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Biopolymers: Reuse, Recycling, and Disposal

Michael Niaounakis

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More will I tell thee too: there is no birth
Of all things mortal, nor end in ruinous death;
But mingling only and interchange of mixed
There is, and birth is but its name with men.

Empedocles

From William Ellery Leonard's *The Fragments of Empedocles* (Chicago: The Open Court Publishing Company, 1908).

Foreword

An outline of certain chapters of this book was presented at the Annual Symposium of Biopolymers, held in Denver, 8-10 October 2010, under the title: Disposal, Recycling and Reuse of Biopolymers - The patent perspective.

The expression biopolymer or bioplastic is used to describe two different terms at the same time, which often leads to confusion. It can mean that the polymer or plastic is biodegradable or that the raw material used is renewable or bio-based. According to the first definition a biodegradable polymer derived from fossil fuel resources is considered as biopolymer. The same applies for a non degradable bio-based polymer; for more details see Chapter 2.

The scope of this book is to present and investigate a novel phenomenon related to the recycling and/or disposal of biopolymers. At first, the idea of recycling these polymers is contradicting with the nature and scope of biodegradable biopolymers. As the current interest of biopolymers is largely based on their biodegradability, to consider recycling these polymers is to ignore one of its most important properties. However, there are good reasons for the recycling of biopolymers. Most commercial biopolymers, such as polylactide (PLA), are not degraded under ordinary conditions even in presence of microorganisms. Furthermore, the disposal of biopolymer articles has the disadvantage of discarding valuable raw materials, which could be efficiently reutilized.

Currently, biopolymers lack economies of scale, representing still a small niche within the overall plastics industry, making up less than 1% of the global plastic market, while their waste streams are small and scattered. Surprisingly enough, there is much activity in patenting on the waste treatment of biopolymers, especially from Japanese universities, institutions and companies. All these patent applicants are poised to benefit from the continuous growth of biopolymers when these materials mature and reach a critical mass, which is necessary for recycling to become profitable.

Not much attention has been paid to the waste management of these materials so far. Meanwhile, biodegradable biopolymers such as polylactide (PLA) are a serious problem when and where they enter either conventional plastics recycling (e.g. of PET) or green-waste composting streams. This problem is expected to grow as biodegradable biopolymers proliferate in residential areas. With the current rate of growth, it is expected that waste issues concerning biopolymers will emerge in the future similarly to the situation of conventional polymers that are currently used.

The book consists of 10 chapters.

Chapter 1 starts with a presentation of the main motivations for using biopolymers. A large section 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 following section investigates the possible sources of biopolymers, including first, second and third generation feedstocks. A separate section is dedicated to the sources of scrap and waste biopolymers, which are intended for recycling.

Chapter 2 clarifies and explains the various terms used to describe biopolymers. A separate section presents the positions of the advocates of bioplastics and oxodegradable polymers and the arguments of each group against the other. In the following section are described the main types and mechanisms of (bio) degradation. The last section reviews the tests methods which have been developed for biodegradable including field tests, simulation tests and laboratory tests.

Chapter 3 describes all the possible ways of reusing discarded biopolymers. A distinction is made between reuse and physical recycling (see Chapter 5).

Chapter 4 examines all the known techniques for the disposal of biopolymers, including landfilling, disposal in soil or water and composting (industrial or home). A separated section summarizes the various microbes (aerobic and anaerobic) and enzymes used for the biodegradation of biopolymers. The following section examines alternative waste disposal systems. The last section describes the destructive thermal methods such as incineration (combustion) and pyrolysis.

Chapter 5 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.

Chapter 6 examines the various methods for the chemical recycling of biopolymers including hydrolysis/alcoholysis, dry heat depolymerization, hydrothermal depolymerization, and the relatively new enzymatic depolymerization technique.

Chapter 7 examines the various techniques of modifying and/or controlling the degradation rate of biopolymers, by suppressing or accelerating the degradation speed at will.

Chapter 8 analyzes and correlates trends in patenting related to the waste management of biopolymers. The methodology includes the collection of statistical data all over the world for the period from 01.01.1990 to 31.08.2012. A separate section presents the prospects and limitations of the main waste treatment options for biopolymers. The next section summarizes the current state of patents in the prior art. The last section reviews the developments of new waste treatment processes and biopolymers.

Chapter 9 presents the regulatory framework of biopolymers by grouping all the international standards related to recycling, disposal, biodegradation (aerobic and anaerobic), composting, and eco-toxicity. A separate group of standards refers to the determination of bio-based content. Other groups of standards refer to Life-Cycle-Assessment (LCA) and eco-labeling. A separate section describes the process of certification.

Chapter 10 constitutes of three parts. The first part reviews the few available economic analyses on the disposal and recycling of waste biopolymers. The second part presents life cycle assessment (LCA) analyses of the main biopolymers, i.e., starch, PLA and polyhydroxyalkanoates (PHAs). The third part examines the possible environmental and health effects resulting from the production, use and waste treatment of biopolymers.

The Appendix contains three tables: Table 1 is a collection of the bibliographic data of all patents related to recycling, reuse or disposal of biopolymers. Table 2 is a collection of the bibliographic data of the patents related to biodegradation on demand. Table 3 is a collection of the bibliographic data of the supplementary patents, which do not refer necessarily to biopolymers, and are used as references to processes and/or materials mentioned in the text.

This book is unique in its coverage encompassing scientific publications as well as patents. Emphasis has been given to patents, since patents refer predominantly to industrial applications and have a potential economic value. Patents, although they represent a substantial part of literature, till recently they were underrepresented in the cited bibliography. Patents are innovative, have an industrial applicability and they are not self-repeated. Although they are not peer reviewed, they have been searched and examined. Most of them come from major industries and international laboratories and the reason for this is possibly the high costs in obtaining and maintaining a patent.

It has to be clarified that the book is not a mere "list" of patents, but rather a critical review of all the available technologies on the issue of the waste management of biopolymers. A patent application is drafted on the so-called "problem-solution" approach; this means that a would-be inventor drafts its patent application by outlining the shortcomings of the prior art and proposing solutions to the stated problem. By summarizing and analyzing all the critical comments of several inventors/applicants on every prior art of each technology, the author was able to build up a clear opinion on the benefits and weaknesses of each technology. Although all this information is indeed available online, it is the author's opinion that is almost impossible for a would-be researcher to retrieve all the available patent literature by simple searching techniques, without prior expertise. At least for the issue of disposal and recycling of biopolymers most of the available patent literature is in Japanese with only a short abstract in English. On the basis of the abstract, an English speaker may consult online a machine translation of the text, which is a very tedious and not always reliable procedure. Furthermore, the relevant literature is scattered in many technical fields making the retrieval and/or combination of all available information difficult.

The book tries to be neutral on several issues surrounding the use of biopolymers and their recycling, reuse or disposal and to present all different arguments (pros and cons). In this context ground is given to both fighting "camps" in the field of degradable polymers, bioplastics and oxodegradable polymers, to present their position. Furthermore, the book keeps a critical eye on unjustified claims of properties which cannot and have not yet been validated or the false use of the term bioplastic or biopolymer for marketing purposes. In the same context, it is noted that there are not enough full scale assessments (LCAs) of biopolymers so far. Therefore, biopolymers have still a long way to go to convince the scientific community and the public that they can form a reliable alternative of polymers or plastics derived from fossil fuel resources.

Several of the commercial products mentioned in the manuscript and the accompanying tables are not anymore available in the market (obsolete). However, since these products are used to exemplify certain aspects of the cited patents, they were kept in the text.

The recycling of natural rubber, the most well known biopolymer, has already been analyzed and reviewed extensively in the past, and will not form part of this book.

One of the most striking results of this survey is the excessively large number of Japanese patent applications related to the waste treatment of biodegradable biopolymers. Actually, Japan has the highest number of patent applications worldwide relating to the waste treatment of biopolymers (66% of all patents). In spite of the large number of patents owned by Japanese companies, only two non-Japanese companies are actively involved on a large scale with the recycling of biopolymers or bioplastics; namely NatureWorks in the USA and Galactic S.A in Europe. However, in view of the large number of patent applications on the recycling of biopolymers future commercial implementation would be expected.

To the best of the author's knowledge there are no books with a similar subject in the market. Useful books, but with a different scope and partial coverage, are the following:

-Handbook of Biodegradable Polymers Handbook of Biodegradable Polymers, 2005, Bastioli, C. (Ed), Smithers Rapra Technology, ISBN: 1859573894.

-Engineering Biopolymers - Markets, Manufacturing, Properties and Applications, 2011, Endres H. J., Siebert-Raths A., Hanser Publications, ISBN: 9781569904619.

-Biodegradable Plastics and Polymers, NIIR board, ISBN: 8178330350.

-Bioplastics In The Waste Stream (CD, online), 2012, iSmithers Rapra Publishing, 2012, ISBN: 9781847359452.

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For Supporting materials and web links to patents, please visit the companion website: http://booksite.elsevier.com/9781455731459

Rijswijk
Dr Michael Niaounakis

Abbreviations of Biopolymers

β-PPL	poly(β-propiolactone)
β-PBL	poly(β-butyrolactone)
γ-PGA	poly(γ-glutamic acid)
ϵ-PL	poly(ϵ-lysine)
CA	cellulose acetate
CAB	cellulose acetate butyrate
CAP	cellulose acetate propionate
CN	cellulose nitrate
P2HB	poly(2-hydroxybutyrate)
P3HB	poly(3-hydroxybutyrate) (or PHB)
P3HB4HB	poly(3-hydroxybutyrate-*co*-4-hydroxybutyrate)
P3HD	poly(3-hydroxydecanoate) (or PHD)
P3HN	poly(3-hydroxynonanoate) (or PHN)
P3HP	poly(3-hydroxypropionate)
P4HB	poly(4-hydroxybutyrate)
P4HB2HB	poly-(4hydroxybutyrate-*co*-2-hydroxybutyrate)
P4HP	poly(-4-hydroxypropionate)
P4HV	poly(4-hydroxyvalerate)
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
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) (PTeMS); (different CAS)
PBSA	poly(butylene succinate-*co*-adipate)
PBSC	poly(butylene succinate-*co*-carbonate)
PBSE	poly(butylene sebacate)
PBSL	poly(butylene succinate-*co*-lactide)
PBST	poly(butylene succinate-*co*-terephthalate)
PCHC	poly(cyclohexene carbonate)
PCL	poly(ϵ-caprolactone)
PDLA	poly(D-lactide)
PDLLA	poly(D,L-lactide)
PDLGA	poly(D,L-lactide-*co*-glycolide)
PDO	polydioxanone (or PDS)
PE	polyethylene (biobased)
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-terephthalate)
PESu	poly(ethylene suberate)
PET	poly(ethylene terephthalate) (biobased)
PEUU	poly(ester urethane urea) (biodegradable)
PGA	polyglycolide, poly(glycolic acid)
PGCL	poly(glycolide-*co*-caprolactone)
PHA	polyhydroxyalkanoate
PHB	polyhydroxybutyrate (or P3HB)
PHBHD	poly(3-hydroxybutryrate-*co*-3-hydroxydecanoate)
PHBHP	poly(3-hydroxybutyrate-co-3-hydroxypropionate)
PHBHx	poly(3-hydroxybutyrate-*co*- 3-hydroxyhexanoate) or poly(hydroxybutyrate-*co*-hydroxyhexanoate)
PHBO	poly(3-hydroxybutyrate-*co*-3-hydroxyoctanoate) (or P3HB/3HO)
PHBHV	poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate)
PHD	polyhydroxydecanoate (or P3HD)
PHHp	poly(3-hydroxyheptanoate)
PHHx	poly(3-hydroxyhexanoate)
PHN	polyhydroxynonanoate (or P3HN)
PHO	poly(3-hydroxyoctanoate)
PHP	poly(3-hydroxypropionate) (or P3HP)
PHSE	poly(hexamethylene sebacate)
PHV	poly(3-hydroxyvalerate)
PLA	polylactide, poly(lactic acid)
PLCL	poly(lactide-*co*-caprolactone)
PLGA	poly(lactide-*co*-glycolide)
PLLA	poly(L-lactide)
PLLGA	poly(L-lactide-*co*-glycolide)
α-PMA	α-type polymalic acid, polymalate
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)
PPS	poly(propylene succinate)
PPT	poly(propylene terephthalate) (biobased); see also PTT
PTeMAT	poly(tetramethylene adipate-*co*-terephthalate); see also poly(butylene adipate-*co*-terephthalate (PBST).
PTeMC	poly(tetramethylene carbonate)
PTMC	poly(trimethylene carbonate)
PTeMS/ 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) (biobased); see also PPT
PU	polyurethane (biobased)
PVOH	poly(vinyl alcohol)
TPS	thermoplastic starch

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