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Tamilselvan Mohan and Karin Stana Kleinschek

Functional Biomaterials

Design and Development for Biotechnology, Pharmacology, and Biomedicine

Volume 1

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Volume 2

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The Editors

Prof. Tamilselvan Mohan
Graz University of Technology
Institute for Chemistry and Technology
of Bio-Based Systems (IBioSys)
Stremayrgasse 9
8010 Graz
Austria

and

University of Maribor
Faculty of Mechanical Engineering
Laboratory for Characterization and
Processing of Polymers
Smetanova Ulica 17
2000 Maribor
Slovenia

Prof. Karin Stana Kleinschek
Graz University of Technology
Institute for Chemistry and Technology
of Bio-Based Systems (IBioSys)
Stremayrgasse 9
8010 Graz
Austria

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The Editors

Prof. Tamilselvan Mohan
Graz University of Technology
Institute for Chemistry and Technology
of Bio-Based Systems (IBioSys)
Stremayrgasse 9
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Prof. Karin Stana Kleinschek
Graz University of Technology
Institute for Chemistry and Technology
of Bio-Based Systems (IBioSys)
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Preface

Broadening the spectrum of biopolymers, their classification, chemical nature, isolation, and characterization is very important for better understanding the usability of biopolymers in new applications. It is also important for the development of completely new materials based on the special properties of polysaccharides (cellulose-based and others) compared to the biomaterials currently used in various high-tech applications (e.g. inorganic materials and non-degradable synthetic polymers). In this context, this book focuses largely on the fundamental knowledge of biopolymers (natural: cellulose and its derivatives; other polysaccharides such as chitosan, glycosaminoglycans (GAG's), etc.; and synthetic ones such as polyethylene terephthalate and others), their origin, classifications, chemical nature, and isolation methods. This book also covers various classical and modern approaches to the transformation of these biopolymers into different forms, from thin films (model surfaces), nanoparticles, nanofibers, to 3D scaffolds. The application of these biopolymer-based multifunctional materials (e.g. 2D thin films to 3D scaffolds) in applications such as biosensors (e.g. for detection of DNA, antibodies, affibodies, and moisture sensors), antifouling surfaces, drug delivery systems, microfluidic devices, microarrays, two-photon absorption lithography, enzymatic digestion systems, wound models, to name a few important areas are also discussed in detail. A library of analytical methods used for the analysis of morphology, structure, shape, thermal, electrical, and surface properties, as well as for the study of solid–liquid interaction of biomaterials, is also covered in detail in this book.

It also provides a comprehensive overview of the latest developments in the applicability of biopolymers, especially polysaccharides, for the production of sustainable biomaterials used in medicine, focusing on potential applications and future developments. Therefore, it is unique and of interest not only to students and scientists but also to industry as well as stakeholders and policy makers. This coincides with recent trends to replace fossil materials with indigenous materials. In addition, readers will get an overview of the specific and very special properties of biopolymers that can be used for the production of sustainable but high-quality functional biomaterials. Overall, this book will contribute to a better understanding of the physicochemical properties of biopolymers and their use in the preparation of completely new materials for various advanced biomedical applications. In summary, there are no books to date that deal exclusively with the classification, isolation, preparation, and characterization of biopolymers and the design of new functional biomaterials, with a particular emphasis on the application of biomaterials in various advanced technological applications.

The content of the book is formulated to serve as a reference for the fundamental understanding of biopolymers/biomaterials and can be used by academicians, industrialists, researchers, graduate, and undergraduate students.

Graz/Austria, April 2022

Tamilselvan Mohan
Karin Stana Kleinschek

1

Definitions and Types of Microbial Biopolyesters and Derived Biomaterials

Martin Koller[1,2]

[1] *University of Graz, Institute of Chemistry, NAWI Graz, Heinrichstrasse 28/VI, 8010 Graz, Austria*
[2] *ARENA – Association for Resource Efficient and Sustainable Technologies, Inffeldgasse 21b, 8010 Graz, Austria*

1.1 Introduction

The increasing quantities of petrol-based plastics used for numerous applications in our daily life are among the most prevailing ecological threats of our days. In this regard, we are steadily confronted with phrases currently circulating in the media such as "plastic contamination of marine ecosystems," "microplastic," "growing garbage dumps," and "bans on everyday plastic materials" such as traditional "plastic shopping bags" or, more recently, cotton swabs with plastic rods or plastic drinking straws. Indeed, the currently produced plastics amount to more than 400 megatons (Mt) annually; their production exploits limited fossil resources, and, after their life span, these plastics need to be disposed of due to their lacking biodegradability [1–3]. In the beginning of 2020, approximately 150 Mt of plastics have already accumulated in the world's oceans alone, estimated to cause perishing of 100 000 marine mammals and about ten times as many birds year by year [4]. Just the other day, the dramatic death of a sperm whale carrying an unbelievable number of around eighty plastic bags in its, making it impossible for the animal to take organic food, and shocked the general public [5]. Only recently, Zheng et al. reported an estimate that, by 2050, the global production of plastics will quadruple, which will be connected with a doubling of plastic waste [6].

In fact, significantly less than one third of plastic waste is recycled in Europe, the rest ends up in landfills or in the environment, or is simply burned [7]. In this context, the increased release of microplastics from recycled food containers, especially from plastic bottles ("Re-PET"), into food, been described [8]. Moreover, it should be noted that recycling of plastic delays, rather than prevents, its final disposal in landfills [9]. Landfilled plastic waste, in turn, returns to the sea via detours, such as wind or river systems, and finally enters the food chain as microplastic and eventually into the human metabolism. This cycle applies to about 500 000 t

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of plastic waste per year in the EU alone. It is self-explanatory that this represents enormous risks for the biosphere and the health of the entire world population. But from the resource-technological perspective as well, our today's dependence on plastic is inadequate, unsustainable, and short sighted not only because current plastics production depends on exploiting limited fossil resources, but also because most plastic products are *per definitionem* designed as disposable products for single use only. This circumstance is a major environmental "fire accelerator"; as typical "end-of-the-pipe" product, plastics donate high short-term benefits through their favorable nature and, at the same time, are available at the discount price.

In particular, microplastics directly endanger food security and human health; starting from their consumption by plankton, such microplastics, which *per definitionem* have particle sizes ranging from 0.1 to 5.000 μm, easily climb up the entire trophic chain, until they finally get accumulated in its top, namely the human metabolism. Only during the last few years, concrete understanding of the detritus mechanisms of microplastic on the ecosystem and the metabolism of animals and humans is developing. In addition to microplastic uptake via the trophic chain, diverse techniques during food production using equipment with plastic parts, in addition to food storage in plastic containers like bottles, are also direct source of microplastic contamination of food, mainly by abrasion and by the currently fashionable use of recycled poly(ethylene terephthalate) (PET) bottles [8]. The documentation and quantification of possible diverse effects of microplastics on human health is currently only in its infancy. In 2018, microparticles in the size of 50–500 μm of a total of nine different petrochemical plastics, predominately poly(propylene) (PP) and PET, were for the first time clearly identified by an Austrian research team in the human intestine [10]. Considering the fact that the deterioration of intestine cells (villi) by microplastics was already demonstrated for fish and nematodes [11], it has to be expected that such microplastic particles also cause negative reactions in the human intestine, such as inflammation or even cancer. Moreover, by intestinal uptake, microplastics could potentially be transported to the blood and lymph system and to various organs.

To change this situation, a reasonable and fair pricing of plastics is required, reflecting not only its benefits but also the damage caused by the high environmental footprint of this end-of-pipe technology. In this way, plastics would no longer be disposed of in bulk; even more important, a fair pricing would, wherever possible, foster the production and implementation of alternative materials like bioinspired alternatives in order to finally find the way out of the "plastic predicament" [4].

1.2 Biopolymers as Bioinspired Alternatives

1.2.1 Defining "Bioplastics" Is No Trivial Task!

Looking back to the very beginnings of the "plastic age," we remember that the first plastic-like polymer indeed was biobased, namely natural *cis*-1,4-poly(isoprene) rubber obtained from the rubber tree *Hevea brasiliensis* (reviewed by Wycherley [12]).

However, especially the decades between 1940 and the turn of the millennium were dominated by synthetic, not biodegradable, polymers of petrochemical origin. As a real alternative to many of the currently used plastics, one can switch to bio-inspired alternatives [13]. In this context, we have to be careful when talking about "bioplastics," which is a scientifically ambiguous expression. It is of major importance to differentiate different groups of "bioplastics":

(a) Plastics that are biobased (originating from renewable resources) and, at the same time, biosynthesized (monomers converted to polymers by the action of living organisms), and biodegradable/compostable. Prime examples: microbial polyhydroxyalkanoates (PHA life cycle). As additional characteristic, PHAs are also biocompatible; hence, they do not exert any negative effect on the biosphere surrounding them (e.g. living organisms, cell lines, ecosystems) according to the standardized ISO 10993 norm. Other natural polymers, which can be processed to generate materials with plastic-like properties (e.g. processing starch to thermoplastic starch [14] – TPS life cycle; see Figure 1.1), or others, e.g. proteins gelatin [15], whey proteins [16], etc., chitin [17], or cellulose [18], which are compatible with PHA and other polymers, also belong to the group of biopolymers *sensu stricto*.

(b) Plastics that are biobased and biodegradable/compostable, but not biosynthesized (monomers converted to polymers by classical chemical methods, often demanding toxic catalysts). Prime example: poly(lactic acid) (PLA), which currently is considered a competitor of PET or poly(styrene) (PS); for the life cycle of PLA, please refer to Figure 1.2. Here, one has to consider high recalcitrance of highly crystalline PLA toward biodegradation and restrictions regarding its *in vivo* biocompatibility [19].

(c) Plastics that are biobased, but neither biosynthesized nor biodegradable/compostable. Prime example: biobased poly(ethylene) (bio-PE), which resorts to chemical conversion of saccharose to ethylene via ethanol and chemical polymerization of ethylene to PE (life cycle; see Figure 1.3). Such "bio-PE" is currently strongly emerging regarding its market volume, which is expected to amount to estimated 300 000 t per year in 2022. In 2018, even the company LEGO™ switched to bio-PE to manufacture their globally famous toy bricks; however, bio-PE is not biodegradable, and its production exploits food resources [20]. Partly, this group also encompasses the "green bottle" commercialized by The Coca Cola™ company, which consists of so-called "biobased PET"; however, this material has a biobased carbon content stemming from renewable resources (the ethylene part) of only 30%, and is not biodegradable/compostable [21].

(d) Other plastics are not biobased and not biosynthesized, but still biodegradable/compostable; they have a petrochemical origin. Prime examples are poly(ε-caprolactone) (PCL [22] life cycle: see Figure 1.4), or the random copolyester poly(butylene adipate terephthalate) (PBAT), which is used for materials commercialized by, e.g. the company BASF SE under the trade name Ecoflex® and follow-up products ([23] life cycle: see Figure 1.5). These materials enter the natural cycle of carbon after being biodegraded; hence, they do not

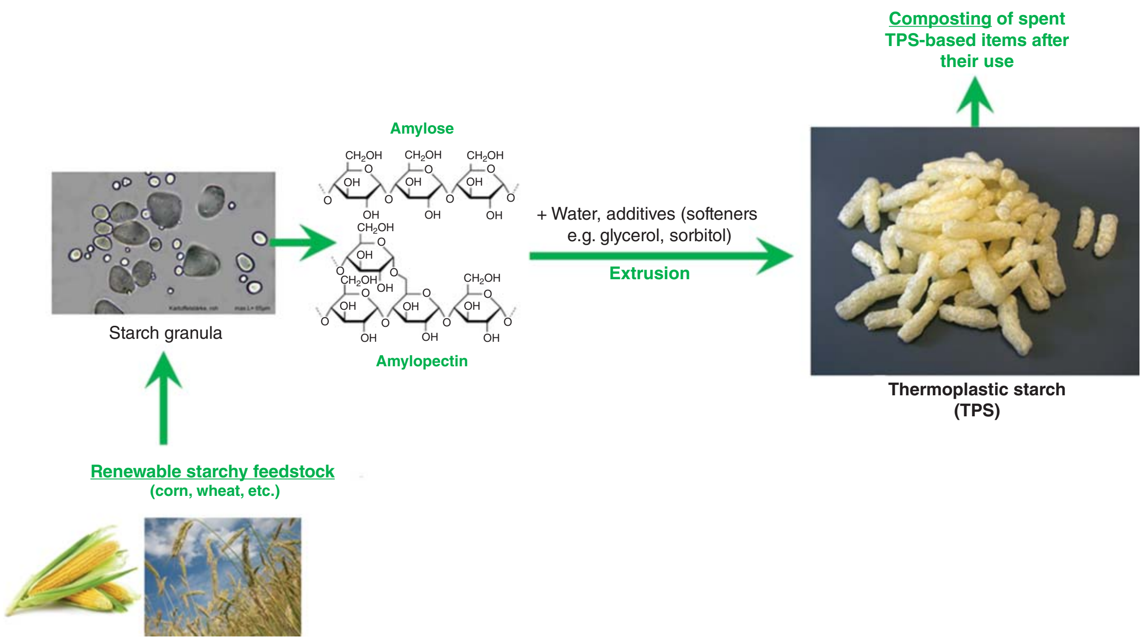

Figure 1.1 Production and life cycle of TPS. Source: Christian Gahle/Wikimedia Commons/CC BY-SA 3.0; atoss/Adobe Stock; Robin/Pixabay.

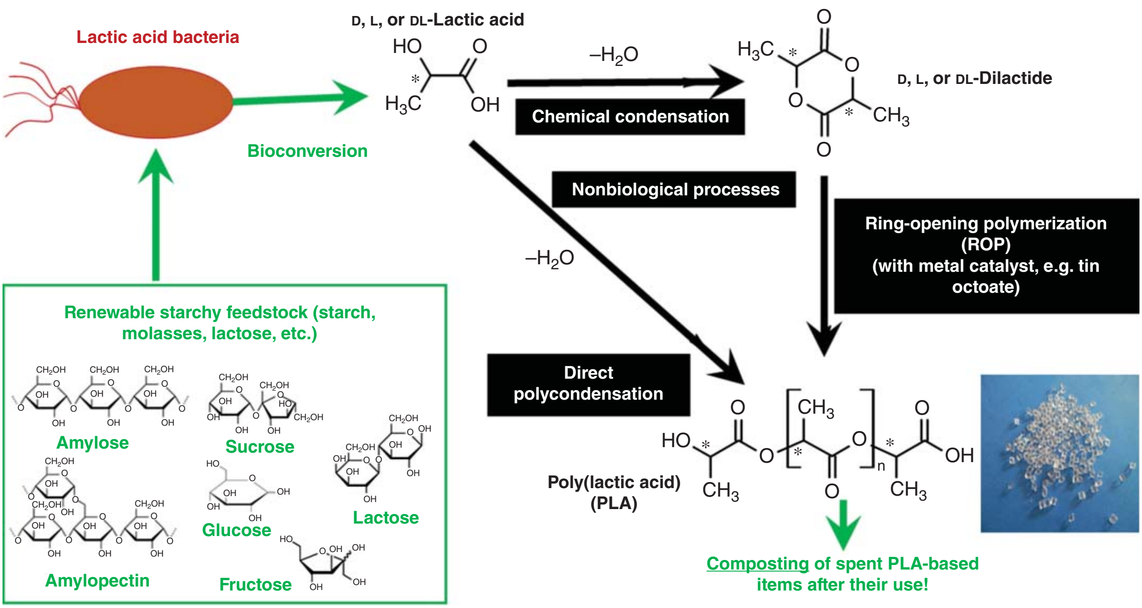

Figure 1.2 Production and life cycle of PLA. The * in the graphic indicates chiral centers. Source: epitavi/Adobe Stock.

Figure 1.3 Production and life cycle of “bio-PE.” Source: lzf/Adobe Stock.