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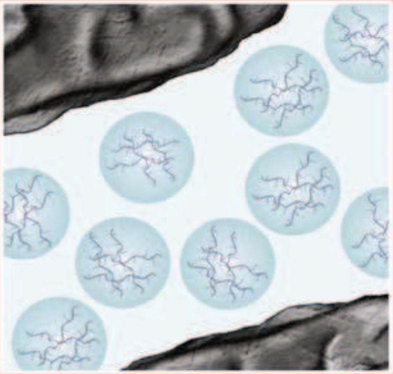

Biopolymers and Biotech Admixtures for Eco-Efficient Construction Materials

Edited by Fernando Pacheco-Torgal, Volodymyr Ivanov, Niranjan Karak and Henk Jonkers

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Edited by

Fernando Pacheco-Torgal, Volodymyr Ivanov, Niranjan Karak and Henk Jonkers

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Contents

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46 **Advanced fibre-reinforced polymer (FRP) composites for structural applications**
Edited by J. Bai
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Edited by F. Pacheco-Torgal, V. W. Y. Tam, J. A. Labrincha, Y. Ding and J. de Brito
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Edited by J. Weerheijm
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Edited by F. Pacheco-Torgal, L. F. Cabeza, J. Labrincha and A. de Magalhães
50 **Advanced composites in bridge construction and repair**
Edited by Y. J. Kim
51 **Rehabilitation of metallic civil infrastructure using fiber-reinforced polymer (FRP) composites**
Edited by V. Karbhari
52 **Rehabilitation of pipelines using fiber-reinforced polymer (FRP) composites**
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53 **Transport properties of concrete: Measurement and applications**
P. A. Claisse
54 **Handbook of alkali-activated cements, mortars and concretes**
F. Pacheco-Torgal, J. A. Labrincha, C. Leonelli, A. Palomo and P. Chindaprasirt
55 **Eco-efficient masonry bricks and blocks: Design, properties and durability**
F. Pacheco-Torgal, P. B. Lourenço, J. A. Labrincha, S. Kumar and P. Chindaprasirt
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61 **Corrosion of steel in concrete structures**
Edited by A. Poursaee
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Edited by K. J. Loh and S. Nagarajaiah
63 **Biopolymers and biotech admixtures for eco-efficient construction materials**
Edited by F. Pacheco-Torgal, V. Ivanov, N. Karak and H. Jonkers

Foreword

The cliché, *never judge a book by its cover,* this time seems especially untrue. The very informative title on the familiar cover of Woodhead Publishing Series in Civil and Structural Engineering inspires confidence and interest.

Key words in the title of the book define its goal: *Ecoefficient Construction Materials*, and simultaneously show the means by which to do that: *biopolymers* and *biotech admixtures.* These characteristics could reduce to the common denominator: *biotech toward sustainable construction.* There is a yardstick of target and the grand scale of engineering ambitions and challenges claimed in this work.

Every material thing comes from something else, and every structure is of construction materials, now mainly from concrete. The construction industry consumes more than 40% of produced energy and about 50% mass of materials the building industry also emits 35% of greenhouse gases. There is no doubt that sustainable development is the fundamental requirement for construction. The notion of sustainable development aspires to the role of a high civilizational ideal. Sustainable development "implies meeting the needs of the present without compromising the ability of future generations to meet their own needs" (Brundtland, 1987). However, a softer definition exists close to the people. Antoine de Saint-Exupery in *The Little Prince* said: *we do not inherit the Earth from our parents; we borrow it from our children.* On first impression, this second definition is a *leitmotif* or underlying theme of the book. Annually over six billion m^3 of concrete is produced around the world. It is unrealistic or even impossible to substitute other materials for this concrete. Nevertheless, it is possible or even necessary to modify concrete to use an adequate admixture (see the book title) to make concrete and construction materials ecoefficient, more environmentally friendly. The book provides basic concepts, production aspects, and environmental impact assessments on the use of biopolymers and biotech admixtures for cement mortar and concrete, as well as for soil stability, wood preservation, and coatings in construction applications including bioadhesives, biofilters, and biobarriers. This knowledge is new but well structured, up-to-date, with an enormous number of references. What is more, on each page a reader feels the need for progress in the face of complexity by making sense of every piece of information. The book is rare that is both scholarly and engaging. It is a great work—a magnum opus: 450 pages and 40 contributors. Contrary to that diversity, from a reader′s point of view it makes the impression of an integral continuity. We can see here the merit of four experienced editors: V. Ivanov (Singapore), W. Karak (India), and H. Jonkers (The Netherlands) under the guideline of Fernando Pacheco-Torgal (Portugal). It is an excellent example of how to make order in informational chaos. Altogether, the contributors could be called the sense makers in the biotech construction material engineering field. The words that were chosen matter to the contributors. They suggest the ideas that the contributors want to bring into the world. The words and sentences can further our plans, fulfill our inspirations. Authors arrange lots of facts, reports, and discoveries in a way that makes it understandable and of value in the engineering field marked by the topical pillars: biotechnology—construction materials—ecology. Readers will feel a familiarity with the architecture of the presented information. What is more, readers feel the right to rely on those information sources and to be professionally active on this area. One of the reasons is a conviction that the authors know their topic and recognize their responsibility, clearly conveyed by the text. Implementing new or even modified construction materials means that we are able to assure durability (often more than 50 years), safety of use, health, and user comfort.

Each chapter shines light on the selected issue: scientific approach for construction biotechnology; biotechnological production; life cycle of biopolymers; biotech admixtures as modifiers for fresh concrete mixture and hardened concrete; microorganism-based bioplasticizers for concrete; fly ash materials; biopolymers for wood preservation; biopolymer coatings, including photocatalytic ones; bioadhesives; biofilters, and biobarriers. Thus, one can outline its edges and depths. The book touches the key problem of how, through experimentation techniques and tests, trials and failures, observations, and theories of construction, researchers have managed to unravel nature's secrets and transform them into technology to achieve progress. Perhaps, the economic aspect is not accented enough.

It is true that biobased admixtures have been used in construction materials for centuries much earlier than the Roman Empire. However, it is also true that contemporary knowledge of this subject is arising almost simultaneously with the appearance of this book. Topicality is one of the extra values of the book.

How we do manage with construction materials in the twenty-first century?—It is one of the basic questions of civilization. Expectations include:

- a new arrangement of the research results,
- a new understanding of the nature of materials,
- a thrust for further development in theory and in application.

The new knowledge will help us to change our activity in our world.

Knowing is not enough, the book also encourages us. It seems that now is the right time. We can lessen our anxiety and follow the book to make progress.

The book appears as the 63rd entry on the list of the Woodhead Publishing Series in Civil and Structural Engineering. Five books published during the last three years have highlighted the significant adjective: *Ecoefficient*. It is not by accident that it exposes the development trend as a megatrend. The book makes a brilliant trace along this way. We have the essential reading.

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Introduction to biopolymers and biotech admixtures for eco-efficient construction materials

1

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1.1 Introduction

For more than half a century the fossil fuel industry has provided the resources for the polymer industry. Independently of the "Peak Oil" never ending discussion (Chapman, 2014), the future scarcity of petroleum resources (Sorrell et al., 2012) is a fact that must be faced sooner or later. Moreover, it does not matter very much that the shale oil euphoria could turn the USA into the world's largest oil producer (Morse, 2014).

Granting the fact, one believes that oil scarcity is not the major issue to be addressed concerning this nonrenewable resource. In the short term, interstate wars and environmental disaster are the major issues. Never before has a commodity triggered so many armed conflicts (Black, 2012). Moreover, since 1973, at least one-quarter of all interstate wars were connected to oil (Verbruggen and van de Graaf, 2013).

States with large oil reserves and unstable political governments tend to instigate conflicts at a rate three and a half times that of comparable states with stable governments and without oil (Colgan, 2013, 2014).

Most importantly, environmental disasters are caused by oil spills like the 1979 *Ixtoc 1* off-shore oil rig blowout, which during nine months released 530 million liters of crude oil into the Gulf of Mexico (Jernelov and Linden, 1981; Patton et al., 1980) causing massive damage to maritime ecosystems (Soto et al., 2014). Add to that the 1989 *Exxon Valdez* oil tanker "small" episode (41 million liters of crude oil) in Alaska that killed hundreds of thousands of seabirds, billions of fish eggs, and many whales and seals (Alford et al., 2014; Malakoff, 2014), and the 2010 British Petroleum (BP)-owned Deep Water Horizon oil spill, which released approximately 780 million liters of crude oil into the Gulf of Mexico (Atlas, 2011). These represent the dark side of crude oil production for which no life-cycle analysis can account.

The latter was considered the worst environmental disaster to have occurred in the USA. According to Costanza et al. (2010), this environmental tragedy was responsible for an almost complete shutdown of the $2.5 billion per year Louisiana fishing industry and was also responsible for a $34–$760 billion loss of ecosystem services in the Mississippi River delta alone. This value exceeds even BP total market value and still

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raises environmental and public health concerns (Ortmann et al., 2012; Wise et al., 2014; Drescher et al., 2014; Gill et al., 2012).

The chronology of other crude oil-related disasters can be seen at Infoplease (2014). In addition, the increase in crude oil transport by oil tankers has led to an increase in collision risk (Morgan et al., 2014).

Because oil exploration is moving into ever-deeper water and into stormier and icier seas, it means increased risks (Jernelov, 2010).

According to Sällh et al. (2015), the share of offshore oil production is expected to increase from 33% to 48% by 2030. This means that the risk of new environmental disasters related to oil production will also increase.

All of the foregoing clearly justifies the search for new and biodegradable polymers based on renewable feedstock.

Recent years have seen a tremendous increase in the number of publication citations on biobased polymers (around 1000% in the last 10 years). However, the fact is that these materials still constitute only a very small fraction of the polymer industry (Babu et al., 2013).

Biopolymers include polymers from agro-resources (polysaccharides, cellulose, starch, chitin, chitosan, and alginates), from microorganisms by fermentation (polyhydroxyalkanoates, such as polyhydroxybutyrate) and from biotechnology via conventional synthesis (polylactides (PLA), polybutadiene succinate, biopolyethylene (PE), polytrimethylene terephthalate, poly-*p*-phenylene) (Avérous and Pollet, 2012). Although some are biodegradable, that is not always the case, like, for instance, PE.

It is clear that the farming practices used to grow biobased feedstock including the fuel required for plowing, harvesting, manufacture, and transport, and the use of herbicides and pesticides, can also have environmental impacts as high as those of petrochemical-based polymers (Yates and Barlow, 2013). However, biopolymers are not associated with armed conflicts, nor are they responsible for large environmental disasters that so often occur in crude oil extraction and transportation. Besides, the reuse of agricultural and biomass waste will contribute to the environmental advantages of biopolymers over traditional petroleum-based polymers (Gopalakrishnan et al., 2012, 2013; Hottle et al., 2013).

1.2 Biopolymers and biotech admixtures for eco-efficient construction materials

Bio-based admixtures have been used in construction materials for centuries. The use of air lime mortars with the addition of vegetable fat goes back to Vitruvius of the Roman Empire (Albert, 1995).

The Romans also had recognized the role of bio-admixtures to improve their building materials; for example, dried blood was used as an air-entraining agent, whereas biopolymers such as proteins served as set retarders for gypsum (Plank, 2003).

The Chinese already have used egg white, fish oil, and blood-based mortars during the construction of the Great Wall due to their imperviousness (Yang, 2012).

In 1507, mortars based on lime mixed with small amounts of vegetable oil added during the slaking process were used in the construction of the Portuguese fortress, “Nossa Senhora da Conceição,” located on Gerum Island, Ormuz, Persian Gulf (Pacheco-Torgal and Jalali, 2011). More than 300 years after the fortress construction, A. W. Stiffe, a Lieutenant of the British Navy, visited the interior of the fortress and made a description of its conservation status for *Geographical Magazine*. He stated that “The mortar used was excellent, and much more durable than the stones” (Rowland, 2006).

The twentieth century became the age of admixtures, the history of which started in the 1920s with the introduction of lignosulfonate, a biopolymer, for Ordinary Portland Cement (OPC) concrete plasticization, the first functional polymer used in construction on a large scale (Plank, 2004).

OPC concrete, a typical civil engineering construction material, is the most used material on Planet Earth. Its production reaches 10,000 million tons/year and in the next 40 years will increase around 100% (Pacheco-Torgal et al., 2013b).

Currently, around 15% of the total OPC concrete production contains chemical admixtures to modify their properties, either in fresh or hardened state. Concrete super plasticizers based on synthetic polymers include melamine, naphthalene condensates, or polycarboxylate copolymers to improve their workability, strength, and durability. Examples of biopolymers used in concrete include lignosulfonate, starch, chitosan, pine root extract, protein hydrolysates, or even vegetable oils. Bioresins based on polyfurfuryl alcohol and produced from agricultural wastes have recently been used with interesting results in engineering structures (Gkaidatzis, 2014).

Biotech admixtures made in fermentation processes by employing bacteria (Pei et al., 2015) or fungi seem to have received an increased attention, because their biosynthesis rate is about two to four times higher than that of plant-based biopolymer (Ivanov et al., 2014). These admixtures include sodium gluconate, xanthan gum, curdlan, or gellan gum. Nevertheless, investigations on the use of biopolymers in OPC are still residual. Of the 8159 Scopus-referenced journal papers published since 2000 and related to OPC, fewer than 1% are related to the use of biopolymers.

The construction industry has become a major field of use for biopolymers. In 2000, an estimated $2 billion in sales was made at the manufacturer’s level, and this growth is expected to continue. Although OPC and dry-mix mortars consume the majority of biopolymers, a great diversity of bio-admixtures with well over 500 different products is now used by other building materials industries (Plank, 2004).

In the next few years, the construction industry will keep on growing at a fast pace just to accommodate urban population increase that will almost double, increasing from approximately 3.4 billion in 2009 to 6.4 billion in 2050 (World Health Organization (WHO, 2014)). Recent estimates on urban expansion suggest that until 2030 urban land cover will increase by 1.2 million km^2 (Seto et al., 2012). Therefore, demand for biopolymer-based construction materials will also increase (Ashby, 2015).

The nanotech advancements that have recently occurred will allow for the development of new and improved biopolymer-based materials. Investigations on cellulose nanocrystals (cellulose elements having at least one dimension in the 1−100 nm range) constitute an important and recent nanotechnology field that will enable the development of eco-efficient high-performance materials (Charreau et al., 2013; Chirayil et al., 2014).

The potential of nanocellulose materials can be perceived from the increase in the number of papers published involving keywords like nanocellulose, cellulose nanocrystals, or cellulose nanocomposites (Figure 1.1).

According to Mariano et al. (2014), the number of papers in this area is expected to increase by a further 500% by at least 2017, leading to an increase in perspective production in the range of 1000% in the following two years. However, the transition from advanced research to practical applications for the built environment is likely to take several years.

Cellulose, being the most abundant organic polymer on Earth and representing about 1.5 trillion tons of the total annual biomass production (Kim et al., 2015), is renewable, biodegradable, and carbon neutral. It has the potential to be processed at industrial-scale quantities and at low cost compared to other materials. The cellulose nanocrystals represent a potential green alternative to carbon nanotubes for reinforcing materials such as polymers and concrete.

Dri et al. (2013) used models based on the atomic structure of cellulose showing that these crystals have a stiffness of 206 GPa, which is comparable to that of steel.

Other authors (Dufresne, 2013) showed that the specific Young's modulus of cellulose nanocrystals, which is the ratio between the Young's modulus and the density of cellulose crystal, is around 85 Jg^{-1}, in comparison to around 25 Jg^{-1} for steel.

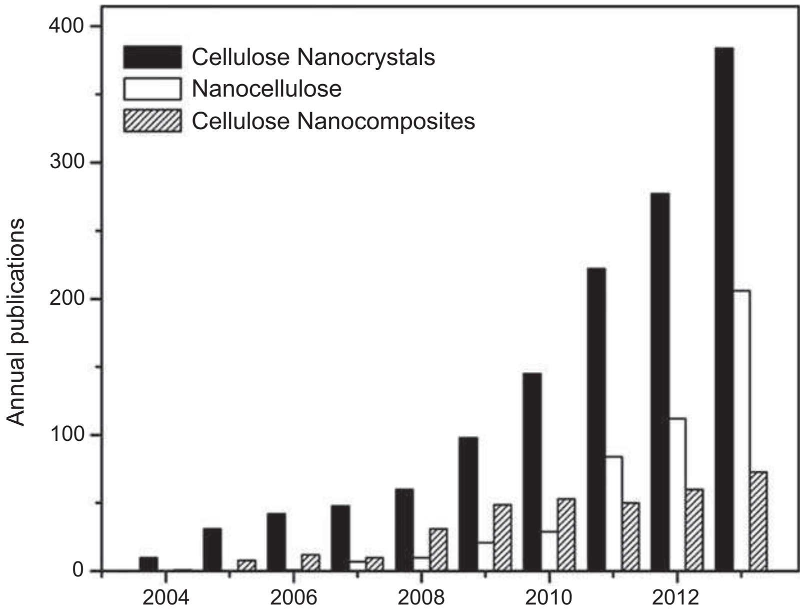

Figure 1.1 Number of publications related with nanocellulose terms during the last decade. Data from main scientific databases. Reprinted from Mariano et al. (2014). Copyright © 2012, with permission from Elsevier.

So far, some uses of nanocrystalline cellulose to improve the modulus of elasticity of cement boards have already been patented (Thomson et al., 2010). The cement industry has a potential nanocellulose market of over 4 million metric tons (Cowie et al., 2014).

Because biopolymers like chitosan, PLA, or starch have poor mechanical performance when compared to synthetic polymers, the use of cellulose nanofibers as reinforcing nanomaterials can help turn those biopolymers into biocomposites with high mechanical strength (Kim et al., 2015).

Cellulose aerogel is another promising application concerning the development of high-performance thermal-insulator building materials (Gavillon and Budtova, 2008; Chen et al., 2014; Nguyen et al., 2014).

Promising results on high-performance nanocellulose-based thermal insulators with fire retardant properties were recently disclosed (Wicklein et al., 2015).

High-performance thermal insulators are materials with a thermal conductivity lower than 0.020 W/m K, whereas current (petroleum-based) insulator materials like expanded polystyrene (EPS) and extruded polystyrene (XPS) have values around 0.03−0.06 W/m K. This is a very important application because the use of thermal insulation materials constitutes the most effective way of reducing heat losses in buildings, thus increasing their energy efficiency. It is worth remembering that the building sector is the largest energy user, responsible for about 40% of the European Union (EU)'s total final energy consumption (Lechtenbohmer and Schuring, 2011). According to the *Energy Road Map 2050* (European Commission, 2011), higher energy efficiency in new and existing buildings is key for the transformation of the EU's energy system. The European Energy Performance of Buildings Directive (EPBD) 2002/91/EC has been recast in the form of Directive 2010/31/EU by the European Parliament on May 19, 2010. One of the new aspects of the EPBD is the introduction of the concept of nearly zero-energy building (Pacheco-Torgal et al., 2013a). Building energy efficiency merits special funding under the HORIZON 2020 EU framework program (Pacheco-Torgal, 2014). In addition, the European market for building energy products and services will reach 80 billion euro by 2023 (Navigant Research, 2014).

Besides, because aerogels are nonflammable, they do not release toxic fumes upon burning as do current insulation materials like EPS or XPS (Pacheco-Torgal et al., 2012), which constitutes an extra advantage.

Some books have already been published concerning biopolymers and biotech admixtures. However, some have absolutely nothing on construction materials, whereas others have just one or two chapters on biobased admixtures for cement and plasters. To the best of my knowledge, none has ever been published that provides a wide view on the subject as does this one. Assembled by a team of leading international expert contributors, this book constitutes an innovative approach on biopolymers and biotech admixtures for eco-efficient construction materials.

1.3 Outline of the book

This book provides an updated state-of-the-art review on the eco-efficiency of biopolymers and biotech admixtures for construction materials. It includes basic concepts, production aspects, environmental impact assessment, the use of biopolymers and biotech admixtures for cement, mortar, and concrete, and covers other construction applications like biobased paintings and coatings, bioadhesives, biofilters, and biobarriers.

The first part of the book encompasses the production of biopolymers for eco-efficient construction materials (Chapters 2−4).

In Chapter 2, basic concepts on biopolymers and biotech admixtures for eco-efficient construction materials are introduced. The different types of biopolymers are reviewed. The case of polysaccharides and their applications in civil engineering are described. Microbial-based bioplastics are covered. Biocements and biogrouts are also covered.

Chapter 3 addresses production aspects of biopolymers and biotech admixtures for eco-efficient construction materials. The following approaches are reviewed: (1) solid or liquid organic wastes, such as food processing, municipal, or mining wastes, used as base materials; (2) aseptic cultivation of microorganisms without sterilization of medium and equipment; and (3) reducing or eliminating the stage of product concentration and purification.

Chapter 4 discusses the life-cycle analysis of biopolymers. The chapter first introduces the concept of biopolymers and the main advantages of shifting from traditional petroleum-derived polymers to biomass-derived polymers. Case studies are reported on the life-cycle assessment of biopolymers used in several sectors with a major focus on the building sector.

Biopolymers and biotech admixtures in cement and mortars are the subject of Part II (Chapters 5−9).

Chapter 5 is concerned with biotech admixtures for enhancing Portland cement hydration. The influence of different polymers including cellulose ethers, hydroxypropylmethyl cellulose, hydroxyethylmethyl cellulose, hydroxyethyl cellulose, chitosan, Diutan gum, gellan gum, xanthan, lignosulfonates, starch, and microcellulose are reviewed.

Chapter 6 covers the utilization of pulp black-liquor waste, a by-product from the papermaking industry as a cement admixture. Its influence on the physical and mechanical properties of cement pastes is analyzed. Infrared spectra and microstructure analysis are included. The optimum pulp black-liquor waste percentage is determined.

Chapter 7 analyzes the use of biopolymer chitosan-based high-performance superplasticizer. The preparation principles and major influence factors as well as the relationship of structure and properties are included. The application properties of the chitosan superplasticizer, such as fluidity, adsorption behavior, and impact on mechanical strength and microstructure of concrete, are studied.

Chapter 8 addresses the case of a new bioproduct produced through fermentation of a mixed culture of microorganisms as a plasticizer in concrete. The bio-admixture has a broad impact on cement and concrete properties probably caused by the various compounds present, and thus the various mechanisms of influence act in a synergetic way. Applications such as plasticizers and viscosity-controlling agents in concrete are discussed. Practical examples of self-compacting and normal concrete are also discussed.

Chapter 9 addresses the performance of fly ash-based geopolymer with kappa-carrageenan biopolymer (KC), a seaweed extract. Mechanical tests are conducted to study the improvement of strength and prepeak toughness, and scanning electron microscopy and Fourier transform infrared are employed to study the microstructural and chemical evolution when different amounts of KC are incorporated in the fly ash-based geopolymer paste specimens.

Part III (Chapters 10–13) deals with biopolymers and biotech admixtures in concrete.

Chapter 10 reviews biopolymers with superplasticizer properties for both fresh and hardened states of concrete. It includes aspects on concrete microstructure and concrete modeling.

Chapter 11 discusses biopolymers with viscosity-enhancing properties for concrete. The chemical structure, modes of action, rheological properties, and impact on cement hydration of commonly used viscosity-enhancing admixtures derived from biological sources are analyzed.

Chapter 12 looks at biotech solutions for concrete repair with enhanced durability. Two different specific systems for biotechnological repair of concrete structures are discussed. The first one covers liquid biobased repair systems for durable repair of cracked and porous concrete surfaces, and the second one addresses biobased mortar systems for repair of larger defects of concrete structures.

Finally, Part IV concerns other biopolymer applications (Chapters 13–18).

Chapter 13 is concerned with biofoam composites. Suggestions for damage prevention including utilization of additives and reinforcements in obtaining multifunctionalities are reported. Common design methodologies used in construction materials are presented.

Chapter 14 addresses the use of biopolymers for wood preservation. It reviews wood-degradative factors, their mechanism of action, and the method for diminishing them.

Chapter 15 is concerned with biopolymers for paintings and coatings. It covers the case of biobased polymers like polyester, poly(ester amide), epoxy, and polyurethane. It presents a typical preparative method for industrial painting based on biopolyester.

Chapter 16 reviews biobased adhesives covering the different existing families of adhesives.

Chapter 17 reviews biopolymers as biofilters and biobarriers. Mechanisms of biofiltration are reviewed. The performance of biopolymer-based barriers is included. The use of biobarriers for the removal of inorganic contaminants from wastewater is also covered.

Chapter 18 closes Part IV with a case study on biopolymers for superhydrophobic photocatalysis coatings, which prevent algae or moss deposits on façade or building roofs.

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