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Biopolymers: Applications and Trends

Michael Niaounakis

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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

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

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

ISBN: 978-0-323-35399-1

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

Publisher: Matthew Deans
Acquisition Editor: David Jackson
Editorial Project Manager: Peter Gane
Production Project Manager: Debbie Clark
Designer: Greg Harris

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

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Foreword

The present book is the third part of a trilogy dedicated to biopolymers. The other two books are: "Biopolymers, Reuse, Recycling and Disposal" (2013), and "Biopolymers: Processing and Products" (2014).

The book gives a detail and full picture of all available applications of biopolymers, and provides a critical review of the prior art and a thorough patent survey. In particular, the book presents every application of biopolymers, which is available in the market, or disclosed in patents, including even some unusual or not well-known applications of biopolymers (see for example Chapter 3, fifth part, and Chapter 4, second part). To the best of author's knowledge most of the information contained in this book, have not been presented before in any other book.

The book consists of 10 chapters. Each chapter is self-contained and stands alone for those interested in a specific subject. Preparatory Chapters 1 and 2 are updated versions of Chapters 1 and 2 of the previous books.

Chapter 1 can be divided roughly into 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. The chapter consists of three parts. The first part reviews the intrinsic properties, which refer to the polymer itself. Among the intrinsic properties are: density, transition temperatures and crystallinity, solubility, gas barrier properties, transparency, and electromagnetic properties. The second part reviews the processing properties, which refer to the behavior of the polymer during forming. Among the processing properties are: viscosity, melt flow index (MFI), and melt strength. The third part reviews the product properties, which refer to the properties of the biopolymer as an entity. 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 investigates the packaging applications of biopolymers. The chapter consists of five parts. The first part gives a short preview of the circumstances that led to the development of packaging materials derived from renewable resources, and the challenges the packaging industry is facing. The second part presents various types of packaging films made of biopolymers including shrink films, cling films, and biaxially oriented films. The third part presents bags, sachets, and nets all made of biopolymers. The fourth part presents various types of containers including multilayered containers, foam containers, and rigid containers, as well as battery packages and bottles. The fifth part examines the use of biopolymers in funeral devices including coffins and urns.

Chapter 4 investigates the applications of biopolymers in agriculture, forestry, and fishery. The chapter consists of two parts. The first part presents the agricultural and forestry applications of biopolymers, and includes ground coverings (mulch films, mulch fabrics), nets, growth substrate media, receptacles (flower-pots or containers), mowers, fertilizers/pesticides, packaging, beehives, and fire-fighting formulations. The second part presents the fishery applications of biopolymers, and includes fishing lines, nets, traps, artificial baits and lures, and aquaculture constructions.

Chapter 5 investigates the main electronic applications of biopolymers. The chapter consists of five parts. The first part previews the major trends of biopolymers in electronics applications. The second part presents a long list of housings and/or enclosures for electronic devices made of biopolymers. The third part presents the use of biopolymers in the manufacture of audio devices. The fourth part presents the use of biopolymers in the manufacture of printed circuit boards (PCB). The fifth part examines the use of biopolymers in insulated wires and cables for electrical and/or electronic devices.

Chapter 6 gives an up-to-date overview of the uses of biopolymers in automotive applications. Biopolymer find applications in interior parts, exterior parts, door components, electrical components, steering fuel and exhaust system, engine, transmission and radiator wheels, HVAC (heating, ventilating, and air conditioning), and hybrid and electrical vehicles.

Chapter 7 investigates the main medical, dental, and pharmaceutical applications of biopolymers. The chapter consists of five parts. The first part presents the main characteristics of the organic and inorganic biopolymers used in the medical sector. The second part gives an extensive overview of a large number of medical applications including uses such as wound enclosures, body implants, and tissue engineering materials. The third part examines drug delivery matrices or vehicles made of biopolymers. The fourth part refers to the dental applications of biopolymers, and the fifth part to applications of biopolymers in diagnostic and therapeutic imaging.

Chapter 8 examines various uses of biopolymers in cosmetic products including cleansing preparations, makeup and other facial preparations, hair care preparations, sunscreen preparations, and manicure and pedicure preparations. A separate part presents accessories, containers, and packages for handling cosmetic substances made of biopolymers.

Chapter 9 reviews the applications of biopolymers in sports, toys, and board games. Biopolymers are used in sports articles including hollow inflatable balls (e.g., soccer balls), badminton and golf equipment, and various sports accessories such as sports shoes, ski boots, snow goggles, etc.

Chapter 10 investigates the building and construction applications of biopolymers. The chapter consists of nine parts. The first three parts overview the main biopolymers that are used either as additives in cement or lime compositions or as matrices in biocomposites, as well as in coatings and adhesives. The next five parts present specific applications of biopolymers including insulation, interior design/decoration, soil erosion, foundations, pavings, and artificial stones. A separate section gives an extensive presentation of the subterranean applications of biopolymers.

Michael Niaounakis
May 2015, 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	Carboxymethyl cellulose
CN	Cellulose nitrate
HEC	Hydroxyethyl cellulose
P2HB	Poly(2-hydroxybutyrate)
P2HBLA	Poly(2-hydroxybutyrate-*co*-lactate)
P3DD	Poly(3-hydroxydodecanoate)
P3HB	Poly(3-hydroxybutyrate) (or PHB or β-PHB)
P3HB4HB	Poly(3-hydroxybutyrate-*co*-4-hydroxybutyrate)
P3HBLA	Poly(3-hydroxybutyrate-*co*-lactate)
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)
P4HHx	Poly(4-hydroxyhexanoate)
P4HP	Poly(4-hydroxypropionate)
P4HV	Poly(4-hydroxyvalerate)
P5HB	Poly(5-hydroxybutyrate)
P5HHx	Poly(5-hydroxyhexanoate)
P5HV	Poly(5-hydroxyvalerate)
P6HHx	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)
PASP	Poly(aspartic acid)
PBA	Poly(butylene adipate)
PBAT	Poly(butylene adipate-*co*-terephthalate)
PBAzT	Poly(butylene azelate-*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)
PBSEAT	Poly(butylene sebacate-*co*-adipate-*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,L-lactide), poly(*rac*-lactide); see also *rac*PLA
PDLGA	Poly(D,L-lactide-*co*-glycolide)
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*-ε-caprolactone)
PGS	Polyglycerol sebacate
PGTMC	Poly(glycolide-*co*-trimethylene carbonate)
PHA	Polyhydroxyalkanoate
PHBHD	Poly(3-hydroxybutyrate-*co*-3-hydroxydecanoate)
PHBHHx	Poly(3-hydroxybutyrate-*co*-3-hydroxyhexanoate), poly(hydroxybutyrate-*co*-hydroxyhexanoate)
PHBHP	Poly(3-hydroxybutyrate-*co*-3-hydroxypropionate)

PHBO	Poly(3-hydroxybutyrate-*co*-3-hydroxyoctanoate)
PHBHV	Poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate)
PHD	Poly(3-hydroxydecanoate) (or P3HD)
PHHp	Poly(3-hydroxyheptanoate)
PHHx	Poly(3-hydroxyhexanoate) or poly(3-hydroxycaproate) (or P3HHx)
PHN	Polyhydroxynonanoate (or P3HN)
PHP	Poly(3-hydroxypropionate) (or P3HP)
PHSE	Poly(hexamethylene sebacate)
PLA	Polylactide, poly(lactic acid)
PLCL	Poly(lactide-*co*-ε-caprolactone)
PLGA	Poly(lactide-*co*-glycolide)
PLDA	poly(L-lactide-*co*-D-lactide)
PLLA	Poly(L-lactide), poly(L-lactic acid)
PLDLLA	poly(L-lactide-*co*-D,L-lactide)
PLLCL	Poly(L-lactide-*co*-ε-caprolactone)
PLLGA	Poly(L-lactide-*co*-glycolide)
PLTMC	Poly(lactide-*co*-trimethylene carbonate)
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)
PPSA	Poly(propylene succinate-*co*-adipate)
PPT	Poly(propylene terephthalate) (bio-based); see also PTT
PSI	Polysuccinimide
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)
***rac*PLA**	Poly(*rac*-lactide); see PDLLA
sbPLA	Stereoblock PLA
scPLA	Stereocomplex PLA
TPS	Thermoplastic starch

Contents

1 Definitions of Terms and Types of Biopolymers

1.1 General

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 material. 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.

1.2 Definition of Terms

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 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 the 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 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

Biopolymers: Applications and Trends. http://dx.doi.org/10.1016/B978-0-323-35399-1.00001-6

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) (PCL) or poly(glycolic acid (PGA))), although some fall into both categories, such as polyhydroxyalkanoates (PHAs).

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 D7026-13

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/g C) through liquid scintillation counting. A bio-based poly(ethylene terephthalate (PET) comprises at least about 0.1 dpm/g C (disintegrations per minute per gram carbon) of ^{14}C [6].

"Compostable" polymer was defined by ASTM D6002-96(2002)e1 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 D6400-12 (for compostable plastics) or D6868-12 (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 D6400-12 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

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

The biopolymers of (type 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 which are