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Biopolymers: State of the Art, New Challenges, and Opportunities

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1.1
Introduction

The term "biopolymers" usually describes polymers produced in a natural way by living species. Their molecular backbones are composed of repeating units of saccharides, nucleic acids, or amino acids and sometimes various additional chemical side chains contributing also to their functionalities.

If the largest part of biopolymers is extracted from biomass, such as polysaccharides from cellulose and proteins from collagen or milk, biopolymers can also be produced from biomonomers using conventional chemical processes as polylactic acid, or directly in microorganisms or genetically modified organisms, as polyhydroxyalkanoates. The genetic manipulation of microorganisms brings a tremendous potentiality for the biotechnological production of biopolymers with tailored properties quite suitable for high-value medical applications such as tissue engineering and drug delivery.

Throughout history, biopolymers have been mainly used by mankind as food, or for making clothing and furniture. Since the industrial time, fossil fuels such as oil are the greatest source in the development and manufacture of almost every commercial product, such as the plastic, which is currently used at a very large scale. But these fuels are not unlimited resources, and environmental concerns over all aspects of using fossil fuels for production and energy must be taken into account. We must act in a sustainable manner, which means that the resources must be consumed at a rate such that they can be restored by natural cycles of our planet. Therefore, today, the renewable nature of biopolymers leads them to a renaissance and a new interest. In the last 20 years, this interest in sustainable products has driven the development of new biopolymers from renewable feedstocks. Biopolymers have to compete with polymers derived from fossil fuel not only because of their functional properties but also in terms of cost. In this respect, biopolymers are competitive when the price of oil is high and the price of feedstocks, such as starch from corn, is low.

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In addition, the biodegradability of biopolymers gives them a specific advantage for the environmental concerns, for example, single-use packaging in food, automotive, or electronics industries [1].

The bionanocomposites deserve a special attention because they form a fascinating interdisciplinary area that brings together biology, materials science, and nanotechnology. Generally, polymer nanocomposites are the result of the combination of polymers and inorganic/organic fillers at the nanometer scale. The extraordinary versatility of these new materials comes from the large choice of biopolymers and fillers available, such as clays, cellulose whiskers, and metal nanoparticles. These new materials have been elaborated thanks to the development of new powerful techniques such as electrospinning [2]. In these materials, the interaction between fillers at the nanometer scale acts as a bridge in the polymer matrix that leads to the enhancement of the mechanical properties of nanocomposites with respect to conventional microcomposites [3]. But, bionanocomposites also add a new dimension because they are biocompatible and/or biodegradable materials. So, they are gradually absorbed and/or eliminated by the body. Their degradation is mainly due to hydrolysis or mediated by metabolic processes. Therefore, nanocomposites present a great interest for biomedical technologies such as tissue engineering, medical implants, dental applications, and controlled drug delivery. Nevertheless, the spread out of these valuable bionanocomposites in our everyday life can only be achieved provided they are easily accessible to consumers in terms of volume. Cellulose whiskers may soon be a challenge for nanoclays that are being used as traditional nanofillers for many applications [4], since they are now produced on an industrial scale.

Food products are also usually made of nanostructured materials based on biopolymers, and the elaboration of nanoparticles based on proteins and/or polysaccharides has recently revolutionized the world of biocompatible and degradable natural biological materials [5]. Therefore, the toolbox that micro- and nanotechnologies offer provides new opportunities for product and process innovations in the food industry. The control of the process and functionality at the nanoscale leads to more sustainable food production. This approach allows the development of nutrient delivery systems with healthy and/or less caloric value nutrients, sensors, and diagnostic devices that can monitor and ensure the safety of food products throughout the food chain. At least, various enhanced packaging concepts extend the shelf life of fresh products or indicate quality deterioration of the packaged product. However, for consumers, the general feeling toward foods that are associated with these new technologies and more particularly nanotechnologies is not totally positive. Thus, it is imperative to develop a good communication of the applications of nanotechnologies that allows the consumers to make an informed decision whether or not they would like to have the benefits of certain applications of nanotechnologies, or whether they do not accept certain risks.

All these driving forces act as stimuli to develop new materials based on biopolymers, and there are many opportunity areas such as industrial, medical, food, consumer products, and pharmaceutical applications for which biopolymers act as stabilizers, thickeners, binders, dispersants, lubricants, adhesives, drug-delivery agents, and so on.

1.2
Biopolymers: A Niche For Fundamental Research in Soft Matter Physics

If, for over half a century, the study of biopolymers has been nearly the reserved field of biochemists and molecular biologists, during the last decade the soft matter physics community has seized this research field. Its purpose is not only for pure intellectual curiosity but also for modeling and understanding various mechanisms involved in the soft matter field, and for the consequences that a better understanding of these biopolymers might lead to. In fact, the fundamental physics underlying the biopolymer behavior and the techniques applied for their study are often similar. With the development of new powerful X-ray sources, new microscopies (cryo-TEM, ultra speed confocal scanning laser microscopy), and the advent of single-molecule techniques [6], polymer physicists are now strongly active in this field and there exists a strong collaboration between biologists and physicists.

For example, biologists can create specific mutations to design molecules for specific studies of the role played by specific groups located at precise points along the chain, for understanding by example the influence of a particular residue on the folding–unfolding process of biopolymer and its influence on the mechanical properties, which can be measured by pulling with an AFM tip [7]. Also, the understanding of the biological molecular machines allows designing synthetic molecules to perform analogous tasks [8].

More generally, most biological macromolecular assemblies are predominantly made from mixtures of stiff biopolymers, and our cells, muscles, and connective tissue owe their remarkable mechanical properties to these complex biopolymer networks. The understanding of their incessant assembly, disassembly, restructuring, active and passive mechanical deformation needs a lot of theoretical modeling efforts because if flexible polymer behavior is well depicted in litterature, the stiffness of these biopolymers and the resulting anisotropic networks that lead to smart mechanical and dynamical properties are far from being understood.

The proteins, which are the major biomacromolecules in our body and play a fundamental role in making our body work, give us another example. As it is well known, proteins have a strong tendency to self-assemble after denaturation and this quasiuniversal mechanism, valuable for all the proteins, can lead to three generic structures, particulate gels around the isoelectric point, isolated amyloid fibrils, and spherulites far away from the isoelectric point [9,10]. Therefore, proteins have appeared as good model systems for understanding and modeling various self-assembling mechanisms, and more particularly the competition between processes of aggregation, gelation, and phase separation that play a major role in the self-assembly of most complex systems. So, a good control of the macroscopic phase separation during the protein self-assembly by kinetically trapping the structure at a particular stage of the process allows to create a large variety of new arrested structures. The linear and nonlinear rheological behaviors of these matrices and the transport properties of various probes inside are

still actively investigated for understanding the relationships between these properties and the structures of the matrices. Such fundamental researches also have societal and medical interests because the aggregation of misfolded protein molecules into so-called amyloid fibrils is directly implicated in many diseases such as Alzheimer's disease. More pleasant, the food industry also utilizes the self-assembling ability of proteins such as the beta-lactoglobulin, a major protein component of milk, to texture foods such as yogurt by forming gels.

The mixtures of biopolymer are well known to display very rich phase behaviors. The understanding of the underlying physics of these phase behavior and of the rheology–morphology relationships of the resulting phases also constitutes a challenge of interest and importance. Such mixtures can also be used as efficient stabilizers for gas bubbles generated using high-throughput devices [11]. Since biomedical applications are targeted, the stability of the bubbles and their monodispersity are key points to be addressed, which can be achieved efficiently by combining biopolymer/protein mixtures and microfluidics.

Functional biopolymer nanoparticles or microparticles formed by heat treatment of globular protein–ionic polysaccharide electrostatic complexes under appropriate conditions are another example of the high potential of biopolymer mixtures [12]. Such biopolymer particles can be used as encapsulation and delivery systems, fat mimetics, lightening agents, or texture modifiers.

1.3 Biopolymers: An Endless Source of Applications

The trend observed for physics also holds for chemistry since biopolymers have become new building blocks from the point of view of macromolecular chemistry in the last decade. This fact owes much to the emergence of new polymerization techniques such as controlled radical polymerization (CRP) and to "Click" chemistry. Processing of these chemical alternatives allows a very good control of the macromolecular architecture, the molar mass distribution, and the functionality of the macromolecules. Block copolymers involving a biopolymer block are nowadays of an easier access, rendering possible the study of their self-assembly in bulk and/or in a selective solvent of one of the blocks. The specificities of the biopolymer block in terms of bioactivity, biocompatibility, and biodegradability allow targeting application fields such as pharmaceutical science for which the self-assemblies (polymersomes, micellar aggregates, microgels, etc.) are used as drug delivery systems with potential targeting properties [13]. In bulk, it should also be said that block copolymers based on a biopolymer block are pretty promising. Actually, the strong segregation force exhibited by most biopolymer blocks with respect to synthetic ones results in an efficient microphase separation despite the small polymerization degrees of each of the blocks. Well-organized thin films with periodicity as small as 5 nm have been obtained for the first time for which applications to soft electronics are expected [14].

1.4
Topics Covered by the Book

This book reviews the recent accomplishments obtained in terms of preparation, characterization, and applications of biopolymers. In the first chapters, general overviews and descriptions of the main concepts and issues regarding the most important biopolymer families are introduced. The synthesis of various biopolymers through the processing of genetic engineering tools or by nature itself is described in Chapters 4, 5, and 11. In each case, the impact of different synthetic conditions on the characteristics of the macromolecules is described in close correlation with their potential from the applicative point of view.

In the same way, Chapters 6–10 focus on the use of biopolymers as material. Each chapter focuses on one type of material such as polymer blends, macro- to nanocomposites, interpenetrated networks (IPN), or hydrogels. In most cases, the elaboration of biomaterials can be rationalized through a modelization approach as depicted in Chapter 24. The resulting practical cases of biopolymer used in our everyday life are described in Chapter 26. Their main advantages in terms of biodegradation, recycling, and life cycle are discussed in Chapter 25.

Biopolymers display interesting properties, not only in bulk but also in solution and at interfaces, as shown in Chapter 23.

The remaining chapters mainly focus on an experimental technique that can be used for gathering information on biopolymers from the point of view of their structure, dynamics, at different length and timescales in bulk or at interfaces. In each case, the background for understanding the technique is given, practical cases are described, and the limits of the technique are discussed. In Chapter 12, the ability of dielectric techniques to access the molecular mobility and chain dynamics of biopolymers and biological systems is addressed. These studies can be nicely complemented at other timescale by running NMR or EPR measurements as shown in Chapters 13 and 14.

Chapters 16–19 describe the use of scattering techniques and of microscopy for investigating the structure of biopolymers at several but complementary length scales. Structural but also mechanical properties of the biopolymers may also be derived from rheological measurements as described in Chapters 20–22. When an accurate knowledge of the chemical composition of the extreme layer of biopolymer surfaces is needed, XPS analysis can be used as detailed in Chapter 15.

1.5
Conclusions

Academic researchers involved in the biopolymer areas often work across various disciplines, physics, soft matter, chemistry, biochemistry, and biology and have developed skills that enable them to transfer their knowledge from one field to another. Thus, these skills should enable them to face some great challenges

including the understanding of the physics of life, the nanoscale design of functional smart materials, the directed assembly of extended structures with targeted properties, and the emergence of physics far from equilibrium. The gap between nature and scientist know-how regarding "tailor-made" biopolymers is still wide, and a biomimetic approach of biopolymer synthesis may need tremendous development of specific genetic engineering tools. Furthermore, one should really have concerns regarding the life cycle of materials involving biopolymers, which are not always their single component, in order to avoid what we are currently facing with their actual homologues based on fossil fuels.

References

1 Johansson, C., Bras, J., Mondragon, I., Nechita, P., Plackett, D., Simon, P. *et al.* (2012) Renewable fibers and bio-based materials for packaging applications – a review of recent developments. *Bioresources*, **7** (2), 2506–2552.

2 Schiffman, J.D. and Schauer, C.L. (2008) A review: electrospinning of biopolymer nanofibers and their applications. *Polym. Rev.*, **48** (2), 317–352.

3 Faruk, O., Bledzki, A.K., Fink, H.P., and Sain, M. (2012) Biocomposites reinforced with natural fibers: 2000–2010. *Prog. Polym. Sci.*, **37** (11), 1552–1596.

4 Paul, D.R. and Robeson, L.M. (2008) Polymer nanotechnology: nanocomposites. *Polymer*, **49**, 3187–3204.

5 Sundar, S., Kundu, J., and Kundu, S.C. (2010) Biopolymeric nanoparticles. *Sci. Technol. Adv. Mater.*, **11** (1), 014104.

6 Deniz, A.A., Mukhopadhyay, S., and Lemke, E.A. (2008) Single-molecule biophysics: at the interface of biology, physics and chemistry. *J. R. Soc. Interface*, **5** (18), 15–45.

7 Alessandrini, A. and Facci, P. (2005) AFM: a versatile tool in biophysics. *Meas. Sci. Technol.*, **16** (6), R65–R92.

8 Kay, E.R., Leigh, D.A., and Zerbetto, F. (2007) Synthetic molecular motors and mechanical machines. *Angew. Chem. Int. Ed.*, **46** (1–2), 72–191.

9 Durand, D., Gimel, J.C., and Nicolai, T. (2002) Aggregation, gelation and phase separation of heat denatured globular proteins. *Physica A – Stat. Mech. Appl.*, **304** (1–2), 253–265.

10 Foegeding, E.A. and Davis, J.P. (2011) Food protein functionality: a comprehensive approach. *Food Hydrocoll.*, **25** (8), 1853–1864.

11 Park, J.I., Tumarkin, E., and Kumacheva, E. (2010) Small, stable, and monodispersed bubbles encapsulated with biopolymers. *Macromol. Rapid Commun.*, **31**, 222–227.

12 Jones, O.G. and McClements, D.J. (2010) Functional biopolymer particles: design, fabrication, and applications. *Compr. Rev. Food Sci. Food Saf.*, **9** (4), 374–397.

13 Schatz, C. and Lecommandoux, S. (2010) Polysaccharide-containing block copolymers: synthesis, properties and applications of an emerging family of glycoconjugates. *Macromol. Rapid Commun.*, **31**, 1664–1684.

14 Cushen, J., Otsuka, I., Bates, C., Halila, S., Fort, S., Rochas, C. *et al.* (2012) Oligosaccharide/silicon-containing block copolymers with 5 nm features for lithographic applications. *ACS Nano*, **6**, 3424–3433.