNA H, 515–528
HORI HIDESHI, 152–182
HORIBE YASUMASA, 242–261, 423–429, 454–458
HORIE TAKESHI, 242–261
HORIMOTO MASAKI, 401–410
HORINKA PAUL R, 439–445
HORIUCHI H, 515–528
HORNSEY ANYA JANE, 345–359
HOROWITZ DANIEL MARK, 199–213
HOSHINO MITSURU, 100–114, 375–386
HOSODA KAZUO, 199–213, 345–359
HOSOHARA SADAO, 401–410
HOSOKAWA NOBUHIRO, 199–213, 469–479
HOSTETLER DONALD E, 469–479
HOTTA SEISHI, 454–458
HOTTA YASUNARI, 199–213, 290–299, 317–325, 454–458
HRABAK OTTO, 199–213, 439–445
HRKACH JEFFREY S, 290–299
HSIAO HSIANG-JEN, 341, 345–359
HSIAO Y-L, 44t–74t
HSIEH HSYUE-JEN, 100–114
HSIEN TZU-YAN, 100–114
HSU Y Y, 290–299
HU LING, 242–261
HUA JIAN-LIN, 242–261
HUANG CHEN-PAO, 270–275
HUANG CHIEN-MING, 290–299
HUANG X, 317–325
HUANG YA-JEN, 423–429
HUANG YANBIN, 290–299
HUANG YU-KAI, 290–299
HUBBELL JEFFREY A, 199–213
HUBER KONRAD, 515–528
HUETTERMANN A, 37
HUETTERMANN J, 44t–74t
HUILLE S, 44t–74t
HUISMAN GJALT W, 44t–74t
HUME NICHOLAS EDWARD, 434, 439–445
HUMMERICH RAINER, 199–213
HUNT RYAN W, 423–429
HUNTER BRIAN KEITH, 199–213
HUTMACHER DIETMAR WERNER, 316–325
HWANG SHI-KUANG, 242–261
HYON SUONG-HYU, 270–275

I

IBA NOBORU, 401–410
IBIM S, 44t–74t
ICHI MASATOSHI, 423–429
ICHIHASHI KUNIO, 152–182
ICHIKAWA KENGO, 375–386
ICHIKAWA YASUSHI, 290–299
ICHIKAWA YOSHITO, 290–299, 454–458
ICHINOSE NAOJI, 401–410
IDEL KARSTEN-JOSEF, 317–325, 469–479
IGUCHI YUJI, 152–182
IHARA TOSHIAKI, 242–261
IHRIG RALF, 469–479
IIDA HIROSHI, 152–182
IIMURO SHIGERU, 401–410
IJI MASATOSHI, 100–114, 242–261
IKADA YOSHITO, 270–275
IKADO SHUHEI, 100–114, 242–261, 317–325
IKEDA NAOKI, 242–261
IKEDA TSUKASA, 242–261
IKEDA YOSHI, 270–275
IKEGAME MIDORI, 401–410
ILMONEN ANU, 454–458
IMAI TOSHIFUMI, 454–458

IMAIZUMI MITSUHIRO, 199–213, 242–261, 345–359
IMAMURA AKIYUK, 199–213
IMAMURA HIDEAKI, 242–261
IMAMURA SHOUJI, 152–182
IMANAKA MAMORU, 100–114
IMANISHI JUN, 242–261
IMON SHUHE, 242–261, 317–325, 375–386
INADA TEIICHI, 152–182
INAGAKI MADOKA, 469–479
INAYAMA TOSHIHIRO, 152–182, 242–261
INCEOGLU FUNDA, 423–429
INGLIS THOMAS L, 374–386
INOKAWA YASUSHI, 242–261
INONE E, 44t–74t
INOUE KAZUHIKO, 100–114, 242–261, 423–429
INOUE SHOZO, 401–410
INOUE TAKASHI, 152–182, 242–261, 439–445
INOUE YOSHIO, 152–182, 317–325
INSOLIA G E, 44t–74t
INUI YUKIKO, 100–114
IOVINE CARMINE P, 469–479
ISAHAYA SADANORI, 152–182
ISHIDA TOSHINOBU, 199–213
ISHIGA SHIGETO, 152–182
ISHIGAMI Y, 515–528
ISHIGURO SHIGEKI, 469–479
ISHIHARA JIRO, 152–182, 242–261
ISHIHARA KAZUHIKO, 199–213, 242–261, 515–528
ISHIHARA KI, 515–528
ISHII AKIRA, 199–213, 290–299, 469–479
ISHII HIROMITSU, 152–182, 242–261
ISHII SHUNTARO, 401–410
ISHII TAKESHI, 375–386
ISHII YUKIKO, 242–261
ISHIKAWA KOICHI, 345–359
ISHINAGA J, 423–429
ISHIOKA RYOJI, 44t–74t, 199–213, 469–479
ISHITOKU TAKESHI, 152–182
ISOBE YASUMITSU, 152–182
ISODA SHINJI, 152–182
ISRAELS RAFEL, 100–114
ITADA MITSUYOSHI, 100–114
ITO DAISUKE, 423–429
ITO FUMIO, 242–261
ITO HIROSHI, 423–429
ITO HISAYOSHI, 270–275
ITO K, 515–528
ITO NORIYUKI, 454–458
ITO TAKESHI, 199–213, 290–299, 375–386, 401–410, 454–458
ITO TAKURO, 100–114, 242–261, 317–325
ITO YUMI, 100–114
ITOH DAISUKE, 100–114, 242–261
ITOH HIROSHI, 152–182
ITSURU SASAHARA, 345–359
IWAI K, 44t–74t
IWAMOTO AKIRA, 152–182, 345–359
IWASAKI SHOHEI, 242–261
IWASAKI YOSHIO, 317–325
IWATA JUNJI, 401–410
IWATA M, 242–261
IWATA MASAHIRO, 454–458
IWATA MASATAKA, 317–325
IWAYA Y, 44t–74t
IWEN MATTHEW L, 439–445
IYAMOTO TAKASHI, 317–325

J

JABBARI E, 44t–74t
JACOBSON HENNING W, 242–261
JAKOB JURGEN, 100–114
JAMIOLKOWSKI D D, 44t–74t
JANE JAY-LIN, 345–359
JANG YUN SUK, 423–429
JANSSEN JANE, 469–479
JEFFERY ANDREW BRUCE, 345–359
JEFFS HYRUM J, 345–359
JENNEN JAY M, 242–261, 375–386
JEON HYUN K, 152–182
JEON SEUNG HO, 375–386
JEON YOUNG SEUNG WO, 345–359
JEONG HYE KYUNG, 423–429
JEROMIN LUTZ, 152–182
JESCHKE KURT, 44t–74t
JIAN D, 44t–74t
JIAN JIAO, 242–261
JIAN WANG, 469–479
JIANZHONG L, 44t–74t
JIAOLIANG YUAN, 152–182
JIAOYU PAN, 199–213
JIN MYONG SONR, 375–386
JO YOUNG MO, 345–359
JOHANSSON CARL-JOHAN, 290–299
JOHANSSON E G, 44t–74t
JOKIAHO KATJA, 454–458
JONES E, 44t–74t
JONES RICHARD ANTHONY LEWIS, 317–325
JONES STUART MICHAEL RUAN, 317–325
JONGBOOM REMIGIUS OENE JULES, 199–213, 270–275, 290–299
JORDAN JOY FRANCINE, 317–325
JUNG CHANG-DO, 152–182
JUNG YOUNGMEE, 242–261

K

KABASHIMA YOHEI, 100–114, 423–429
KADOTA J, 469–479
KAGEYAMA YASUSHI, 152–182
KAGEYAMA YUKAKO, 401–410
KAIBING HUANG, 469–479
KAITIAN XU, 199–213
KAJIMARU HIROSHI, 199–213
KAJIYAMA T, 44t–74t
KAKU TOSHIYUKI, 317–325, 454–458
KAKUSCHKE ROLF, 270–275
KAMADA MINOR, 152–182
KAMATA YUKIRO, 345–359
KAMEI RYOSUKE, 345–359
KAMEOKA TAIJI, 375–386
KAMEYAMA HIROKAZU, 152–182, 242–261
KAMIKAWA HIROO, 100–114
KAMIKAWA M, 44t–74t
KAMIKURA MASAO, 152–182
KAMIO KATSUHISA, 199–213, 345–359
KAMIYA SOICHIRO, 152–182, 242–261
KAMMERER HANS HERMANN, 454–458
KAMMERSTETTER HERIBERT, 375–386
KAN YOSHIHIRO, 401–410
KANAMORI KENJI, 100–114, 242–261, 423–429
KANAMORI TAKESHI, 44t–74t
KANAZAWA SHINICHI, 100–114, 290–299, 375–386
KANDA TAIJI, 152–182
KANEKO HIROAKI, 401–410
KANEKO TOMOAKI, 317–325
KANEMOTO NAOTAKA, 401–410
KANN YELENA, 290–299
KANNAN GANESH, 100–114, 515–528
KANO FUMIHISA, 454–458
KANZAWA TAKESHI, 152–182, 375–386
KAO CORP, 242–261
KAPPEN FRANS, 469–479
KARASAWA TAIZO, 317–325
KARHUKETO HANNU TAPANI, 375–386, 439–445
KARTHAEUSER JOACHIM, 345–359
KARTVELISHVILI T M, 44t–74t
KASAHARA RUMIKO, 375–386
KASAI ATSUSHI, 242–261
KASAI MIKIO, 100–114, 242–261
KASHIMA TAKESHI, 375–386, 469–479
KASKE KENT, 345–359
KATAYAMA T, 515–528
KATO R, 44t–74t
KATO S, 515–528
KATO SHUNICHI, 290–299, 454–458, 515–528
KATO TAKEO, 454–458
KATO YASUUMAZAWA, 100–114, 401–410
KATO YUKIO, 100–114, 242–261
KATSARAVA RAMAZ, 44t–74t
KATSURA SHINJI, 44t–74t
KATZSCHNER GREGOR, 515–528
KAUFFMAN THOMAS F, 469–479
KAUSHIVA B D, 44t–74t
KAWABATA HAYAHITO, 401–410
KAWADA KEN-ICHI, 423–429
KAWAGUCHI TATSUYA, 100–114, 242–261
KAWAGUCHI Y, 515–528
KAWAHARA MITSUHIRO, 423–429
KAWAI N, 515–528
KAWAKAMI YUKICHIKA, 100–114, 375–386
KAWAKITA SHUNICHI, 317–325
KAWALEC MICHAL, 290–299
KAWAMOTO HISAFUMI, 345–359
KAWAMOTO KENJI, 317–325, 454–458
KAWAMURA YASUO, 100–114, 242–261
KAWANO AKIRA, 100–114, 317–325
KAWANO KIYOSHI, 100–114, 290–299, 375–386
KAWASAKI H, 515–528
KAWASHIMA MASAKI, 199–213
KAWASHIMA N, 515–528
KAWK NO YUN, 452–458
KE ZENG, 317–325
KE ZHOU, 317–325

KEHL KARL, 345–359
KELA LAURA, 454–458
KELLY JR WILLIAM E, 242–261
KEMMISH DAVID JOHN, 469–479
KEMPF WOLFGANG, 152–182
KENJI YAO, 100–114
KERITSIS D, 515–528
KERN OTTO, 242–261
KESLING JR HAVEN S, 469–479
KHARAZIPOUR A, 44t–74t
KHEMANI KISHAN, 152–182
KHUSRAWY MALIHA, 152–182
KIDAI O, 44t–74t
KIDO HIROSHI, 317–325
KIDO TAKAYASU, 152–182
KIM CHEOL JOO, 401–410
KIM D H, 44t–74t
KIM DO, 152–182
KIM DOE, 152–182
KIM DONG JIN, 317–325
KIM GUN POONG, 270–275
KIM HONG SOO, 423–429
KIM JAEHO, 290–299
KIM JI HYANG, 270–275
KIM MAN SOO, 362, 375–386
KIM O JIN, 423–429
KIM SANG PIL, 423–429
KIM SANG-HEON, 242–261
KIM SI MIN, 317–325
KIM SON NGUYEN, 199–213
KIM SOO HYUN, 242–261
KIM SSANG OK, 345–359
KIM WON IL, 401–410
KIM YOUNG JIN, 401–410
KIM YOUNG MIN, 345–359
KIM YUN JO, 317–325
KIMIZU MITSUGI, 401–410
KIMURA HIDEHARU, 290–299
KIMURA HIDEJI, 345–359
KIMURA ISAO, 454–458
KIMURA KOICHI, 423–429, 439–445
KIMURA KUNIO, 375–386, 401–410, 454–458
KIMURA TOSHIAKI, 100–114, 401–410
KIMURA YOSHIHARU, 91–92, 100–114, 122, 189, 199–213, 242–261, 401–410, 433, 439–445
KIMURA YUKITAKA, 401–410
KINO TORU, 345–359
KIRIE YOZO, 152–182
KISHI ATSUSHI, 345–359
KISHIDA HISANOR, 44t–74t
KISHIGAMI KAZUHIKO, 401–410
KISHIMOTO HIROAKI, 242–261
KISSEL THOMAS, 290–299
KITAGAWA IYUKI, 317–325
KITAGAWA SATORU, 317–325
KITAHARA YASUHIRO, 100–114, 152–182, 242–261, 345–359, 375–386
KITAMURA MAMORU, 401–410
KITAZAWA TAKEO, 199–213
KITAZONO EIICHI, 401–410
KITORA SHUICHI, 100–114
KITORA YUJI, 423–429
KITOU SATOSHI, 317–325
KITSUMOTO HIROTOSHI, 454–458
KIUCHI YUKIHIRO, 242–261
KLEIN M H, 44t–74t
KLIMESCH ROGER, 152–182
KO KAI-JEN, 423–429
KOBAYASHI AKIO, 270–275
KOBAYASHI FUMINORI, 242–261, 270–275
KOBAYASHI GENTA, 100–114
KOBAYASHI HISATO, 317–325, 375–386
KOBAYASHI KAZUHIRO, 152–182
KOBAYASHI MASAKAZU, 375–386
KOBAYASHI NAOKI, 100–114, 242–261, 317–325
KOBAYASHI SADAYUKI, 152–182, 375–386
KOBAYASHI YOSHIHIKO, 423–429
KOBORI TADASHI, 469–479
KOBUNE MOMOO, 317–325
KOCH HELMUT, 44t–74t
KOCH R, 44t–74t
KOCHEM KARL-HEINZ, 375–386
KODAMA SAI, 152–182, 242–261
KOEHLER GERNOT, 152–182
KOEHNLECHNER R, 515–528
KOELLNER M, 494, 515–528
KOGA TAKANORI, 317–325
KOGAMI AKINOBU, 242–261
KOGER THURMAN JOHN II, 375–386
KOGURE MASAHITO, 152–182, 515–528
KOHLHAMMER KLAUS, 152–182
KOIDE MASASHI, 423–429
KOIDE S, 439–445
KOIKE YUTAKA, 375–386
KOJIMA MAKOTO, 469–479
KOJIMA MITSURU, 401–410
KOLESKE JOSEPH VICTOR, 152–182
KOLLS B, 44t–74t
KOLSTAD JEFFREY JOHN, 100–114, 152–182, 242–261, 290–299, 439–445
KOMURA AKIMASA, 317–325
KONDO T, 44t–74t
KONDO YOSHIKAZU, 100–114, 152–182, 401–410
KONISHI N, 501, 515–528
KONISHI TADASHI, 401–410
KONO MONICHIRO, 454–458
KONO TOSHINORI, 242–261
KORI TOMOYUKI, 423–429
KORPELA HEIKKI, 375–386
KOSAKA H, 515–528
KOSEKI EIICHI, 401–410
KOSEKI HIDEKAZU, 100–114, 152–182, 199–213, 242–261, 401–410, 423–429
KOSITRUANGCHAI NAPAWAN, 423–429
KOSKAN L P, 44t–74t
KOSSA W C, 44t–74t
KOTANI TERUMITSU, 345–359
KOUNO AKIRA, 242–261, 317–325
KOUYAMA TOSHITAKA, 100–114, 375–386
KOWALCZUK MAREK, 290–299
KOYAMA MASATOSHI, 152–182, 242–261
KOYANAGI KENJI, 317–325
KOZAKI SHINYA, 454–458
KRAGNESS ERIC, 345–359
KRICHELDORF HANS R, 44t–74t
KRIEG G, 467, 492, 515–528
KRIEGEL R M, 44t–74t
KROATH HANS, 199–213, 439–445
KRONER MATTHIAS, 44t–74t
KRUTAK J J SR, 515–528
KRUTAK JAMES J, 152–182
KUBO MASAHIKO, 454–458
KUBO TAKAYOSHI, 152–182, 345–359, 515–528
KUCKERT E, 515–528
KUENKEL ANDREAS, 345–359
KUI WANG, 317–325
KUIJSTERMANS FRANCISCUS PETRUS, 345–359
KUMAKI JIRO, 152–182, 242–261, 375–386
KUMAZAWA SADANORI, 152–182, 242–261, 345–359
KUME TAMIKAZU, 290–299
KUNST A, 44t–74t
KUO CHIH-YING, 152–182
KUO PEI Y, 100–114
KUPHAL JEFFREY A, 152–182
KURATA YASUYUKI, 439–445
KURCOK PIOTR, 290–299
KURDIKAR DEVDATT L, 100–114, 199–213, 270–275
KURIAN JOSEPH V, 401–410
KURIHARA HIDESHI, 401–410
KURIHASHI TOR, 454–458
KURISAKA TAKAYUKI, 317–325
KURIYAMA TAKU, 242–261
KURODA IWAO, 199–213
KUROKI TAKAYUKI, 100–114, 242–261, 317–325, 375–386
KUROSAKI H, 505, 515–528
KURTH THOMAS M, 345–359
KURUHARA NANAKO, 270–275
KUUSIPALO JURKKA, 423–429, 439–445
KUWABARA JUN, 152–182
KUYAMA HIROKI, 152–182, 242–261
KUYAMA KAZUNORI, 317–325
KWON M, 44t–74t
KWON OH HYEONG, 401–410
KWON YOUNG DO, 152–182
KWON YOUNG-CHUL, 152–182

L

LACOURSE NORMAN L, 345–359
LAFFEND L A, 44t–74t
LAFFERTY ROBERT M, 100–114
LAGARON CABELLO JOSE MARIA, 423–429
LAI JUIN Y, 100–114
LAKE JOHN ALLEN, 152–182
LAMBERT BYRON, 44t–74t
LANGE WOLFGANG, 270–275
LANGER ROBERT S, 290–299
LANSBURY PETER T JR, 290–299
LAPCIKOVA MONIKA, 439–445
LAPOINTE PATRICK, 454–458
LARGMAN THEODORE C O ALLIED CO, 242–261
LAUFFENBURGER PATRICK, 401–410
LAURENCIN C, 44t–74t
LAVASANIFAR AFSANEH, 199–213

LAVEC RODERIK, 152–182
LAY GUSTAV, 152–182
LE GUILLAUME, 270–275
LECKEY RICHARD ANTHONY, 423–429
LEE CHUL KYU, 452–458
LEE GUN KYU, 345–359
LEE HYUNG-TAK, 152–182
LEE J W, 44t–74t
LEE JAE SIK, 423–429
LEE JAEHONG, 152–182
LEE JI EUN, 345–359
LEE JONG SEONG, 375–386
LEE KEUN H, 290–299
LEE KUN PIL, 270–275
LEE MARK S, 375–386
LEE MIN WOO, 423–429
LEE S W, 44t–74t
LEE SI YOUNG, 345–359
LEE WAN KHENG VICTOR, 317–325
LEE YONG CHIAH VINCENT, 317–325
LEE YONG HOON, 270–275
LEE YOUNG-JUN, 152–182
LENDLEIN ANDREAS, 290–299
LENG DOUGLAS ELLIS, 199–213
LENGES G M, 515–528
LENTZ DAVID JOHN, 152–182
LEPOUTRE PIERRE F, 199–213, 375–386, 439–445
LEUFGENS MARKUS, 152–182
LEWIS DAVID N, 469–479
LEWIS TERRY W, 469–479
LI CHIA-HUNG, 341, 345–359
LI FENGKUI, 152–182, 290–299, 375–386
LI KUAN-JU, 423–429
LI WEI, 375–386
LI YOUXIN, 290–299
LI Z-J, 44t–74t
LIDDELL JOHN MACDONALD, 199–213, 270–275, 439–445
LIM DAE HWI, 345–359
LIN WEN-JOUE, 423–429
LIN YANG, 317–325
LINDNER CHRISTIAN, 152–182
LIU CHANGDENG, 317–325
LIU MIMI, 423–429
LIU RUOJIN, 423–429
LIU WENGUANG, 290–299
LLEMANN ERIC, 199–213
LOERCKS JUERGEN, 152–182, 317–325
LOHMANN JEROME, 345–359
LOMBI ROBERTO, 100–114, 152–182, 345–359
LONGO EUGENIO, 345–359
LOOMIS GARY L, 401–410
LOOS ROBERT, 345–359, 375–386
LOPEZ RUBIO AMPARO, 423–429
LÖRCKS L JÜJRGEN, 469–479
LORENZ K, 44t–74t
LOTAN NOAH, 290–299
LOW K C, 44t–74t
LOWE CHARLES E, 100–114
LOWRANCE DOROUGH GEORGE, 242–261
LOYEN KARINE, 270–275
LU L, 44t–74t
LU W-C, 44t–74t
LUDA M P, 515–528
LUGAO ADEMAR BENEVOLO, 317–325
LUHUA ZHONG, 152–182
LUIJKX ROMAIN, 242–261
LUNT JAMES, 152–182
LUTTERMANN K, 515–528
LUTZ MICHAEL, 199–213

M

MA WENGUANG, 152–182
MAASE MATTHIAS, 199–213
MACFARLANE DOUGLAS R, 199–213
MACHIDA TOSHINORI, 317–325
MACHOVA LUDKA, 439–445
MACKEY LARRY NEIL, 401–410
MADELEINE D G, 515–528
MADISON LARA, 44t–74t
MAEDA KOICHIRO, 401–410
MAEDA MASAHIRO, 454–458
MAEDA NOBORU, 242–261
MAEDA YUHE, 401–410
MAEHARA H, 515–528
MAEKAWA YOSHIHIRO, 401–410
MAGILL J H, 44t–74t
MAGISTRALI PAOLO, 439–445
MAHISHI LATA HANAMANTRAO, 17
MAJCHERCZYK A, 44t–74t
MAKUUCHI KEIZO, 290–299, 345–359
MALFROID PIERRE, 152–182
MARCHESSAULT ROBERT HENRY, 199–213, 290–299, 375–386, 439–445, 454–458
MARCUSSON ANDERS, 345–359
MARES FRANK C O ALLIED CORPORA, 242–261
MARGAM CHANDRASEKARAN, 317–325
MARK ARTHUR M, 375–386
MARTIN ALISHA, 317–325
MARTIN DAVID P, 44t–74t
MARTIN INGRID, 100–114
MARTINEZ SANZ MARTA, 423–429
MARTINI FRANCESCO, 375–386
MARUYAMA YUZURU, 317–325
MASAAKI NISHIOKA, 100–114
MASAHARU FUTAKAWA, 345–359
MASAHIRO MORIYAMA, 100–114
MASARO LAURENT, 454–458
MASAYA IKUNO, 100–114
MASAYUKI OKOSHI, 100–114
MASHBURN LARRY E, 327, 345–359, 401–410
MASSONNE KLEMENS, 199–213
MASUDA TOYOHIKO, 100–114, 290–299
MASUMURA NOBUYUKI, 317–325
MATHIEU CYRILLE, 270–275
MATSUBARA W, 515–528
MATSUDA TAKAAKI, 401–410
MATSUDA YASUSHI, 401–410
MATSUHASHI SETSU, 317–325
MATSUI HITOSHI, 152–182, 242–261
MATSUI MASAO, 100–114, 152–182, 242–261, 401–410
MATSUMOTO AKIHIRO, 199–213
MATSUMOTO HIROSHIGE, 100–114, 290–299, 375–386, 401–410
MATSUMOTO KATSUO, 152–182, 515–528
MATSUMOTO KEIJI, 270–275
MATSUMOTO KIYOICHI, 375–386
MATSUMOTO TATSUYA, 345–359
MATSUMURA KAZUYA, 401–410
MATSUMURA KAZUYUKI, 242–261
MATSUMURA S, 515–528
MATSUNAGA ATSUSHI, 401–410
MATSUNAGA KEIJI, 375–386
MATSUNAGA MAMIKO, 401–410
MATSUO SHIGERU, 152–182
MATSUO T, 44t–74t
MATSUOKA EIICHI, 401–410
MATSUOKA FUMIO, 100–114, 345–359, 401–410, 423–429
MATSUOKA HIROYUKI, 439–445
MATSUSHITA HIROYUKI, 152–182
MATSUSHITA TERUKI, 152–182
MATSUYAMA KIYOSHI, 270–275
MATSUZAKI KAZUHIKO, 152–182
MAUCH FREDERIC, 345–359
MAY J R, 44t–74t
MAZZOCCHETTI LAURA, 290–299
MCANENEY LANNEN GWYNNE EVELYN, 454–458
MCCARTHY KEVIN T, 439–445
MCCARTHY STEPHEN P, 152–182
MCDANIEL JOSEPH B, 375–386
MCDANIEL K G, 44t–74t
MCELMURY DONALD E, 469–479
MCENEANY RYAN J, 401–410
MEAH A R Y, 44t–74t
MEHLTRETTER CHARLES L, 375–386
MEINANDER KERSTIN, 290–299
MELIK DAVID HARRY, 242–261
MENCELOGLU YUSUF ZIYA, 423–429
MENDON SHARATHKUMAR K, 469–479
MENTINK LEON, 199–213
MERICLE ROBERT W, 44t–74t
MERKER R L, 44t–74t
MERMINGIS CONSTANTINOS, 345–359
MESSAGER A, 44t–74t
METZNER KLAUS, 100–114
MIAO Q, 44t–74t
MIERAU UTA, 44t–74t, 152–182
MIHALIK MICHAL, 152–182, 242–261
MIHARA MAKOTO, 152–182
MIHARA TAKASHI, 152–182
MIJOLOVIC D, 44t–74t
MIKHAIL MICHEL DR, 242–261
MIKI YASUHIRO, 199–213, 439–445
MIKOS A G, 44t–74t
MIKSIC BORIS A, 242–261
MILIZIA TIZIANA, 152–182
MILLS STEPHEN, 454–458
MIMURA KOJI, 375–386
MIN LI, 152–182, 242–261, 423–429
MINAMI M, 515–528
MINAMI SABURO, 469–479
MINAMI SHUNSUKE, 152–182
MINAZU HIROSHI, 199–213, 439–445
MINE TAKAKIYO, 152–182

MING-YI T D, 515–528
MINOWA TOSHIYUKI, 199–213
MISHIMA KENJI, 270–275
MISRA MANJUSRI, 152–182, 290–299, 423–429
MITA KOZO, 375–386
MITA T, 515–528
MITCHELL T, 44t–74t
MITO OSAMU, 401–410
MITOMI HIROSHI, 290–299
MITSUHASHI KIMIYUKI, 469–479
MITSURU, 345–359
MIURA HIROMITSU, 100–114
MIURA HITOMI, 152–182
MIURA MITSUO, 152–182
MIYAGAWA TOSHIO, 345–359
MIYAKE MUNEHIRO, 375–386
MIYAKE YUICHI, 423–429
MIYAMOTO KENJI, 270–275
MIYAMOTO TAKASHI, 100–114, 199–213, 290–299, 317–325, 439–445, 454–458, 469–479
MIYASHITA AKIRA, 423–429
MIYASHITA KAZUHISA, 375–386
MIYASHITA YOU, 375–386
MIYAZAKI KEIKO, 242–261, 375–386
MIYOSHI MASANAO, 375–386
MIZUMA HIROKAZU, 152–182
MIZUMURA TAKESHI, 317–325
MIZUNO AKIRA, 44t–74t
MIZUNO KATSUTOSHI, 290–299, 423–429
MIZUNO UTAKO, 469–479
MOCHIZUKI KATSUHIKO, 100–114, 401–410
MOCHIZUKI MASATSUGU, 401–410
MOCHIZUKI T, 515–528
MOELLER MICHAEL, 469–479
MOHANTY AMAR K, 152–182, 290–299, 423–429
MOIREAU PATRICK, 199–213
MOLENVELD KARIN, 345–359
MOMOSE KATSUSHI, 270–275
MOMOSE YOSHIAKI, 345–359
MONTADOR JAMES HENRY, 317–325, 439–445
MONTINO ALESSANDRO, 100–114, 152–182
MOORE L, 515–528
MOORE T G, 44t–74t
MORI FUMIHIKO, 515–528
MORI HIROKI, 317–325
MORI HIROYUKI, 242–261, 317–325
MORI KEIJI, 317–325
MORI MASAHIRO, 152–182
MORI TAKUMI, 317–325
MORI YUKIKO, 270–275
MORIKAWA AKIRA, 375–386
MORIMOTO KAZUKI, 152–182
MORIMOTO OSAMU, 317–325, 469–479
MORIOKA TATSUTA, 401–410
MORITA KENJI, 345–359, 375–386
MORIYA MASAFUMI, 199–213
MORIYA SHINOBU, 242–261, 375–386, 401–410
MORIYAMA M, 515–528
MORIYAMA TAKESHI, 152–182
MOROHASHI N, 515–528
MORSCHBACKER A L R D, 44t–74t
MOSCA ROBERTO, 439–445
MOSSEVELD HENK, 152–182
MOTIKA STEPHEN ANDREW, 375–386
MOTOMIYA T, 515–528
MOTOYAMA TORU, 515–528
MUEHLBAUER UDO, 44t–74t
MUELLER M, 44t–74t
MUELLER VOLKER, 44t–74t
MUKAI KATSUYUKI, 423–429
MUKOYAMA M, 44t–74t
MULUKUTLA PRASAD, 290–299, 423–429
MURAFUJI Y, 44t–74t
MURAKAMI TADASHI, 290–299
MURAKAMI TEI, 290–299, 345–359
MURATA M, 515–528
MURATA SHIGERU, 152–182, 242–261
MURDOCH JOSEPH R, 401–410
MUSSO SI, 515–528
MUTAGAMI SHIYOUGO, 401–410
MYERS SASHA B, 242–261, 375–386
MYLLYMAEKI VESA, 199–213

N

NABESHIMA KOJI, 515–528
NAEGELE H, 44t–74t
NAGAHAMA M, 506–507, 515–528
NAGAI AKIRA, 152–182
NAGAO KEN, 242–261
NAGAO TAKASHI, 152–182, 242–261
NAGAOKA KOICHI, 401–410
NAGARAJAN V, 44t–74t
NAGASAWA KAZUYUKI, 270–275, 375–386
NAGASAWA NAOTANE, 290–299
NAGASAWA NAOTSUGU, 100–114, 290–299
NAGASHIMA TAKASHI, 242–261
NAGOSHI TOSHIHARU, 317–325
NAISBY ANDREW J, 317–325
NAITO HIROSHI, 152–182, 345–359
NAITO IKUO, 454–458
NAKADA TOMOYUKI, 100–114, 242–261, 345–359
NAKAE TSUNAHIRO, 152–182, 345–359, 515–528
NAKAGAWA KUNIYOSHI, 401–410
NAKAGAWA YOSHIHIRO, 317–325
NAKAJIMA JUNJI, 100–114, 242–261
NAKAJIMA M, 515–528
NAKAJIMA TADASHI, 469–479
NAKAMURA AKINOBU, 423–429
NAKAMURA C, 44t–74t
NAKAMURA K, 501, 506–507, 515–528
NAKAMURA NOBUO, 375–386
NAKAMURA RIKIYA, 242–261
NAKAMURA SHINYA, 345–359
NAKANO MASARU, 423–429
NAKANO MICHIHIKO, 44t–74t
NAKANO MITSURU, 100–114
NAKANO YUKIHIRO, 375–386
NAKAO HIROSHI, 317–325
NAKAO SUGURU, 242–261
NAKAOKI TAKAHIKO, 345–359
NAKASUGI HISAHIKO, 345–359
NAKATA TOMOYUKI, 100–114, 152–182, 242–261
NAKATSUBO FUMIAKI, 469–479
NAKAYAMA NAOKI, 345–359
NAKAZAWA HIROMOTO, 345–359, 423–429
NAKAZAWA KENJI, 242–261
NALAWADE SAMEER, 345–359
NAM BYEONG UK, 100–114
NAM SEUNG BAIK, 242–261
NAM YOUN WOO, 345–359
NANGERONI JAMES FRANCIS, 100–114, 439–445
NANJO KAZUNARI, 375–386
NANJO RYOJI, 423–429
NARAAYANAN S S, 515–528
NARASIMHAN KARUNAKARAN, 199–213
NARAYAN RAMANI, 152–182
NARIBAYASHI IKUYA, 242–261
NARITA JUNICHI, 242–261, 317–325
NARITA SHUSAKU, 401–410
NARUTAKI TOMOMITSU, 199–213
NASCIMENTO JEFTER FERNANDES, 100–114, 152–182, 242–261, 423–429
NATAL MANUEL, 44t–74t
NATARAJAN SRIRAM, 317–325
NATSUME TATSUYA, 242–261
NATSUME YOSUKE, 375–386
NAVARINI FRANCO, 375–386
NAWABY A VICTORIA, 345–359
NEAL CHARLES WILLIAM, 199–213
NEBIRU E D, 515–528
NEENAN T X, 44t–74t
NENOV NIKOLAY, 199–213
NESS EVERETT ALAN, 454–458
NEVALAINEN KIMMO, 423–429, 434, 439–445
NEWTON ALAN BRANFORD, 152–182
NGUYEN QUI LONG, 152–182
NGUYEN SOPHIE, 290–299
NICOLAS F, 44t–74t
NICOLINI MATTEO, 345–359
NIEHOFF RAYMOND LOUIS, 199–213
NIEMI MARIA, 290–299
NIES BERTHOLD, 469–479
NIIKURA ISAMU, 290–299
NIIMI TATSUO, 242–261
NIITSU HIROMI, 100–114
NIIZAKI MI, 515–528
NIIZEKI KOICHI, 199–213
NIKU-PAAVOLA M-L, 44t–74t
NING K, 44t–74t
NISHIDA HARUO, 498, 515–528
NISHIDA HIROFUMI, 423–429
NISHIDA TOSHIO, 345–359
NISHIHARA SHUNICHI, 317–325
NISHIIKE HARUKI, 199–213, 469–479
NISHIJIMA KATSUNORI, 345–359
NISHIMURA ATSUO, 100–114
NISHIMURA HIROSHI, 100–114, 375–386
NISHIMURA MOTOKATSU, 401–410
NISHIOKA MASAAKI, 100–114
NISHIOKA YASUHIRO, 152–182
NITTO DENKO CORP, 469–479
NIU CHUNLIANG, 423–429

NIX CARLTON, 454–458
NODA AKIRA, 375–386
NODA ISAO, 100–114, 199–213, 401–410, 469–479, 515–528
NODA MITSUO, 242–261
NODERA AKIO, 152–182
NOEL BAPTIST JAMES, 100–114
NOETZOLD S, 44t–74t
NOGAMI HISASHI, 199–213
NOGUCHI HIROSHI, 242–261
NOGUCHI TSUTOMU, 242–261, 317–325
NOMOTO TSUYOSHI, 454–458
NOMURA NOBUYOSHI, 44t–74t
NONAKA SHUICHI, 100–114, 401–410
NONOKAWA RYUJI, 152–182
NOORDEGRAAF JAN, 345–359
NORTHOLT MARTIN DINANT, 199–213, 439–445
NORTON R, 515–528

O

OBARA CHOJI, 345–359
OBERHAUSER JAMES, 44t–74t
O'BRIEN WILLIAM GEORGE, 317–325
OBUCHI SEIJI, 100–114, 242–261, 345–359
OBUCHI SHOJI, 100–114, 152–182, 242–261
OCHI TAKASHI, 100–114, 401–410
OCHIAI TETSUYA, 345–359
ODA NAONOBU, 317–325, 375–386
ODA TOMOKO, 152–182
O'DONNELL HUGH JOSEPH, 401–410
OELSCHLAEGER PETER, 152–182
OFFERGELD HEINZ, 100–114, 242–261
OGAITO MAKOTO, 375–386
OGAMI AKINOBU, 345–359, 423–429
OGAWA ASUKA, 454–458
OGAWA NORIKO, 270–275
OGAWA RYOHEI, 152–182
OGAWA TOSHIO, 100–114, 317–325
OGOSHI IKUO, 242–261
OH SEOK BIN, 152–182
OHARA HARUO, 423–429, 515–528
OHARA TORU, 317–325
OHKUBO K, 44t–74t
OHKURA MASATOSHI, 317–325
OHME HIROYUKI, 152–182
OHTA SHUN-ICHI, 345–359, 423–429
OHYAMA MASAHIKO, 345–359
OIKAWA MASAHARU, 345–359
OKA K, 44t–74t
OKA TATSUYA, 317–325
OKA YOSHIYUKI, 152–182, 345–359
OKABAYASHI A, 515–528
OKADA TAKAO, 345–359
OKADA TAKU, 454–458
OKADO H, 515–528
OKAMOTO HIROTAKA, 100–114
OKAMOTO K, 515–528
OKAMOTO MASAMI, 345–359, 423–429
OKAMOTO T, 515–528
OKAMOTO YOSHIHARU, 469–479
OKINO YOSHIRO, 199–213
OKIWA YUTAKA, 100–114
OKOROAFOR MICHAEL O, 317–325
OKSMAN KRISTIINA, 423–429
OKUBO TSUTOMU, 242–261
OKUDA TOHR, 345–359
OKUDAIRA TADASHI, 317–325
OKUYA MASAHIRO, 199–213
OKUYAMA HISASHI, 454–458
OKUYAMA HISATSUGU, 242–261
OKUYAMA KAZUNORI, 317–325, 454–458
OMORI KEIICHI, 375–386
OMORI TAKEMITSU, 423–429
OMORI YUMIKO, 439–445
OMOTO S, 515–528
OMURA YOSHIHIKO, 469–479
ONISHI HAYAMI, 199–213, 515–528
ONISHI KATSUMI, 152–182
ONO TOSHIHIKO, 100–114, 242–261
ONO TSUTOMU, 401–410
ONOE YOSUKE, 152–182
OOGI YUTAKA, 345–359
OOME HIROKAZ, 242–261
OPITZ GUNTRAM, 152–182
ORSOLINI P, 44t–74t
ORTH P, 515–528
OSAKADA FUMIO, 270–275
OSAKI MISA, 375–386
OSAKI TAKUJI, 401–410
OSANAI Y, 515–528
OSAWA SATOSHI, 100–114, 317–325
OSENBAUM SONJA, 242–261
OSHIDA YASUNORI, 152–182
OSONE SATOSHI, 375–386
OTA HAJIME, 345–359
OTA MASAAKI, 242–261, 423–429, 515–528
OTA SEIJI, 423–429
OTA SEIYA, 401–410
OTA TAKAYUKI, 242–261
OTAGURO MASAZO, 401–410
OTEY FELIX HAROLD, 152–182, 375–386
OTOME S, 44t–74t
OTOMO TAKASHI, 242–261
OURA MAKOTO, 375–386
OYAMA KANAKO, 375–386
OYAMA MASAHIKO, 152–182, 345–359
OZASA TERUO, 317–325
OZAWA MASAAKI, 100–114, 242–261
OZAWA NORIAKI, 454–458
OZAWA SATOMI, 317–325
OZEKI EIICHI, 152–182, 375–386

P

PACHEKOSKI WAGNER MAURICIO, 100–114, 152–182, 242–261, 423–429
PACK JI-WON, 152–182
PADWA ALLEN R, 242–261, 290–299
PAGGA UDO, 199–213
PAIK IN KYU, 345–359
PALLMANN H, 515–528
PAOLILLI TRACY A, 317–325
PARHAM W W, 515–528
PARK BYUNG SIK, 423–429
PARK JAE HYUNG, 345–359
PARK JONG SOON, 423–429
PARK KI MOON, 375–386
PARK YANG HO, 423–429
PARONEN TIMO PETTERI, 199–213
PARRA DUCLERC FERNANDES, 317–325
PARTON BRIAN, 454–458
PARULEKAR YASHODHAN, 423–429
PASTER MARK D, 100–114, 199–213, 270–275
PATHAK CHANDRASHEKHAR P, 199–213
PATONAY G, 515–528
PATTERSON THOMAS E, 327, 345–359, 401–410
PAUL CHARLES W, 469–479
PAVLACKOVA MIROSLAVA, 152–182, 242–261
PAWLOSKI ADAM R, 345–359
PAYNE R G, 44t–74t
PAZOS J F, 44t–74t
PEIKAI MIU, 317–325
PEIPEI ZHANG, 317–325
PELLINGRA SALVATORE, 375–386
PELTONEN SOILI, 199–213
PENG T, 515–528
PENGYANG DENG, 242–261, 423–429
PENHALE D, 44t–74t
PENTTINEN TAPANI, 423–429, 439–445
PEOPLES OLIVER P, 44t–74t
PERAZZO LUIGI, 375–386
PEREGO GABRIELE, 317–325
PFEIFFER THOMAS, 515–528
PFITZER J, 44t–74t
PHAN DEAN VAN, 199–213
PICHON THOMAS, 152–182, 290–299
PIERRE JEAN R, 100–114, 439–445
PIPPER GUNTER, 44t–74t
PITZI THOMAS J, 345–359
PLAVEC RODERIK, 242–261
PLIJTER JOHANNES, 152–182
POLISTINA ROCCO ALBERT, 100–114
POLLOCK MARK A, 152–182
POMMERANZ WINFRIED, 152–182, 317–325, 469–479
PONCE PATRICIA, 317–325
PONTI ROBERTO, 100–114, 152–182
POTTS JAMES E, 152–182
PRADEL JEAN-LAURENT, 270–275
PRAVATA LAURENT, 467–479
PRESCOTT A G, 44t–74t
PRESTON JOSEPH R, 152–182, 242–261
PUCCI J, 44t–74t
PUISIEUX FRANCIS, 199–213, 270–275
PULETTI PAUL P, 469–479
PURNAMA PURBA, 242–261
PYRAH KEITH, 44t–74t

Q

QINGWEN GUAN, 423–429
QUINN PHILIP JAMES, 345–359
QUINTANAR-GUERRERO DAVID, 199–213
QVINTUS-LEINO P, 44t–74t

R

RAFAT MEHRDAD, 290–299
RAJA LAZMINARIYAN L, 317–325
RAKU TAKAO, 100–114

RAMACHANDER TURAGA VENKATA NAGA, 17
RAMESH NATARAJAN S, 345–359
RAMP JAMES W, 199–213
RAMUS J S, 44t–74t
RANDALL BRIAN S, 401–410
RANDALL JED RICHARD, 152–182
RAPTHEL INNO, 270–275
RAUN-LUELLEMANN A, 44t–74t
RAUSCHER DAVID, 290–299
RAWAL SHUBAN KISHEN, 17
RAWLINS JAMES W, 469–479
RAY-CHAUDHURI DILI K, 469–479
RAYKOVITZ GARY, 469–479
REHM HELGA, 100–114, 199–213
REHM JOHANNES, 152–182
REICH PETER, 454–458
REICHLE ALAN JOHN, 423–429
REID TOBY SIMON OLIVER, 242–261
REIGHARD TRICIA S, 375–386
REN LIQUN, 375–386
RENBUTSU EIKO, 469–479
RENXU YUAN, 242–261
REYNES P, 44t–74t
RHIM HANNONG, 290–299
RI KANSHIN, 454–458
RIEBEL MICHAEL J, 375–386
RIEBEL MILTON, 375–386
RIEGERT THEODORE E, 375–386
RIESS R, 515–528
RINNAI R, 469–479
RITTER WOLFGANG, 152–182
ROBERT CHRISTOPHE, 469–479
ROBESON LLOYD M, 152–182
ROGERS ROBIN DON, 199–213
ROKICKI ANDRZEJ, 375–386
ROLFES EMILY R, 345–359
ROMEO AURELIO, 199–213
RONCORONI VITTORIO, 375–386
ROOREN D B, 515–528
ROOSE PATRICE, 152–182, 290–299
ROSENBAUM MANFRED, 375–386
ROSENBAUM MARLIES, 375–386
ROSENBAUM SONJA, 375–386
ROSENDALE DAVID, 100–114, 242–261
ROTH WILLIAM B, 375–386
ROTHE THOMAS, 152–182
ROY KRISHNENDU, 317–325
RUSSELL CHRISTINE, 454–458
RUSSELL SCOTT O, 100–114
RUYIN WANG, 423–429
RYAN CHRISTOPHER MICHAEL, 152–182, 401–410, 439–445, 469–479
RYU SEUNG CHAN, 152–182

S

SACHETTO JEAN-PIERRE, 152–182
SAEKI T, 515–528
SAFAEI-NIKOUEI NAZILA, 199–213
SAGAWA Y, 44t–74t
SAHOO S, 152–182
SAIGUSA KOTAKU, 270–275
SAIKA MASAAKI, 439–445
SAIKI NORITSUGU, 401–410
SAIMOTO HIROYUKI, 469–479
SAINAI NAOFUMI, 199–213, 242–261
SAKAGUCHI MASAKAZU, 345–359
SAKAGUCHI TOSHIKI, 317–325
SAKAI ATSUSHI, 345–359
SAKAI SHIGEKAZU, 454–458
SAKAI TAKAAKI, 100–114, 401–410
SAKAI TAKASHI, 242–261
SAKAIRI K, 345–359
SAKAMOTO JUN, 375–386
SAKAMOTO NAOYA, 152–182
SAKASHITA KEIICHI, 152–182
SAKIDA FUMIE, 152–182, 375–386
SAKOBE TADAYUKI, 401–410
SALANITRO JOSEPH P, 152–182
SAMANT K, 515–528
SAMPATH BANGARU, 345–359
SAMUEL JOHNSON K, 290–299
SANADA AKIRA, 469–479
SANDERS JEREMY KEITH MORRIS, 199–213
SANDLER JAN KURT WALTER, 345–359
SANO TOSHIMICHI, 242–261
SASAKI HIDEHIRO, 345–359
SASAKI M, 44t–74t
SASAKI S, 44t–74t
SASAMOTO TAI, 317–325
SASE Y, 44t–74t
SASHI A, 515–528
SASHITA KAZUYUKI, 242–261
SATAKE MAKOTO, 401–410
SATANI SHOICHI, 242–261, 375–386
SATGURUNATHAN RAJASINGHAM, 199–213, 439–445
SATO DAISUKE, 242–261
SATO HIROYUKI, 152–182, 242–261, 270–275
SATO NOBUO, 100–114, 375–386
SATO TAKASHI, 100–114
SATO TAKU, 375–386, 423–429
SATOMI YOSHIE, 469–479
SAUER M, 494, 515–528
SAVILL KAREN, 439–445
SAWA KOUICHI, 375–386
SAWADA HIDEYUKI, 454–458
SAWADA SEIJI, 423–429
SAWAI TORU, 100–114, 375–386
SAWAI YUMIKO, 401–410
SAWAMURA SHINYA, 469–479
SAWAOKA RYUJI, 423–429
SAWARA MASAAKI, 345–359
SAWARA TETSUYA, 423–429
SAWHNEY AMARPREET S, 199–213
SAYED AZIZ EL, 515–528
SCANDOLA MARIASTELLA, 290–299
SCHAFFER JUERGEN, 100–114
SCHEER FREDERIC, 152–182
SCHEIRS JOHN, 152–182, 242–261
SCHENNINK GERALDUS GERARDUS JOHANNES, 152–182, 242–261, 345–359
SCHERTZ DAVID MICHAEL, 290–299
SCHEUCHENSTUHL WILLIBALD, 199–213, 439–445
SCHILKE FRANK, 469–479
SCHILLING KEVIN H, 242–261
SCHINDLER ANTON, 345–359
SCHLEMMER LOTHAR, 152–182
SCHMIDT ANNETTE, 290–299
SCHMIDT HARALD, 152–182, 317–325, 469–479
SCHMIDT JOACHIM, 100–114, 199–213
SCHMIECHEN HELMUTH, 100–114, 199–213
SCHMITT C, 494, 515–528
SCHMITT EDWARD EMIL, 100–114
SCHNEIDER ALLAN K, 242–261, 375–386
SCHOENBERG JULES E, 290–299, 469–479
SCHOENWEITZ CLAUDIA, 515–528
SCHOLLMEYER JULIE, 152–182
SCHORNICK GUNNAR, 152–182
SCHROETER JOHANNE, 375–386
SCHUEBEL R, 515–528
SCHUEMANN UWE, 469–479
SCHUHMANN MICHAEL, 375–386
SCHULTHEIS M W, 44t–74t
SCHULZ A, 494, 515–528
SCHULZE JOACHIM, 44t–74t
SCHULZ-SCHLITTE WOLFGANG, 317–325, 469–479
SCHUMACHER KARL-HEINZ, 199–213
SCHUTTE GERRIT, 469–479
SCHWARK DWIGHT W, 439–445
SCOTT A, 44t–74t
SEEGER S, 494, 515–528
SEELIGER URSULA, 152–182, 199–213
SEIFRIED BERNHARD, 270–275
SEKI MASAO, 152–182, 290–299
SEKIGUCHI KUNITAKA, 317–325
SEKIGUCHI YUKA, 469–479
SELA MARION, 100–114
SELIN JOHAN-FREDRIK, 242–261, 290–299
SELWOOD ALAN, 375–386
SEMP B AT, 515–528
SENDA HIROKI, 469–479
SENDA KENICHI, 199–213, 345–359, 439–445
SENG F, 515–528
SENIOR PETER JAMES, 100–114, 199–213
SEO MIN HYO, 270–275
SEO YEONG BUM, 423–429
SERIZAWA SHIN, 100–114, 242–261, 423–429
SERPELLONI MICHEL, 199–213
SERTORI DURAO ANTONIO, 242–261
SHAH SAMIR, 345–359
SHALABY W S, 44t–74t
SHAOHONG ZHOU, 317–325
SHARAK MATTHEW L, 469–479
SHARMA SURAJ, 423–429
SHARP JAMES SINCLAIR, 317–325
SHEN LIE PENG, 423–429
SHI BO, 375–386
SHIBA YOSHITO, 199–213
SHIBATA MASUMI, 242–261
SHIBATA MITSUHIRO, 423–429
SHIBAZAKI SATOKO, 199–213, 290–299, 454–458
SHIBUYA MASAHIRO, 345–359
SHICHIDA HIROAKI, 290–299, 423–429
SHIDA HIROTAKA, 152–182

SHIFENG WANG, 423–429
SHIFRIN SHARI, 451, 454–458
SHIGA KENJI, 242–261
SHIGEMASA YOSHIHRO, 469–479
SHIIKI ZENYA, 100–114, 375–386
SHIKATA NORIKI, 375–386
SHIMADA TAKASHI, 152–182
SHIMENO KATSUYA, 469–479
SHIMIZU HIROSHI, 152–182
SHIMIZU TAKEO, 152–182, 290–299, 401–410
SHIMIZU TOSHIYUKI, 152–182, 375–386
SHIMURA HIROMI, 242–261, 317–325
SHIN H, 44t–74t
SHIN KYUNG MOO, 152–182
SHINKAWA TAKEO, 401–410
SHINNUMADATE HIROSHI, 317–325, 375–386
SHINO KATSUYA, 199–213, 290–299, 454–458
SHINODA HOSEI, 345–359, 375–386
SHINODA NORIMASA, 242–261, 375–386, 401–410
SHINOHARA MITSURU, 345–359
SHINOHARA RUMI, 317–325
SHINOZAKI HIROKI, 345–359
SHIOTANI TAKENAGA, 44t–74t
SHIOTANI TAKESHI, 100–114
SHIOYA SATORU, 345–359
SHIRAHAMA R, 44t–74t
SHIRAI YOSHITO, 498, 515–528
SHIRAISHI AKIHIKO, 375–386
SHIRAKI YASUICHIROU, 469–479
SHIRASAWA DAISUKE, 199–213
SHIRO FUKUYAMA, 100–114
SHISEIDO CO LTD, 317–325
SHIYONG XIA, 242–261
SHO KENGYO, 423–429
SIDMAN K R, 44t–74t
SIGELKO WILMER LIST, 199–213
SILBIGER JAKOB, 37, 152–182
SILVA BIZZARRI PABLO, 242–261
SIMON A, 515–528
SINCLAIR RICHARD G, 152–182, 242–261, 375–386
SITZMANN STEFAN, 375–386
SKOG MARIA, 242–261
SKORPENSKE R G, 44t–74t
SKRALY FRANK A, 44t–74t
SKUPIN GABRIEL, 152–182, 515–528
SOEDERGAARD ANDERS, 290–299
SOERENS DAVE A, 290–299
SOHGAWA Y-H, 44t–74t
SOKOLL K K, 44t–74t
SOLODAR A JOHN, 100–114, 199–213
SOMMER E J, 491, 515–528
SON JONG-SEOK, 242–261
SONG GI SANG, 317–325
SONG JI YOUNG, 152–182
SOULA G, 44t–74t
SOUNDERS FRANK LINWOOD, 199–213
SOYAMA MAKOTO, 242–261
SPAWN TERENCE D, 242–261, 375–386
SPEER DREW V, 439–445
SPIES MANFRED, 469–479
SRUBAR III WILFRED V, 417, 423–429
STAERKE DIRK, 152–182
STAGEMAN JOHN FREDERICK, 199–213
STAMBOULIDES CHRISTOS, 242–261
STAPPERS FRANK H M, 270–275
STARK KURT, 375–386
STASSIN FABRICE, 345–359
STEGMANN VEIT, 199–213
STEINKE TOBIAS HEINZ, 345–359
STEPHENS HENRY M, 375–386
STEPTO ROBERT F T, 152–182
STERZEL HANS-JOSEF, 100–114, 152–182, 317–325, 345–359
STEVENS M M, 44t–74t
STOCK L R II, 44t–74t
STOWELL WILLIAM J, 152–182
STOYE HARTMUT, 270–275
STRAUSER FRED E, 100–114, 199–213
STREMPEL FRIEDRICH, 100–114, 270–275
STRICKER HERBERT, 242–261
STUUT P I, 44t–74t
SUBRAMANIAN N S, 515–528
SUEOKA MASANORI, 375–386
SUGA KEIKO, 242–261, 375–386
SUGA YUTA, 454–458
SUGAI MASAHIRO, 242–261, 317–325
SUGANO GEN, 270–275
SUGANO HARUYUKI, 152–182
SUGI MASAHIRO, 242–261
SUGIMOTO MARIKO, 375–386
SUGIMOTO NOBUNARI, 375–386
SUGISAWA TOYOO, 317–325
SUGISHIMA MASAMI, 439–445
SUGIURA NOBUYUKI, 199–213, 469–479
SUGIYAMA HIROKO, 199–213
SUGIYAMA YASUNORI, 317–325
SUKIGARA MASAYUKI, 100–114, 345–359
SULING CARLHANS, 152–182
SUMI T, 44t–74t
SUMIDA N, 515–528
SUMMERVILLE S, 44t–74t
SUN HSIANG-NING, 469–479
SUWA YOSHIHITO, 454–458
SUZUKI AKIHIRO, 242–261
SUZUKI AKIRA, 199–213, 317–325, 454–458
SUZUKI ATSUSHI, 242–261
SUZUKI F, 515–528
SUZUKI KAZUHIKO, 100–114, 152–182, 242–261, 317–325, 345–359, 375–386
SUZUKI KENSUKE, 270–275
SUZUKI KENYA, 439–445
SUZUKI MASAHIRO, 152–182, 242–261
SUZUKI MASATO, 100–114, 242–261, 317–325
SUZUKI SATORU, 100–114
SUZUKI TAKEHIKO, 199–213
SUZUKI TAKEHISA, 439–445
SUZUKI YOSHINORI, 152–182
SWATLOSKI RICHARD PATRICK, 199–213
SYRE PEDER, 423–429

T

TABATA HISATAKA, 375–386
TABEYA TOSHIHIRO, 152–182, 290–299
TACHIKA HIROSHI, 242–261
TADROS RAEF M, 100–114
TAGLIAFERRO A, 515–528
TAGUCHI T, 44t–74t
TAHARA SHU, 375–386
TAHERI KAMBIZ, 242–261
TAINAKA JUNICHI, 345–359
TAKAGI JUN, 100–114, 152–182, 242–261, 317–325, 368, 375–386, 515–528
TAKAGI MASATOSHI, 199–213, 439–445, 469–479
TAKAGI SIGEYUKI, 152–182
TAKAGI YOSHINORI, 199–213, 439–445
TAKAHARA MASATO, 199–213, 469–479
TAKAHASHI A, 515–528
TAKAHASHI ISAMU, 152–182
TAKAHASHI KATSUJI, 152–182
TAKAHASHI MAKOTO, 44t–74t
TAKAHASHI RYOTA, 454–458
TAKAHASHI SHUJI, 401–410
TAKAHIRA HITOSHI, 469–479
TAKANAGA HIDETOSHI, 401–410
TAKASE YOSHIHIKO, 242–261
TAKASHIMA KAZUNORI, 44t–74t
TAKEDA KEIJI, 152–182, 290–299
TAKEDA KIYOSHI, 152–182
TAKEDA KUNIHIKO, 242–261
TAKEISHI HIROYUKI, 423–429
TAKENAKA AKIRA, 152–182, 242–261
TAKEUCHI FUMIYO, 439–445
TAKEUCHI HISATO, 100–114
TAKIYAMA EIICHIRO, 44t–74t, 152–182, 290–299, 345–359
TALEYARKHAN RUSI P, 434, 439–445
TAM KOCK FYE, 316–325
TAMAI MASAJI, 270–275
TAN KIM CHENG, 316–325
TAN YEN-CHU, 423–429
TANAKA HIDEYUKI, 199–213, 469–479
TANAKA J, 44t–74t
TANAKA KAZUYA, 100–114, 242–261, 375–386
TANAKA MASAHIDE, 152–182
TANAKA MASAKI, 242–261
TANAKA MASAO, 515–528
TANAKA SUMINORI, 423–429
TANAKA SYUKICHI, 242–261
TANG REGINALD TING-HONG C O AL, 242–261
TANGELDER ROBERT, 152–182
TANIFUJI YOICHI, 375–386
TANIGUCHI KEIKO, 401–410
TANIGUCHI MASAYUKI, 317–325
TANIYAMA YOICHI, 270–275
TANNER CANDACE M, 152–182
TAO LIU, 317–325
TAO LUO, 469–479
TAPLIN WALTER, 317–325
TARUMOTO HIROYUKI, 345–359
TASHIRO TAKESHI, 375–386
TATEISHI KENJI, 375–386
TAYA NAOKI, 242–261, 375–386
TAYAUCHI MASATO, 242–261, 375–386
TAYLOR PHILIP LOUIS, 152–182, 199–213, 439–445

TEETERS WILBER O, 44t–74t
TEJIMA TOMOJI, 375–386
TELESCA ROSANNA, 317–325
TEMELLI FERAL, 270–275
TEOH SWEE HIN, 316–325
TERADA SHIGENORI, 152–182, 242–261, 317–325, 368, 375–386
TERADA T, 515–528
TERADO YUJI, 469–479
THAMES SHELBY F, 469–479
THIES CURT, 270–275
THOENY-MEYER LINDA CHRISTIANE, 345–359
THOMA MARKUS, 152–182
THOMPSON DARRELL R, 44t–74t
TIETZ R F, 44t–74t
TIETZ WOLFGANG, 44t–74t
TIMM DELMAR C, 100–114
TIMMERMANN R, 44t–74t
TO SHIN, 152–182, 401–410
TOBITA ETSUO, 44t–74t
TOBITA HISANORI, 100–114
TOHMIYA NAOKO, 100–114
TOKIWA TOMOO, 345–359
TOKIWA YUTAKA, 152–182, 242–261
TOKORO HISAO, 345–359
TOKORO TOSHIO, 345–359
TOKUNAGA YASUYUKI, 469–479
TOKUSHIGE YUJI, 375–386
TOMANOVA KATARINA, 152–182, 242–261
TOMKA IVAN, 128, 148, 152–182, 232–233
TOMORI MASAHIKO, 345–359
TONE SEIJI, 152–182
TONGMIN CAI, 242–261
TOPOLKARAEV VASILY A, 401–410
TORII H, 44t–74t
TOTANI YOSHIYUKI, 152–182
TOYAMA TATSUYA, 317–325
TOYOHARA KIYOTSUNA, 152–182, 401–410
TOZAKI HIROYUKI, 375–386
TRANTOLO DEBRA J, 290–299
TRAVIS JR WILLIAM C, 44t–74t
TRENNERT MARIKA, 100–114, 199–213
TRIPATHI GYANENDRA, 17
TROUTMAN MALISA, 439–445
TRUNCELLITO-SIMONI JEANNETTE, 439–445
TRUONG MYHANH T, 469–479
TSAI FU-JYA DANIEL, 401–410
TSUBAKI TADAHIRO, 454–458
TSUGAWA HIROYUKI, 401–410
TSUJI HIDETO, 44t–74t
TSUJI MASASHI, 152–182
TSUJIMOTO KEI, 317–325
TSUKADA NORIAKI, 345–359
TSUKUDA KAZUAKI, 199–213
TSUNEIZUMI Y, 515–528
TSURUSAKI YOSHIYUKI, 242–261, 317–325, 469–479
TSUSHIMA YOSUKE, 199–213, 439–445
TULLOS TINA L, 439–445
TURATI DANIELE, 345–359
TUREK CAROLINE M, 454–458
TURNER PETER DERYCK, 199–213, 439–445
TWEED EDWARD CARL, 375–386

U
UCHIDA NOBUYUKI, 423–429
UCHIDA TAKASHI, 152–182
UCHIKI KOHICHI, 345–359, 375–386
UCHIUMI Y, 515–528
UEDA AKIHIKO, 375–386
UEDA KAZUE, 100–114, 199–213, 242–261, 345–359, 423–429
UEDA MASANORI, 345–359
UEDA SHUHEI, 375–386
UEHARA TAKESHI, 515–528
UEKI TAKAYUKI, 375–386
UEMATSU TAKASHI, 317–325
UENO YOSHIAKI, 454–458
UERDINGEN ERIC, 199–213
UERDINGEN WALTER, 152–182
UGELSTAD JOHN, 187–188, 199–213
UMEYAMA HIROSHI, 317–325
UNI CHARM CORP, 317–325
UNO KEIICHI, 375–386, 401–410, 439–445, 454–458
UNRININ TOSHIFUMI, 152–182, 375–386
UPFAL JONATHAN, 199–213
URAYAMA HIROSHI, 44t–74t
URAYAMA YUJI, 242–261
URTTI ARTO OLAVI, 199–213
USUGI SHINICHI, 152–182
USUKI ARIMITSU, 100–114
UYAMA HIROSHI, 242–261, 317–325

V
VACANTI JOSEPH P, 290–299
VAN DER MEIJDEN JACOBUS, 152–182
VAN DIJK-WOLTHUIS WENDELMOED N, 199–213
VAN EGDOM EDWARD, 270–275
VAN HORN BRETT L, 345–359
VAN SCHIJNDEL RENEE JOSIE GIDE, 270–275
VAN SOEST JEROEN JOHANNES GERA, 152–182, 270–275
VANDERHOFF JOHN W, 187–188, 199–213
VANDERVEKEN YVES, 152–182
VANLAUTEM NOEL, 100–114, 199–213
VERBERNE PETRUS, 290–299
VERNON GARY, 100–114, 242–261
VERWEIJ ADAM BASTIAAN, 44t–74t
VETRECIN ROBERT, 317–325
VICINO JOSE RICARDO DE LELLO, 100–114
VIETTO PAOLO, 375–386
VIIKARI L, 44t–74t
VLOT TONNY, 290–299
VOIGT MICHAEL, 44t–74t
VUORENPAEAE JANI, 199–213

W
WADA KENZO, 152–182
WADAHARA EISUKE, 423–429
WADDINGTON SIMON DOMINIC, 375–386, 439–445
WAGLAND ALISON MARY, 439–445
WALLAJAPET PALANI RAJ RAMASWAM, 317–325
WALLENBERGER F T, 44t–74t
WALTER EARL RICHARD, 152–182
WAMPFLER-VON ROTZ BRUNO KARL, 345–359
WANG CHUN-SHAN, 423–429
WANG DA M, 100–114
WANG DONGHAI, 454–458
WANG FOSONG, 152–182
WANG JAMES HONGXUE, 152–182, 290–299, 375–386, 401–410
WANG XIANHONG, 152–182, 454–458
WANG YAN, 152–182
WANG YIH-WEN, 152–182
WANG YUNBING, 44t–74t
WANIBE HIROTAKA, 100–114, 242–261, 317–325
WANICZEK HELMUT, 152–182
WARZELHAN VOLKER, 152–182, 199–213, 345–359
WASHINO MASAHIRO, 401–410
WATANABE AKIHITO, 242–261
WATANABE AKIKO, 242–261
WATANABE FUMIO, 290–299, 454–458
WATANABE ICHIJI, 152–182
WATANABE JIRO, 290–299, 454–458
WATANABE KATSUJI, 270–275
WATANABE SUKETAKA, 317–325
WATANABE TAKAHIRO, 152–182
WATANABE TAKAKO, 375–386
WATANABE TAKAYUKI, 100–114, 152–182, 242–261, 345–359, 375–386
WATANABE TOMOKO, 401–410
WATANABE YASUYUKI, 199–213
WAY TUN-FUN, 242–261
WEAVER M A, 515–528
WEBER KARL, 152–182
WEI LI, 469–479
WEI ZHAO, 242–261
WEICHUAN LU, 199–213
WENDELIN G, 515–528
WENFU ZHU, 199–213
WENRUI TANG, 317–325
WERLE E E, 44t–74t
WERTHEIM BRIGITTE C, 401–410
WESSELMANN ULRICH, 469–479
WESTEPPE UWE, 317–325, 469–479
WESTERHOF HENK, 469–479
WESTHOFF RICHARD P, 152–182, 375–386
WEUSTHUIS RUUD ALEXANDER, 199–213, 439–445
WHELAN JASON, 100–114
WHITE ALAN W, 100–114, 152–182
WHITE CHRISTOPHER R, 317–325
WHITED G, 44t–74t
WHITEHOUSE ROBERT S, 152–182, 199–213, 290–299, 469–479
WIDEMAN GREGORY JAMES, 152–182
WIERER KONRAD ALFONS, 152–182
WILDI ROBERT H, 270–275

WILLETT JULIOS, 152–182
WILLIAMS SIMON F, 44t–74t
WILLMOUTH FRANK MARTIN, 152–182
WILLOCQ J, 515–528
WINGLER FRANK, 152–182
WISE DONALD L, 290–299
WITT MICHAEL RALPH JUERGEN, 345–359
WITT U, 515–528
WITZKE DAVID ROY, 100–114, 152–182, 242–261, 290–299, 439–445
WNUK ANDREW JULIAN, 242–261, 375–386
WOHLRABE FRANK C, 375–386
WOLFRUM J, 494, 515–528
WON CHEE-YOUB, 290–299
WOODSON B R, 44t–74t
WOOL RICHARD P, 152–182
WRIGHT LEONARD FEREDRICK, 100–114, 199–213
WRIST PETER E, 199–213, 375–386, 439–445
WU ROY, 100–114
WU RU-YU, 152–182
WUENNING M, 44t–74t
WUENNING P, 37

X
XIANGBIN ZENG, 242–261
XIANGNAN ZHANG, 152–182, 242–261, 423–429
XIAO FENGFEI, 454–458
XIAO M, 515–528
XIAOJUAN WANG, 199–213
XIAOMING MA, 317–325
XIAOPING LAN, 152–182
XIONG TAO, 152–182
XU DAN, 454–458
XU Y, 515–528

Y
YACKABONIS WILLIAM E, 345–359
YAGI TOSHIAKI, 100–114, 290–299
YAGINUMA MASAKI, 317–325
YAHIAOUI ALI, 317–325
YAHIRO SHUJI, 152–182
YAKUSHIDOH KENICHI, 375–386
YAMA S, 515–528
YAMA SHINKO, 152–182, 345–359
YAMADA AKIFUMI, 199–213, 317–325
YAMADA FUTOSHI, 401–410
YAMADA KAZUNOBU, 199–213, 345–359, 423–429
YAMADA NAOAKI, 317–325
YAMADA SHINICHIRO, 242–261
YAMADA TAKAYUKI, 242–261
YAMADA TAKEMIKI, 375–386, 423–429
YAMADA TAKEYOSHI, 375–386
YAMADA TOSHIHIRO, 401–410
YAMADA TOSHIO, 375–386
YAMADA YOSHIHISA, 423–429
YAMAGATA Y, 515–528
YAMAGISHI MASANAO, 345–359
YAMAGUCHI AKIHIRO, 317–325, 375–386
YAMAGUCHI MASAYUKI, 152–182
YAMAGUCHI TERUHIRO, 199–213, 242–261, 345–359, 375–386, 439–445, 515–528
YAMAGUCHI YUJI, 317–325
YAMAMOTO HISAO, 401–410
YAMAMOTO I, 515–528
YAMAMOTO MASAKAZU, 317–325
YAMAMOTO MOTONORI, 152–182, 199–213
YAMAMOTO TAKASHI, 401–410
YAMAMURA GOUHEI, 375–386
YAMANAKA TAKESHI, 469–479
YAMANE HIDEKI, 100–114
YAMANE KAZUYUKI, 100–114, 152–182, 242–261, 270–275, 439–445
YAMAOKA HIROAKI, 375–386
YAMAOKA TETSUJI, 401–410
YAMASHITA ROKUYA, 242–261
YAMASHITA SEIJI, 152–182
YAMASHITA TAKEHIKO, 242–261
YAMAZAKI KAZUHIKO, 317–325
YAMAZAKI MASAHIRO, 270–275
YAMAZAKI YUTAKA, 454–458
YAN TANG, 317–325
YANAGISAWA TSUNENORI, 100–114, 242–261
YANG XIN, 375–386
YANO TAKUMA, 345–359, 423–429
YANO TETSUYA, 454–458
YANO TORU, 152–182
YAO K, 515–528
YASUI MITSUO, 375–386
YASUI SHIGEYUKI, 423–429
YASUMITSU REI, 401–410
YATSUZUKA MICHIHIRO, 100–114
YEO BOON HON, 317–325
YIBIN XU, 242–261
YINXI ZHANG, 423–429
YIPENG WANG, 317–325
YODA KAORU, 152–182
YOKOI SEIJI, 401–410
YOKOMIZO OSAMU, 345–359
YOKOSUKA M, 506–507, 515–528
YOKOYAMA MASAO, 401–410
YONEHARA HIROSHIGE, 423–429
YONG ZHANG, 423–429
YOO YOON JONG, 423–429
YOON CHANG WON, 423–429
YOON JEE YOUNG, 345–359
YOSHIDA HIROJI, 401–410
YOSHIDA IKUNORI, 345–359
YOSHIDA KAZUNORI, 242–261
YOSHIDA KOJI, 270–275
YOSHIDA MASAHIRO, 100–114
YOSHIDA MINORU, 152–182, 375–386
YOSHIDA MITSUHIRO, 152–182
YOSHIDA SHIGETO, 375–386
YOSHIDA SHINJI, 401–410
YOSHIDA TAKASHI, 375–386
YOSHIDA YASUNORI, 242–261
YOSHIE NAOKO, 317–325
YOSHIE SATOMI, 469–479
YOSHIGA NORIO, 100–114
YOSHIHARA TOSHIAKI, 317–325
YOSHII FUMIO, 100–114, 290–299, 345–359
YOSHIKAWA SEISHI, 152–182, 515–528
YOSHIMOTO SEI, 345–359
YOSHIMURA KAZUKO, 242–261, 345–359, 423–429
YOSHIMURA MASAFUMI, 242–261
YOSHIMURA MASAJI, 152–182
YOSHINO TAIKI, 152–182
YOSHIOKA TAKAHIDE, 152–182, 345–359
YOSHITOME HIDEO, 401–410
YOSOMIYA RYUTOKU, 423–429
YOU YOUNG SUN, 362, 375–386
YOUNG TERRILL ALAN, 242–261, 375–386
YPACEK FRANTISEK, 439–445
YU GA-ER, 290–299
YU XIAOYAN, 423–429
YUAN YIN, 242–261, 423–429
YUHONG L, 44t–74t
YUI YASUSHI, 317–325
YUKE ZHONG, 242–261
YUKINO TOSHINORI, 44t–74t
YUKSEL K UMIT, 345–359
YUMING GUO, 317–325
YUN SHEN, 401–410
YUUCHI MINAKO, 454–458

Z
ZAALISHVILI M M, 44t–74t
ZACHMANN G, 515–528
ZANETTI M, 515–528
ZEIN IWAN, 316–325
ZELLER HEINZ, 44t–74t
ZELLER MARK ASHTON, 423–429
ZGAVERDEA ALINA CORINA, 152–182
ZHAN XUEDONG, 454–458
ZHANG JIANWEI, 270–275
ZHANG LIZHEN, 423–429
ZHANG QINGXIN, 423–429
ZHANG QIUCHEN PETER, 317–325
ZHANG SU SHE, 345–359
ZHANG TONGTONG, 152–182
ZHANG YELI, 290–299
ZHAO FENGHUA, 423–429
ZHAO XIAOJIANG, 152–182
ZHENMING CHEN, 423–429
ZHIFEI CHEN, 199–213
ZHIKAI TAO, 317–325
ZHONG LUHUA, 290–299
ZHONGHUA B, 44t–74t
ZHOU QINGHAI, 152–182
ZHOU Z-Z, 44t–74t
ZHU LINFANG, 454–458
ZHU X, 44t–74t
ZHU X-X, 44t–74t
ZHUOHUA TAN, 423–429
ZIERENBERG BERND, 242–261
ZIMMERMAN SCOTT ALLEN, 439–445
ZOU WAN KANG, 454–458
ZUCCATO ALESSANDRO, 317–325
ZUPANCICH JOHN ANDREW, 44t–74t

Index of Patents

Note: Page numbers with "f" and "t" denote figures and tables, respectively.

A

AR042799 A1, 401–410
AR059725 A1, 290–299
AR062138 A1, 242–261
AR072203 A1, 290–299
AR072204 A1, 345–359
AR072205 A1, 290–299
AR205109 A1, 100–114
AR213619 A1, 44t–74t
AR223433 A1, 152–182
AR230840 A1, 152–182
AR244703 A1, 44t–74t
AR245159 A1, 375–386
AR247411 A1, 152–182
AT101035 T, 242–261
AT106409 T, 44t–74t
AT109813 T, 152–182
AT113635 T, 152–182
AT131831 T, 44t–74t
AT139573 T, 270–275
AT145657 T, 44t–74t
AT150058 T, 100–114, 152–182
AT152130 T, 152–182
AT152466 T, 152–182
AT155161 T, 100–114, 152–182
AT156166 T, 152–182
AT163304 T, 44t–74t
AT163883 T, 375–386
AT167886 T, 375–386
AT170575 T, 401–410
AT171076 T, 44t–74t
AT171465 T, 152–182
AT173753 T, 469–479
AT177054 T, 317–325
AT177768 T, 290–299
AT179196 T, 199–213
AT179757 T, 199–213, 439–445
AT187477 T, 469–479
AT192765 T, 290–299
AT193718 T, 439–445
AT198980 T, 290–299
AT199383 T, 100–114, 152–182
AT200501 T, 44t–74t
AT205869 T, 152–182
AT207104 T, 199–213, 401–410, 469–479
AT209669 T, 44t–74t
AT210702 T, 152–182
AT211157 T, 242–261
AT217331 T, 345–359
AT218585 T, 44t–74t
AT218601 T, 44t–74t
AT219782 T, 290–299
AT219786 T, 439–445
AT224414 T, 152–182
AT225378 T, 290–299
AT230772 T, 317–325
AT234894 T, 44t–74t
AT236207 T, 44t–74t
AT238068 T, 199–213
AT242272 T, 270–275
AT242295 T, 152–182
AT245671 T, 345–359
AT252114 T, 199–213, 270–275, 290–299
AT254531 T, 439–445
AT264355 T, 152–182
AT265485 T, 152–182
AT265493 T, 199–213
AT266434 T, 290–299
AT275603 T, 423–429
AT277208 T, 401–410
AT285432 T, 44t–74t
AT286929 T, 345–359
AT290047 T, 199–213, 469–479
AT300423 T, 242–261
AT306905 T, 44t–74t
AT314410 T, 100–114, 401–410
AT321803 T, 44t–74t
AT323736 T, 345–359
AT328035 T, 100–114
AT332949 T, 469–479
AT335795 T, 454–458
AT336537 T, 199–213
AT337382 T, 199–213, 401–410, 469–479
AT340825 T, 152–182
AT342793 T, 423–429
AT342936 T, 242–261
AT346878 T, 44t–74t
AT348643 T, 439–445
AT349476 T, 44t–74t, 100–114, 152–182
AT354600 T, 44t–74t
AT354607 T, 375–386
AT356847 T, 317–325
AT356903 B, 44t–74t
AT357468 T, 44t–74t
AT364708 T, 199–213
AT368770 B, 152–182
AT373684 T, 345–359
AT376433 T, 44t–74t
AT377060 T, 152–182, 469–479
AT383386 T, 469–479
AT383462 T, 401–410
AT384615 B, 44t–74t
AT386075 T, 290–299
AT388182 T, 100–114
AT394452 T, 152–182
AT395319 B, 270–275
AT398655 T, 152–182
AT403694 T, 199–213
AT407967 T, 242–261
AT434045 T, 44t–74t
AT437992 T, 401–410
AT444983 T, 44t–74t
AT448266 T, 290–299
AT448274 T, 44t–74t
AT450146 T, 100–114
AT450556 T, 100–114, 242–261
AT452940 T, 152–182
AT459687 T, 152–182
AT461942 T, 199–213
AT468372 T, 152–182
AT469035 T, 44t–74t
AT478696 T, 439–445
AT478909 T, 290–299
AT482999 T, 152–182, 375–386
AT489415 T, 100–114, 242–261
AT492389 T, 375–386
AT504630 T, 242–261
AT505462 A1, 515–528
AT506395 T, 439–445
AT506489 A1, 515–528
AT506489 B1, 515–528
AT509985 T, 152–182
AT510898 T, 290–299, 469–479
AT514748 T, 152–182
AT518912 T, 152–182
AT518932 T, 152–182, 469–479
AT522571 T, 199–213
AT523552 T, 345–359
AT525423 T, 345–359
AT529242 T, 375–386
AT531757 T, 152–182
AT533811 T, 345–359
AT536386 T, 345–359
AT538176 T, 100–114, 242–261
AT547476 T, 152–182
AT552958 T, 515–528
AT66685 T, 375–386
AT84806 T, 199–213
AT99719 T, 152–182
ATA673778 A, 152–182

AU1041676 A, 44t–74t
AU1056895 A, 100–114
AU1112995 A, 317–325
AU1275088 A, 44t–74t
AU1278000 A, 44t–74t
AU1446599 A, 44t–74t
AU1552200 A, 44t–74t
AU1650992 A, 100–114, 152–182
AU1670592 A, 152–182
AU1680688 A, 199–213
AU1680995 A, 100–114, 401–410
AU1709099 A, 100–114
AU1774700 A, 44t–74t
AU1854301 A, 152–182, 290–299
AU1858288 A, 44t–74t
AU1876399 A, 44t–74t
AU1942999 A, 44t–74t
AU2001272206 B2, 423–429
AU2001287015 B2, 44t–74t
AU2001297782 B2, 345–359
AU2002225713 A8, 515–528
AU2002236346 A1, 469–479
AU2002237289 A1, 152–182
AU2002252982 B2, 152–182
AU2002309622 B2, 469–479
AU2002309683 B2, 401–410
AU2002310868 B2, 375–386
AU2002310868 B8, 375–386
AU2002316857 B2, 375–386
AU2002324595 B2, 242–261
AU2002338496 B2, 242–261
AU2002343784 B2, 100–114, 242–261
AU2002343784 C1, 100–114, 242–261
AU2002347788 A1, 199–213
AU2002347788 B2, 199–213
AU2002348306 A1, 439–445
AU2002349540 A1, 345–359
AU2002349540 B2, 345–359
AU2002350935 A1, 317–325
AU2002357605 A1, 44t–74t
AU2002357605 B2, 44t–74t
AU2002357605 B9, 44t–74t
AU2003201583 B2, 454–458
AU2003213398 A1, 100–114
AU2003215495 A1, 439–445
AU2003215495 B2, 439–445
AU2003220893 A1, 317–325
AU2003225805 A1, 345–359, 401–410
AU2003225805 A8, 345–359, 401–410
AU2003231482 A1, 515–528
AU2003241542 A1, 290–299
AU2003242308 A1, 44t–74t
AU2003252345 A1, 515–528
AU2003264393 A1, 100–114
AU2003266709 A1, 270–275
AU2003277546 A1, 199–213, 439–445
AU2003293173 A1, 401–410
AU2003293173 A8, 401–410
AU2003297236 A1, 317–325
AU2004215733 A1, 242–261
AU2004312517 A1, 242–261
AU2004312517 B2, 242–261
AU2005209541 A1, 270–275
AU2005209541 B2, 270–275
AU2005285159 A1, 375–386
AU2006229153 A1, 152–182, 345–359
AU2006280452 A1, 454–458
AU2006289625 A1, 290–299
AU2006289625 B2, 290–299
AU2006322085 A1, 401–410
AU2007218992 A1, 100–114, 152–182, 242–261
AU2007218993 A1, 100–114, 242–261, 423–429
AU2007218994 A1, 100–114
AU2007218995 A1, 100–114, 242–261
AU2007218996 A1, 100–114, 242–261
AU2007277961 A1, 242–261, 317–325
AU2007277961 B2, 242–261, 317–325
AU2007278752 A1, 242–261
AU2007285951 A1, 270–275
AU2007285951 B2, 270–275
AU2007292008 A1, 401–410
AU2007302005 A1, 152–182
AU2007302005 B2, 152–182
AU2007302010 A1, 152–182
AU2007302010 B2, 152–182
AU2007313630 A1, 152–182
AU2007321746 A1, 515–528
AU2007321746 B2, 515–528
AU2007329122 A1, 44t–74t
AU2008211581 A1, 345–359
AU2008211581 B2, 345–359
AU2008241682 A1, 345–359
AU2008241682 B2, 345–359
AU2008264647 A1, 100–114
AU2008264647 B2, 100–114
AU2008282212 A1, 317–325
AU2008331448 A1, 44t–74t
AU2009202657 A1, 317–325
AU2009214810 A1, 515–528
AU2009229151 A1, 44t–74t
AU2009311259 A1, 152–182, 242–261
AU2009322983 A1, 345–359
AU2010206743 A1, 439–445
AU2010237248 A1, 515–528
AU2010237249 A1, 488, 495, 502, 515–528
AU2010243295 A1, 44t–74t
AU2010251208 A1, 152–182
AU2010251208 B2, 152–182
AU2010254741 A1, 270–275
AU2010276083 A1, 152–182
AU2010280940 A1, 515–528
AU2010294423 A1, 515–528
AU2010294818 A1, 375–386
AU2010312243 A1, 242–261
AU2010312244 A1, 242–261
AU2010331906 A1, 44t–74t
AU2010334423 A1, 152–182
AU2010337977 A1, 152–182
AU2011206716 A1, 345–359
AU2011251907 A1, 345–359
AU2011256163 A1, 515–528
AU2011277960 A1, 152–182
AU2011291705 A1, 401–410
AU2012226557 A1, 152–182
AU2068188 A, 44t–74t
AU2097097 A, 242–261
AU2124177 A, 100–114
AU2198083 A, 199–213
AU2352288 A, 242–261
AU2432295 A
AU2467300 A, 199–213, 270–275, 290–299
AU2509397 A, 317–325
AU2571302 A, 515–528
AU2582702 A, 290–299, 469–479
AU2623100 A, 44t–74t
AU2684095 A, 199–213, 439–445
AU2693997 A, 469–479
AU2727884 A, 199–213
AU2784599 A, 290–299
AU2798492 A, 345–359
AU2836392 A, 152–182
AU2870895 A, 469–479
AU2887689 A, 152–182
AU2913495 A, 345–359
AU2925395 A, 152–182
AU2978195 A, 44t–74t
AU3081700 A, 270–275
AU3114095 A, 152–182, 199–213, 439–445
AU3188295 A, 199–213
AU3264297 A, 199–213
AU3360197 A, 199–213
AU3521984 A, 44t–74t
AU3843889 A, 44t–74t
AU3877200 A, 290–299
AU3932395 A, 439–445
AU3976278 A, 152–182
AU4027700 A, 44t–74t
AU4223889 A, 133–135, 152–182
AU4286701 A, 423–429
AU4349600 A, 44t–74t
AU4351800 A, 44t–74t
AU4429399 A, 199–213
AU4533993 A, 375–386
AU4557496 A, 44t–74t
AU4557496 A, 100–114, 152–182
AU4583302 A, 345–359
AU4631196 A, 199–213, 439–445
AU4644700 A, 44t–74t
AU4668996 A, 199–213
AU4717996 A, 44t–74t
AU4787096 A, 44t–74t
AU4856096 A, 152–182
AU4882501 A, 199–213
AU4952296 A, 152–182
AU4958401 A, 152–182
AU5040799 A, 423–429, 439–445
AU5080001 A, 270–275
AU512448 B2, 100–114
AU5133293 A, 469–479
AU5156799 A, 199–213
AU5159896 A, 439–445
AU5277696 A, 439–445
AU5278601 A, 345–359
AU529981 B2, 100–114, 199–213
AU5316296 A, 242–261
AU5350294 A, 439–445
AU537455 B2, 152–182
AU5426894 A, 152–182
AU543991 B2, 44t–74t
AU5472198 A, 44t–74t

AU5497273 A, 152–182
AU5523499 A, 44t–74t
AU5560680 A, 100–114, 199–213
AU5588090 A, 152–182
AU5588190 A, 152–182
AU560653 B2, 44t–74t
AU5664098 A, 44t–74t
AU5703490 A, 152–182
AU572811 B2, 199–213
AU5750090 A, 152–182
AU576795 B2, 44t–74t
AU5806490 A, 152–182
AU5837694 A, 375–386
AU5860798 A, 199–213
AU5862501 A, 454–458
AU5921390 A, 152–182
AU5926899 A, 345–359
AU599612 B2, 345–359
AU599761 B2, 44t–74t
AU602110 B2, 44t–74t
AU603076 B2, 375–386
AU605883 B2, 44t–74t
AU609194 B2, 242–261
AU610594 B2, 199–213
AU617411 B2, 152–182
AU623012 B2, 152–182
AU628175 B2, 152–182
AU633928 B2, 152–182
AU634123 B2, 152–182
AU636570 B, 44t–74t
AU637685 B2, 152–182
AU641603 B2, 152–182
AU6429901 A, 199–213
AU643154 B2, 469–479
AU6439800 A, 345–359
AU6499896 A, 199–213, 401–410, 469–479
AU6515986 A, 345–359
AU658180 B2, 100–114, 152–182
AU659353 B2, 469–479
AU6601286 A, 375–386
AU660266 B2, 439–445
AU664831 B2, 100–114, 152–182
AU6667696 A, 317–325
AU674361 B2, 152–182
AU677787 B2, 270–275
AU681589 B2, 375–386
AU681862 B2, 375–386
AU684303 B2, 242–261, 290–299
AU685135 B2, 469–479
AU6890796 A, 199–213, 469–479
AU689130 B2, 469–479
AU690304 B2, 345–359
AU691317 B2, 44t–74t
AU6943196 A, 439–445
AU695820 B2, 152–182
AU6971598 A, 100–114, 199–213
AU6974398 A, 199–213
AU699166 B2, 469–479
AU703156 B2, 100–114
AU705499 B2, 152–182
AU710136 B2, 199–213, 469–479
AU7220601 A, 423–429
AU7259698 A, 401–410
AU729239 B2, 469–479
AU729305 B2, 44t–74t
AU733819 B2, 439–445
AU742248 B2, 401–410
AU746769 B2, 199–213
AU7481591 A, 152–182
AU7486798 A, 44t–74t
AU750072 B2, 423–429, 439–445
AU751610 B2, 44t–74t
AU7516294 A, 242–261, 290–299
AU751861 B2, 290–299
AU7586298 A, 439–445
AU760358 B, 44t–74t
AU7604894 A, 469–479
AU760508 B2, 199–213, 270–275, 290–299
AU765200 B2, 270–275
AU766760 B2, 345–359
AU770579 B2, 44t–74t
AU775913 B2, 44t–74t
AU778081 B2, 44t–74t
AU778497 B2, 44t–74t
AU7822275 A, 100–114
AU7996291 A, 270–275
AU8133694 A, 44t–74t
AU8410882 A, 44t–74t
AU8506898 A, 439–445
AU8587998 A, 100–114
AU8701501 A, 44t–74t
AU9105091 A, 100–114, 152–182
AU9396898 A, 290–299
AU9820098 A, 100–114

B

BE1018716 A3, 515–528
BE1018850 A3, 515–528
BE1018882 A3, 515–528
BE1019608 A3, 515–528
BE654236 A, 93–94, 100–114
BE721809 A, 469–479
BE758156 A4, 242–261
BE799132 A1, 152–182
BE802562 A1, 152–182
BE837935 A1, 39–41
BE850332 A1, 81, 100–114
BE870457 A1, 147–148, 152–182
BE888829 A1, 44t–74t
BR0007703 A, 199–213, 270–275, 290–299
BR0007703 B1, 199–213, 270–275, 290–299
BR0013315 A, 44t–74t
BR0113483 A, 152–182
BR0113483 B1, 152–182
BR0115158 A, 515–528
BR0202107 A, 345–359
BR0209393 A, 469–479
BR0211556 A, 242–261
BR0213106 A, 199–213
BR0314749 A, 270–275
BR0315787 A, 199–213, 439–445
BR0317157 A, 317–325
BR0317787 A, 401–410
BR7531268 A, 100–114
BR7600499 A, 44t–74t
BR7806072 A, 152–182
BR8306929 A, 199–213
BR8605989 A, 375–386
BR8704814 A, 44t–74t
BR8800838 A, 44t–74t
BR8803120 A, 44t–74t
BR8803404 A, 44t–74t
BR8803664 A, 152–182
BR8806902 A, 199–213
BR8900350 A, 152–182
BR9002600 A, 152–182
BR9002601 A, 152–182
BR9002792 A, 152–182
BR9002853 A, 152–182
BR9003200 A, 152–182
BR9104633 A, 152–182
BR9106821 A, 242–261
BR9107138 A, 100–114, 152–182
BR9205258 A, 100–114, 152–182
BR9305657 A, 439–445
BR9306621 A, 375–386
BR9306756 A, 270–275
BR9407212 A, 242–261, 290–299
BR9506664 A, 100–114, 401–410
BR9509685 A, 152–182
BR9714065 A, 44t–74t
BR9806955 A, 44t–74t
BR9809136 A, 439–445
BR9815471 A, 401–410
BR9815471 B1, 401–410
BR9907968 A, 290–299
BR9907968 B1, 290–299
BR9909283 A, 100–114, 439–445
BR9909283 B1, 100–114, 439–445
BR9913784 A, 345–359
BR9913784 B1, 345–359
BR9916691 A, 270–275
BR9916691 B1, 270–275
BRPI0413432 A, 199–213
BRPI0413559 A, 199–213
BRPI0515700 A, 375–386
BRPI0519835 A2, 152–182
BRPI0520831 A2, 313, 317–325
BRPI0600681 A, 100–114, 152–182, 242–261
BRPI0600683 A, 100–114, 242–261, 423–429
BRPI0600782 A, 100–114
BRPI0600783 A, 100–114, 242–261
BRPI0600787 A, 100–114, 242–261
BRPI0601137 A, 44t–74t
BRPI0605169 A, 44t–74t
BRPI0605173 A, 44t–74t
BRPI0612775 A2, 515–528
BRPI0620442 A2, 100–114
BRPI0620556 A2, 401–410
BRPI0708460 A2, 290–299
BRPI0715054 A2, 242–261
BRPI0715276 A2, 152–182
BRPI0716443 A2, 401–410
BRPI0716663 A2, 270–275

C

CA1011028 A1, 152–182
CA1045548 A1, 100–114
CA1087345 A1, 44t–74t
CA1089136 A1, 152–182

CA1091600 A1, 100–114
CA1110384 A1, 152–182
CA1133686 A, 515–528
CA1171579 A1, 152–182, 375–386
CA1186438 A1, 44t–74t
CA1218175 A1, 152–182
CA1219101 A1, 199–213
CA1274339 A1, 44t–74t
CA1283051 C, 345–359
CA1288922 C, 375–386
CA1292168 C, 270–275
CA1292818 C, 401–410
CA1293170 C, 199–213
CA1311237 C, 44t–74t
CA1324477 C, 152–182
CA1328711 C, 44t–74t
CA1333770 C, 242–261
CA1334224 C, 152–182
CA1340020 C, 199–213
CA1340634 C, 44t–74t
CA2016976 A1, 152–182
CA2017654 A1, 152–182
CA2017655 A1, 152–182
CA2017655 C, 152–182
CA2018785 A1, 152–182
CA2019084 A1, 152–182
CA2020150 A1, 152–182
CA2029747 A1, 124–125, 152–182
CA2029747 C, 152–182
CA2037340 A1, 152–182
CA2037340 C, 152–182
CA2060650 A1, 152–182
CA2068368 A1, 375–386
CA2076038 A1, 199–213, 367, 375–386, 431, 439–445
CA2076038 C, 199–213, 375–386, 439–445
CA2079535 A1, 469–479
CA2079768 A1, 152–182
CA2079768 C, 152–182
CA2082051 A1, 152–182
CA2083697 A1, 268, 270–275
CA2084994 A1, 100–114, 152–182
CA2084994 C, 100–114, 152–182
CA2087444 A1, 152–182
CA2087444 C, 152–182
CA2095536 A1, 100–114, 152–182
CA2095536 C, 100–114, 152–182
CA2098220 A1, 503–504, 515–528
CA2107018 A1, 345–359
CA2121507 C, 515–528
CA2124846 A1, 439–445
CA2124846 C, 439–445
CA2126849 A1, 469–479
CA2126849 C, 469–479
CA2127463 A1, 290–299
CA2127463 C, 290–299
CA2127754 A1, 392–393, 401–410
CA2137794 A1, 270–275
CA2138120 A1, 375–386
CA2138120 C, 375–386
CA2147857 A1, 152–182
CA2153807 A1, 375–386
CA2153807 C, 375–386
CA2153998 A1, 317–325
CA2168041 A1, 242–261, 290–299
CA2168041 C, 242–261, 290–299
CA2173753 A1, 469–479
CA2177065 A1, 317–325
CA2181791 A1, 100–114
CA2181791 C, 100–114
CA2181795 A1, 100–114, 401–410
CA2181795 C, 100–114, 401–410
CA2194001 A1, 345–359
CA2194681 A1, 469–479
CA2194681 C, 469–479
CA2196698 A1, 290–299
CA2196698 C, 290–299
CA2197782 A1, 199–213
CA2202676 A1, 41
CA2205071 A1, 152–182
CA2205071 C, 152–182
CA2205072 A1, 44t–74t
CA2205072 C1, 44t–74t
CA2217541 A1, 152–182
CA2217640 A1, 439–445
CA2226864 A1, 199–213, 401–410, 469–479
CA2226864 C, 199–213, 401–410, 469–479
CA2231568 A1, 242–261
CA2251821 A1, 469–479
CA2251829 A1, 317–325
CA2263290 A1, 44t–74t
CA2275033 A1, 44t–74t
CA2275033 C, 44t–74t
CA2277279 A1, 44t–74t
CA2287952 A1, 401–410
CA2287952 C, 401–410
CA2288661 A1, 290–299
CA2291172 A1, 439–445
CA2291172 C, 439–445
CA2298327 A1, 242–261
CA2298327 C, 242–261
CA2313192 A1, 44t–74t
CA2313516 A1, 44t–74t
CA2313516 C, 44t–74t
CA2314151 A1, 44t–74t
CA2316190 A1, 290–299
CA2316190 C, 290–299
CA2325046 A1, 100–114, 439–445
CA2325046 C, 100–114, 439–445
CA2333005 A1, 199–213
CA2336898 A1, 423–429, 439–445
CA2336898 C, 423–429, 439–445
CA2342723 A1, 44t–74t
CA2344378 A1, 345–359
CA2344378 C, 345–359
CA2350418 C, 44t–74t
CA2355206 A1, 283, 290–299
CA2357032 A1, 270–275
CA2357032 C, 270–275
CA2360801 A1, 44t–74t
CA2360801 C, 44t–74t
CA2361722 A1, 199–213, 270–275, 290–299
CA2361722 C, 199–213, 270–275, 290–299
CA2368470 A1, 44t–74t
CA2368470 C, 44t–74t
CA2368617 A1, 290–299
CA2368617 C, 290–299
CA2369758 A1, 44t–74t
CA2369758 C, 44t–74t
CA2370330 A1, 44t–74t
CA2370330 C, 44t–74t
CA2370357 A1, 44t–74t
CA2370357 C, 44t–74t
CA2380616 C, 44t–74t
CA2388585 A1, 345–359
CA2388585 C, 345–359
CA2389245 A1, 152–182, 290–299
CA2415642 A1, 423–429
CA2419180 A1, 345–359
CA2419180 C, 345–359
CA2419429 A1, 44t–74t
CA2419429 C, 44t–74t
CA2419574 A1, 152–182
CA2419574 C, 152–182
CA2423601 C, 515–528
CA2425935 A1, 345–359
CA2425935 C, 345–359
CA2434763 A1, 152–182
CA2434763 C, 152–182
CA2443161 A1, 375–386
CA2443161 C, 375–386
CA2445845 A1, 375–386
CA2445885 A1, 469–479
CA2445885 C, 469–479
CA2446092 A1, 401–410
CA2446092 C, 401–410
CA2462460 A1, 199–213
CA2462460 C, 199–213
CA2464635 A1, 100–114
CA2464635 C, 100–114, 242–261
CA2468929 A1, 469–479
CA2468929 C, 469–479
CA2472420 A1, 375–386
CA2472420 C, 375–386
CA2473519 A1, 454–458
CA2476431 A1, 439–445
CA2478883 A1, 199–213
CA2486312 A1, 44t–74t
CA2499607 A1, 270–275
CA2503590 A1, 44t–74t, 199–213, 439–445
CA2533553 A1, 199–213
CA2534619 A1, 199–213
CA2541366 A, 30
CA2546107 A1, 199–213
CA2550009 A1, 242–261
CA2550009 C, 242–261
CA2568765 A1, 30
CA2578635 A1, 375–386
CA2578635 C, 375–386
CA2583529 A1, 375–386
CA2598470 A1, 100–114, 199–213, 439–445
CA2602145 A1, 199–213
CA2602145 C, 199–213
CA2620378 A1, 401–410
CA2621824 A1, 290–299
CA2628565 A1, 401–410
CA2630563 A1, 375–386
CA2631449 A1, 100–114
CA2631449 C, 100–114
CA2641922 A1, 100–114, 152–182, 242–261
CA2641924 A1, 100–114, 242–261, 423–429
CA2641925 A1, 100–114

CA2641926 A1, 100–114, 242–261
CA2641927 A1, 100–114, 242–261
CA2644444 A1, 290–299
CA2658794 A1, 242–261, 317–325
CA2659123 A1, 242–261
CA2660612 A1, 270–275
CA2662105 A1, 152–182
CA2662400 A1, 401–410
CA2662446 A1, 152–182
CA2666341 A1, 515–528
CA2666341 C, 515–528
CA2668902 A1, 515–528
CA2670850 A1, 317–325
CA2672476 A1, 345–359
CA2672476 C, 345–359
CA2675473 A1, 345–359
CA2692189 A1, 100–114
CA2692189 C, 100–114
CA2694935 A1, 317–325
CA2699868 A1, 345–359
CA2710098 A1, 100–114, 242–261
CA2710098 C, 100–114, 242–261
CA2712709 A1, 242–261
CA2715048 A1, 515–528
CA2718279 A1, 44t–74t
CA2722282 A1, 454–458
CA2722940 A1, 152–182
CA2727016 A1, 290–299
CA2733581 A1, 317–325
CA2733616 A1, 44t–74t
CA2734102 A1, 44t–74t
CA2739669 A1, 317–325
CA2740142 A1, 345–359
CA2742933 A1, 152–182, 242–261
CA2743866 A1, 439–445
CA2745223 A1, 345–359
CA2762988 A1, 152–182
CA2763986 A1, 152–182
CA2768708 A1, 152–182
CA2774742 A1, 375–386
CA2775121 A1, 345–359
CA2775703 A1, 44t–74t, 100–114, 242–261
CA2776946 A1, 242–261
CA2776948 A1, 242–261
CA2778582 A1, 345–359
CA2782989 A1, 44t–74t
CA2787222 A1, 345–359
CA2794960 A1, 270–275
CA2797285 A1, 345–359
CA2801706 A1, 270–275
CA2807164 A1, 401–410
CA2828190 A1, 152–182
CA2833131 A1, 44t–74t
CA2833131 A1, 152–182, 242–261
CA2836044 A1, 439–445
CA2840783 A1, 375–386
CA2844149 A1, 515–528
CA982007 A1, 242–261
CH250077 A, 37
CH573752 A5, 242–261
CH618455 A5, 100–114
CH635355 A5, 44t–74t
CH644880 A5, 152–182
CH644881 A5, 152–182
CH657369 A5, 44t–74t
CH680590 A5, 152–182
CN100344679 C, 345–359
CN100344680 C, 345–359
CN100365050 C, 199–213
CN100378138 C, 152–182
CN100378186 C, 469–479
CN100379803 C, 242–261
CN100379806 C, 100–114, 439–445
CN100381501 C, 199–213
CN100384937 C, 100–114, 242–261
CN100413906 C, 100–114
CN100419023 C, 242–261
CN100419034 C, 454–458
CN100427153 C, 423–429
CN100429338 C, 100–114, 401–410
CN100432124 C, 270–275
CN100434475 C, 242–261
CN100436271 C, 44t–74t
CN100439439 C, 152–182
CN100447199 C, 100–114
CN100475808 C, 515–528
CN100523064 C, 345–359
CN100528544 C, 100–114
CN101007853 A, 199–213
CN101007853 B, 199–213
CN101009979 A, 317–325
CN101023133 A, 152–182
CN101023133 B, 152–182
CN101024843 A, 44t–74t
CN101035861 A, 152–182
CN101035861 B, 152–182
CN101124280 A, 100–114, 199–213, 439–445
CN101125929 A, 290–299
CN101130627 A, 485, 515–528
CN101130627 B, 515–528
CN101133121 A, 242–261
CN101133121 B, 242–261
CN101146663 A, 345–359
CN101146663 B, 345–359
CN101146851 A, 287, 290–299
CN101151310 A, 152–182, 345–359
CN101151310 B, 152–182, 345–359
CN101175819 A, 423–429
CN101175819 B, 423–429
CN101184597 A, 345–359
CN101184597 B, 345–359
CN101225221 A, 305–306, 317–325
CN101225221 B, 317–325
CN101230129 A, 482, 515–528
CN101238161 A, 44t–74t
CN101238161 B, 44t–74t
CN101268123 A, 270–275
CN101268123 B, 270–275
CN101268125 A, 345–359
CN101268125 B, 345–359
CN101275009 A, 485, 488, 515–528
CN101275009 B, 515–528
CN101296958 A, 44t–74t
CN101296958 B, 44t–74t
CN101305052 A, 290–299
CN101305052 B, 290–299
CN101321828 A, 401–410
CN101321828 B, 401–410
CN101326056 A, 401–410
CN101346416 A, 199–213
CN101346416 B, 199–213
CN101370860 A, 345–359
CN101370860 B, 345–359
CN101384662 A2, 100–114
CN101389677 A, 100–114
CN101395199 A, 290–299
CN101395199 B, 290–299
CN101469072 A, 222, 242–261, 418, 423–429
CN101469072 B, 242–261, 423–429
CN101470366 A, 454–458
CN101470366 B, 454–458
CN101484528 A, 100–114, 152–182
CN101484528 B, 100–114, 152–182
CN101495290 A, 242–261, 317–325
CN101495290 B, 242–261, 317–325
CN101495568 A, 152–182
CN101495568 B, 152–182
CN101503521 A, 222, 242–261, 414, 423–429
CN101516996 A, 242–261
CN101516996 B, 242–261
CN101516997 A, 152–182
CN101516997 B, 152–182
CN101522797 A, 152–182
CN101528844 A, 152–182
CN101528844 B, 152–182
CN101528994 A, 401–410
CN101535018 A, 515–528
CN101535397 A, 270–275
CN101535397 B, 270–275
CN101538400 A, 188, 199–213
CN101541887 A, 152–182
CN101541887 B, 152–182
CN101589097 A, 152–182
CN101628972 A, 18
CN101628972 B, 44t–74t
CN1016346 B, 44t–74t
CN101646539 A, 345–359
CN101646539 B, 345–359
CN101657428 A, 199–213
CN101657470 A, 199–213
CN101657470 B, 199–213
CN101665618 A, 152–182
CN101665618 B, 152–182
CN101668779 A, 199–213
CN101668779 B, 199–213
CN101675101 A, 345–359
CN101675101 B, 345–359
CN101678642 A, 317–325
CN101678642 B, 317–325
CN101678920 A, 317–325
CN101678920 B, 317–325
CN101679733 A, 401–410
CN101775199 A, 124, 152–182
CN101775199 B, 152–182
CN101778902 A, 100–114
CN101778902 B, 100–114
CN101784588 A, 242–261
CN101784588 B, 242–261
CN101809223 A, 152–182, 290–299
CN101809223 B, 152–182, 290–299
CN101815454 A, 317–325
CN101918211 A, 152–182, 375–386

CN101942182 A, 152–182
CN101942182 B, 152–182
CN101942183 A, 152–182
CN101942183 B, 152–182
CN101945743 A, 515–528
CN101945749 A, 100–114, 375–386
CN101970530 A, 44t–74t
CN101970547 A, 242–261
CN102002148 A, 17
CN102002148 B, 44t–74t
CN102007192 A, 469–479
CN102027059 A, 152–182
CN102027059 B, 152–182
CN102056985 A, 152–182
CN102071492 A, 398, 401–410
CN102086322 A, 454–458
CN102089351 A, 44t–74t
CN102105311 A, 152–182
CN102105311 B, 152–182
CN102112519 A, 290–299
CN102112559 A, 375–386
CN102115576 A, 152–182
CN102119178 A, 152–182
CN102119186 A, 469–479
CN102119186 B, 469–479
CN102131796 A, 44t–74t
CN102167890 A, 242–261
CN102167893 A, 375–386
CN102167893 B, 375–386
CN102167894 A, 222, 242–261, 419, 423–429
CN102167894 B, 242–261, 423–429
CN102171289 A, 100–114
CN102177195 A, 345–359
CN102181137 A, 138, 152–182
CN102190874 A, 100–114
CN102197067 A, 152–182
CN102197067 B, 152–182
CN102239185 A, 44t–74t
CN102264912 A, 515–528
CN102282197 A, 152–182, 242–261
CN102325931 A, 100–114, 401–410
CN102348672 A, 515–528
CN102348673 A, 515–528
CN102348772 A, 439–445
CN102357943 A, 515–528
CN102369234 A, 270–275
CN102369234 B, 270–275
CN102372911 A, 220, 242–261
CN102395719 A, 401–410
CN102395720 A, 401–410
CN102407633 A, 345–359
CN102414247 A, 44t–74t
CN102438832 A, 152–182, 375–386
CN102459391 A, 44t–74t
CN102471473 A, 44t–74t
CN102482369 A, 515–528
CN102482447 A, 515–528
CN102482461 A, 152–182
CN102498151 A, 515–528
CN102498151 B, 515–528
CN102504311 A, 310, 317–325
CN102504503 A, 416, 423–429
CN102504503 B, 423–429
CN102504506 A, 126, 152–182
CN102532832 A, 412, 423–429
CN102549094 A, 469–479
CN102549094 B, 469–479
CN102573818 A, 345–359
CN102574374 A, 152–182
CN102575076 A, 100–114, 242–261
CN102575131 A, 469–479
CN102575132 A, 469–479
CN102582173 A, 345–359
CN102585200 A, 44t–74t
CN102603643 A, 199–213
CN102617999 A, 345–359
CN102627935 A, 460, 469–479
CN102627935 B, 469–479
CN102665635 A, 152–182
CN102675207 A, 199–213
CN102712801 A, 345–359
CN1027726 C, 44t–74t
CN102791793 A, 152–182
CN102834458 A, 242–261
CN102862282 A, 270–275
CN102869724 A, 242–261
CN102884115 A, 345–359
CN102892817 A, 375–386
CN102892820 A, 242–261, 375–386
CN102892826 A, 345–359
CN102892936 A, 515–528
CN102898667 A, 100–114
CN102918086 A, 270–275
CN102971432 A, 44t–74t
CN102993653 A, 370–371, 375–386
CN103003360 A, 152–182
CN103003362 A, 152–182
CN103025933 A, 401–410
CN103030791 A, 419, 423–429
CN103061162 A, 421, 423–429
CN103097128 A, 317–325
CN103097441 A, 375–386
CN1031314 A, 44t–74t
CN1031380 A, 44t–74t
CN103154338 A, 401–410
CN1032213 C, 152–182
CN103228713 A, 464, 469–479
CN103232694 A, 100–114
CN103260840 A, 242–261
CN103261259 A, 290–299
CN103261299 A, 345–359
CN1032919 C, 152–182
CN103305053 A, 452, 454–458
CN103429503 A, 439–445
CN103429675 A, 454–458
CN103459498 A, 152–182, 242–261
CN1034872 C, 152–182
CN1036215 A, 152–182
CN103703077 A, 375–386
CN1048549 A, 152–182
CN1048551 A, 152–182
CN1048552 A, 152–182
CN1050390 A, 152–182
CN1050391 A, 152–182
CN1062740 A, 100–114, 152–182
CN1068277 C, 375–386
CN1071341 C, 100–114, 401–410
CN1071342 C, 152–182
CN1072245 C, 100–114, 152–182
CN1075527 C, 44t–74t
CN1076358 C, 100–114, 152–182
CN1085493 A, 375–386
CN1088723 C, 345–359
CN1097603 C, 100–114
CN1131281 C, 100–114, 152–182
CN1139936 A, 100–114, 401–410
CN1142839 A, 100–114
CN1156465 A, 345–359
CN1170418 A, 152–182
CN1170419 A, 44t–74t
CN1176997 C, 242–261
CN1181098 A, 152–182
CN1183423 A, 100–114, 152–182
CN1183426 A, 100–114, 152–182
CN1183427 A, 100–114, 152–182
CN1183428 A, 100–114, 152–182
CN1183429 A, 100–114, 152–182
CN1183433 A, 100–114, 152–182
CN1211424 C, 152–182, 290–299
CN1215119 C, 152–182
CN1216568 A, 317–325
CN1226307 C, 270–275
CN1230288 C, 423–429
CN1230466 C, 242–261
CN1236901 C, 345–359
CN1237096 C, 317–325
CN1239579 C, 199–213
CN1245428 C, 345–359
CN1246387 C, 44t–74t
CN1247658 C, 152–182
CN1250482 A, 44t–74t
CN1250603 C, 44t–74t
CN1259176 A, 401–410
CN1261466 C, 242–261
CN1279984 C, 439–445
CN1280333 C, 100–114, 242–261
CN1281482 A, 44t–74t
CN1293100 C, 199–213, 270–275, 290–299
CN1298852 C, 44t–74t
CN1299393 A, 100–114, 439–445
CN1300247 C, 242–261
CN1306021 A, 44t–74t
CN1307259 C, 152–182
CN1308395 C, 44t–74t
CN1323326 A, 345–359
CN1324082 C, 242–261
CN1324891 A, 44t–74t, 100–114, 152–182
CN1325543 C, 100–114
CN1335857 A, 270–275
CN1337969 A, 199–213, 270–275, 290–299
CN1379818 A, 44t–74t
CN1390869 A, 345–359
CN1391596 A, 152–182, 290–299
CN1392197 A, 242–261
CN1417239 A, 242–261
CN1417256 A, 217–218, 242–261
CN1430506 A, 199–213
CN1436803 A, 24
CN1441823 A, 199–213
CN1446144 A, 345–359
CN1447738 A, 423–429
CN1468273 A, 152–182

CN1473171 A, 515–528
CN1473875 A, 242–261
CN1489616 A, 152–182
CN1495223 A, 345–359
CN1522282 A, 44t–74t
CN1524115 A, 469–479
CN1524897 A, 242–261
CN1525986 A, 100–114
CN1537140 A, 242–261
CN1564848 A, 152–182
CN1596279 A, 345–359
CN1596282 A, 199–213
CN1608093 A, 100–114, 242–261
CN1633313 A, 439–445
CN1639235 A, 100–114
CN1643092 A, 454–458
CN1652976 A, 44t–74t
CN1678777 A, 100–114, 401–410
CN1681884 A, 100–114
CN1690105 A, 100–114, 290–299
CN1694963 A, 270–275
CN1711316 A, 44t–74t
CN1748003 A, 242–261
CN1768115 A, 152–182, 375–386
CN1768115 B, 152–182, 375–386
CN1777795 A, 100–114
CN1793198 A, 152–182
CN1807505 A, 242–261
CN1807505 B, 242–261
CN1809611 A, 152–182
CN1810877 A, 345–359
CN1810877 B, 345–359
CN1827686 A, 100–114, 242–261
CN1827686 B, 100–114, 242–261
CN1836068 A, 199–213
CN1845970 A, 152–182, 242–261
CN1847279 A, 44t–74t
CN1847279 B, 44t–74t
CN1850300 A, 412, 423–429
CN1867630 A, 242–261
CN1872902 A, 242–261
CN1906248 A, 100–114
CN1906248 B, 100–114
CN1911460 A, 439–445
CN1914030 A, 100–114
CN1914255 A, 270–275
CN1914278 A, 242–261
CN1914279 A, 242–261
CN1914279 B, 242–261
CN1922255 A, 242–261
CN1922255 B, 242–261
CN1926126 A, 515–528
CN1931902 A, 345–359
CN1938378 A, 100–114, 242–261
CN1974526 A, 44t–74t
CN1974526 B, 44t–74t
CN1974660 A, 242–261
CN1974660 B, 242–261
CN87105988 A, 44t–74t
CO6551719 A2, 152–182
CO6561769 A2, 152–182
CY1107044 T1, 44t–74t
CY1107549 T1, 439–445
CZ20003072 A3, 290–299
CZ20020269 A3, 515–528
CZ282950 B6, 152–182
CZ285748 B6, 100–114, 152–182
CZ292145 B6, 152–182
CZ293001 B6, 44t–74t
CZ303404 B6, 290–299
CZ9002644 A3, 152–182
CZ9203901 A3, 100–114, 152–182
CZ9600822 A3, 44t–74t
CZ9602192 A3, 100–114
CZ9602211 A3, 100–114, 401–410
CZ9701437 A3, 152–182
CZ9701465 A3, 44t–74t
CZ9902516 A3, 44t–74t

D

DD239609 A1, 100–114, 196, 199–213
DD297988 A5, 152–182
DD298416 A5, 152–182
DE10100667 A1, 434, 439–445
DE10104829 A1, 372, 375–386
DE10121150 A1, 375–386
DE10151386 A1, 38
DE10151386 C2, 44t–74t
DE102005018086 A1, 100–114, 290–299
DE102005027861 A1, 515–528
DE102005027861 B4, 515–528
DE102005056432 A1, 44t–74t
DE102005062608 A1, 197, 199–213
DE102007032746 A1, 290–299
DE102009029035 A1, 152–182
DE102009042008 A1, 375–386
DE102010061931 A1, 454–458
DE102011011173 A1, 412, 423–429
DE102011016918 A1, 421, 423–429
DE102011017126 A1, 412, 423–429
DE102011077447 A1, 152–182
DE102011086224 A1, 100–114
DE102012202822 A1, 462, 464, 469–479
DE10256492 A1, 448, 454–458
DE10313939 A1, 152–182
DE10321616 A1, 439–445
DE10358779 A1, 469–479
DE10358779 B4, 469–479
DE112005000965 T5, 515–528
DE112005002471 T5, 152–182
DE112006000594 T5, 290–299, 375–386
DE112006000699 T5, 290–299
DE1800834 A1, 469–479
DE1800834 B2, 469–479
DE19504899 A1, 332–333, 344–359, 419, 423–429
DE19504899 B4, 345–359, 423–429
DE19505186 A1, 44t–74t
DE19522147 A1, 490, 515–528
DE19522147 C2, 515–528
DE19530449 A1, 494, 515–528
DE19615151 A1, 460, 469–479
DE19615348 A1, 312, 317–325
DE19623464 A1, 345–359
DE19623778 A1, 100–114
DE19637404 A1, 497, 515–528
DE19637404 B4, 515–528
DE19638686 A1, 199–213
DE19648616 A1, 141, 152–182
DE19700902 A1, 37
DE19700903 A1, 37
DE19700905 A1, 37
DE19700907 A1, 37
DE19701015 A1, 37
DE19739992 A1, 490, 515–528
DE19740027 A1, 490, 515–528
DE19750846 C1, 152–182
DE19754418 A1, 29
DE19816881 A1, 492, 515–528
DE19816881 B4, 515–528
DE19829200 A1, 490, 515–528
DE19848873 A1, 495, 515–528
DE19852034 C1, 38
DE19901743 A1, 490, 515–528
DE19924772 A1, 268, 270–275
DE19934259 A1, 44t–74t
DE19934259 A1, 515–528
DE19938008 A1, 336–337, 345–359
DE202005022027 U1, 375–386
DE202006001693 U1, 469–479
DE2062604 A1, 242–261
DE2322440 A1, 152–182
DE2335348 A1, 152–182
DE2513159 A1, 100–114
DE2602994 A1, 44t–74t
DE2602994 C2, 44t–74t
DE260415 T1, 44t–74t
DE266603 T1, 44t–74t
DE2701278 A1, 100–114
DE2839908 A1, 152–182
DE3116655 A, 515–528
DE3148618 A1, 44t–74t
DE3206751 A1, 345–359
DE3206751 C2, 345–359
DE3218151 A1, 265, 270–275
DE327505 T1, 152–182
DE3314188 A1, 138, 152–182
DE3428640 A1, 265, 270–275
DE3428640 C2, 270–275
DE3689650 T2, 242–261
DE3734223 A1, 229, 242–261
DE3751964 T2, 44t–74t
DE3752176 T2, 199–213
DE3752381 T2, 44t–74t
DE3842072 C1, 483, 515–528
DE3876521 T2, 44t–74t
DE3877678 T2, 199–213
DE3879320 T2, 100–114
DE3882047 T2, 152–182
DE3888046 T2, 44t–74t
DE3888046 T3, 44t–74t
DE3889751 T2, 44t–74t
DE4007882 A1, 100–114, 242–261
DE4029167 A, 515–528
DE4038732 A1, 140, 152–182
DE4040158 A1, 194, 199–213, 431, 439–445
DE4116404 A1, 140, 152–182
DE4213323 A1, 515–528
DE4231477 A1, 494, 515–528
DE4234620 A1, 345–359
DE4239781 A1, 339, 345–359

DE4244000 A1, 375–386
DE4300420 A1, 122, 152–182
DE4313136 A1, 100–114, 317–325
DE4327024 A1, 29
DE4331747 A1, 37
DE4340914 A1, 515–528
DE4406172 A1, 290–299
DE4406172 C2, 290–299
DE4440837 A1, 44t–74t
DE4440858 A1, 152–182
DE539541 T1, 100–114, 152–182
DE553394 T1, 469–479
DE59902150 G, 44t–74t
DE60005932 T2, 199–213, 270–275, 290–299
DE60009428 T2, 454–458
DE60012381 T2, 242–261
DE60016878 T2, 152–182
DE60026983 E
DE60029971 T2, 44t–74t
DE60034045 T2, 44t–74t
DE60036845 T2, 242–261
DE60036863 T2, 44t–74t
DE60038010 T2, 290–299
DE60105398 T2, 423–429
DE60122732 T2, 199–213
DE60123968 T2, 423–429
DE60124929 T2, 44t–74t
DE60132525 T2, 152–182
DE602004009764 T2, 152–182, 469–479
DE60209310 T2, 242–261
DE60209587 T2, 454–458
DE60213080 T2, 469–479
DE60214913 T2, 152–182
DE60215511 T2, 242–261
DE60218764 T2, 317–325
DE60222326 T2, 100–114
DE60222496 T2, 345–359
DE60224505 T2, 469–479
DE60224530 T2, 401–410
DE60224530 T3, 401–410
DE60224729 T2, 100–114
DE60225445 T2, 100–114
DE60303642 T2, 100–114
DE60307423 T2, 454–458
DE60309787 T2, 242–261
DE60310540 T2, 439–445
DE68904326 T2, 270–275
DE68904326 T3, 270–275
DE68928209 T2, 152–182
DE68928209 T3, 152–182
DE68928817 T2, 44t–74t
DE69005702 T2, 152–182
DE69009323 T2, 152–182
DE69011431 T2, 152–182
DE69030527 T2, 152–182
DE69033806 T2, 152–182
DE69115673 T2, 44t–74t
DE69125170 T2, 100–114, 152–182
DE69125965 T2, 152–182
DE69132548 T2, 100–114, 152–182
DE69133554 T2, 100–114, 152–182
DE69203713 T2, 469–479
DE69212557 T2, 152–182
DE69213304 T2, 375–386
DE69216114 E, 515–528
DE69220754 T2, 100–114, 152–182
DE69224772 T2, 375–386
DE69224772 T3, 375–386
DE69227878 T2, 44t–74t
DE69228010 E, 515–528
DE69303282 T2, 270–275
DE69306308 T2, 515–528
DE69317423 T2, 375–386
DE69317474 T2, 317–325
DE69317474 T3, 317–325
DE69328822 T2, 439–445
DE69329903 T2, 290–299
DE69400638 T2, 317–325
DE69411382 T2, 375–386
DE69411382 T3, 375–386
DE69412948 T2, 401–410
DE69414854 T2, 469–479
DE69416857 T2, 317–325
DE69417265 T2, 290–299
DE69422053 T2, 469–479
DE69425599 T2, 454–458
DE69431408 T2, 44t–74t
DE69431483 T2, 242–261, 292–299
DE69431523 T2, 152–182
DE69432189 T2, 100–114
DE69507898 T2, 439–445
DE69521321 T2, 152–182, 199–213, 439–445
DE69529075 T2, 469–479
DE69530203 T2, 345–359
DE69534715 T2, 100–114, 401–410
DE69601590 T2, 469–479
DE69602176 T2, 199–213
DE69602351 T2, 199–213, 439–445
DE69616067 T2, 199–213, 401–410, 469–479
DE69617905 T2, 152–182
DE69622040 T2, 439–445
DE6962569 T2, 317–325
DE69634410 T2, 199–213, 469–479
DE69636049 T2, 100–114
DE69636485 T2, 199–213, 401–410, 469–479
DE69707547 T2, 100–114, 317–325
DE69709320 T2, 242–261
DE69720516 T2, 44t–74t
DE69721265 T2, 199–213
DE69728875 T2, 199–213
DE69730771 T2, 100–114, 375–386
DE69730897 T2, 100–114, 375–386
DE69805848 T2, 44t–74t
DE69806262 T2, 290–299
DE69819902 T2, 439–445
DE69819902 T3, 439–445
DE69826457 T2, 401–410
DE69834248 T2, 345–359
DE69834726 T2, 100–114
DE69837141 T2, 44t–74t
DE69837914 T2, 199–213
DE69906099 E, 44t–74t
DE69908655 T2, 270–275
DE69918233 T2, 152–182, 242–261
DE69920703 T2, 423–429, 439–445
DE69923210 T2, 345–359
DE69923210 T3, 345–359
DE69927841 T2, 44t–74t
DE69932818 T2, 199–213
DE9219143 U1, 152–182
DK0400531 T3, 152–182
DK0400532 T3, 152–182
DK0404723 T3, 152–182
DK0479043 T3, 270–275
DK0479964 T3, 152–182
DK0495056 T3, 44t–74t
DK0539541 T3, 100–114, 152–182
DK0542155 T3, 152–182
DK0542155 T4, 152–182
DK0553394 T3, 469–479
DK0615532 T3, 439–445
DK0637641 T3, 401–410
DK0647184 T3, 375–386
DK0652969 T3, 270–275
DK0708804 T3, 469–479
DK0711314 T3, 242–261, 290–299
DK0711314 T5, 242–261, 290–299
DK0758669 T3, 152–182
DK0792310 T3, 44t–74t
DK0797609 T3, 290–299
DK0809666 T3, 44t–74t
DK0809666 T4, 44t–74t
DK0885261 T3, 242–261
DK0910412 T3, 199–213
DK0927219 T3, 199–213
DK0961805 T3, 152–182
DK0981381 T3, 44t–74t
DK1023378 T3, 290–299, 439–445
DK1040127 T3, 44t–74t
DK1074570 T3, 152–182
DK1127086 T3, 345–359
DK1127086 T4, 345–359
DK1163019 T3, 44t–74t
DK1168934 T3, 290–299
DK1227129 T3, 152–182
DK1264850 T3, 345–359
DK1366104 T3, 469–479
DK143450 B, 469–479
DK143450 C, 469–479
DK1458805 T3, 199–213
DK1492581 T3, 439–445
DK16082 A, 44t–74t
DK166360 B, 44t–74t
DK171316 B1, 44t–74t
DK173005 B1, 199–213
DK174534 B1, 152–182
DK175252 B1, 242–261
DK1764118 T3, 439–445
DK1793994 T3, 375–386
DK1838784 T3, 152–182
DK2032649 T3, 152–182
DK2101974 T3, 515–528
DK2252440 T3, 515–528
DK32076 A, 44t–74t
DK358488 A, 44t–74t,
DK36789 A, 44t–74t, 152–182
DK407778 A, 152–182
DK444388 A, 44t–74t
DK46690 A, 44t–74t
DK549486 A, 345–359
DK561588 A, 242–261
DK698688 A, 199–213
DK720634 T3, 44t–74t
DK73380 A, 100–114, 199–213
DK737219 T3, 290–299

DK792309 T3, 152–182
DK809664 T3, 44t–74t
DK819147 T3, 152–182
DK907681 T3, 199–213
DK918825 T3, 44t–74t
DK946624 T3, 44t–74t
DK961805 T3, 44t–74t
DOP2007000032 A, 100–114, 242–261
DOP2007000033 A, 100–114
DOP2007000034 A, 100–114, 242–261, 423–429
DOP2007000036 A, 100–114, 242–261
DOP2007000038 A, 100–114, 152–182, 242–261

E
E19852081 C1, 44t–74t
EA008535 B1, 199–213
EG20102 A, 375–386
EP0014490 A1, 100–114, 199–213
EP0014490 B1, 100–114, 199–213
EP0015123 A1, 13–15, 100–114, 196, 199–213
EP0015123 B1, 100–114, 199–213
EP0032802 A1, 147–149, 152–182, 362, 375–386
EP0032802 B1, 152–182, 375–386
EP0036699 A1, 100–114, 199–213
EP0036699 B1, 100–114, 199–213
EP0036699 B2, 100–114, 199–213
EP0046335 A2, 13–15
EP0051667 A1, 44t–74t
EP0051667 B1, 44t–74t
EP0052459 A1, 15
EP0052460 A1, 137, 152–182
EP0052460 B1, 152–182
EP0058480 A1, 375–386
EP0058480 B1, 375–386
EP0069497 A2, 15
EP0069497 A3, 44t–74t
EP0069497 B1, 44t–74t
EP0078609 A2, 366, 375–386
EP0078609 A3, 375–386
EP0078609 B1, 375–386
EP0087847 A1, 345–359
EP0094536 A2, 270–275
EP0094536 A3, 270–275
EP0094536 B1, 270–275
EP0104731 A2, 390, 401–410
EP0104731 A3, 401–410
EP0104731 B1, 401–410
EP0105399 A1, 138, 152–182
EP0105399 B1, 152–182
EP0113443 A1, 199–213
EP0113443 A3, 199–213
EP0113443 B1, 199–213
EP0124309 A2, 196, 199–213
EP0124309 A3, 199–213
EP0142950 A2, 44t–74t
EP0142950 A3, 44t–74t
EP0142950 B1, 44t–74t
EP0168095 A1, 199–213
EP0168095 B1, 199–213
EP0171603 A1, 270–275
EP0171603 B1, 270–275
EP0223708 A2, 344–359
EP0223708 A3, 345–359
EP0223708 B1, 345–359
EP0226061 A2, 242–261
EP0226061 A3, 242–261
EP0226061 B1, 242–261
EP0226439 A1, 366, 375–386
EP0226439 B1, 375–386
EP0260415 A2, 41
EP0260415 A3, 44t–74t
EP0260415 B1, 44t–74t
EP0261572 A1, 44t–74t
EP0265116 A2, 197, 199–213
EP0265116 A3, 199–213
EP0265116 B1, 199–213
EP0266603 A1, 41
EP0272902 A2, 44t–74t
EP0272902 A3, 44t–74t
EP0274961 A1, 190, 199–213
EP0275796 A1, 270–275
EP0275796 B1, 270–275
EP0275796 B2, 270–275
EP0298920 A2, 44t–74t
EP0298920 A3, 44t–74t
EP0298920 B1, 44t–74t
EP0301632 A1, 152–182
EP0301632 B1, 152–182
EP0304293 A2, 100–114
EP0304293 A3, 100–114
EP0304293 B1, 100–114
EP0304401 A2, 44t–74t
EP0304401 A3, 44t–74t
EP0304401 B1, 44t–74t
EP0304401 B2, 44t–74t
EP0311065 A1, 242–261
EP0327505 A2, 152–182
EP0327505 A3, 152–182
EP0327505 B1, 152–182
EP0327505 B2, 152–182
EP0330180 A1, 266, 270–275
EP0330180 B1, 270–275
EP0330180 B2, 270–275
EP0349505 A2, 16
EP0349505 B1, 44t–74t
EP0360818 A1, 152–182
EP0363549 A1, 199–213
EP0363549 B1, 199–213
EP0371627 A2, 448, 454–458
EP0371627 A3, 454–458
EP0373372 A2, 515–528
EP0373372 A3, 515–528
EP0373372 B1, 515–528
EP0400531 A1, 149, 152–182
EP0400531 B1, 152–182
EP0400532 A1, 149, 152–182
EP0400532 B1, 152–182
EP0402826 A1, 152–182
EP0404723 A2, 140, 152–182
EP0404723 A3, 152–182
EP0404723 B1, 152–182
EP0404728 A2, 140, 152–182
EP0404728 A3, 152–182
EP0405918 A1, 199–213
EP0407350 A2, 140, 152–182
EP0407350 A3, 152–182
EP0408503 A2, 140, 152–182
EP0408503 B1, 152–182
EP0440165 A2, 100–114
EP0444880 A2, 128, 152–182
EP0444880 A3, 152–182
EP0444880 B1, 152–182
EP0446852 A2, 91, 100–114, 242–261
EP0446852 A3, 100–114, 242–261
EP0466050 A1, 100–114
EP0473726 A1, 152–182
EP0473726 A4, 152–182
EP0476416 A2, 515–528
EP0476416 A3, 515–528
EP0479043 A1, 100–114, 267, 270–275
EP0479964 A1, 152–182
EP0479964 B1, 152–182
EP0495056 A1, 44t–74t
EP0495056 B1, 44t–74t
EP0510998 A2, 371, 375–386
EP0510998 A3, 375–386
EP0510998 B1, 375–386
EP0514137 A2, 372, 375–386
EP0514137 A3, 375–386
EP0514137 B1, 375–386
EP0514137 B2, 375–386
EP0533144 A2, 16, 100–114
EP0533144 A3, 100–114
EP0533144 B1, 44t–74t
EP0535065 A1, 270–275
EP0535994 A1, 128, 149, 152–182
EP0535994 B1, 152–182
EP0539541 A1, 100–114, 152–182
EP0539541 B1, 100–114, 152–182
EP0539544 A1, 152–182
EP0539544 B1, 152–182
EP0542155 A2, 128, 140, 148, 152–182
EP0542155 A3, 152–182
EP0542155 B1, 152–182
EP0542155 B2, 152–182
EP0553394 A1, 469–479
EP0553394 B1, 469–479
EP0559785 A1, 100–114, 152–182
EP0559785 B1, 100–114, 152–182
EP0560823 A1, 152–182
EP0566948 A1, 515–528
EP0566948 B1, 515–528
EP0573042 A1, 500–501, 515–528
EP0573042 B1, 515–528
EP0576993 A2, 308, 317–325, 422
EP0576993 A3, 317–325
EP0576993 B1, 317–325
EP0576993 B2, 317–325
EP0592911 A1, 336, 345–359
EP0601390 A1, 345–359
EP0603876 A1, 372, 375–386
EP0613927 A2, 447, 454–458
EP0613927 A3, 454–458
EP0613927 B1, 454–458
EP0616621 A1, 515–528
EP0616621 B1, 515–528
EP0618948 A1, 469–479
EP0619732 A1, 290–299
EP0619732 A4, 290–299
EP0619732 B1, 290–299
EP0628533 A1, 515–528

EP0637641 A1, 401–410
EP0637641 B1, 401–410
EP0641817 A2, 44t–74t
EP0641817 A3, 44t–74t
EP0641817 B1, 44t–74t
EP0647184 A1, 375–386
EP0647184 B1, 375–386
EP0652969 A1, 270–275
EP0652969 B1, 270–275
EP0669959 A1, 152–182
EP0680522 A1, 317–325
EP0680522 B1, 317–325
EP0683207 A2, 242–261
EP0683207 A3, 242–261
EP0683207 B1, 242–261
EP0695321 A1, 375–386
EP0695321 B1, 375–386
EP0695321 B2, 375–386
EP0700961 A2, 515–528
EP0700961 A3, 515–528
EP0700961 B1, 515–528
EP0708804 A1, 469–479
EP0708804 B1, 469–479
EP0711314 A1, 242–261, 290–299
EP0711314 B1, 242–261, 290–299
EP0711314 B9, 242–261, 290–299
EP0711326 A1, 152–182
EP0711326 A4, 152–182
EP0711326 B1, 152–182
EP0720634 A1, 44t–74t
EP0720634 B1, 44t–74t
EP0723572 A1, 469–479
EP0723572 B1, 469–479
EP0731754 A1, 317–325
EP0731754 B1, 317–325
EP0736563 A1, 375–386
EP0737219 A1, 290–299
EP0737219 B1, 290–299
EP0739368 A1, 100–114
EP0739368 B1, 100–114
EP0741177 A2, 465, 469–479
EP0741177 A3, 469–479
EP0741177 B1, 469–479
EP0741178 A2, 465, 469–479
EP0741178 A3, 469–479
EP0741753 A1, 100–114, 401–410
EP0741753 B1, 100–114, 401–410
EP0746543 A1, 44t–74t
EP0746543 A4, 44t–74t
EP0746543 B1, 44t–74t
EP0758669 A2, 152–182
EP0758669 A3, 152–182
EP0758669 B1, 152–182
EP0759451 A2, 515–528
EP0766719 A1, 199–213, 439–445
EP0767810 A1, 345–359
EP0767810 A4, 345–359
EP0767810 B1, 345–359
EP0772464 A1, 469–479
EP0772464 B1, 469–479
EP0772654 B1, 152–182, 199–213, 439–445
EP0776371 A1, 199–213
EP0780428 A1, 87, 91, 100–114
EP0780428 B1, 100–114
EP0792309 A1, 152–182
EP0792309 B1, 152–182
EP0792310 A1, 44t–74t
EP0792310 B1, 44t–74t
EP0795190 A1, 439–445
EP0795190 B1, 439–445
EP0797609 A1, 290–299
EP0797609 B1, 290–299
EP0802219 A2, 92, 100–114, 310, 317–325
EP0802219 A3, 100–114, 317–325
EP0802219 B1, 100–114, 317–325
EP0803532 A1, 368, 375–386
EP0804506 A2, 152–182
EP0804506 B1, 152–182
EP0805175 A1, 83–85, 100–114, 361, 364–365, 375–386
EP0805175 B1, 100–114, 375–386
EP0805176 A1, 83–85, 100–114, 364–365, 375–386
EP0805176 B1, 100–114, 375–386
EP0808373 A1, 199–213, 439–445
EP0808373 B1, 199–213, 439–445
EP0809664 A1, 44t–74t
EP0809664 B1, 44t–74t
EP0809666 A1, 44t–74t
EP0809666 B2, 44t–74t
EP0809669 A1, 199–213
EP0809669 B1, 199–213
EP0812877 A2, 329, 345–359
EP0812877 A3, 345–359
EP0812877 B1, 345–359
EP0819058 A1, 439–445
EP0819147 A1, 152–182
EP0819147 B1, 152–182
EP0831996 A1, 439–445
EP0839170 A1, 199–213, 401–410, 469–479
EP0839170 B1, 199–213, 401–410, 469–479
EP0842217 A1, 317–325
EP0842977 A2, 152–182
EP0848759 A2, 100–114
EP0848759 B1, 100–114
EP0850988 A1, 199–213, 469–479
EP0850988 A4, 199–213, 469–479
EP0850988 B1, 199–213, 469–479
EP0866839 A1, 439–445
EP0866839 B1, 439–445
EP0875505 A2, 515–528
EP0885261 A1, 242–261
EP0885261 B1, 242–261
EP0894118 A1, 317–325
EP0894122 A1, 469–479
EP0896013 A1, 136, 152–182
EP0898590 A1, 290–299
EP0899274 A1, 277–278, 290–299
EP0907681 A1, 199–213
EP0907681 B1, 199–213
EP0910412 A1, 199–213
EP0910412 B1, 199–213
EP0918633 A1, 375–386
EP0918825 A1, 44t–74t
EP0927219 A1, 199–213
EP0927219 B1, 199–213
EP0946624 A1, 44t–74t
EP0946624 B1, 44t–74t
EP0960206 A1, 44t–74t
EP0961805 A1, 44t–74t, 152–182
EP0961805 B1, 44t–74t
EP0961805 B1, 152–182
EP0973930 A1, 199–213
EP0973930 B1, 199–213
EP0974615 A1, 308–309, 317–325
EP0974615 B1, 317–325
EP0975788 A1, 100–114, 199–213
EP0977912 A1, 401–410
EP0977912 B1, 401–410
EP0980894 A4, 152–182, 242–261
EP0980894 B1, 152–182, 242–261
EP0981381 A2, 44t–74t
EP0981381 B1, 44t–74t
EP0981666 A1, 439–445
EP0984039 A1, 290–299
EP0984039 A4, 290–299
EP0989159 A1, 345–359
EP0989159 A4, 345–359
EP0989159 B1, 345–359
EP0996670 A1, 100–114
EP0996670 B1, 100–114
EP0998381 A1, 439–445
EP0998381 B1, 439–445
EP0998381 B2, 439–445
EP1003441 A1, 290–299
EP1003441 A4, 290–299
EP1023378 A1, 290–299, 439–445
EP1023378 B1, 290–299, 439–445
EP1029890 A2, 242–261
EP1029890 B1, 242–261
EP1037943 A1, 44t–74t
EP1040127 A1, 44t–74t
EP1040127 B1, 44t–74t
EP1041105 A2, 239–261
EP1041105 A3, 242–261
EP1042388 A1, 44t–74t
EP1056487 A1, 290–299
EP1056487 B1, 290–299
EP1070097 A1, 100–114, 439–445
EP1074570 A2, 152–182
EP1074570 A3, 152–182
EP1074570 B1, 152–182
EP1086164 A1, 199–213
EP1086164 B1, 199–213
EP1094944 A1, 423–429, 439–445
EP1094944 B1, 423–429, 439–445
EP1095977 A1, 152–182, 288–299
EP1097967 A2, 128–130, 152–182
EP1097967 A3, 152–182
EP1097967 B1, 152–182
EP1105715 A1, 515–528
EP1106640 A2, 20–21
EP1106640 A3, 44t–74t
EP1107069 A1, 452, 454–458
EP1107069 B1, 454–458
EP1108737 A2, 20–21
EP1108737 A3, 44t–74t
EP1108751 A1, 242–261
EP1108751 B1, 242–261
EP1112319 A1, 44t–74t
EP1112319 B1, 44t–74t
EP1116746 A2, 242–261

EP1116746 A3, 242–261
EP1127086 A1, 345–359
EP1127086 A4, 345–359
EP1127086 B1, 345–359
EP1127086 B2, 345–359
EP1129131 A1, 515–528
EP1129139 A1, 44t–74t
EP1129139 B1, 44t–74t
EP1129140 A1, 44t–74t
EP1129140 B1, 44t–74t
EP1130149 A1, 401–410
EP1130149 A4, 401–410
EP1130149 B1, 401–410
EP1131056 A1, 44t–74t
EP1131056 B1, 44t–74t
EP1132446 A2, 199–213, 401–410, 469–479
EP1132446 A3, 199–213, 401–410, 469–479
EP1132446 B1, 199–213, 401–410, 469–479
EP1134258 A1, 419–420, 423–429
EP1155041 A1, 270–275
EP1155041 B1, 270–275
EP1159301 A1, 199–213, 270–275, 290–299
EP1159301 B1, 199–213, 270–275, 290–299
EP1163019 A1, 44t–74t
EP1163019 B1, 44t–74t
EP1168934 A1, 290–299
EP1168934 A4, 290–299
EP1168934 B1, 290–299
EP1171006 A1, 44t–74t
EP1171006 A4, 44t–74t
EP1171006 B1, 44t–74t
EP1188781 A1, 152–182
EP1188781 A4, 152–182
EP1188781 B1, 152–182
EP1194463 A1, 44t–74t
EP1194463 A4, 44t–74t
EP1194463 B1, 44t–74t
EP1200194 A1, 44t–74t
EP1204700 A1, 345–359
EP1204700 B1, 345–359
EP1204755 A2, 44t–74t
EP1204755 B1, 44t–74t
EP1208208 A2, 44t–74t
EP1208208 B1, 44t–74t
EP1210379 A1, 44t–74t
EP1210379 A4, 44t–74t
EP1210379 B1, 44t–74t
EP1222303 A2, 44t–74t
EP1225196 A1, 312, 317–325
EP1227129 A1, 125, 152–182
EP1227129 B1, 152–182
EP1236753 A1, 465–466, 469–479
EP1241231 A1, 485, 506, 515–528
EP1256606 A2, 447–448, 454–458
EP1256606 A3, 454–458
EP1256606 B1, 454–458
EP1263871 A1, 423–429
EP1263871 B1, 423–429
EP1264850 A1, 327, 345–359
EP1264850 B1, 345–359
EP1266984 A1, 100–114, 390–391
EP1266984 B1, 100–114
EP1270659 A1, 242–261
EP1270659 B1, 242–261
EP1277465 A1, 199–213
EP1294814 A2, 454–458
EP1302502 A1, 199–213
EP1302502 A4, 199–213
EP1302502 B1, 199–213
EP1309434 A1, 423–429
EP1309434 A4, 423–429
EP1309434 B1, 423–429
EP1311582 A1, 152–182
EP1311582 A4, 152–182
EP1311582 B1, 152–182
EP1312642 A1, 242–261
EP1313794 A2, 44t–74t
EP1313794 B1, 44t–74t
EP1330503 A2, 290–299, 469–479
EP1330503 B1, 290–299, 469–479
EP1332030 A1, 345–359
EP1332030 A4, 345–359
EP1332030 B1, 345–359
EP1332173 A2, 515–528
EP1360235 A1, 152–182
EP1360235 B1, 152–182
EP1366104 A2, 469–479
EP1366104 B1, 469–479
EP1375592 A1, 99–114
EP1375592 B1, 100–114
EP1378538 A1, 338, 345–359
EP1383847 A1, 469–479
EP1383847 B1, 469–479
EP1385700 A1, 242–261
EP1385700 B1, 242–261
EP1385899 A1, 375–386
EP1385899 B1, 375–386
EP1388562 A1, 242–261
EP1388562 B1, 242–261
EP1395415 A1, 375–386
EP1395415 B1, 375–386
EP1397537 A1, 401–410
EP1397537 B1, 401–410
EP1397537 B2, 401–410
EP1404738 A1, 100–114
EP1404738 B1, 100–114
EP1412425 A1, 242–261
EP1412425 B1, 242–261
EP1416946 A2, 345–359
EP1416946 A4, 345–359
EP1445282 A1, 152–182
EP1445282 A4, 152–182
EP1449864 A1, 100–114, 242–261
EP1449864 A4, 100–114, 242–261
EP1449864 B1, 100–114, 242–261
EP1449869 A1, 345–359
EP1449869 A4, 345–359
EP1456285 A1, 317–325
EP1458805 A2, 199–213
EP1458805 B1, 199–213
EP1460107 A1, 44t–74t
EP1460107 A4, 44t–74t
EP1460107 B1, 44t–74t
EP1463619 A1, 100–114
EP1463619 A4, 100–114
EP1463619 B1, 100–114
EP1470199 A1, 454–458
EP1470199 B1, 454–458
EP1477535 A1, 439–445
EP1484356 A1, 100–114
EP1484356 A4, 100–114
EP1484356 B1, 100–114
EP1484357 A1, 340, 345–359
EP1484371 A2, 435, 439–445
EP1484371 A3, 439–445
EP1491575 A1, 317–325
EP1491575 A4, 317–325
EP1491575 B1, 317–325
EP1492581 A1, 439–445
EP1492581 B1, 439–445
EP1514891 A1, 189, 193–194, 196, 199–213
EP1514891 B1, 199–213
EP1544250 A1, 100–114
EP1544250 A4, 100–114
EP1544250 B1, 100–114
EP1548053 A1, 515–528
EP1548161 A1, 100–114, 401–410
EP1548161 A4, 100–114, 401–410
EP1548161 B1, 100–114, 401–410
EP1550724 A1, 270–275
EP1555209 A1, 44t–74t
EP1564235 A1, 18
EP1564235 B1, 44t–74t
EP1566409 A1, 199–213, 439–445
EP1566409 A4, 44t–74t
EP1575842 A2, 317–325
EP1576213 A2, 401–410
EP1586647 A1, 44t–74t
EP1589076 A1, 423–429
EP1589076 A4, 423–429
EP1601737 A1, 152–182, 469–479
EP1601737 B1, 152–182, 469–479
EP1603987 A1, 152–182, 469–479
EP1603987 B1, 152–182, 469–479
EP1605017 A1, 242–261
EP1605017 A4, 242–261
EP1605017 B1, 242–261
EP1608700 A1, 152–182
EP1608700 B1, 152–182
EP1609819 A1, 152–182, 375–386
EP1609819 A4, 152–182, 375–386
EP1609819 B1, 152–182, 375–386
EP1624024 A1, 336, 345–359
EP1624024 A4, 345–359
EP1624024 B1, 345–359
EP1627332 A2, 100–114
EP1636298 A1, 345–359
EP1636299 A1, 345–359
EP1636299 B1, 345–359
EP1654415 A1, 199–213
EP1659149 A1, 222, 242–261
EP1659149 A4, 242–261
EP1664125 A1, 199–213
EP1664125 B1, 199–213
EP1674551 A1, 236–237, 242–261
EP1679349 A1, 152–182, 242–261
EP1683828 A2, 345–359
EP1683828 A3, 345–359
EP1683828 B1, 345–359
EP1685201 A1, 199–213
EP1692224 A1, 469–479
EP1704180 A1, 242–261

EP1704180 A4, 242–261
EP1704180 B1, 242–261
EP1710075 A4, 100–114
EP1712576 A1, 44t–74t
EP1717263 A1, 270–275
EP1717263 A4, 270–275
EP1728818 A1, 242–261
EP1736510 A1, 100–114, 242–261
EP1736510 A4, 100–114, 242–261
EP1736510 B1, 100–114, 242–261
EP1741536 A1, 487–488, 515–528
EP1741707 A1, 498, 515–528
EP1741707 A4, 515–528
EP1762655 A1, 401–410
EP1764118 A2, 439–445
EP1764118 A3, 439–445
EP1764118 B1, 439–445
EP1785449 A2, 317–325
EP1785449 A3, 317–325
EP1790677 A1, 242–261
EP1790678 A1, 44t–74t
EP1790678 B1, 44t–74t
EP1792941 A1, 152–182
EP1792941 B1, 152–182
EP1793994 A2, 375–386
EP1793994 A4, 375–386
EP1793994 B1, 375–386
EP1793995 A2, 375–386
EP1793995 A4, 375–386
EP1813652 A1, 317–325
EP1813652 B1, 317–325
EP1816164 A1, 100–114
EP1816164 A4, 100–114
EP1816164 A8, 100–114
EP1816174 A2, 463, 469–479
EP1816174 A3, 469–479
EP1816174 B1, 469–479
EP1838784 A1, 152–182
EP1838784 B1, 152–182
EP1849833 A1, 100–114, 199–213, 439–445
EP1849833 A4, 100–114, 199–213, 439–445
EP1860138 A1, 419–420, 423–429
EP1860153 A1, 242–261
EP1860153 A4, 242–261
EP1860153 B1, 242–261
EP1865021 A1, 152–182, 345–359
EP1865021 A4, 152–182, 345–359
EP1867348 A2, 44t–74t
EP1867348 A3, 44t–74t
EP1867348 B1, 44t–74t
EP1870220 A1, 345–359
EP1870222 A1, 345–359
EP1870431 A1, 345–359
EP1870431 A4, 345–359
EP1870431 B1, 345–359
EP1874996 A2, 199–213
EP1887029 A1, 375–386
EP1887029 A4, 375–386
EP1907182 A1, 515–528
EP1907182 B1, 515–528
EP1911809 A1, 423–429
EP1911809 A4, 423–429
EP1914258 A1, 100–114, 242–261
EP1914258 B1, 100–114, 242–261
EP1920106 A1, 401–410
EP1920106 B1, 401–410
EP1921098 A1, 44t–74t
EP1921098 A4, 44t–74t
EP1921098 B1, 44t–74t
EP1934289 A2, 290–299
EP1934289 A4, 290–299
EP1935945 A1, 152–182, 469–479
EP1944333 A1, 345–359
EP1944333 A4, 345–359
EP1945690 A1, 44t–74t
EP1947145 A2, 152–182
EP1947145 A3, 152–182
EP1947145 B1, 152–182
EP1954571 A2, 375–386
EP1956120 A1, 401–410
EP1956120 A4, 401–410
EP1957582 A2, 401–410
EP1957589 B1, 454–458
EP1964879 A1, 242–261
EP1964879 B1, 242–261
EP1965636 A2, 100–114
EP1965636 B1, 100–114
EP1967603 A2, 317–325
EP1967603 A3, 317–325
EP1970399 A1, 270–275
EP1970399 A4, 270–275
EP1970399 B1, 270–275
EP1975195 A1, 345–359
EP1975195 A4, 345–359
EP1987075 A1, 100–114
EP1991601 A1, 290–299
EP1991601 B1, 290–299
EP1992468 A2, 375–386
EP1999189 A1, 290–299
EP1999189 B1, 290–299
EP2022818 A1, 515–528
EP2022818 A4, 515–528
EP2022818 B1, 515–528
EP2025713 A1, 100–114
EP2028218 A1, 222, 242–261
EP2032649 A1, 152–182
EP2041341 A1, 290–299, 401–410
EP2041341 A4, 290–299, 401–410
EP2041341 B1, 290–299, 401–410
EP2045292 A1, 152–182
EP2045292 A4, 152–182
EP2045292 B1, 152–182
EP2047967 A1, 242–261, 317–325
EP2052030 A1, 242–261
EP2060665 A1, 401–410
EP2060665 A4, 401–410
EP2064284 A1, 152–182
EP2064284 B1, 152–182
EP2065435 A1, 90, 100–114, 221, 234–235, 242–261
EP2069431 A2, 270–275
EP2069431 A4, 270–275
EP2074175 A2, 152–182
EP2079767 A1, 515–528
EP2079767 A4, 515–528
EP2079794 A1, 423–429
EP2079794 A4, 423–429
EP2079794 B1, 423–429
EP2080787 A1, 152–182
EP2080787 A4, 152–182
EP2087033 A1, 152–182
EP2088198 A2, 44t–74t
EP2088198 A3, 44t–74t
EP2089460 A1, 345–359
EP2089460 B1, 345–359
EP2099735 A2, 44t–74t
EP2101974 A1, 515–528
EP2112199 A1, 122, 152–182
EP2115053 A1, 345–359
EP2115053 A4, 345–359
EP2118070 A1, 199–213
EP2118143 A1, 199–213
EP2121766 A1, 199–213
EP2133386 A1, 345–359
EP2133386 A4, 345–359
EP2133386 B1, 345–359
EP2135724 A1, 345–359
EP2135734 A1, 317–325
EP2135734 A4, 317–325
EP2135734 B1, 317–325
EP2137249 A2, 345–359
EP2137250 A2, 345–359
EP2138542 A1, 401–410
EP2141191 A1, 313, 317–325
EP2151395 A1, 317–325
EP2151395 A4, 317–325
EP2151464 A1, 290–299
EP2151464 A4, 290–299
EP2162475 A1, 44t–74t
EP2162475 B1, 44t–74t
EP2169005 A1, 100–114
EP2169005 A4, 100–114
EP2178423 A2, 317–325
EP2178967 A1, 152–182
EP2181142 A1, 242–261
EP2181145 A1, 439–445
EP2181145 B1, 439–445
EP2185637 A1, 345–359
EP2185637 B1, 345–359
EP2199456 A1, 152–182, 290–299
EP2199456 A4, 152–182, 290–299
EP2202274 A2, 152–182
EP2202274 A3, 152–182
EP2202274 B1, 152–182
EP2222459 A1, 375–386
EP2222459 A4, 375–386
EP2236548 A2, 317–325
EP2236548 A3, 317–325
EP2236548 B1, 317–325
EP2238195 A1, 44t–74t
EP2241605 A2, 152–182, 469–479
EP2241605 A3, 152–182, 469–479
EP2245102 A1, 469–479
EP2246402 A1, 423–429
EP2246402 A4, 423–429
EP2246402 B1, 423–429
EP2252440 A1, 515–528
EP2252440 B1, 515–528
EP2255951 A1, 375–386
EP2256149 A1, 242–261
EP2265659 A2, 44t–74t
EP2285890 A1, 152–182
EP2285890 B1, 152–182
EP2285901 A1, 152–182
EP2291429 A2, 290–299

EP2291429 B1, 290–299
EP2291430 A1, 290–299
EP2295218 A1, 515–528
EP2296879 A1, 152–182, 375–386
EP2297212 A1, 152–182
EP2297212 A4, 152–182
EP2305324 A1, 44t–74t
EP2311896 A1, 469–479
EP2321294 A2, 44t–74t
EP2323788 A1, 317–325
EP2323788 A4, 317–325
EP2325246 A2, 199–213
EP2325246 A3, 199–213
EP2329961 A1, 152–182
EP2329961 B1, 152–182
EP2330157 A1, 375–386
EP2334719 A2, 345–359
EP2336244 A1, 100–114
EP2344577 A1, 317–325
EP2345688 A1, 152–182
EP2345688 A4, 152–182
EP2346922 A1, 290–299
EP2346922 B1, 290–299
EP2348122 A1, 515–528
EP2348122 A4, 515–528
EP2352781 A1, 152–182, 242–261
EP2352781 A4, 152–182, 242–261
EP2356184 A1, 439–445
EP2357209 A1, 152–182
EP2363434 A1, 92, 100–114
EP2370508 A1, 345–359
EP2376538 A1, 44t–74t
EP2389421 A1, 439–445
EP2389421 A4, 439–445
EP2392570 A1, 44t–74t
EP2419395 A1, 515–528
EP2419395 B1, 515–528
EP2419395 B8, 515–528
EP2419396 A1, 515–528
EP2419396 B1, 515–528
EP2422005 A1, 401–410
EP2422005 B1, 401–410
EP2424937 A2, 44t–74t
EP2429598 A2, 469–479
EP2432830 A1, 152–182
EP2432830 B1, 152–182
EP2433796 A1, 152–182, 375–386
EP2436814 A1, 401–410
EP2436814 A4, 401–410
EP2439228 A2, 270–275
EP2450388 A1, 44t–74t
EP2451860 A2, 44t–74t
EP2456620 A1, 152–182
EP2456620 A4, 152–182
EP2462189 A1, 515–528
EP2462189 B1, 515–528
EP2475689 A1, 515–528
EP2475689 B1, 515–528
EP2480222 A1, 345–359
EP2480222 A4, 345–359
EP2480411 A1, 375–386
EP2480589 A1, 515–528
EP2480710 A1, 317–325
EP2492325 A1, 469–479
EP2492327 A1, 469–479
EP2492327 A4, 469–479
EP2492328 A1, 469–479
EP2493978 A1, 242–261
EP2493979 A1, 242–261
EP2513325 A2, 44t–74t
EP2515817 A2, 152–182
EP2515817 A4, 152–182
EP2519567 A2, 152–182
EP2519579 A1, 242–261, 375–386
EP2524004 A2, 345–359
EP2524945 A1, 242–261
EP2524945 A4, 242–261
EP2524945 B1, 242–261
EP2535041 A1, 290–299
EP2545120 A1, 152–182
EP2551301 A1, 368, 375–386
EP2553000 A1, 270–275
EP2553000 A4, 270–275
EP2559725 A, 495–496, 507, 515–528
EP2567936 A1, 423–429
EP2567936 A4, 423–429
EP2569363 A1, 345–359
EP2572020 A2, 515–528
EP2573133 A1, 345–359
EP2575771 A1, 270–275
EP2580277 A1, 345–359
EP2582757 A1, 152–182
EP2583994 A1, 375–386
EP2589489 A2, 317–325
EP2589489 A4, 317–325
EP2593514 A2, 152–182
EP2593514 A4, 152–182
EP2607415 A1, 375–386
EP2607415 A4, 375–386
EP2607529 A1, 401–410
EP2607529 A4, 401–410
EP2612959 A1, 401–410
EP2612959 A4, 401–410
EP2617771 A2, 345–359
EP2617771 A3, 345–359
EP2644643 A1, 469–479
EP2647682 A1, 469–479
EP2655487 A2, 317–325
EP2657269 A1, 290–299
EP2657279 A1, 345–359
EP2658906 A2, 345–359
EP2683623 A1, 439–445
EP2683773 A2, 152–182
EP2690129 A2, 345–359
EP2690129 A3, 345–359
EP2705096 A2, 454–458
EP2707222 A1, 439–445
EP327505 A2, 138
ES2006417 T3, 44t–74t
ES2031151 T3, 270–275
ES2031151 T5, 270–275
ES2031529 T3, 199–213
ES2032537 T3, 152–182
ES2035949 T3, 199–213
ES2039315 T1, 152–182
ES2039315 T3, 152–182
ES2039315 T5, 152–182
ES2051888 T3, 44t–74t
ES2051888 T5, 44t–74t
ES2053798 T3, 44t–74t
ES2053801 T3, 44t–74t
ES2058868 T3, 152–182
ES2061589 T3, 242–261
ES2062177 T3, 152–182
ES2067437 T1, 469–479
ES2067437 T3, 469–479
ES2078406 T3, 270–275
ES2080958 T3, 44t–74t
ES2095494 T3, 515–528
ES2100855 T3, 152–182
ES2103806 T3, 152–182
ES2103943 T3, 100–114, 152–182
ES2113542 T3, 375–386
ES2115258 T3, 44t–74t
ES2115583 T3, 199–213
ES2121741 T3, 44t–74t
ES2122205 T3, 401–410
ES2122792 T3, 44t–74t
ES2122792 T5, 44t–74t
ES2123533 T3, 152–182
ES2123533 T5, 152–182
ES2128704 T3, 290–299
ES2146751 T3, 290–299
ES2147918 T3, 44t–74t
ES2154655 T3, 44t–74t
ES2156210 T3, 44t–74t
ES2156893 T3, 290–299
ES2162088 T3, 199–213, 401–410, 469–479
ES2163565 T3, 152–182
ES2168652 T3, 44t–74t
ES2170364 T3, 242–261
ES2175821 T3, 44t–74t
ES2178491T T3, 44t–74t
ES2183631 T3, 44t–74t
ES2183878 T3, 152–182
ES2186689 T3, 290–299
ES2186723 T3, 469–479
ES2188648 T3, 100–114
ES2196385 T3, 44t–74t
ES2198579 T3, 199–213
ES2200586 T3, 270–275
ES2201173 T3, 152–182
ES2203500 T3, 345–359
ES2209813 T3, 199–213, 270–275, 290–299
ES2219247 T3, 152–182
ES2221053 T3, 199–213
ES2221363 T3, 290–299
ES2225503 T3, 423–429
ES2226410 T3, 423–429, 439–445
ES2230689 T3, 401–410
ES2235516 T3, 345–359
ES2235516 T5, 345–359
ES2251236 T3, 44t–74t
ES2251716 T3, 100–114
ES2260835 T3, 345–359
ES2266506 T3, 469–479
ES2271522 T3, 454–458
ES2272582 T3, 152–182
ES2274996 T3, 242–261
ES2275724 T3, 44t–74t
ES2276084 T3, 439–445
ES2278424 T3, 100–114, 152–182
ES2281147 T3, 44t–74t
ES2283572 T3, 375–386
ES2285770 T3, 44t–74t

ES2294064 T3, 345–359
ES2295021 T3, 44t–74t
ES2297385 T3, 152–182, 469–479
ES2298135 T3, 290–299
ES2299555 T3, 469–479
ES2301658 T3, 100–114
ES2305201 T3, 152–182
ES2306273 T3, 152–182
ES2315737 T3, 242–261
ES2333038 T3, 44t–74t
ES2336491 T3, 100–114
ES2343326 T3, 199–213
ES2344000 T3, 44t–74t
ES2345518 T3, 152–182
ES2349424 T3, 439–445
ES2351526 T3, 290–299
ES2362405 T3, 290–299, 469–479
ES2366541 T3, 152–182
ES2368093 T3, 152–182
ES2369811 A1, 423–429
ES2369811 B1, 423–429
ES2371069 T3, 152–182, 469–479
ES2371756 T3, 199–213
ES2372235T T3, 44t–74t
ES2372988 T3, 345–359
ES2374740 T3, 375–386
ES2376281 T3, 152–182
ES2379361 T3, 100–114, 242–261
ES2382530 T3, 152–182
ES2385105 T3, 515–528
ES2394653 T3, 515–528
ES2394953 T3, 44t–74t
ES2395057 T3, 44t–74t
ES2401990 T3, 345–359
ES2426774 T3, 290–299
ES2445337 T3, 100–114
ES358639 A1, 469–479
ES444484 A1, 44t–74t
ES473389 A1, 152–182
ES8103169 A1, 100–114, 199–213
ES8207564 A1, 44t–74t

F
FI100302 B, 242–261
FI100977 B, 152–182
FI102478 B, 152–182
FI102760 B, 152–182
FI102760 B1, 152–182
FI105040 B, 242–261
FI107541 B1, 270–275
FI108038 B1, 199–213
FI108460 B, 375–386
FI110413 B, 375–386
FI112083 B, 242–261, 290–299
FI112624 B, 423–429
FI115138 B, 100–114, 152–182
FI116142 B1, 199–213
FI117440 B, 44t–74t
FI117510 B1, 152–182
FI117898 B1, 199–213
FI118223 B1, 152–182
FI20000496 A, 100–114, 152–182
FI20031301 A, 199–213
FI20060360 A, 152–182
FI52523 B, 242–261
FI52523 C, 242–261
FI782826 A, 152–182
FI87225 B, 44t–74t
FI87225 C, 44t–74t
FI874504 A, 199–213
FI880929 A, 44t–74t
FI883117 A, 44t–74t
FI883720 A, 44t–74t
FI884604 A, 242–261
FI885767 A, 199–213
FI890406 A, 152–182
FI925333 A, 270–275
FI925978 A, 100–114, 152–182
FI93022 B, 44t–74t
FI93022 C, 44t–74t
FI932450 A, 100–114, 152–182
FI935282 A, 345–359
FI945264 A, 290–299
FI946071 A, 375–386
FI950284 A, 270–275
FI951637 A, 439–445
FI952162 A, 152–182
FI953411 A, 375–386
FI960158 A, 469–479
FI960433 A, 242–261, 290–299
FI961022 A, 242–261
FI96219 B, 199–213
FI96219 C, 199–213
FI962251 A, 317–325
FI962627 A, 199–213
FI962996 A, 100–114, 401–410
FI962997 A, 100–114
FI96610 B, 199–213
FI96610 C, 199–213
FI970679 A, 199–213
FI972059 A, 152–182
FI972060 A, 44t–74t
FI972638 A, 375–386
FI973358 A, 44t–74t
FI973359 A, 44t–74t
FI973364 A, 199–213
FI981558 A, 423–429, 439–445
FI99125 C, 290–299
FR1585311 A, 469–479
FR2088548 A1, 242–261
FR2088548 B1, 242–261
FR2184657 A1, 152–182
FR2184657 B3, 152–182
FR2265412 A1, 100–114
FR2265412 B1, 100–114
FR2299356 A1, 44t–74t
FR2338291 A1, 100–114
FR2403354 A1, 152–182
FR2403354 B1, 152–182
FR2446859 A1, 100–114, 196, 199–213
FR2446859 B1, 100–114, 199–213
FR2567149 A1, 196, 199–213
FR2567149 B1, 199–213
FR2608942 A1, 199–213
FR2608988 A1, 266, 270–275
FR2608988 B1, 270–275
FR2618441 A1, 146, 152–182
FR2618441 B1, 152–182
FR2709500 A1, 401–410
FR2782999 A1, 131
FR2782999 B1, 44t–74t
FR2786098 A1, 28
FR2859729 A1, 199–213
FR2859729 B1, 199–213
FR2862310 A1, 194, 199–213
FR2902434 A1, 135–136, 152–182
FR2902434 B1, 152–182
FR2905378 A1, 146, 152–182
FR2905378 B1, 152–182
FR2918383 A1, 131, 152–182, 281, 290–299
FR2918383 B1, 152–182, 290–299
FR2927629 A1, 465–466, 469–479
FR2927629 B1, 469–479
FR2957351 A1, 152–182
FR2957351 B1, 152–182
FR2970713 A1, 270–275
FR2973386 A1, 231, 242–261
FR2973386 B1, 242–261
FR2974811 A1, 454–458
FR2981359 A1, 454–458
FR2981359 B1, 454–458

G
GB1043518 A, 100–114
GB1239636 A, 469–479
GB1421233 A, 152–182
GB1425624 A, 282–283, 290–299
GB1490425 A, 100–114
GB1502082 A, 44t–74t
GB1568719 A, 100–114
GB1590261 A, 20
GB1600496 A, 152–182
GB2086404 A, 44t–74t
GB2107320 A, 513–528
GB2205323 A, 34
GB2205323 B, 44t–74t
GB2206888 A, 34
GB2206888 B, 44t–74t
GB2208651 A, 34
GB2208651 B, 44t–74t
GB2214918 A, 152–182
GB2243327 A, 367, 375–386
GB2284477 A, 491, 515–528
GB2284477 B, 515–528
GB2291648 A, 146, 152–182, 194, 199–213, 431, 439–445
GB2291648 B, 152–182, 199–213, 439–445
GB2456564 A, 451, 454–458
GB2461147 A, 448, 454–458
GB2461147 B, 454–458
GB2488811 A, 123, 152–182
GB965349 A, 361–362, 375–386
GR3002778 T3, 375–386
GR3004152 T3, 270–275
GR3004198 T3, 199–213
GR3006550 T3, 44t–74t
GR3006969 T3, 199–213
GR3018034 T3, 100–114, 270–275
GR3018122 T3, 270–275
GR3022577 T3, 44t–74t
GR3023472 T3, 152–182
GR3023869 T3, 152–182
GR3024078 T3, 100–114, 152–182

GR3026335 T3, 375–386
GR3030372 T3, 290–299
GR3034115 T3, 290–299
GR3035425 T3, 44t–74t
GR74902 A1, 44t–74t
GR88300163 T1, 44t–74t
GR92300067 T1, 152–182
GT200000029 A, 345–359

H

HK1006847 A1, 152–182
HK1007755 A1, 152–182
HK1009643 A1, 375–386
HK1025607 A1, 401–410
HK1031887 A1, 44t–74t
HK1036466 A1, 100–114, 439–445
HK1041708 A1, 100–114, 152–182
HK1059414 A1, 423–429
HK1072205 A1, 439–445
HK1076120 A, 199–213
HK1078601 A1, 100–114
HK1084687 A1, 152–182, 469–479
HK1085504 A1, 152–182, 469–479
HK1097412 A1, 242–261
HK1107286 A1, 439–445
HK1125395 A1, 290–299
HU0001972 A2, 44t–74t
HU0100466 A2, 290–299
HU0100466 A3, 290–299
HU0201525 A2, 515–528
HU0201931 A2, 345–359
HU0402591 A2, 439–445
HU204858 B, 199–213
HU205954 B, 152–182
HU205963 B, 152–182
HU206510 B, 152–182
HU211429 B, 152–182
HU212028 B, 152–182
HU216971 B, 100–114, 152–182
HU218160 B, 100–114
HU222543 B1, 290–299
HU222853 B1, 152–182
HUT45734 A, 199–213
HUT49895 A, 44t–74t
HUT52130 A, 44t–74t
HUT54392 A, 152–182
HUT54393 A, 152–182
HUT54402 A, 152–182
HUT55813 A, 152–182
HUT61791 A, 152–182
HUT63644 A, 100–114, 152–182
HUT68437 A, 152–182
HUT75180 A, 100–114
HUT75658 A, 44t–74t
HUT77057 A, 44t–74t
HUT77198 A, 152–182

I

ID23288 A, 100–114
ID23288 A, 401–410
ID23445 A, 44t–74t
ID23491 A, 100–114
IE47745 B1, 152–182
IE51287 B1, 44t–74t
IE61041 B1, 44t–74t
IE62111 B1, 199–213
IE62505 B1, 242–261
IE781873 L, 152–182
IE872618 L, 199–213
IE881026 L, 199–213
IE883040 L, 242–261
IE890281 L, 152–182
IE902117 A1, 152–182
IE902117 L, 152–182
IE902174 A1, 152–182
IE902174 L, 152–182
IE902379 A1, 152–182
IE914155 A1, 100–114, 152–182
IL137299 A, 290–299
IL157964 A, 375–386
IL158424 A, 375–386
IL161124 A, 199–213
IL196761 A, 242–261
IL48799 A, 44t–74t
IL84032 A, 199–213
IL86922 A, 44t–74t
IL87397 A, 44t–74t
IL87973 A, 242–261
IL89096 A, 152–182
IL90714 A, 44t–74t
IL94495 A, 152–182
IL94587 A, 152–182
IN167499 A1, 44t–74t
IN170801 A1, 199–213
IN172788 A1, 44t–74t
IN174313 A1, 152–182
IN175171 A1, 44t–74t
IT1050278 B, 100–114
IT1057070 B, 44t–74t
IT1082451 B, 100–114
IT1109078 B, 152–182
IT1198449 B, 199–213
IT1233599 B, 152–182
IT1234783 B, 152–182
IT1277799 B1, 317–325
IT1380839 B, 515–528
IT986290 B, 152–182
ITBO950462 A1, 439–445
ITMI20061844 A1, 152–182
ITMI20061845 A1, 152–182
ITMI20100865 A1, 345–359
ITTO20010057 A1, 152–182
ITVR950068 A1, 317–325

J

JP2000007789 A, 191, 199–213
JP2000007815 A, 333–335, 345–359
JP2000007816 A, 332–333, 335–336, 345–359
JP2000017038 A, 136, 152–182, 337, 345–359
JP2000053792 A, 342, 345–359
JP2000086965 A, 219–220, 242–261
JP2000094573 A, 309, 317–325
JP2000095898 A, 140, 152–182
JP2000096491 A, 314, 317–325
JP2000103005 A, 309, 317–325
JP2000103006 A, 309, 317–325
JP2000103879 A, 309, 317–325
JP2000108202 A, 309, 317–325
JP2000109045 A, 374–386
JP2000136261 A, 345–359
JP2000136435 A, 90, 100–114
JP2000160034 A, 415, 423–429
JP2000280410 A, 239–261
JP2000302956 A, 242–261
JP2000319446 A, 132–133, 152–182
JP2000504355 A, 44t–74t
JP2000506204 A, 242–261
JP2000508699 A, 469–479
JP2000508700 A, 317–325
JP2000509428 A, 44t–74t
JP2000515853 A, 199–213
JP2000516878 A, 375–386
JP2001011294 A, 188–189, 199–213
JP2001018290 A, 310–311, 317–325
JP2001040078 A, 503, 515–528
JP2001098065 A, 18–20
JP2001098104 A, 339, 345–359
JP2001131433 A, 340, 345–359
JP2001162676 A, 91, 100–114
JP2001166537 A, 454–458
JP2001187817 A, 44t–74t
JP2001187818 A, 44t–74t
JP2001226571 A, 242–261, 369–370, 375–386
JP2001261797 A, 90, 100–114, 278–280, 290–299
JP2001288273 A, 264, 270–275
JP2001294792 A, 450, 454–458
JP2001303478 A, 189, 199–213
JP2001323052 A, 281–282, 290–299
JP2001329072 A, 411, 423–429
JP2001329082 A, 307, 317–325
JP2001335710 A, 414, 423–429
JP2001354223 A, 90–91, 304, 317–325
JP2001354802 A, 100–114, 152–182
JP2001354841 A, 199–213
JP2001501652 A, 199–213
JP2001522412 A, 401–410
JP2001523999 A, 290–299
JP2001525473 A, 44t–74t
JP2002003607 A, 192, 199–213
JP2002012687 A, 239–240, 242–261
JP2002017384 A, 510, 515–528
JP2002017385 A, 510, 515–528
JP2002020525 A, 339–340, 345–359
JP2002030208 A, 278–280, 290–299
JP2002069206 A, 285, 290–299
JP2002069279 A, 125, 152–182
JP2002069303 A, 416, 423–429
JP2002069341 A, 450, 454–458
JP2002069352 A, 290–299, 450, 454–458
JP2002080703 A, 229, 242–261
JP2002097359 A, 449, 454–458
JP2002105298 A, 417, 423–429
JP2002105371 A, 451, 454–458
JP2002114900 A, 240, 242–261
JP2002121240 A, 307, 317–325
JP2002138139 A, 44t–74t
JP2002146170 A, 364, 375–386
JP2002161155 A, 311, 317–325
JP2002173535 A, 190, 199–213
JP2002179891 A, 220, 242–261
JP2002179898 A, 220–221, 242–261

JP2002179971 A, 451, 454–458
JP2002210886 A, 317–325
JP2002226623 A, 485, 515–528
JP2002234117 A, 369, 375–386
JP2002248047 A, 395, 401–410
JP2002249696 A, 451, 454–458
JP2002256088 A, 307, 317–325
JP2002275379 A, 515–528
JP2002302567 A, 337–338, 345–359
JP2002317066 A, 327–328, 345–359
JP2002320499 A, 510–511, 515–528
JP2002356640 A, 450, 454–458
JP2002371259 A, 469–479
JP2002371431 A, 100–114
JP2002503160 A, 439–445
JP2002503524 A, 290–299
JP2002509968 A, 100–114, 439–445
JP2002513449 A, 439–445
JP2002517582 A, 199–213
JP2002519222 A, 423–429, 439–445
JP2002524627 A, 345–359
JP2002528585 T, 515–528
JP2002529567 A, 44t–74t
JP2002529568 A, 44t–74t
JP2002530323 A, 44t–74t
JP2002534981 A, 44t–74t
JP2002539854 A, 44t–74t
JP2002541308 A, 290–299
JP2002542339 A, 44t–74t
JP2002542349 A, 44t–74t
JP2002542352 A, 44t–74t
JP2002543220 A, 270–275
JP2002544335 A, 199–213, 270–275, 290–299
JP2003010030 A, 395, 401–410
JP2003012984 A, 454–458
JP2003020355 A, 328, 345–359
JP2003020390 A, 229, 242–261
JP2003026757 A, 345–359
JP2003039524 A, 328, 345–359
JP2003041435 A, 391, 401–410
JP2003049374 A, 389, 401–410
JP2003073495 A, 338, 345–359
JP2003073532 A, 242–261
JP2003079388 A, 511–512, 515–528
JP2003082140 A, 371
JP2003082160 A, 127–128, 375–386
JP2003096285 A, 121, 152–182
JP2003103595 A, 335, 345–359
JP2003103628 A, 363, 375–386
JP2003103632 A, 369, 375–386
JP2003128768 A, 100–114, 152–182
JP2003128900 A, 488, 499, 515–528
JP2003138140 A, 242–261
JP2003147248 A, 450, 454–458
JP2003165570 A, 315, 317–325, 450, 454–458
JP2003175569 A, 315, 317–325, 450, 454–458
JP2003176289 A, 515–528
JP2003182266 A, 315, 317–325, 450, 454–458
JP2003183488 A, 133, 152–182
JP2003192883 A, 225–226, 242–261
JP2003192884 A, 7–8
JP2003192925 A, 236, 242–261
JP2003221464 A, 100–114, 152–182
JP2003226801 A, 91, 100–114
JP2003253009 A, 100–114
JP2003261661 A, 44t–74t
JP2003261704 A, 328, 345–359
JP2003277595 A, 188, 199–213
JP2003286401 A, 135, 152–182
JP2003292640 A, 317–325
JP2003293220 A, 388–389, 401–410
JP2003300927 A, 508, 515–528
JP2003301066 A, 328, 345–359
JP2003301152 A, 469–479
JP2003311876 A, 309, 317–325
JP2003313214 A, 286, 290–299
JP2003313307 A, 215–216, 242–261
JP2003321600 A, 189, 199–213, 433, 439–445
JP2003327737 A, 328, 345–359
JP2003328229 A, 401–410
JP2003507022 A, 44t–74t
JP2003513133 A, 152–182, 290–299
JP2004002776 A, 369, 375–386
JP2004002871 A, 191, 199–213
JP2004010842 A, 135, 152–182
JP2004018681 A, 100–114
JP2004018744 A, 194, 199–213
JP2004027136 A, 216, 242–261
JP2004044002 A, 400–410
JP2004057134 A, 304, 317–325
JP2004058352 A, 328, 345–359
JP2004067801 A, 242–261
JP2004083890 A, 345–359
JP2004084156 A, 100–114, 152–182
JP2004091968 A, 90, 100–114, 399, 401–410
JP2004099883 A, 188–189, 199–213
JP2004143315 A, 133, 152–182
JP2004149679 A, 371, 375–386
JP2004161931 A, 100–114
JP2004168798 A, 451, 454–458
JP2004175831 A, 412, 423–429
JP2004175999 A, 17
JP2004190025 A, 236, 242–261
JP2004204143 A, 216, 242–261
JP2004204219 A, 189, 199–213
JP2004204365 A, 396, 401–410
JP2004204406 A, 90, 100–114, 399, 401–410
JP2004204407 A, 100–114, 399, 401–410
JP2004216378 A, 488, 499, 515–528
JP2004218182 A, 399, 401–410
JP2004223786 A, 314–315, 317–325
JP2004231797 A, 462, 469–479
JP2004231910 A, 411–412, 423–429
JP2004237543 A, 422–429
JP2004238564 A, 451, 454–458
JP2004244457 A, 100–114, 216, 242–261
JP2004262971 A, 242–261
JP2004263168 A, 44t–74t
JP2004269865 A, 267, 270–275
JP2004270094 A, 400–410
JP2004277682 A, 363, 375–386
JP2004277748 A, 439–445
JP2004277931 A, 399, 401–410
JP2004290130 A, 513, 515–528
JP2004307662 A, 328, 345–359
JP2004308077 A, 495, 515–528
JP2004323804 A, 188–189, 199–213
JP2004345150 A, 91, 100–114
JP2004359763 A, 304, 317–325
JP2004359892 A, 229, 242–261
JP2004503415 A, 423–429
JP2004506792 A, 152–182
JP2004507600 A, 44t–74t
JP2004512419 A, 290–299, 469–479
JP2004513200 A, 515–528
JP2004518781 A, 152–182
JP2004518808 A, 152–182
JP2004533551 A, 401–410
JP2004534135 A, 100–114
JP2004536941 A, 242–261
JP2004537136 A, 345–359
JP2004538178 A, 100–114
JP2005002289 A, 341, 345–359
JP2005002302 A, 266, 270–275
JP2005008733 A, 190–191, 199–213
JP2005008997 A, 395, 401–410
JP2005014966 A, 310–311, 317–325
JP2005023512 A, 389, 401–410
JP2005036104 A, 229, 242–261
JP2005048303 A, 395, 401–410
JP2005060689 A, 222, 242–261, 345–359
JP2005060850 A, 395, 401–410
JP2005068306 A, 339, 345–359
JP2005082710 A, 515–528
JP2005089751 A, 199–213
JP2005105245 A, 423–429
JP2005120118 A, 242–261
JP2005120119 A, 236, 242–261
JP2005131856 A, 495, 501, 515–528
JP2005132901 A, 495, 501, 515–528
JP2005139441 A, 92, 100–114
JP2005146425 A, 396, 401–410
JP2005154477 A, 469–479
JP2005162871 A, 236, 242–261
JP2005194383 A, 312–313, 317–325
JP2005200600 A, 221, 242–261
JP2005200663 A, 266, 270–275
JP2005211041 A, 19
JP2005232228 A, 135, 137, 152–182
JP2005232232 A, 137, 152–182
JP2005248062 A, 220, 242–261
JP2005248139 A, 220, 242–261
JP2005263997 A, 421–429
JP2005264155 A, 18
JP2005298401 A, 508, 515–528
JP2005306943 A, 100–114, 290–299
JP2005307078 A, 414, 423–429
JP2005307359 A, 393, 401–410
JP2005320426 A, 17
JP2005325336 A, 290–299
JP2005330211 A, 508, 515–528
JP2005505639 A, 469–479
JP2005506401 A, 199–213
JP2005511840 A, 317–325
JP2005515290 A, 454–458
JP2005516736 A, 439–445
JP2006009007 A, 152–182
JP2006022472 A, 100–114, 152–182
JP2006063308 A, 364, 375–386
JP2006068225 A, 395–396, 401–410
JP2006070091 A, 462, 469–479
JP2006077063 A, 146, 152–182
JP2006083262 A, 222, 242–261
JP2006089687 A, 190–191, 199–213
JP2006097166 A, 395, 401–410

JP2006104335 A, 152–182
JP2006111836 A, 452, 454–458
JP2006124439 A, 312, 317–325
JP2006130847 A, 85, 100–114, 373, 375–386
JP2006130848 A, 373, 375–386
JP2006131705 A, 462, 469–479
JP2006137892 A, 508–509, 515–528
JP2006160867 A, 435, 439–445
JP2006176731 A, 242–261
JP2006182017 A, 365, 375–386
JP2006233192 A, 338, 345–359
JP2006274231 A, 501, 515–528
JP2006274520 A, 399, 401–410
JP2006282750 A, 338, 345–359
JP2006282753 A, 345–359
JP2006291205 A, 44t–74t
JP2006326952 A, 421–429
JP2006335874 A, 242–261
JP2006512506 A, 401–410
JP2006518780 A, 242–261
JP2006518799 A, 152–182, 469–479
JP2006519293 A, 152–182, 469–479
JP2007001940 A, 507, 515–528
JP2007002160 A, 506, 515–528
JP2007023176 A, 506, 515–528
JP2007031538 A, 495, 501, 515–528
JP2007051202 A, 506–507, 515–528
JP2007070422 A, 462, 469–479
JP2007070517 A, 412–413, 423–429
JP2007092022 A, 287, 290–299
JP2007099663 A, 508–509, 515–528
JP2007100104 A, 121, 152–182
JP2007112867 A, 371, 375–386
JP2007126653 A, 242–261
JP2007138377 A, 100–114, 152–182
JP2007146163 A, 44t–74t
JP2007154002 A, 278–280, 290–299, 417, 423–429
JP2007182484 A, 287, 290–299
JP2007191548 A, 122
JP2007191625 A, 122, 152–182
JP2007197523 A, 317–325
JP2007197602 A, 264, 270–275
JP2007210889 A, 506, 515–528
JP2007224113 A, 501, 515–528
JP2007230284 A, 393, 401–410
JP2007238691 A, 507, 515–528
JP2007246707 A, 231, 242–261
JP2007254509 A, 371, 375–386
JP2007262319 A, 345–359
JP2007270372 A, 396, 401–410
JP2007277389 A, 501, 515–528
JP2007284495 A, 484, 515–528
JP2007307719 A, 422–429
JP2007308626 A, 463, 469–479
JP2007308660 A, 92, 100–114
JP2007314797 A, 290–299
JP2007314913 A, 393, 401–410
JP2007326290 A, 366, 375–386
JP2007331154 A, 313, 317–325
JP2007511631 A, 199–213
JP2007517126 A, 242–261
JP2007524715 A, 152–182
JP2008001837 A, 287, 290–299
JP2008007611 A, 509, 515–528
JP2008013657 A, 450–451, 454–458
JP2008013658 A, 450–451, 454–458
JP2008030306 A, 242–261, 317–325
JP2008038142 A, 144–145, 152–182
JP2008043905 A, 313, 317–325
JP2008044363 A, 370–371, 375–386
JP2008050351 A, 501–502, 515–528
JP2008050446 A, 515–528
JP2008063356 A, 122, 152–182
JP2008063697 A, 313, 317–325
JP2008069299 A, 229–230, 242–261
JP2008100413 A, 485, 515–528
JP2008115503 A, 44t–74t
JP2008138060 A, 435, 439–445
JP2008155385 A, 373–386
JP2008179713 A, 507, 515–528
JP2008195834 A, 143–144, 152–182, 221, 242–261
JP2008201679 A, 499, 515–528
JP2008201680 A, 499, 515–528
JP2008208258 A, 515–528
JP2008231048 A, 498–499, 515–528
JP2008239830 A, 439–445
JP2008254794 A, 317–325
JP2008255349 A, 152–182
JP2008260205 A, 309–310, 317–325
JP2008265117 A, 373, 375–386
JP2008274222 A, 515–528
JP2008274228 A, 412, 423–429
JP2008285610 A, 310, 317–325
JP2008291268 A, 121–122, 152–182
JP2008308693 A, 100–114
JP2008513234 A, 375–386
JP2008527120 A, 152–182
JP2008535483 A, 199–213
JP2009001622 A, 100–114
JP2009029757 A, 505, 515–528
JP2009030068 A, 100–114, 242–261
JP2009062502 A, 345–359
JP2009072759 A, 505, 515–528
JP2009079220 A, 199–213
JP2009084581 A, 345–359
JP2009084759 A, 399, 401–410
JP2009091588 A, 345–359
JP2009133022 A, 397, 401–410
JP2009138085 A, 364, 375–386
JP2009144152 A, 100–114, 242–261
JP2009161655 A, 484, 515–528
JP2009162957 A, 454–458
JP2009167225 A, 289–299
JP2009167539 A, 399, 401–410
JP2009185108 A, 100–114, 196, 199–213
JP2009202465 A, 100–114, 375–386
JP2009242520 A, 226, 242–261
JP2009242545 A, 505, 515–528
JP2009242728 A, 337, 345–359
JP2009249508 A, 507, 515–528
JP2009270228 A, 396–397, 401–410
JP2009280932 A, 397, 401–410
JP2009507110 A, 290–299
JP2009508598 A, 44t–74t
JP2009518555 A, 401–410
JP2009527593 A, 100–114, 152–182, 242–261
JP2009527594 A, 100–114, 242–261, 423–429
JP2009527596 A, 100–114, 242–261
JP2009527597 A, 100–114, 242–261
JP2009528416 A, 290–299
JP2009540088 A, 152–182
JP2009544826 A, 242–261
JP2010005948 A, 484–485, 515–528
JP2010018640 A, 439–445
JP2010024576 A, 397, 401–410
JP2010037463 A, 469–479
JP2010059423 A, 152–182
JP2010070621 A, 220, 242–261
JP2010084001 A, 100–114
JP2010132886 A, 515–528
JP2010138389 A, 515–528
JP2010138390 A, 515–528
JP2010143947 A, 136, 152–182
JP2010144091 A, 304, 317–325
JP2010150721 A, 100–114, 401–410
JP2010174170 A, 450, 454–458
JP2010175841 A, 452, 454–458
JP2010254812 A, 44t–74t
JP2010255135 A, 401–410
JP2010260900 A, 230, 242–261
JP2010270425 A, 401–410
JP2010500937 A, 270–275
JP2010502801 A, 152–182
JP2010502811 A, 423–429
JP2010505017 A, 152–182
JP2010505018 A, 152–182
JP2010506965 A, 515–528
JP2010508425 A, 152–182
JP2010509413 A, 515–528
JP2010513604 A, 345–359
JP2010516884 A, 345–359
JP2010518166 A, 199–213
JP2010518244 A, 199–213
JP2010518245 A, 199–213
JP2010525099 A, 345–359
JP2010526163 A, 345–359
JP2010535120 A, 317–325
JP2010536973 A, 242–261
JP2010538791 A, 345–359
JP2011063821 A, 423–429
JP2011088957 A, 469–479
JP2011088958 A, 469–479
JP2011088959 A, 469–479
JP2011089006 A, 439–445
JP2011111541 A, 220, 242–261
JP2011116984 A, 454–458
JP2011140656 A, 152–182, 469–479
JP2011162480 A, 499, 515–528
JP2011168798 A, 242–261
JP2011178932 A, 100–114
JP2011190426 A, 198–213
JP2011219736 A, 22
JP2011252102 A, 460, 469–479
JP2011506628 A, 44t–74t
JP2011510148 A, 242–261
JP2011511105 A, 44t–74t
JP2011514850 A, 515–528
JP2011518241 A, 152–182
JP2011526949 A, 152–182, 375–386
JP2011526950 A, 152–182
JP2011527348 A, 44t–74t
JP2012040787 A, 345–359
JP2012066588 A, 515–528

JP2012067157 A, 439–445
JP2012111203 A, 464, 469–479
JP2012111204 A, 464, 469–479
JP2012111205 A, 464, 469–479
JP2012111206 A, 464, 469–479
JP2012111207 A, 464, 469–479
JP2012111208 A, 464, 469–479
JP2012111217 A, 464, 469–479
JP2012111914 A, 464, 469–479
JP2012111915 A, 464, 469–479
JP2012111916 A, 469–479
JP2012111918 A, 464, 469–479
JP2012111919 A, 469–479
JP2012111955 A, 270–275
JP2012116888 A, 464, 469–479
JP2012116889 A, 469–479
JP2012131072 A, 242–261
JP2012229404 A, 242–261
JP2012246421 A, 303, 317–325
JP2012505288 A, 345–359
JP2012507614 A, 152–182, 242–261
JP2012515835 A, 439–445
JP2012523442 A, 515–528
JP2012523443 A, 515–528
JP2013039425 A, 290–299
JP2013043959 A, 236, 242–261
JP2013079356 A, 236, 242–261
JP2013193336 A, 317–325
JP2013194175 A, 412, 423–429
JP2013501111 A, 515–528
JP2013504634 A, 515–528
JP2013506032 A, 345–359
JP2013513397 A, 44t–74t
JP2013515822 A, 242–261, 375–386
JP2013521396 A, 152–182
JP2013527204 A, 270–275
JP2013527338 A, 515–528
JP2013530301 A, 345–359
JP2013532209 A, 152–182
JP2013535353 A, 317–325
JP2507731 B2, 44t–74t
JP2513091 B2, 199–213, 423–429
JP2527523 B2, 100–114, 152–182
JP2564386 B2, 199–213
JP2631050 B2, 152–182
JP2635218 B2, 317–325
JP2636186 B2, 345–359, 423–429
JP2648308 B2, 199–213
JP2651884 B2, 152–182
JP2655796 B2, 345–359
JP2670680 B2, 270–275
JP2739896 B2, 270–275
JP2742630 B2, 152–182
JP2763303 B2, 242–261
JP2777757 B2, 100–114
JP2815260 B2, 401–410
JP2821986 B2, 515–528
JP2825969 B2, 290–299
JP2842649 B2, 44t–74t
JP2883809 B2, 401–410
JP2892964 B2, 401–410
JP2997995 B2, 199–213, 469–479
JP3040794 B2, 152–182
JP3076797 B2, 152–182
JP3079716 B2, 44t–74t
JP3085459 B2, 317–325
JP3085460 B2, 317–325
JP3085461 B2, 317–325
JP3097754 B2, 152–182
JP3105020 B2, 242–261
JP3137198 B2, 152–182
JP3138196 B2, 152–182
JP3196895 B2, 317–325
JP3203355 B2, 515–528
JP3206747 B2, 317–325
JP3211651 B2, 375–386
JP3229978 B2, 345–359
JP3240676 B2, 345–359
JP3267369 B2, 515–528
JP3270087 B2, 345–359
JP3270088 B2, 345–359
JP3279768 B2, 152–182
JP3280666 B2, 44t–74t
JP3290496 B2, 242–261
JP3302145 B2, 375–386
JP3308335 B2, 100–114
JP3312213 B2, 454–458
JP3319531 B2, 401–410
JP3329350 B2, 401–410
JP3334338 B2, 242–261
JP3342579 B2, 44t–74t
JP3344759 B2, 345–359
JP3347440 B2, 242–261, 375–386
JP3348752 B2, 152–182, 242–261
JP3353117 B2, 242–261
JP3355026 B2, 401–410
JP3356825 B2, 515–528
JP3359744 B2, 375–386
JP3359764 B2, 100–114, 242–261
JP3362040 B2, 100–114, 152–182
JP3363589 B2, 152–182
JP3364494 B2, 375–386
JP3369185 B2, 242–261, 290–299
JP3383256 B2, 242–261
JP3390571 B2, 44t–74t
JP3391133 B2, 242–261
JP3393124 B2, 100–114, 152–182
JP3394063 B2, 375–386
JP3410075 B2, 375–386
JP3411168 B2, 100–114
JP3411289 B2, 152–182
JP3415103 B2, 242–261
JP3419127 B2, 242–261
JP3419575 B2, 100–114, 401–410
JP3431042 B2, 152–182
JP3434622 B2, 44t–74t
JP3434628 B2, 401–410
JP3436368 B2, 439–445
JP3439621 B2, 242–261
JP3440915 B2, 100–114, 290–299
JP3452583 B2, 44t–74t
JP3459258 B2, 44t–74t
JP3472644 B2, 242–261
JP3473441 B2, 317–325
JP3476325 B2, 317–325
JP3477642 B2, 317–325
JP3487608 B2, 515–528
JP3493472 B2, 44t–74t
JP3493744 B2, 454–458
JP3503127 B2, 515–528
JP3506425 B2, 242–261
JP3512208 B2, 515–528
JP3523944 B2, 199–213, 439–445
JP3530178 B2, 100–114, 152–182
JP3550782 B2, 345–359
JP3558060 B2, 454–458
JP3570850 B2, 290–299
JP3583097 B2, 515–528
JP3592718 B2, 469–479
JP3592819 B2, 242–261
JP3597809 B2, 242–261
JP3616465 B2, 199–213
JP3623795 B2, 469–479
JP3634937 B2, 423–429
JP3638416 B2, 317–325
JP3647689 B2, 44t–74t
JP3655619 B2, 375–386
JP3666172 B2, 152–182
JP3671547 B2, 242–261
JP3674152 B2, 242–261
JP3680136 B2, 44t–74t
JP3680988 B2, 290–299
JP3698533 B2, 469–479
JP3707240 B2, 242–261
JP3711409 B2, 401–410
JP3716730 B2, 423–429
JP3718636 B2, 375–386
JP3725428 B2, 44t–74t
JP3731838 B2, 100–114, 375–386
JP3732125 B2, 345–359
JP3732135 B2, 345–359
JP3742842 B2, 100–114
JP3747592 B2, 100–114
JP3748832 B2, 242–261
JP3753254 B2, 152–182, 242–261
JP3759067 B2, 290–299
JP3759155 B2, 270–275
JP3772426 B2, 375–386
JP3773057 B2, 439–445
JP3773335 B2, 152–182
JP3773526 B2, 270–275
JP3775668 B2, 199–213, 439–445
JP3783199 B2, 317–325
JP3785011 B2, 454–458
JP3802680 B2, 152–182, 345–359
JP3806320 B2, 401–410
JP3808400 B2, 345–359
JP3810354 B2, 345–359
JP3852958 B2, 100–114
JP3861500 B2, 199–213
JP3866465 B2, 100–114
JP3880073 B2, 401–410
JP3892745 B2, 345–359
JP3902916 B2, 515–528
JP3929434 B2, 44t–74t
JP3938609 B2, 469–479
JP3942883 B2, 317–325, 454–458
JP3945264 B2, 100–114
JP3946958 B2, 199–213, 270–275, 290–299
JP3960797 B2, 44t–74t
JP3962576 B2, 454–458
JP3966043 B2, 401–410
JP3971289 B2, 423–429
JP3992966 B2, 454–458
JP4006457 B2, 515–528

JP4011512 B2, 345–359
JP4034036 B2, 290–299
JP4040567 B2, 401–410
JP4059192 B2, 401–410
JP4071683 B2, 242–261
JP4073052 B2, 100–114, 375–386
JP4075611 B2, 100–114, 401–410
JP4088980 B2, 454–458
JP4093595 B2, 401–410
JP4105600 B2, 317–325
JP4113989 B2, 199–213, 401–410, 469–479
JP4114443 B2, 100–114, 401–410
JP4118313 B1, 507, 515–528
JP4119756 B2, 401–410
JP4140804 B2, 515–528
JP4145193 B2, 100–114
JP4154994 B2, 152–182
JP4171823 B2, 515–528
JP4177992 B2, 515–528
JP4179585 B2, 317–325
JP4190261 B2, 454–458
JP4194558 B2, 100–114
JP4213200 B2, 345–359
JP4222023 B2, 401–410
JP4231781 B2, 100–114
JP4232377 B2, 152–182
JP4238174 B2, 100–114, 290–299
JP4242109 B2, 469–479
JP4254368 B2, 401–410
JP4256779 B2, 100–114, 242–261
JP4273391 B2, 317–325
JP4277040 B2, 152–182
JP4297680 B2, 100–114
JP4299490 B2, 345–359
JP4307254 B2, 100–114
JP4311204 B2, 345–359
JP4316285 B2, 375–386
JP4328244 B2, 423–429
JP4335987 B2, 100–114
JP4348960 B2, 100–114, 242–261
JP4354996 B2, 401–410
JP4359718 B2, 515–528
JP4368525 B2, 199–213
JP4382909 B2, 199–213
JP4420052 B2, 317–325
JP4458422 B2, 515–528
JP4472348 B2, 439–445
JP4476803 B2, 44t–74t
JP4486561 B2, 515–528
JP4490633 B2, 469–479
JP4517069 B2, 515–528
JP4530670 B2, 317–325
JP4530809 B2, 100–114, 375–386
JP4541085 B2, 199–213
JP4548591 B2, 242–261
JP4553733 B2, 199–213, 439–445
JP4562316 B2, 100–114
JP4570855 B2, 270–275
JP4581181 B2, 423–429
JP4581420 B2, 152–182
JP4582871 B2, 345–359
JP4583537 B2, 242–261, 375–386
JP4588980 B2, 423–429
JP4600278 B2, 152–182
JP4600278 B2, 375–386
JP4604797 B2, 401–410
JP4605640 B2, 401–410
JP4610603 B2, 454–458
JP4621885 B2, 44t–74t
JP4622259 B2, 152–182
JP4623833 B2, 401–410
JP4625548 B2, 199–213
JP4628649 B2, 242–261
JP4629217 B2, 242–261
JP4632866 B2, 423–429
JP4635292 B2, 270–275
JP4644374 B2, 44t–74t
JP4647413 B2, 515–528
JP4650339 B2, 423–429
JP4653098 B2, 199–213
JP4653162 B2, 345–359
JP4655342 B2, 290–299
JP4656056 B2, 152–182
JP4659351 B2, 242–261
JP4664106 B2, 345–359
JP4664502 B2, 423–429
JP4665073 B2, 515–528
JP4694110 B2, 199–213
JP4697821 B2, 345–359
JP4697861 B2, 345–359
JP4704456 B2, 100–114, 242–261
JP4708457 B2, 100–114
JP4716634 B2, 44t–74t
JP4724111 B2, 152–182, 469–479
JP4726989 B2, 423–429
JP4733694 B2, 345–359
JP4745540 B2, 469–479
JP4746861 B2, 152–182
JP4747366 B2, 515–528
JP4748698 B2, 345–359
JP4767690 B2, 100–114
JP4777606 B2, 242–261
JP4794365 B2, 375–386
JP4795518 B2, 290–299, 454–458
JP4807834 B2, 345–359
JP4815171 B2, 423–429
JP4817321 B2, 515–528
JP4819350 B2, 439–445
JP4842502 B2, 152–182
JP4843141 B2, 44t–74t
JP4850550 B2, 375–386
JP4863684 B2, 375–386
JP4871436 B2, 469–479
JP4872149 B2, 317–325
JP4891490 B2, 454–458
JP4894263 B2, 242–261
JP4910270 B2, 242–261
JP4916105 B2, 375–386
JP4927256 B2, 44t–74t
JP4932721 B2, 44t–74t
JP4942436 B2, 242–261
JP4948440 B2, 515–528
JP4962662 B2, 242–261
JP4971449 B2, 423–429
JP4972012 B2, 100–114, 375–386
JP4973848 B2, 100–114, 242–261
JP4977292 B2, 270–275
JP4986325 B2, 44t–74t
JP5004247 B2, 345–359
JP5007504 B2, 317–325
JP5023065 B2, 401–410
JP5031144 B2, 44t–74t
JP5037249 B2, 375–386
JP5044337 B2, 345–359
JP5045030 B2, 515–528
JP5054978 B2, 242–261
JP5061868 B2, 375–386
JP5076499 B2, 152–182, 345–359
JP5079321 B2, 152–182, 469–479
JP5089133 B2, 242–261
JP5093834 B2, 270–275
JP5093872 B2, 375–386
JP5097982 B2, 152–182
JP51100194 A, 44t–74t
JP5136551 B2, 317–325
JP5136880 B2, 515–528
JP5138150 B2, 199–213
JP5138224 B2, 199–213
JP5157035 B2, 152–182
JP5161466 B2, 515–528
JP5167540 B2, 290–299
JP5174017 B2, 152–182
JP5193475 B2, 515–528
JP5197604 B2, 152–182
JP5200548 B2, 401–410
JP5212685 B2, 375–386
JP5217056 B2, 401–410
JP5232985 B2, 270–275
JP5246645 B2, 423–429
JP5264176 B2, 345–359
JP5264850 B2, 199–213
JP5274251 B2, 100–114
JP5274845 B2, 345–359
JP5280656 B2, 515–528
JP5291461 B2, 152–182
JP5309298 B2, 152–182
JP5339670 B2, 100–114
JP5357056 B2, 345–359
JP5376373 B2, 515–528
JPH01103641 A, 152–182
JPH01104635 A, 343, 345–359
JPH01216918 A, 270–275
JPH01502991 A, 199–213
JPH0197615 A, 44t–74t
JPH02117 A, 242–261
JPH0214228 A, 152–182
JPH0216930 B2, 44t–74t
JPH02200475 A, 454–458
JPH02202403 A, 515–528
JPH02218719 A, 44t–74t
JPH02503324 A, 152–182
JPH0263055 B2, 401–410
JPH0263056 B2, 401–410
JPH03149255 A, 152–182
JPH03157450 A, 152–182
JPH03224492 A, 100–114
JPH0324101 A, 152–182
JPH0331328 A, 152–182
JPH0331333 A, 152–182
JPH03500139 A, 44t–74t
JPH0355492 B2, 44t–74t
JPH03732 A, 44t–74t
JPH0374444 A, 152–182
JPH0379645 A, 152–182
JPH0379646 A, 152–182

JPH039127 B2, 44t–74t
JPH0413710 A, 30
JPH04189822 A, 284, 290–299
JPH04189823 A, 284, 290–299
JPH04220456 A, 100–114, 242–261
JPH04246425 A, 515–528
JPH04264125 A, 100–114, 270–275
JPH04304244 A, 328, 345–359
JPH04334448 A, 195–196, 199–213, 423–429
JPH04335060 A, 229, 242–261
JPH04506832 A, 152–182
JPH0465425 A, 100–114
JPH0469186 B2, 152–182
JPH0470342 B2, 152–182
JPH05148352 A, 30
JPH05170965 A, 345–359
JPH05170966 A, 345–359
JPH05178977 A, 506, 515–528
JPH05271458 A, 340, 345–359
JPH05271638 A, 469–479
JPH05320524 A, 152–182
JPH05321025 A, 390, 401–410
JPH05331315 A, 128, 152–182
JPH0543772 A, 145, 152–182
JPH0548258 B2, 44t–74t
JPH05501686 A, 44t–74t
JPH05507410 A, 270–275
JPH0552749 B2, 242–261
JPH0564982 B2, 345–359
JPH0581239 B2, 199–213
JPH0593049 A, 100–114
JPH0613176 B, 515–528
JPH0615604 B2, 152–182
JPH06172501 A, 44t–74t
JPH06190853 A, 345–359
JPH06207047 A, 152–182
JPH06212511 A, 392, 401–410
JPH0623836 A, 375–386
JPH06240004 A, 494–495, 515–528
JPH06240045 A, 494, 515–528
JPH06248104 A, 342, 345–359
JPH06256480 A, 365, 375–386
JPH06256481 A, 365, 375–386
JPH06263892 A, 143, 242–261
JPH06264343 A, 392–393, 401–410
JPH06271694 A, 345–359
JPH06287347 A, 375–386
JPH06293841 A, 345–359
JPH06297458 A, 494, 515–528
JPH06299054 A, 88, 100–114
JPH06306264 A, 231, 242–261
JPH06313063 A, 130, 152–182
JPH06315935 A, 494, 515–528
JPH0641481 B2, 44t–74t
JPH0643516 B2, 199–213
JPH0649266 A, 500–501, 515–528
JPH0649276 A, 152–182
JPH06500149 A, 152–182
JPH06502676 A, 100–114, 152–182
JPH06503110 A, 152–182
JPH06504558 A, 100–114, 152–182
JPH06504799 A, 242–261
JPH0662839 B2, 152–182
JPH0662928 B2, 469–479
JPH066307 B2, 44t–74t
JPH0668041 B2, 152–182
JPH0673191 A, 515–528
JPH0674340 B2, 375–386
JPH068370 A, 317–325
JPH0693998 B2, 199–213
JPH07109413 A, 136, 152–182
JPH0711044 A, 515–528
JPH07126970 A, 392, 401–410
JPH07173271 A, 361, 375–386
JPH07177826 A, 229, 242–261, 375–386
JPH07195814 A, 314, 317–325
JPH0725936 B2, 152–182
JPH0725938 B2, 152–182
JPH07300720 A, 390, 401–410
JPH07309863 A, 506, 515–528
JPH07310236 A, 393, 401–410
JPH07330954 A, 129–130, 152–182
JPH0747623 B2, 44t–74t
JPH0748769 A, 392–393, 401–410
JPH0749459 B, 44t–74t
JPH07502069 A, 469–479
JPH07504227 A, 439–445
JPH07504939 A, 439–445
JPH07506622 A, 290–299
JPH07507074 A, 515–528
JPH07509131 A, 270–275
JPH0757827 B2, 152–182
JPH075788 B2, 152–182
JPH0778167 B2, 152–182
JPH0797545 A, 311–312, 317–325
JPH0811206 A, 367, 375–386
JPH08150658 A, 367–368, 375–386
JPH08157798 A, 461–462, 469–479
JPH08183898 A, 88, 100–114, 398, 401–410
JPH08188671 A, 128, 152–182
JPH08188706 A, 367, 375–386
JPH08193165 A, 91, 100–114, 242–261
JPH08199052 A, 232, 242–261
JPH08199053 A, 229, 242–261
JPH08231837 A, 240, 242–261
JPH08244781 A, 312, 317–325
JPH08245866 A, 122, 152–182, 229, 242–261
JPH08246320 A, 401–410
JPH08252823 A, 92, 100–114
JPH08253617 A, 345–359
JPH08253619 A, 504, 515–528
JPH0827296 A, 371, 375–386
JPH0827362 A, 125, 152–182
JPH0827363 A, 88, 100–114
JPH08283557 A, 232, 242–261
JPH08284016 A, 390, 401–410
JPH08290526 A, 374–386
JPH08302265 A, 452, 454–458
JPH08319445 A, 449–450, 454–458
JPH083432 A, 225–226, 242–261
JPH0834913 A, 242–261
JPH0841214 A, 412, 423–429
JPH08500062 A, 375–386
JPH08502552 A, 152–182
JPH08503500 A, 152–182
JPH08505415 A, 375–386
JPH08505825 A, 317–325
JPH08512066 A, 44t–74t
JPH0892417 A, 345–359, 423–429
JPH0892518 A, 449, 454–458
JPH09111107 A, 123, 152–182
JPH09125016 A, 463, 469–479
JPH09151310 A, 369–370, 375–386
JPH09157954 A, 399, 401–410
JPH09169896 A, 369, 375–386
JPH09169897 A, 413–414, 423–429
JPH09221587 A, 240, 242–261
JPH09233956 A, 375–386
JPH09235360 A, 375–386
JPH09241417 A, 504, 515–528
JPH09278991 A, 87, 91, 100–114
JPH09296103 A, 229, 242–261
JPH09316310 A, 135, 152–182
JPH09500157 A, 469–479
JPH09501456 A, 242–261, 290–299
JPH09505615 A, 469–479
JPH09506303 A, 317–325
JPH09508423 A, 100–114
JPH09508424 A, 100–114, 401–410
JPH0959337 A, 515–528
JPH0977904 A, 515–528
JPH0977910 A, 199–213, 469–479
JPH0978494 A, 194, 199–213, 432–433, 439–445
JPH0995849 A, 393, 401–410
JPH10101911 A, 188, 199–213
JPH10138433 A, 308, 317–325
JPH10152572 A, 345–359
JPH10152602 A, 130, 152–182
JPH10158369 A, 225–226, 242–261
JPH10158485 A, 130, 152–182
JPH10219012 A, 307, 317–325
JPH10237401 A, 463, 469–479
JPH1024518 A, 308, 317–325
JPH10251498 A, 135, 152–182
JPH10273582 A, 416, 423–429
JPH10274494 A, 132, 152–182
JPH10287733 A, 284–285, 290–299
JPH10324766 A, 345–359
JPH10330527 A, 343, 345–359
JPH1034807 A, 309, 317–325
JPH1036553 A, 501, 515–528
JPH1036650 A, 240, 242–261
JPH10503102 A, 469–479
JPH10503227 A, 152–182, 199–213, 439–445
JPH10504459 A, 199–213
JPH10508640 A, 152–182
JPH10510394 A, 439–445
JPH10512010 A, 152–182
JPH1060136 A, 100–114, 375–386
JPH1060137 A, 100–114, 375–386
JPH1086307 A, 239–240, 242–261
JPH1087975 A, 225–226, 242–261
JPH11106628 A, 91, 100–114
JPH11116709 A, 310, 317–325
JPH11124443 A, 422–429
JPH11147269 A, 307, 317–325
JPH11158452 A, 461–462, 469–479
JPH11279311 A, 342, 345–359
JPH11323113 A, 229, 242–261
JPH11335401 A, 152–182
JPH11335475 A, 303, 317–325
JPH1135693 A, 265, 270–275
JPH11500157 A, 44t–74t
JPH11500468 A, 44t–74t

JPH11500476 A, 199–213
JPH11500613 A, 199–213, 439–445
JPH11509142 A, 439–445
JPH11510194 A, 199–213, 401–410, 469–479
JPH1160716 A, 467, 469–479
JPH1192712 A, 192–193, 199–213
JPH9263651 A, 374–386
JPS2218719 A, 44t–74t
JPS4936597 B1, 242–261
JPS4955740 A, 152–182
JPS51116079 A, 100–114
JPS5233137 B1, 469–479
JPS5287169 A, 100–114
JPS5490248 A, 152–182
JPS5599195 A, 100–114, 199–213
JPS56149444 A, 152–182, 375–386
JPS57111349 A, 152–182
JPS57150393 A, 152–182
JPS57152893 A, 375–386
JPS57500613 A, 44t–74t
JPS58206637 A, 270–275
JPS59130533 A, 199–213
JPS59205992 A, 199–213
JPS59206815 A, 152–182
JPS59500251 A, 345–359
JPS5959419 A, 401–410
JPS60214745 A, 44t–74t
JPS60221424 A, 44t–74t
JPS6135790 A, 199–213
JPS6136321 A, 6–7
JPS6142531 A, 270–275
JPS6169431 A, 390, 401–410
JPS62144663 A, 242–261
JPS62164743 A, 345–359
JPS62209144 A, 375–386
JPS6254475 B2, 100–114, 199–213
JPS63105003 A, 199–213
JPS63172762 A, 145–146, 152–182
JPS63230701 A, 44t–74t
JPS63232840 A, 199–213
JPS63240936 A, 270–275
JPS63241024 A, 401–410
JPS6429404 A, 44t–74t

K

KR0130073 B1, 44t–74t
KR0139046 B1, 152–182
KR100220443 B1, 100–114, 152–182
KR100233184 B1, 100–114, 375–386
KR100233487 B1, 152–182
KR100244057 B1, 100–114, 375–386
KR100245905 B1, 100–114, 152–182
KR100262356 B1, 375–386
KR100266488 B1, 199–213, 401–410, 469–479
KR100366483 B1, 44t–74t
KR100382568 B1, 290–299
KR100451527 B1, 199–213, 270–275, 290–299
KR100504214 B1, 401–410
KR100566707 B1, 515–528
KR100652533 B1, 270–275
KR100655914 B1, 418, 423–429
KR100657936 B1, 423–429
KR100778793 B1, 199–213
KR100785997 B1, 44t–74t
KR100804442 B1, 270–275
KR100806985 B1, 242–261
KR100830022 B1, 515–528
KR100836271 B1, 415, 423–429
KR100865097 B1, 317–325
KR100867424 B1, 423–429
KR100898359 B1, 317–325
KR100923833 B1, 345–359
KR100942443 B1, 100–114
KR100944893 B1, 44t–74t
KR100945060 B1, 454–458
KR100954924 B1, 100–114
KR100955024 B1, 375–386
KR100955437 B1, 375–386
KR100967336 B1, 375–386
KR100989116 B1, 152–182
KR101010385 B1, 242–261
KR101030231 B1, 371, 375–386
KR101039649 B1, 242–261
KR101045446 B1, 152–182, 375–386
KR101050338 B1, 345–359
KR101067141 B1, 152–182
KR101105292 B1, 270–275
KR101118895 B1, 152–182
KR101139031 B1, 152–182
KR101148691 B1, 152–182
KR101152973 B1, 100–114, 242–261
KR101158487 B1, 100–114
KR110010638 B1, 345–359
KR110018895 B1, 44t–74t
KR20000058110 A, 242–261
KR20010002589 A, 270–275
KR20010012198 A, 401–410
KR20010055721 A, 44t–74t
KR20010057068 A, 44t–74t
KR20010108052 A, 270–275
KR20010108128 A, 199–213, 270–275, 290–299
KR20020059364 A, 44t–74t
KR20020083949 A, 454–458
KR20020096888 A, 242–261
KR20030016294 A, 199–213
KR20030068147 A, 515–528
KR20030069984 A, 152–182
KR20040014193 A, 242–261
KR20040065550 A, 199–213
KR20040066148 A, 345–359
KR20040097126 A, 439–445
KR20040097146 A, 100–114
KR20040104742 A, 44t–74t
KR20050027060 A, 199–213
KR20050057167 A, 100–114
KR20050058484 A, 100–114, 401–410
KR20050085432 A, 317–325
KR20050088141 A, 401–410
KR20050120675 A, 152–182, 375–386
KR20060003580 A, 418, 423–429
KR20060010716 A, 242–261
KR20060047208 A, 100–114, 290–299
KR20060086288 A, 345–359
KR20060107330 A, 44t–74t
KR20060125871 A, 270–275
KR20070008522 A, 199–213
KR20070009584 A, 100–114, 242–261
KR20070009625 A, 515–528
KR20070055956 A, 44t–74t
KR20070065325 A, 152–182
KR20070073767 A, 152–182
KR20070078053 A, 317–325
KR20070094844 A, 152–182
KR20070105990 A, 100–114, 199–213, 439–445
KR20070106679 A, 375–386
KR20070119632 A, 290–299, 375–386
KR20070122461 A, 290–299
KR20080000572 A, 152–182, 345–359
KR20080011321 A, 375–386
KR20080015367 A, 290–299
KR20080036854 A, 415, 423–429
KR20080039336 A, 423–429
KR20080046655 A, 44t–74t
KR20080065973 A, 290–299
KR20080072815 A, 345–359
KR20080074206 A, 401–410
KR20080087774 A, 317–325
KR20080098048 A, 290–299
KR20080103052 A, 100–114
KR20080109010 A, 515–528
KR20090008110 A, 362, 375–386
KR20090008111 A, 362, 375–386
KR20090014382 A, 345–359
KR20090023336 A, 100–114
KR20090023737 A, 242–261, 317–325
KR20090024709 A, 152–182
KR20090048612 A, 401–410
KR20090053909 A, 270–275
KR20090054434 A, 242–261
KR20090054454 A, 152–182
KR20090073824 A, 452–458
KR20090086132 A, 375–386
KR20090092806 A, 515–528
KR20090096454 A, 375–386
KR20090109106 A, 199–213
KR20090109107 A, 199–213
KR20090109556 A, 199–213
KR20090125139 A, 345–359
KR20100007869 A, 317–325
KR20100014717 A, 317–325
KR20100016017 A, 401–410
KR20100018605 A, 100–114
KR20100027438 A, 152–182
KR20100044232 A, 242–261
KR20100079986 A, 135, 152–182
KR20100103783 A, 44t–74t
KR20100120212 A, 515–528
KR20100126317 A, 44t–74t
KR20100131244 A, 270–275
KR20100131482 A, 242–261
KR20110007259 A, 515–528
KR20110008312 A, 152–182
KR20110025730 A, 152–182
KR20110037928 A, 152–182, 375–386
KR20110038642 A, 290–299
KR20110045097 A, 44t–74t
KR20110063345 A, 454–458
KR20110064122 A, 135, 152–182
KR20110079715 A, 345–359
KR20110094345 A, 44t–74t
KR20110095293 A, 152–182, 242–261
KR20110098970 A, 100–114, 401–410

KR20110108736 A, 135, 152–182
KR20110117183 A, 439–445
KR20120001539 A, 317–325
KR20120007733 A, 345–359
KR20120012780 A, 401–410
KR20120014243 A, 44t–74t
KR20120015440 A, 515–528
KR20120023624 A, 44t–74t
KR20120026039 A, 152–182, 375–386
KR20120027425 A, 44t–74t
KR20120066005 A, 152–182
KR20120084447 A, 345–359
KR20120097948 A, 398, 401–410
KR20120099384 A, 515–528
KR20120108798 A, 152–182
KR20120109571 A, 242–261, 375–386
KR20120113220 A, 152–182
KR20120116995 A, 242–261
KR20120125628 A, 345–359
KR20120126066 A, 152–182
KR20120126769 A, 242–261
KR20130005389 A, 423–429
KR20130014717 A, 100–114
KR20130089159 A, 375–386
KR20130092405 A, 345–359
KR20130100260 A, 152–182
KR20130108277 A, 375–386
KR20130109002 A, 345–359
KR20130109972 A, 515–528
KR20130114344 A, 242–261
KR20130117798 A, 469–479
KR920002702 B1, 199–213
KR920010645 B1, 152–182
KR960002225 B1, 199–213
KR960006410 B1, 44t–74t
KR960008112 B1, 100–114, 152–182
KR970006082 B1, 242–261
KR977007206 A, 152–182

L
LU90462 A, 44t–74t
LV12151 A, 100–114, 152–182
LV12151 B, 100–114, 152–182

M
MX142986 A, 44t–74t
MX169228 B, 375–386
MX169930 B, 44t–74t
MX172659 B, 152–182
MX184254 B, 515–528
MX2007002442 A, 375–386
MX2008010889 A, 100–114
MX2008011345 A, 290–299
MX2009000526 A, 401–410
MX2009001688 A, 270–275
MX2009002380 A, 401–410
MX2009004892 A, 515–528
MX2009006045 A, 345–359
MX2009006387 A, 375–386
MX2010001049 A, 317–325
MX2010007943 A, 44t–74t
MX2010008248 A, 515–528
MX2011001623 A, 317–325
MX2011001726 A, 44t–74t
MX2011003767 A, 345–359
MX2011011366 A, 44t–74t
MX2012001027 A, 152–182
MX2012001088 A, 515–528
MX2012002137 A, 515–528
MX2012006944 A, 44t–74t
MX2012007266 A, 152–182
MX2012007627 A, 152–182
MX2013000379 A, 152–182
MX2013001128 A, 401–410
MX209461 B, 152–182
MX220923 B, 199–213, 270–275, 290–299
MX226463 B, 270–275
MX9102312 A, 100–114, 152–182
MX9303853 A, 375–386
MX9306143 A, 439–445
MX9603065 A, 100–114, 401–410
MX9700046 A, 345–359
MX9701249 A, 199–213
MX9703537 A, 44t–74t
MX9703538 A, 152–182
MX9800592 A, 199–213, 401–410, 469–479
MX9804764 A, 199–213
MXPA00011963 A, 199–213
MXPA01002680 A, 345–359
MXPA01006641 A, 270–275
MXPA01007503 A, 199–213, 270–275, 290–299
MXPA02000573 A, 290–299
MXPA02004230 A, 152–182, 290–299
MXPA02008854 A, 290–299
MXPA03005805 A, 290–299
MXPA03005807 A, 290–299
MXPA03009926 A, 375–386
MXPA03009933 A, 375–386
MXPA03010031 A, 469–479
MXPA04003029 A, 199–213
MXPA04007898 A, 439–445
MXPA04011846 A, 290–299
MXPA05006144 A, 317–325
MXPA05006874 A, 401–410
MXPA06013551 A, 44t–74t
MXPA10009905 A, 44t–74t
MXPA11007535 A, 44t–74t
MXPA11010716 A, 515–528
MY145412 A, 152–182

N
NL1007735 C2, 44t–74t
NL1008497 C2, 199–213, 439–445
NL1009449 C6, 44t–74t
NL1010926 C2, 270–275
NL1033719 C2, 345–359
NL1036039 C, 345–359
NL174728 C, 44t–74t
NL188166 C, 44t–74t
NL6814218 A, 469–479
NL7103263 A, 242–261
NL7306280 A, 152–182
NL7600881 A, 44t–74t
NL7700308 A, 100–114
NL7809320 A, 152–182
NL8120177 A, 44t–74t
NL9401037 A, 199–213, 439–445
NL990036 I1, 44t–74t
NL990036 I2, 44t–74t
NO132784 B, 242–261
NO132784 C, 242–261
NO174208 B, 199–213
NO174208 C, 199–213
NO175374 B, 199–213
NO175374 C, 199–213
NO176304 B, 242–261
NO176304 C, 242–261
NO179213 B, 152–182
NO20002947 A, 44t–74t
NO20011910 A, 515–528
NO20033334 A, 152–182
NO20041774 A, 199–213
NO20043843 A, 439–445
NO20062798 A, 199–213
NO300579 B1, 375–386
NO302999 B1, 44t–74t
NO303394 B1, 44t–74t
NO307521 B1, 152–182
NO309042 B1, 439–445
NO310921 B1, 290–299
NO315120 B1, 152–182
NO315121 B1, 44t–74t
NO315203 B1, 44t–74t
NO315204 B1, 44t–74t
NO315906 B1, 401–410
NO322142 B1, 199–213
NO330519 B1, 152–182
NO783106 A, 152–182
NO864507 A, 345–359
NO874251 A, 199–213
NO882919 A, 44t–74t
NO883547 A, 44t–74t
NO884474 A, 242–261
NO885570 A, 199–213
NO890361 A, 152–182
NO900878 A, 44t–74t
NO902347 A, 152–182
NO902348 A, 152–182
NO902602 A, 152–182
NO903013 A, 152–182
NO914797 A, 152–182
NO925049 A, 100–114, 152–182
NO934265 A, 345–359
NO942035 A, 439–445
NO944985 A, 375–386
NO950241 A, 270–275
NO951158 A, 199–213
NO960153 A, 469–479
NO962751 A, 290–299
NO963104 A, 100–114
NO965492 A, 199–213, 439–445
NO970738 A, 199–213
NO972226 A, 152–182
NO972227 A, 44t–74t
NO973766 A, 44t–74t
NO973767 A, 44t–74t
NO991356 A, 199–213
NO995357 A, 401–410
NO995734 A, 439–445
NZ188382 A, 152–182
NZ197036 A, 44t–74t
NZ201054 A, 44t–74t
NZ206486 A, 199–213
NZ221994 A, 199–213
NZ225245 A, 44t–74t

NZ225779 A, 44t–74t
NZ226514 A, 242–261
NZ227762 A, 152–182
NZ230246 A, 152–182
NZ234018 A, 152–182
NZ234091 A, 152–182
NZ234315 A, 152–182
NZ240799 A, 100–114, 152–182
NZ254186 A, 270–275
NZ257216 A, 439–445
NZ271513 A, 242–261, 290–299
NZ276325 A, 100–114
NZ279627 A, 100–114, 401–410
NZ289416 A, 152–182
NZ336663 A, 44t–74t
NZ336718 A, 44t–74t
NZ501274 A, 401–410
NZ501695 A, 439–445
NZ506328 A, 345–359
NZ519353 A, 345–359
NZ523669 A, 423–429
NZ532076 A, 199–213
NZ534682 A, 439–445
NZ552936 A, 345–359
NZ575069 A, 242–261
NZ593179 A, 152–182, 242–261
NZ597829 A, 152–182

P
PH19415 A, 199–213
PH25687 A, 44t–74t
PH25687 A, 152–182
PH25985 A, 44t–74t
PH26025 A, 199–213
PH27063 A, 44t–74t
PH30236 A, 242–261
PL156365 B1, 44t–74t
PL156368 B1, 44t–74t
PL159070 B1, 152–182
PL174799 B1, 100–114, 152–182
PL178568 B1, 100–114
PL181098 B1, 100–114, 401–410
PL2032649 T3, 152–182
PL206185 B1, 199–213
PL2089460 T3, 345–359
PL273393 A1, 44t–74t
PL274156 A1, 44t–74t
PL277424 A1, 152–182
PL285383 A1, 152–182
PL285384 A1, 152–182
PL285673 A1, 152–182
PL285754 A1, 152–182
PL285861 A1, 152–182
PL297375 A1, 100–114, 152–182
PL301609 A1, 375–386
PL315682 A1, 100–114, 401–410
PL315691 A1, 100–114
PL320223 A1, 44t–74t
PL321599 A1, 152–182
PL334520 A1, 44t–74t
PL354035 A1, 44t–74t
PL354035 A1, 515–528
PL371517 A1, 439–445
PL376044 A1, 270–275
PL376558 A1, 44t–74t
PT1040127 E, 44t–74t
PT1042388 E, 44t–74t
PT104888 A, 44t–74t
PT1074570 E, 152–182
PT1094944 E, 423–429, 439–445
PT1127086 E, 345–359
PT1163019 E, 44t–74t
PT1204755 E, 44t–74t
PT1366104 E, 469–479
PT1412425 E, 242–261
PT1492581 E, 439–445
PT1603987 E, 152–182, 469–479
PT1764118 E, 439–445
PT1991601 E, 290–299
PT2202274 E, 152–182
PT2285890 E, 152–182
PT615532 E, 439–445
PT73035 A, 44t–74t
PT73035 B, 44t–74t
PT792309 E, 152–182
PT792310 E, 44t–74t
PT797609 E, 290–299
PT819147 E, 152–182
PT85908 A, 199–213
PT85908 B, 199–213
PT866839 E, 439–445
PT87881 A, 44t–74t
PT87881 B, 44t–74t
PT88231 A, 44t–74t
PT88231 B, 44t–74t
PT88703 A, 242–261
PT88703 B, 242–261
PT89556 A, 152–182
PT89556 B, 152–182
PT910412 E, 199–213
PT94364 B, 152–182
PT94383 A, 152–182
PT94542 A, 152–182
PT94594 A, 152–182
PT946624 E, 44t–74t
PT977912 E, 401–410
PT981381 E, 44t–74t

R
RU1799387 C, 44t–74t
RU2002114915 A, 345–359
RU2004124243 A, 454–458
RU2004124718 A, 439–445
RU2005113285 A, 270–275
RU2005117628 A, 44t–74t
RU2006110878 A, 44t–74t
RU2007112465 A, 375–386
RU2008129640 A, 100–114
RU2008139288 A, 290–299
RU2009109258 A, 270–275
RU2009112385 A, 152–182
RU2009114684 A, 152–182
RU2009114686 A, 152–182
RU2009122359 A, 515–528
RU2010137909 A, 515–528
RU2011107123 A, 44t–74t
RU2026321 C1, 152–182
RU2073037 C1, 152–182
RU2095379 C1, 100–114, 152–182
RU2127313 C1, 270–275
RU2137784 C1, 100–114
RU2144047 C1, 100–114, 401–410
RU2215542 C2, 290–299
RU2308976 C2, 439–445
RU2363586 C2, 375–386
RU2398806 C2, 454–458
RU2412804 C1, 515–528
RU2413412 C2, 100–114
RU2418818 C2, 290–299
RU2447101 C2, 152–182
RU2457223 C2, 270–275

S
SE361599 B, 242–261
SE418189 B, 44t–74t
SE455791 B, 44t–74t
SE462284 B, 152–182
SE462284 C, 152–182
SE7600760 A, 44t–74t
SE7700296 A, 100–114
SE7809716 A, 152–182
SE8200068 A, 44t–74t
SE8503650 L, 152–182
SG101495 A1, 345–359
SG124395 A1, 345–359
SG126853 A1, 44t–74t
SG132645 A1, 44t–74t
SG144167 A1, 345–359
SG161236 A1, 44t–74t
SG165337 A1, 290–299
SG178083 A1, 152–182
SG194040 A1, 152–182, 242–261
SG47625 A1, 152–182
SG47812 A1, 100–114, 401–410
SG47853 A1, 100–114, 152–182
SG47881 A1, 515–528
SG49114 A1, 100–114
SG50508 A1, 152–182
SG65587 A1, 375–386
SI1492581 T1, 439–445
SI1764118 T1, 439–445
SI1838784 T1, 152–182
SI2101974 T1, 515–528
SI2295218 T1, 515–528
SK146393 A3, 375–386
SK262011 A3, 152–182, 242–261
SK279993 B6, 100–114, 152–182
SK390192 A3, 100–114, 152–182
SK94299 A3, 44t–74t
SK962002 A3, 515–528
SK96996 A3, 100–114, 401–410
SK97096 A3, 100–114
SU1016314 A1, 30
SU1612999 A3, 44t–74t

T
TR200002450 T2, 290–299
TR24428 A, 152–182
TR27656 A, 375–386
TW200811240 A, 100–114
TW200817459 A, 290–299
TW200831601 A, 242–261
TW200831725 A, 401–410
TW200840879 A, 317–325

TW200909512 A, 401–410
TW201002756 A, 44t–74t
TW201005031 A, 412, 423–429
TW201012846 A, 290–299
TW201022328 A, 290–299
TW201022341 A, 345–359
TW201024349 A, 152–182
TW201031700 A, 100–114, 401–410
TW201038786 A, 401–410
TW201043661 A, 231, 242–261
TW201105739 A, 152–182, 375–386
TW201114791 A, 44t–74t
TW201114852 A, 439–445
TW201121783 A, 152–182
TW201209089 A, 345–359
TW201211152 A, 290–299
TW201219463 A, 375–386
TW201229105 A, 375–386
TW201233718 A, 345–359
TW201238996 A, 290–299
TW201245326 A, 290–299
TW201335209 A, 290–299
TW201341448 A, 242–261
TW211035 A, 515–528
TW383316 B, 100–114
TW385320 B, 100–114
TW387914 B, 152–182
TW512158 B, 345–359
TW574309 B, 242–261
TWI225012 B, 317–325
TWI227721 B, 152–182
TWI238834 B, 100–114
TWI255837 B, 242–261
TWI257399 B, 345–359
TWI294444 B, 242–261
TWI302550 B, 242–261
TWI321600 B, 100–114, 401–410
TWI331164 B, 100–114
TWI331621 B, 317–325
TWI377226 B, 152–182
TWI378971 B, 152–182
TWI382056 B, 100–114
TWI387534 B, 375–386
TWI388592 B, 152–182
TWI389972 B, 242–261

U
US1943176 A, 196, 199–213
US1995970 A, 4–5, 228–229, 242–261
US2001000742 A1, 375–386
US2001003636 A1, 454–458
US2001004665 A1, 44t–74t
US2001007899 A1, 44t–74t
US2001009769 A1, 44t–74t
US2001023274 A1, 199–213
US2001024631 A1, 199–213
US2001031297 A1, 44t–74t
US2001045518 A1, 491, 515–528
US2002002252 A1, 100–114
US20020052445 A1, 368, 375–386
US2002010327 A1, 290–299
US2002032254 A1, 199–213
US2002040485 A1, 44t–74t
US2002042481 A1, 290–299
US2002059001 A1, 342, 345–359
US2002061943 A1, 44t–74t
US2002061943 A1, 152–182
US2002061944 A1, 100–114
US2002068810 A1, 469–479
US2002082363 A1, 24
US2002090687 A1, 17
US2002128382 A1, 290–299
US2002128384 A1, 280–281, 290–299
US2002130436 A1, 515–528
US2002131952 A1, 199–213
US2002136848 A1, 290–299
US2002156150 A1, 44t–74t
US2002160201 A1, 317–325
US2002161169 A1, 290–299
US2002173558 A1, 44t–74t
US2002188041 A1, 401–410
US2002188071 A1, 152–182
US2002192456 A1, 327, 345–359, 401–410
US2003018128 A1, 290–299
US2003038405 A1, 100–114
US2003082756 A1, 44t–74t
US2003083394 A1, 345–359
US2003083440 A1, 242–261
US2003088052 A1, 100–114
US2003096126 A1, 439–445
US2003100645 A1, 242–261
US2003105178 A1, 345–359
US2003109605 A1, 401–410
US2003119959 A1, 242–261
US2003125431 A1, 100–114, 242–261
US2003125508 A1, 100–114, 242–261
US2003125509 A1, 290–299
US2003135020 A1, 317–325
US2003148688 A1, 392–393, 401–410
US2003157351 A1, 199–213
US2003157674 A1, 44t–74t
US2003166735 A1, 345–359
US2003166748 A1, 118, 152–182
US2003166779 A1, 118, 152–182
US2003180524 A1, 423–429
US2003181630 A1, 199–213
US2003203987 A1, 454–458
US2003204028 A1, 124–125, 152–182
US2003208034 A1, 515–528
US2003219562 A1, 439–445
US2003232929 A1, 278–280, 290–299
US2004023028 A1, 20
US2004024141 A1, 235, 239–240, 242–261
US2004028927 A1, 423–429
US2004029988 A1, 345–359
US2004034128 A1, 100–114
US2004034163 A1, 345–359
US2004039092 X6, 100–114
US2004053381 A1, 44t–74t
US2004068058 A1, 152–182
US2004092613 A1, 345–359
US2004093831 A1, 375–386
US2004102596 A1, 345–359
US2004122165 A1, 290–299
US2004127123 A1, 306, 317–325
US2004143072 A1, 469–479
US2004161622 A1, 242–261
US2004172675 A1, 44t–74t
US2004185282 A1, 375–386
US2004225065 A1, 242–261
US2004230001 A1, 145, 152–182
US2004231559 A1, 469–479
US2004242803 A1, 152–182
US2004247807 A1, 439–445
US2005001358 A1, 44t–74t
US2005026529 A1, 401–410
US2005032923 A1, 345–359
US2005043462 A1, 423–429
US2005058712 A1, 199–213
US2005095679 A1, 27–28
US2005107578 A1, 44t–74t
US2005112182 A1, 469–479
US2005124786 A1, 317–325
US2005137332 A1, 125–126, 152–182
US2005158364 A1, 345–359
US2005163745 A1, 44t–74t
US2005163819 A1, 345–359
US2005165142 A1, 100–114
US2005175801 A1, 44t–74t
US2005182196 A1, 152–182
US2005182204 A1
US2005182228 A1, 345–359
US2005203258 A1, 100–114, 401–410
US2005209377 A1, 242–261
US2005215662 A1, 454–458
US2005215672 A1, 290–299, 423–429
US2005233425 A1, 515–528
US2005242466 A, 86, 100–114, 290–299
US2005250931 A1, 488, 499, 515–528
US2005253292 A1, 100–114
US2005287358 A1, 374–386
US2005288399 A1, 152–182
US2006035860 A1, 515–528
US2006045940 A1, 362–363, 375–386
US2006051603 A1, 372, 375–386
US2006100313 A1, 100–114
US2006140842 A1, 345–359
US2006142421 A1, 242–261
US2006147695 A1, 423–429
US2006167122 A1, 338, 345–359
US2006204727 A1, 317–325
US2006229375 A1, 44t–74t
US2006241287 A1, 197, 199–213
US2006247390 A1, 290–299, 469–479
US2006257616 A1, 396, 401–410
US2006258833 A1, 199–213, 439–445
US2006264539 A1, 152–182
US2006276575 A1, 242–261
US2006283340 A1, 483, 515–528
US2007014752 A1, 306, 317–325
US2007032577 A1, 152–182, 375–386
US2007037912 A1, 423–429
US2007043145 A1, 448, 454–458
US2007054073 A1, 375–386
US2007060687 A1, 152–182, 242–261
US2007071879 A1, 439–445
US2007071926 A1, 439–445
US2007073051 A1, 199–213
US2007088099 A1, 199–213
US2007100037 A1, 217, 242–261
US2007100051 A1, 515–528
US2007102836 A1, 270–275
US2007116909 A1, 370–371, 375–386
US2007117908 A1, 24, 127, 152–182

US2007123725 A1, 44t–74t
US2007128436 A1, 401–410
US2007135929 A1, 44t–74t
US2007139667 A1, 100–114
US2007160782 A1, 100–114
US2007172611 A1, 100–114
US2007172663 A1, 312, 317–325
US2007215300 A1, 199–213
US2007243374 A1, 469–479
US2007259195 A1, 100–114
US2007260019 A1, 152–182
US2007280899 A1, 44t–74t
US2007293591 A1, 515–528
US2007299170 A1, 100–114, 242–261
US2007299170 X6, 100–114
US2008004454 A1, 515–528
US2008023162 A1, 199–213
US2008033093 A1, 423–429
US2008033097 A1, 152–182
US2008036119 A1, 286–287, 290–299
US2008048365 A1, 515–528
US2008051490 A1, 44t–74t
US2008051506 A1, 345–359
US2008071015 A1, 242–261
US2008095823 A1, 44t–74t
US2008103232 A, 148
US2008103232 A1, 152–182
US2008108772 A1, 420, 423–429
US2008118963 A1, 270–275
US2008132134 A1, 345–359, 401–410
US2008139702 A1, 242–261
US2008146686 A1, 345–359
US2008147034 A1, 362, 375–386
US2008160166 A1, 439–445
US2008161505 A1, 100–114, 199–213, 439–445
US2008167409 A1, 242–261
US2008182924 A1, 152–182
US2008194739 A1, 242–261
US2008194807 A1, 199–213
US2008194808 A1, 199–213
US2008194834 A1, 199–213
US2008213209 A1, 290–299
US2008214713 A1, 242–261
US2008237910 A1, 485, 515–528
US2008258357 A1, 90–91, 100–114
US2008259054 A1, 100–114
US2008262151 A1, 152–182
US2008274885 A1, 100–114
US2008280081 A1, 375–386
US2008315020 A1, 515–528
US2008317818 A1, 290–299
US2009012194 A1, 345–359
US2009018235 A1, 100–114, 242–261, 423–429
US2009023836 A1, 100–114, 242–261
US2009030094 A1, 44t–74t
US2009030112 A1, 100–114, 242–261
US2009030160 A1, 290–299
US2009036639 A1, 317–325
US2009043000 A1, 100–114
US2009048368 A1, 152–182
US2009069463 A, 100–114
US2009074999 A1, 375–386
US2009082484 A1, 345–359
US2009082491 A1, 100–114, 152–182, 242–261
US2009093550 A1, 345–359
US2009093575 A1, 423–429
US2009099270 A1, 515–528
US2009118462 A1, 270–275
US2009123728 A1, 345–359
US2009124723 A1, 290–299
US2009127915 A, 44t–74t
US2009131545 A1, 345–359
US2009148713 A1, 375–386
US2009155611 A1, 373, 375–386
US2009156713 A1, 242–261
US2009162683 A1, 100–114, 242–261
US2009170020 A1, 452, 454–458
US2009175921 A1, 44t–74t
US2009186990 A1, 100–114
US2009197994 A1, 423–429
US2009208695 A1, 401–410
US2009221204 A1, 401–410
US2009226655 A1, 242–261, 317–325
US2009246430 A1, 44t–74t
US2009258175 A1, 345–359
US2009270524 A1, 152–182, 345–359
US2009275692 A1, 100–114, 152–182
US2009291607 A1, 401–410
US2009311455 A1, 152–182
US2009312456 A1, 242–261
US2009325444 A1, 345–359, 401–410
US2009326130 A, 364, 375–386
US2009326152 A1, 144, 152–182
US2010003434 A1, 152–182
US2010003457 A1, 317–325
US2010004362 A1, 401–410
US2010028512 A1, 22
US2010029793 A1, 345–359
US2010040904 A1, 308–309, 317–325
US2010056689 A1, 375–386
US2010056700 A1, 136, 152–182
US2010069691 A1, 44t–74t
US2010086718 A1, 152–182
US2010087556 A1, 345–359
US2010089287 A1, 467, 469–479
US2010098928 A1, 345–359
US2010105835 A1, 100–114
US2010105841 A1, 401–410
US2010112252 A1, 317–325
US2010112357 A1, 152–182
US2010120932 A1, 345–359
US2010130652 A1, 242–261
US2010130699 A1, 401–410
US2010135601 A1, 152–182
US2010136338 A1, 345–359
US2010140205 A1, 317–325
US2010167048 A1, 152–182
US2010175691 A1, 32, 502
US2010184915 A1, 290–299
US2010203348 A1, 439–445
US2010213202 A1, 375–386
US2010216902 A1, 515–528
US2010255326 A1, 317–325
US2010272940 A1, 43
US2010279135 A1, 423–429
US2010298460 A1, 44t–74t
US2010305280 A1, 152–182, 469–479
US2010311131 A1, 44t–74t
US2010311886 A1, 242–261
US2010330315 A1, 469–479
US2010330382 A1, 308–309, 317–325, 375–386
US2011008555 A1, 439–445
US2011015310 A1, 152–182, 290–299
US2011027590 A1, 100–114, 375–386
US2011042841 A1, 270–275
US2011049763 A1, 515–528
US2011054099 A1, 242–261
US2011065825 A1, 8–11
US2011071235 A1, 486, 515–528
US2011071247 A1, 152–182
US2011076511 A1, 308–309, 317–325
US2011086950 A1, 242–261
US2011101573 A1, 100–114
US2011124778 A1, 152–182
US2011130502 A1, 448, 454–458
US2011130513 A1, 263, 270–275
US2011135707 A1, 44t–74t
US2011135924 A1, 469–479
US2011152818 A1, 127, 152–182
US2011159288 A1, 32
US2011165370 A1, 100–114, 401–410
US2011178213 A1, 242–261
US2011184115 A1, 242–261
US2011189414 A, 152–182
US2011190430 A1, 375–386
US2011190456 A1, 100–114
US2011196076 A1, 152–182
US2011201069 A1, 515–528
US2011213104 A1, 44t–74t
US2011217430 A1, 333
US2011218257 A1, 345–359
US2011218278 A1, 100–114
US2011229700 A1, 439–445
US2011237710 A1, 199–213
US2011237750 A1, 368, 375–386
US2011245456 A1, 267, 270–275
US2011251349 A1, 290–299
US2011260355 A1, 375–386
US2011262669 A1, 44t–74t
US2011262683 A1, 100–114, 401–410
US2011262720 A1, 375–386
US2011269873 A1, 152–182
US2011275729 A1, 290–299
US2011287102 A1, 44t–74t
US2011287105 A1, 265, 270–275
US2011293865 A1, 290–299
US2011306693 A1, 345–359
US2011319509 A1, 411, 423–429
US2012007267 A, 345–359
US2012009420 A1, 332, 338–339, 345–359
US2012015142 A1, 127–128, 152–182
US2012029228 A1, 515–528
US2012053256 A1, 341, 345–359
US2012053259 A1, 287–288, 290–299
US2012053261 A1, 469–479
US2012064789 A1, 401–410
US2012064791 A1, 401–410
US2012070679 A1, 152–182, 375–386
US2012071591 A1, 152–182
US2012077028 A1, 469–479
US2012077887 A1, 469–479

US2012077905 A1, 152–182
US2012077954 A1, 469–479
US2012078155 A1, 469–479
US2012080822 A1, 152–182
US2012095169 A1, 44t–74t
US2012095207 A1, 199–213
US2012116049 A1, 515–528
US2012128924 A1, 515–528
US2012142854 A1, 375–386
US2012142910 A1, 199–213
US2012142958 A1, 515–528
US2012149920 A1, 44t–74t
US2012156780 A1, 304, 306, 317–325
US2012165422 A1, 100–114, 242–261
US2012165554 A1, 515–528
US2012189860 A1, 290–299
US2012201983 A1, 439–445
US2012202058 A1, 469–479
US2012202925 A1, 417, 423–429
US2012208015 A1, 469–479
US2012208017 A1, 469–479
US2012211927 A1, 278–280, 290–299
US2012213959 A1, 375–386
US2012214213 A1, 16
US2012216705 A1, 199–213
US2012223459 A1, 345–359
US2012225961 A1, 345–359
US2012239135 A1, 44t–74t
US2012245292 A1, 118, 136, 152–182
US2012259047 A1, 217, 242–261
US2012270978 A1, 242–261, 375–386
US2012289618 A1, 218, 242–261, 419
US2012289658 A1, 392, 401–410
US2012296044 A1, 152–182, 375–386
US2012296045 A1, 152–182, 375–386
US2012302671 A1, 242–261
US2012315416 A1, 152–182
US2012315454 A1, 152–182
US2012316275 A1, 375–386
US2012328806 A1, 152–182
US2012329920 A1, 242–261
US2013004760 A1, 363–364, 375–386
US2013012631 A1, 242–261
US2013018142 A1, 100–114
US2013029124 A1, 368, 375–386
US2013030129 A1, 100–114
US2013059141 A, 345–359
US2013059154 A1, 345–359
US2013065055 A1, 345–359
US2013085185 A1, 15
US2013085212 A1, 423–429
US2013093119 A1, 242–261
US2013101849 A1, 270–275
US2013109781 A1, 145, 152–182
US2013116352 A1, 345–359
US2013131209 A1, 270–275
US2013131225 A1, 242–261
US2013136922 A1, 317–325
US2013137788 A1, 375–386
US2013137803 A1, 401–410
US2013143057 A1, 317–325
US2013143064 A1, 317–325
US2013149511 A1, 375–386
US2013150468 A1, 345–359
US2013157367 A1, 401–410
US2013169127 A1, 242–261
US2013197161 A1, 152–182, 375–386
US2013211014 A1, 152–182
US2013220173 A1, 423–429
US2013225761 A1, 199–213
US2013236723 A1, 469–479
US2013253121 A1, 152–182, 375–386
US2013266767 A1, 345–359
US2013288056 A1, 345–359
US2013288322 A1, 515–528
US2013289221 A1, 290–299
US2013295376 A1, 423–429
US2013337530 A1, 152–182
US2014005624 A1, 152–182
US2014011921 A1, 152–182
US2014023806 A1, 375–386
US2014039096 A1, 242–261
US2014039435 A1, 152–182
US2014050868 A1, 454–458
US2014065914 A1, 401–410
US2014072746 A1, 290–299
US2051025 A, 468–479
US2102937 A, 469–479
US2111762 A, 20
US2362511 A, 4–5
US2668162 A, 94, 100–114
US2676945 A, 364, 375–386
US2703316 A, 362, 375–386
US3036959 A, 100–114
US3044942 A, 100–114
US3116351 A, 361–362, 375–386
US3275610 A, 100–114, 366, 375–386
US3297033 A, 100–114
US3355307 A, 468
US3468853 A, 93–94, 100–114
US3487033 A, 468–479
US3498957 A, 228–229, 242–261
US3619222 A, 37
US3632687 A, 146, 152–182
US3636956 A, 228–229, 242–261
US3636956 X6, 242–261
US3668157 A, 138, 152–182
US3668157 X6, 152–182
US3734979 A, 146, 152–182
US3737440 A, 100–114
US3762979 A, 146, 152–182
US3867324 A, 146, 152–182
US3902497 A, 100–114
US4016117 A, 152–182
US4021388 A, 152–182
US4045418 A, 362, 375–386
US4057537 A, 5
US4078331 A, 43
US4079038 A, 39–41
US4093709 A, 44t–74t
US4101533 A, 100–114
US4131648 A, 39–41
US4133784 A, 149, 152–182
US4137280 A, 147, 152–182
US4138344 A, 44t–74t
US4141087 A, 20
US4177177 A, 187–188, 199–213
US4180646 A, 39–41
US4218350 A, 152–182
US4236349 A, 43
US4298013 A, 513–528
US4304767 A, 44t–74t
US4310684 A, 100–114, 199–213
US4324709 A, 152–182
US4324907 A, 196, 199–213
US4337181 A, 152–182, 375–386
US4393167 A, 152–182
US4427614 A, 375–386
US4440921 A, 42
US4450150 A, 28
US4471077 A, 270–275
US4490326 A, 23–24
US4490326 X6, 44t–74t
US4495174 A, 42
US4502888 A, 199–213
US4506045 A, 152–182
US4537738 A, 401–410
US4562245 A, 199–213
US4620999 A, 44t–74t
US4645664 A, 270–275
US4673438 A, 34
US4702917 A, 345–359
US4705604 A, 199–213
US4719246 A, 6–7, 388, 401–410
US4757128 A, 44t–74t
US4770931 A, 147, 152–182
US4789724 A, 44t–74t
US4826493 A, 375–386
US4863655 A, 329, 345–359
US4876331 A, 100–114
US4880592 A, 375–386
US4880622 A, 42, 152–182
US4900361 A, 44t–74t
US4900654 A, 152–182
US4912149 A, 138, 152–182
US4942005 A, 152–182
US4946938 A, 42
US4968350 A, 199–213
US5004664 A, 451, 454–458
US5009586 A, 515–528
US5032683 A, 195, 199–213
US5049322 A, 199–213
US5095054 A, 34
US5100669 A, 270–275
US5102448 A, 454–458
US5116890 A, 199–213
US5118528 A, 270–275
US5124371 A, 152–182
US5135966 A, 152–182
US5138029 A, 100–114
US5169889 A, 464–465, 469–479
US5171308 A, 20–21
US5180765 A, 231, 242–261
US5201921 A, 515–528
US5206087 A, 152–182
US5213976 A, 100–114, 270–275
US5229528 A, 500, 515–528
US5238968 A, 345–359
US5252271 A, 345–359
US5252646 A, 464–465, 469–479
US5256711 X6, 152–182
US5264614 A, 503, 515–528

US5264617 A, 503, 515–528
US5264626 A, 500, 515–528
US5268507 A, 500, 515–528
US5275774 A, 44t–74t
US5280055 A, 152–182
US5292860 A, 100–114
US5312850 A, 464–465, 469–479
US5314934 A, 152–182
US5315010 A, 28
US5329127 A, 515–528
US5334520 A, 270–275
US5334634 A, 152–182
US5338822 A, 439–445
US5340646 A, 375–386
US5342969 A, 497, 515–528
US5348983 A, 345–359
US5358475 A, 242–261
US5359026 A, 242–261, 290–299
US5362777 A, 232–233
US5378792 A, 345–359
US5382611 A, 44t–74t
US5382611 A, 44t–74t
US5382611 X6, 44t–74t
US5391423 A, 375–386
US5391764 A, 44t–74t
US5397819 A, 515–528
US5399665 A, 290–299
US5405564 A, 44t–74t
US5410016 A, 197–213
US5422053 A, 345–359
US5427614 A, 34
US5427614 X6, 44t–74t
US5434004 A, 375–386
US5439688 A, 19
US5439953 A, 152–182
US5443780 A, 363, 375–386
US5446079 A, 100–114, 152–182
US5446123 A, 439–445
US5451456 A, 199–213, 375–386, 439–445
US5461136 A, 515–528
US5462982 A, 152–182
US5462983 A, 152–182
US5475080 A, 439–445
US5484881 A, 439–445
US5498692 A, 100–114
US5502116 A, 100–114, 401–410
US5510619 A, 515–528
US5521233 A, 451, 454–458
US5523372 A, 345–359
US5534616 A, 375–386
US5536564 A, 100–114, 401–410
US5536807 A, 439–445
US5539081 A, 439–445
US5553714 A, 515–528
US5556711 A, 317–325
US5559171 A, 100–114, 152–182
US5569692 A, 152–182
US5574076 A, 469–479
US5578382 A, 375–386
US5579038 A, 454–458
US5580911 A, 100–114, 152–182
US5583114 A, 469–479
US5583187 A, 469–479
US5585191 A, 439–445
US5594095 A, 242–261, 290–299
US5599858 A, 100–114, 152–182
US5599891 A, 188, 199–213
US5602227 A, 100–114
US5610241 A, 278–280, 290–299
US5644020 A, 44t–74t
US5646217 A, 152–182
US5654381 A, 290–299
US5700344 A, 469–479
US5710190 A, 327, 345–359
US5711842 A, 469–479
US5713991 A, 454–458
US5714573 A, 152–182
US5728847 A, 515–528
US5733951 A, 44t–74t
US5753724 A, 469–479
US5756651 A, 242–261
US5763513 A, 242–261
US5763564 A, 439–445
US5773562 A, 439–445
US5780704 A, 515–528
US5798435 A, 242–261, 290–299
US5798436 A, 439–445
US5798440 A, 270–275
US5840777 A, 345–359
US5853639 A, 100–114, 375–386
US5874124 A, 439–445
US5883199 A, 123, 125, 152–182
US5883199 X6, 152–182
US5889135 A, 44t–74t
US5891936 A, 199–213
US5900322 A, 100–114, 152–182
US5900322 X6, 100–114, 152–182
US5908917 A, 100–114, 375–386
US5908918 A, 231, 242–261
US5914188 A, 100–114, 317–325
US5922832 A, 152–182
US5929196 A, 290–299
US5936045 A, 20
US5952405 A, 290–299
US5952433 A, 280–281
US5952433 X6, 290–299
US5952450 A, 152–182
US5952460 A, 199–213
US5955068 A, 44t–74t
US5958480 A, 199–213, 439–445
US5972093 A, 439–445
US5977250 A, 199–213, 439–445
US5981694 A, 439–445
US5990266 A, 100–114
US5993530 A, 199–213, 469–479
US5998552 A, 242–261, 290–299
US6018004 A, 152–182
US6024784 A, 194, 199–213, 439–445
US6025028 A, 439–445
US6042820 A, 44t–74t
US6043063 A, 100–114, 199–213
US6046248 A, 20
US6046248 X6, 44t–74t
US6071982 A, 290–299
US6077916 A, 12, 42
US6087471 A, 199–213
US6093791 A, 439–445
US6096809 A, 152–182
US6096810 A, 290–299, 439–445
US6103858 A, 199–213
US6103858 X6, 199–213
US6110983 A, 345–359
US6114042 A, 152–182
US6114495 A, 100–114, 439–445
US6117928 A, 242–261
US6121033 A, 100–114
US6121410 A, 439–445
US6136905 A, 242–261
US6139948 A, 100–114, 317–325
US6143863 A, 439–445
US6143947 A, 393, 401–410
US6153664 A, 290–299
US6156929 A, 221, 242–261
US6160084 A, 290–299
US6180686 B1, 345–359
US6183814 B1, 439–445
US6191176 B1, 100–114
US6197380 B1, 439–445
US6201034 B1, 152–182
US6201083 B1, 290–299, 439–445
US6228501 B1, 345–359, 423–429
US6228934 B1, 199–213
US6235816 B1, 152–182
US6235825 B1, 152–182, 242–261
US6245537 B1, 44t–74t
US6258924 B1, 44t–74t
US6280855 B1, 44t–74t
US6284838 B1, 44t–74t
US6287604 B1, 44t–74t
US6291597 B1, 242–261, 290–299
US6297347 B1, 44t–74t
US6303677 B1, 152–182
US6306821 B1, 44t–74t
US6307003 B1, 469–479
US6312732 B1, 44t–74t
US6322899 B1, 375–386
US6323276 B2, 199–213
US6342304 B1, 44t–74t
US6342304 B1, 100–114, 152–182
US6353086 B1, 100–114, 439–445
US6365680 B1, 469–479
US6388047 B1, 290–299
US6399716 B2, 44t–74t
US6410096 B1, 199–213, 439–445
US6414108 B1, 44t–74t
US6417294 B1, 100–114
US6428767 B1, 23
US6432600 B2, 454–458
US6462105 B1, 242–261
US6465569 B1, 345–359
US6482341 B1, 44t–74t
US6495631 B1, 152–182
US6497903 B1, 199–213
US6500897 B2, 290–299
US6503538 B1, 44t–74t
US6506873 B1, 401–410
US6509397 B1, 44t–74t
US6509537 B1, 515–528
US6514733 B1, 44t–74t
US6515054 B1, 152–182
US6534599 B2, 290–299
US6544607 B1, 242–261

US6548569 B1, 44t–74t
US6552124 B2, 290–299
US6559244 B1, 290–299
US6573308 B1, 345–359
US6573340 B1, 152–182
US6583219 B2, 290–299
US6600008 B1, 317–325
US6605262 B2, 199–213
US6607996 B1, 401–410
US6610981 B2, 515–528
US6617448 B2, 290–299
US6620869 B2, 100–114
US6623749 B2, 44t–74t
US6624244 B2, 345–359
US6630171 B1, 44t–74t
US6645584 B1, 423–429, 439–445
US6645622 B2, 100–114
US6649732 B2, 317–325
US6656984 B1, 199–213
US6677386 B1, 199–213, 270–275, 290–299
US6706106 B1, 44t–74t
US6709668 B2, 290–299
US6709763 B2, 439–445
US6713595 B2, 44t–74t
US6716911 B2, 199–213
US6720374 B2, 242–261
US6726756 B1, 454–458
US6730252 B1, 316–325
US6755915 B1, 270–275
US6787613 B2, 152–182
US6803443 B1, 152–182
US6811599 B2, 423–429
US6815079 B2, 375–386
US6815529 B2, 44t–74t
US6818686 B1, 152–182, 290–299
US6824599 B2, 199–213
US6835764 B2, 423–429
US6838493 B2, 44t–74t
US6864296 B2, 345–359
US6867239 B2, 345–359
US6867247 B2, 44t–74t
US6881763 B2, 345–359
US6884432 B2, 44t–74t
US6890872 B2, 401–410
US6916857 B2, 290–299
US6916861 B2, 454–458
US6921430 B2, 469–479
US6943214 B2, 152–182
US6946506 B2, 401–410
US6951956 B2, 100–114, 242–261
US6953622 B2, 401–410
US6958369 B2, 152–182
US6987138 B2, 100–114
US7037983 B2, 290–299
US7052776 B2, 439–445
US7053151 B2, 290–299
US7064113 B2, 515–528
US7067300 B2, 44t–74t
US7067596 B2, 152–182
US7067611 B2, 100–114
US7094840 B2, 290–299, 469–479
US7128969 B2, 375–386
US7144634 B2, 242–261
US7148272 B2, 44t–74t
US7160592 B2, 439–445
US7160977 B2, 152–182
US7169588 B2, 44t–74t
US7173080 B2, 423–429
US7179883 B2, 44t–74t
US7208535 B2, 100–114
US7214414 B2, 152–182
US7226615 B2, 345–359
US7241832 B2, 152–182
US7244442 B2, 44t–74t
US7265160 B2, 345–359
US7265188 B2, 152–182
US7268190 B2, 152–182
US7268205 B2, 44t–74t
US7297394 B2, 152–182
US7364768 B2, 439–445
US7364875 B2, 44t–74t
US7368160 B2, 375–386
US7396667 B2, 515–528
US7419709 B2, 439–445
US7439283 B2, 100–114
US7445835 B2, 423–429
US7452491 B2, 100–114
US7455999 B2, 44t–74t
US7465770 B2, 469–479
US7467585 B2, 515–528
US7491754 B2, 199–213, 439–445
US7501464 B2, 242–261
US7504556 B2, 44t–74t
US7531585 B2, 100–114, 242–261
US7550541 B2, 152–182
US7553900 B2, 152–182
US7553923 B2, 44t–74t
US7557224 B2, 515–528
US7563830 B2, 345–359
US7588632 B2, 454–458
US7598305 B2, 515–528
US7608593 B2, 515–528
US7615183 B2, 375–386
US7619025 B2, 423–429
US7666501 B2, 401–410
US7670545 B2, 100–114
US7678444 B2, 375–386
US7700500 B2, 317–325
US7713601 B2, 375–386
US7718718 B2, 152–182, 375–386
US7718720 B2, 242–261
US7728100 B2, 270–275
US7762482 B2, 515–528
US7763715 B2, 199–213
US7767744 B2, 515–528
US7790069 B2, 242–261
US7799837 B2, 44t–74t
US7803298 B2, 290–299
US7846987 B2, 345–359
US7854880 B2, 100–114
US7863343 B2, 345–359
US7863382 B2, 152–182
US7868101 B2, 469–479
US7872056 B2, 345–359
US7879440 B2, 100–114
US7906135 B2, 44t–74t
US7910645 B2, 242–261
US7919543 B2, 454–458
US7919631 B2, 199–213
US7928167 B2, 152–182, 469–479
US7947754 B2, 345–359
US7951438 B2, 375–386
US7964696 B2, 44t–74t
US7968026 B1, 317–325
US7972669 B2, 345–359
US7985778 A1, 515–528
US7998545 B2, 375–386
US8002399 B2, 454–458
US8003719 B2, 242–261
US8003721 B2, 100–114, 152–182
US8003731 B2, 152–182
US8043679 B2, 152–182
US8048502 B2, 44t–74t
US8049065 B2, 44t–74t
US8057818 B2, 345–359
US8066923 B2, 401–410
US8067485 B2, 242–261
US8067492 B2, 469–479
US8071007 B1, 317–325
US8071124 B2, 345–359
US8084551 B2, 242–261
US8101253 B2, 152–182
US8101688 B2, 100–114, 401–410
US8114522 B2, 423–429
US8133558 B2, 375–386
US8133562 B2, 317–325
US8148453 B2, 100–114
US8148518 B2, 199–213
US8153343 B2, 454–458
US8153782 B2, 199–213
US8182889 B2, 439–445
US8182901 B2, 317–325
US8202450 B2, 242–261
US8207240 B2, 44t–74t
US8222354 B2, 44t–74t
US8231889 B2, 44t–74t
US8232343 B2, 152–182
US8232348 B2, 242–261
US8263197 B2, 375–386
US8268901 B2, 345–359
US8268913 B2, 152–182, 375–386
US8283389 B2, 345–359
US8293826 B2, 242–261
US8299148 B2, 401–410
US8324298 B2, 152–182
US8329856 B2, 270–275
US8334348 B2, 290–299
US8362145 B2, 152–182
US8372512 B2, 345–359
US8372917 B2, 152–182, 375–386
US8378027 B2, 152–182
US8389107 B2, 375–386
US8392851 B2, 100–114
US8419997 B2, 515–528
US8420707 B2, 345–359
US8420746 B2, 290–299
US8431218 B2, 152–182
US8431677 B2, 515–528
US8431683 B2, 515–528
US8440748 B2, 242–261
US8444905 B2, 152–182, 375–386
US8445593 B2, 152–182
US8461262 B2, 401–410
US8470420 B2, 375–386
US8470421 B2, 317–325

US8481620 B2, 152–182
US8481675 B2, 515–528
US8501445 B2, 515–528
US8512852 B2, 152–182, 375–386
US8513329 B2, 152–182
US8513379 B2, 515–528
US8529617 B2, 44t–74t
US8546490 B2, 152–182, 375–386
US8563140 B2, 439–445
US8586658 B2, 100–114
US8586821 B2, 152–182
US8592641 B2, 375–386
US8628718 B2, 290–299
USRE36548 E, 100–114
USRE38158 E1, 469–479

W

W201119826 A, 270–275
WO0001530 A1, 422–429, 433, 439–445
WO0014154 A1, 44t–74t
WO0015684 A1, 327, 345–359
WO0024819 A1, 515–528
WO0027923 A1, 35–38
WO0027924 A1, 44t–74t
WO0030618 A1, 44t–74t
WO0040617 A1, 267, 270–275
WO0043523 A2, 16
WO0043523 A3, 44t–74t
WO0056376 A1, 15
WO0056376 A9, 44t–74t
WO0060956 A1, 278–280, 290–299
WO0062630 A1, 20
WO0063263 A1, 44t–74t
WO0063268 A1, 44t–74t
WO0065140 A1, 394, 401–410
WO0069916 A1, 195, 199–213, 264, 270–275, 288, 290–299
WO0070331 A1, 492, 515–528
WO0073380 A1, 270–275
WO0076483 A1, 267, 270–275
WO0100730 A1, 221, 242–261
WO0102087 A1, 187–188, 190–192, 199–213
WO0107166 A1, 37, 489, 491, 515–528
WO0111070 A3, 44t–74t
WO0112706 A1, 345–359
WO0112833 A2, 23
WO0112833 A3, 44t–74t
WO0130905 A1, 150, 152–182, 290–299
WO0168762 A1, 423–429
WO0168890 A2, 265, 270–275
WO0168890 A3, 270–275
WO0170846 A1, 122, 152–182
WO0180835 A1, 190, 199–213
WO0190262 A2, 448, 454–458
WO0190262 A3, 454–458
WO0196449 A1, 192–193, 199–213
WO02053610 A1, 280–281, 290–299
WO02053641 A1, 280–281, 290–299
WO02053641 A9, 290–299
WO02059199 A1, 123, 125, 152–182
WO0206023 A1, 414, 423–429
WO02070583 A2, 469–479
WO02070583 A3, 469–479
WO02070583 A8, 469–479
WO02072699 A1, 152–182
WO02072699 A8, 152–182
WO02085284 A2, 345–359
WO02085284 A3, 345–359
WO02087851 A1, 363, 375–386
WO02087877 A1, 240, 242–261
WO02088230 A1, 373, 375–386
WO02088271 A1, 460, 468–479
WO02090629 A1, 391–392, 401–410
WO0214043 A1, 328, 340, 345–359
WO0216468 A1, 118, 152–182
WO0218477 A2, 29
WO0234857 A2, 278–280, 290–299, 462, 469–479
WO0234857 A3, 290–299, 469–479
WO0236675 A2, 500, 515–528
WO0236675 A3, 515–528
WO0236675 A8, 515–528
WO03006525 A1, 93–94, 100–114
WO03011959 A1, 242–261
WO03014224 A1, 145, 152–182
WO03016015 A1, 90–91, 100–114
WO03022927 A1, 418, 423–429
WO03029329 A2, 196, 199–213
WO03029329 A3, 199–213
WO03037956 A9, 100–114, 242–261
WO03043815 A1, 434, 439–445
WO03046060 A1, 341–342, 345–359
WO03050170 A1, 303–304, 317–325
WO03057781 A, 7–8
WO03062334 A1, 449, 454–458
WO03068289 A1, 439–445
WO03074593 A1, 91, 100–114
WO03078493 A2, 345–359, 401–410
WO03078493 A3, 345–359, 401–410
WO03082963 A1, 314, 317–325
WO03091238 A1, 498, 515–528
WO03097468 A1, 11–12
WO03106521 A1, 290–299
WO2003037956 A1, 88, 100–114, 217, 242–261
WO2004013217 A1, 515–528
WO2004020708 A1, 89–90, 100–114, 398, 401–410
WO2004022650 A, 100–114
WO2004033700 A1, 267–268, 270–275
WO2004041936 A1, 16, 199–213, 439–445
WO2004058314 A2, 317–325
WO2004061172 A2, 387–388, 401–410
WO2004061172 A3, 401–410
WO2004063282 A1, 416, 423–429
WO2004069930 A1, 239–240, 242–261
WO2004076550 A1, 242–261
WO2004076550 A8, 242–261
WO2004076582 A1, 124, 152–182, 469–479
WO2004076583 A1, 152–182, 460, 469–479
WO2004085533 A1, 152–182
WO2004087812 A1, 128, 152–182, 375–386
WO2004095319 A2, 100–114
WO2004095319 A3, 100–114
WO2004108805 A1, 345–359
WO2004108806 A1, 345–359
WO2005017001 A1, 196, 199–213
WO2005017252 A1, 196, 199–213
WO2005023873 A1, 196, 199–213
WO2005026245 A1, 512–513, 515–528
WO2005040282 A1, 136–137, 152–182, 232, 242–261
WO2005052056 A1, 93, 100–114
WO2005052075 A, 199–213
WO2005056680 A1, 466, 469–479
WO2005061626 A1, 236, 242–261
WO2005066256 A1, 226, 242–261
WO2005072944 A1, 85, 100–114
WO2005073285 A1, 269–275
WO2005078018 A1, 278–280, 290–299, 414, 423–429
WO2005097894 A1, 90–91, 100–114, 226, 242–261
WO2005105775 A1, 498, 515–528
WO2005105908 A1, 504–505, 515–528
WO2006001081 A1, 196, 199–213
WO2006012917 A1, 232, 242–261
WO2006022430 A1, 399–410
WO2006026546 A2, 375–386
WO2006026546 A3, 375–386
WO2006030951 A1, 117, 136, 152–182
WO2006031568 A2, 375–386
WO2006031568 A3, 375–386
WO2006038506 A1, 145, 152–182
WO2006054493 A1, 89, 237, 242–261
WO2006074815 A1, 126, 152–182
WO2006088241 A1, 91–92, 100–114, 189, 199–213, 433, 439–445
WO2006095526 A, 242–261
WO2006098159 A1, 286–287, 290–299, 363, 375–386
WO2006103913 A1, 287, 290–299
WO2006103926 A1, 328, 345–359
WO2006103928 A1, 335, 345–359
WO2006103969 A1, 135, 152–182, 328, 335, 345–359
WO2006103970 A1, 339, 345–359
WO2006116126 A2, 199–213
WO2006121118 A1, 369–370, 375–386
WO2006124349 A2, 401–410
WO2006124349 A3, 401–410
WO2007003659 A1, 515–528
WO2007008755 A2, 317–325
WO2007008755 A3, 317–325
WO2007015371 A1, 416, 423–429
WO2007020904 A1, 30
WO2007021377 A2, 454–458
WO2007021377 A3, 454–458
WO2007022080 A2, 418, 423–429
WO2007022080 A3, 423–429
WO2007025582 A1, 396, 401–410
WO2007028258 A2, 289–299
WO2007028258 A3, 290–299
WO2007029688 A1, 395, 401–410
WO2007033418 A1, 30
WO2007034805 A1, 263–264, 270–275
WO2007047844 A2, 401–410
WO2007047844 A3, 401–410
WO2007052543 A1, 345–359
WO2007052587 A1, 435, 439–445
WO2007061944 A2, 375–386
WO2007061944 A3, 375–386
WO2007067435 A2, 391, 401–410
WO2007067435 A3, 401–410

WO2007074042 A2, 100–114
WO2007074042 A3, 100–114
WO2007083705 A1, 327–328, 335, 345–359
WO2007086623 A1, 423–429
WO2007094477 A1, 87, 100–114
WO2007095708 A1, 100–114, 152–182, 232, 242–261
WO2007095709 A1, 100–114, 228, 232, 242–261, 413, 415, 423–429
WO2007095710 A1, 100–114
WO2007095711 A1, 100–114, 232, 242–261
WO2007095712 A1, 100–114, 242–261
WO2007099056 A1, 286, 290–299
WO2007102488 A1, 507, 515–528
WO2007107808 A1, 283, 290–299
WO2007142106 A1, 100–114
WO2007144529 A1, 152–182
WO2008004490 A1, 100–114, 123, 152–182
WO2008008068 A1, 283, 290–299, 391, 401–410
WO2008011668 A1, 222–223, 242–261
WO2008012981 A1, 217, 242–261, 304, 317–325
WO2008022127 A2, 264, 270–275
WO2008022127 A3, 270–275
WO2008028915 A1, 152–182
WO2008028918 A1, 152–182
WO2008029934 A1, 388, 401–410
WO2008037744 A2, 130–131, 152–182
WO2008037744 A3, 152–182
WO2008037749 A2, 130–131, 152–182
WO2008038648 A1, 20, 123, 152–182
WO2008045516 A1, 496, 515–528
WO2008050945 A1, 413, 415, 423–429
WO2008055240 A1, 152–182
WO2008056989 A2, 423–429
WO2008058303 A1, 481–482, 496, 515–528
WO2008067627 A2, 42–43
WO2008067627 A3, 44t–74t
WO2008072114 A1, 375–386
WO2008076755 A1, 329–330, 336–337, 345–359
WO2008090590 A1, 133, 152–182
WO2008093284 A1, 338, 345–359
WO2008100566 A1, 199–213
WO2008100569 A1, 199–213
WO2008100577 A1, 199–213
WO2008120807 A1, 388–390, 401–410
WO2008123367 A1, 136, 337–338, 345–359
WO2008126660 A1, 335, 345–359
WO2008129688 A1, 310–311, 317–325
WO2008130225 A2, 339, 343, 345–359
WO2008130226 A2, 345–359
WO2008130226 A3, 345–359
WO2008146905 A1, 281–282, 290–299
WO2008149918 A1, 310–311, 317–325
WO2008155980 A1, 91–92, 100–114
WO2009018380 A2, 317–325
WO2009022195 A1, 148, 152–182
WO2009024812 A1, 435, 439–445
WO2009027357 A1, 242–261
WO2009038783 A1, 342, 345–359
WO2009041518 A1, 152–182, 278–280, 290–299
WO2009045176 A1, 316–325
WO2009070858 A1, 38–39
WO2009081362 A1, 514–528
WO2009092825 A1, 231, 242–261
WO2009095363 A1, 30
WO2009100473 A1, 482, 515–528
WO2009104372 A1, 421–429
WO2009107425 A1, 11, 88, 92, 100–114, 364–365, 375–386
WO2009115672 A1, 469–479
WO2009120457 A2, 22
WO2009120457 A3, 44t–74t
WO2009125872 A1, 236–237, 242–261
WO2009130205 A1, 152–182
WO2009137058 A1, 126, 152–182
WO2010002668 A1, 152–182, 375–386
WO2010002668 A8, 152–182, 375–386
WO2010002669 A1, 152–182
WO2010008445 A2, 290–299
WO2010008445 A3, 290–299
WO2010008447 A1, 286, 290–299
WO2010010696 A1, 133, 152–182
WO2010013483 A1, 368, 375–386
WO2010016514 A1, 462–464, 469–479
WO2010019944 A, 317–325
WO2010022966 A2, 6t
WO2010022966 A3, 44t–74t
WO2010022966 A8, 44t–74t
WO2010032197 A1, 439–445
WO2010038537 A1, 85, 100–114
WO2010040707 A1, 312, 317–325
WO2010041936 A2, 337, 345–359
WO2010041936 A3, 345–359
WO2010044112 A1, 283–284, 290–299
WO2010044112 A8, 290–299
WO2010047370 A1, 144, 152–182
WO2010050482 A1, 515–528
WO2010051589 A1, 128–129, 152–182, 223, 242–261
WO2010059562 A1, 434, 439–445
WO2010065053 A1, 335, 345–359
WO2010074015 A1, 89–90, 100–114, 398, 401–410
WO2010083356 A1, 44t–74t
WO2010085569 A1, 434–435, 439–445
WO2010118954 A1, 488, 495, 502, 515–528
WO2010118955 A1, 488, 495, 502, 515–528
WO2010122806 A1, 393, 396, 401–410
WO2010123095 A1, 18–19
WO2010125490 A2, 44t–74t
WO2010125490 A3, 44t–74t
WO2010133560 A1, 141, 152–182
WO2010134454 A, 152–182, 375–386
WO2010137514 A1, 393, 401–410
WO2010139056 A1, 132, 152–182
WO2010140865 A2, 270–275
WO2010140865 A3, 270–275
WO2010142507 A2, 460, 466–479
WO2010142507 A3, 469–479
WO2010151872 A1, 317–325, 375–386
WO2011002004 A1, 7–8, 152–182
WO2011005664 A2, 25
WO2011005664 A3, 44t–74t
WO2011009165 A1, 152–182
WO2011015433 A1, 489, 495, 502, 515–528
WO2011015433 A9, 515–528
WO2011024023 A1, 193–194, 199–213
WO2011029648 A1, 495, 502, 515–528
WO2011032727 A1, 374–386
WO2011038071 A1, 515–528
WO2011038081 A1, 332, 345–359
WO2011038248 A1, 317–325
WO2011040905 A1, 93, 100–114, 219, 237, 239, 242–261
WO2011047486 A1, 198–213
WO2011049111 A1, 463–464, 469–479
WO2011049115 A1, 462–463, 469–479
WO2011049116 A1, 463–464, 469–479
WO2011050479 A1, 242–261
WO2011050480 A1, 242–261
WO2011056924 A2, 197, 199–213
WO2011056924 A3, 199–213
WO2011073874 A2, 31–32
WO2011073874 A3, 44t–74t
WO2011073874 A4, 44t–74t
WO2011073874 A9, 44t–74t
WO2011077304 A2, 152–182
WO2011077304 A3, 152–182
WO2011080623 A2, 140–141, 152–182
WO2011080623 A3, 152–182
WO2011082052 A1, 228, 230, 242–261, 363, 375–386
WO2011086030 A2, 337, 343, 345–359
WO2011086030 A3, 345–359
WO2011110567 A, 146, 152–182
WO2011120155 A1, 269–275
WO2011122080 A1, 236–237, 242–261
WO2011132537 A1, 439–445
WO2011138485 A1, 420, 423–429
WO2011141573 A1, 339, 345–359
WO2011145391 A1, 345–359
WO2011145461 A1, 341, 345–359
WO2011146562 A2, 485, 515–528
WO2011146562 A3, 515–528
WO2011149689 A1, 270–275
WO2011153653 A1, 345–359
WO2011157691 A1, 137, 152–182
WO2011162046 A1, 364, 375–386
WO2012002707 A2, 313, 317–325
WO2012002707 A3, 317–325
WO2012004402 A1, 27
WO2012007857 A2, 152–182
WO2012008784 A2, 329, 345–359
WO2012008784 A3, 345–359
WO2012012064 A1, 217–218, 242–261, 278–280
WO2012017832 A1, 265–266, 270–275
WO2012023465 A1, 371, 375–386
WO2012023594 A1, 400–410
WO2012029710 A1, 397–398, 401–410
WO2012030819 A1, 466, 469–479
WO2012030821 A1, 469–479
WO2012030822 A1, 469–479
WO2012030823 A1, 469–479
WO2012043219 A1, 236, 242–261
WO2012070526 A1, 464, 469–479
WO2012078315 A1, 375–386
WO2012086192 A1, 216, 242–261
WO2012086226 A1, 284, 290–299
WO2012086305 A1, 345–359
WO2012087616 A2, 317–325
WO2012087616 A3, 317–325

WO2012091366 A2, 345–359
WO2012091366 A3, 345–359
WO2012098340 A1, 270–275
WO2012099357 A2, 335, 345–359
WO2012099357 A3, 345–359
WO2012102792 A1, 290–299
WO2012112266 A1, 290–299
WO2012120199 A1, 434, 439–445
WO2012120309 A2, 152–182
WO2012120309 A3, 152–182
WO2012121296 A1, 264–265, 270–275
WO2012121960 A1, 343, 345–359
WO2012131252 A1, 242–261
WO2012133037 A1, 264–265, 270–275
WO2012133039 A1, 264–265, 270–275
WO2012138282 A1, 345–359
WO2012141660 A1, 124, 152–182, 242–261
WO2012149407 A1, 191, 199–213
WO2012150349 A2, 447, 454–458
WO2012150349 A3, 454–458
WO2012158511 A1, 434, 439–445
WO2013005914 A1, 419, 423–429
WO2013006464 A2, 375–386
WO2013006781 A2, 345–359
WO2013006781 A3, 345–359
WO2013006781 A9, 345–359
WO2013007760 A1, 147, 152–182
WO2013012705 A1, 100–114
WO2013016444 A2, 232, 242–261
WO2013016444 A3, 242–261
WO2013017431 A1, 375–386
WO2013017895 A1, 336, 345–359
WO2013021772 A1, 364
WO2013026784 A1, 515–528
WO2013029018 A1, 415, 423–429
WO2013030300 A1, 335, 345–359
WO2013038068 A1, 449, 454–458
WO2013038770 A1, 368, 375–386
WO2013039266 A1, 8
WO2013041561 A1, 434, 439–445
WO2013046487 A1, 237, 242–261
WO2013048738 A1, 146–147, 152–182
WO2013049161 A1, 44t–74t
WO2013053774 A2, 453–458
WO2013053774 A3, 454–458
WO2013058056 A1, 345–359
WO2013061834 A1, 284, 290–299
WO2013077210 A1, 138, 144, 152–182
WO2013080788 A1, 373, 375–386
WO2013087903 A1, 30
WO2013108817 A, 135, 152–182
WO2013131649 A1, 226, 242–261
WO2013140868 A1, 311, 317–325
WO2013154255 A1, 230–231, 242–261
WO2014001922 A1, 147, 152–182
WO2014023319 A1, 194–195, 199–213
WO8103278 A1, 39–41
WO8302955 A1, 329, 343, 345–359
WO8808011 A1, 191, 199–213
WO8808869 A1, 152–182
WO9000067 A1, 44t–74t
WO9001521 A1, 133–135, 152–182
WO9014388 A1, 148, 152–182
WO9106681 A1, 149, 152–182
WO9113207 A1, 194, 199–213, 375–386, 431, 439–445
WO9116375 A1, 140, 152–182
WO9202559 A1, 34
WO9204413 A1, 231, 242–261
WO9209654 A2, 32, 100–114, 117, 127, 152–182
WO9209654 A3, 100–114, 152–182
WO9210539 A1, 152–182
WO9219680 A1, 89, 100–114, 128, 152–182
WO9220740 A1, 152–182
WO9308014 A1, 345–359
WO9309172 A1, 494, 515–528
WO9400293 A, 367, 375–386
WO9402622 A1, 268, 270–275
WO9407940 A1, 188, 199–213
WO9407949 A1, 432, 439–445
WO9409760 A1, 277–278, 290–299
WO9410257 A1, 464–465, 469–479
WO9411440 A2, 124–125, 152–182
WO9411440 A3, 152–182
WO9416000 A1, 366–367, 375–386
WO9417220 A1, 308, 317–325
WO9500479 A1, 44t–74t
WO9502649 A1, 459–460, 469–479
WO9504097 A1, 242–261, 285, 290–299
WO9504108 A1, 129, 152–182
WO9508594 A1, 44t–74t
WO9510577 A1, 464–465, 469–479
WO9514740 A1, 20–21
WO9515260 A1, 311, 317–325
WO9518169 A1, 285, 290–299
WO9520614 A1, 100–114
WO9520615 A1, 100–114, 390, 401–410
WO9523175 A1, 280–281, 290–299
WO9529710 A1, 20
WO9600263 A1, 194, 199–213, 431, 439–445
WO9600746 A1, 345–359
WO9603159 A1, 467, 469–479
WO9603468 A1, 152–182, 199–213, 439–445
WO9606178 A, 199–213
WO9615173 A1, 125–126, 152–182
WO9615174 A1, 20
WO9617369 A1, 431, 439–445
WO9622330 A2, 136, 152–182
WO9622330 A3, 152–182
WO9624682 A1, 194, 199–213, 431, 439–445
WO9625446 A1, 20–21
WO9625448 A1, 44t–74t
WO9625452 A1, 190, 199–213
WO9631303 A1, 432, 439–445
WO9631347 A1, 432, 439–445
WO9631561 A1, 129, 152–182
WO9704036 A1, 199–213, 401–410, 459, 466, 469–479
WO9705193 A1, 305–306, 317–325
WO9708931 A2, 100–114
WO9708931 A3, 100–114
WO9710292 A1, 187, 195, 199–213, 459, 469–479
WO9712946 A1, 434, 439–445
WO9721762 A1, 188, 199–213
WO9732929 A1, 242–261
WO9734953 A1, 242–261
WO9740111 A1, 317–325, 469–479
WO9742249 A1, 290–299
WO9749762 A1, 193, 199–213
WO9800170 A1, 197–213
WO9806785 A1, 37
WO9812245 A1, 191, 199–213
WO9828080 A1, 490, 515–528
WO9828357 A1, 27
WO9831825 A1, 44t–74t
WO9846782 A1, 100–114, 196, 199–213
WO9846783 A1, 196, 199–213
WO9847445 A1, 289–299
WO9850611 A1, 401–410
WO9851812 A2, 16
WO9851812 A3, 44t–74t
WO9853141 A1, 432–433, 439–445
WO9854244 A1, 338, 342, 345–359
WO9901278 A1, 372, 375–386
WO9904948 A1, 431–432, 439–445
WO9905207 A1, 88–89, 100–114
WO9906456 A1, 280–281, 290–299
WO9914268 A1, 285–286, 290–299, 432, 439–445
WO9925756 A1, 149, 152–182
WO9928366 A1, 98, 100–114
WO9929733, 138–139
WO9929768 A1
WO9932536 A1, 12–13
WO9933558 A1, 187–188, 190–192, 199–213
WO9942147 A, 290–299
WO9945067 A1, 123, 152–182, 242–261
WO9946332 A1, 285, 290–299
WO9964498 A1, 192, 199–213

Y

YU114690 A, 152–182
YU117990 A, 152–182
YU126590 A, 152–182
YU126788 A, 44t–74t
YU154488 A, 44t–74t
YU45506 B, 44t–74t
YU45508 B, 44t–74t

Z

ZA200100251 A, 423–429, 439–445
ZA200103577 A, 44t–74t
ZA200308081 A, 375–386
ZA200309278 A, 375–386
ZA200402610 A, 199–213
ZA200406448 A, 439–445
ZA200901007 A, 270–275
ZA7100808 A, 242–261
ZA7302749 A, 152–182
ZA7600493 A, 44t–74t
ZA7805208 A, 152–182
ZA8103269 A, 44t–74t
ZA8707559 A, 199–213
ZA8804695 A, 44t–74t
ZA8805889 A, 44t–74t
ZA8807535 A, 242–261
ZA8900692 A, 152–182
ZA8909905 A, 345–359
ZA9305179 A, 270–275
ZA9500657 A, 100–114
ZA9811205 A, 44t–74t