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SURFACE MODIFICATION OF BIOPOLYMERS: AN OVERVIEW

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1.1 INTRODUCTION

Among various materials used in our everyday life, polymers play the most imperative role along with their use in a number of industries for versatile applications [1–3]. Polymers have been known to play a key role in the economy of the most of the countries of modern world since last century [4, 5]. Polymers have been frequently classified into natural and synthetic polymers [6, 7]. Although natural polymers were frequently used by the people of earlier civilization for a number of applications directly/indirectly, usage of synthetic polymers has dominated the modern world especially the last few decades [8–11]. Synthetic polymers have even replaced some of the commonly used metallic materials due to their enormous advantages such as light weight, chemical/water resistant, versatility, decent mechanical/thermal properties, and easy tailor ability [12–15]. Both natural and synthetic polymers can be easily distinguished depending upon their inherent properties and their structural property

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relationship [16]. However, during the last few years, sustainable development through the use of environmentally friendly materials has become the hottest topic of conversation as well as research all around the globe [17, 18]. In this direction, the usage of materials that can be procured from our nature is rising rapidly for a number of applications [19, 20]. In fact the materials obtained from the nature are becoming a potentially viable alternative to a number of traditional synthetic materials that are generally synthesized from petroleum-based resources [21–23]. The effective utilization of the materials obtained from nature offers a number of challenges for their successful usage as well as offers new opportunities from the economic and environmental point of view [24, 25]. The past few decades has seen a pronounced advancement in the development of new eco-friendly materials that are procured from bio-based biopolymers for vast applications [26–28]. Different kinds of bio-based biopolymers represent a renewable feedstock of materials for different usage [29, 30]. The renewable feedstock of biopolymers extensively depends upon the availability of bio-based resources in different regions of the world, the new developments in the use of these materials, and the agricultural production as most of the biopolymers are directly/indirectly related to the field of agriculture [31, 32]. Applications of any biopolymer material in a particular application stresses on the specific physical, chemical, thermal, mechanical, economic, and degradation properties so as to offer significant advantages over their synthetic counterpart [33, 34]. In addition to these requirements, the easy availability of these biopolymeric materials is one of the most significant parameters in their commercialization as it is directly related to the final cost of the material in the market [35, 36]. Different kinds of biopolymer-based materials found in the nature can play one of the key roles in the modern industries to make the final product green [37, 38]. The use of biopolymer-based materials ranges from house hold applications to advanced applications in the defense [39, 40]. Different kinds of biopolymers depending upon their compositions can be used in a number of applications as follows: biomedical (e.g., stent, drug-delivery vehicles), food packaging, polymer composites for structural applications, as electrolyte for energy storage in super capacitor/battery, adhesives, cosmetic industries, and most frequently in textile industries [41, 42].

1.2 STRUCTURES OF SOME COMMERCIALY IMPORTANT BIOPOLYMERS

Among the various biopolymer materials, a few materials such as natural cellulosic fibers, starch, agar, chitosan, and poly(3-hydroxyalkanoates) (PHAs), are being used in a number of applications [24, 43–49]. In the following section, we briefly describe some of the commercially important biopolymers, as their detailed introduction along with their modification/applications has been given in the upcoming chapters.

1.2.1 Natural Fibers

Among the various fibers available naturally/synthetically, natural cellulosic fibers are of much importance due to their intrinsic properties [48–50]. These fibers have been reported to be used by human beings for thousands of years ago starting from early civilization in the formation of bridges for on-foot passage as well as in naval

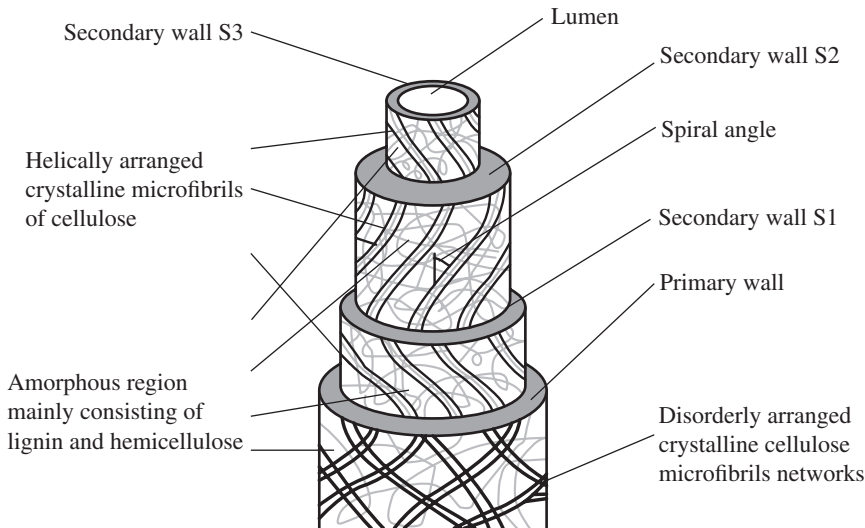


FIGURE 1.1 Structure of lignocellulosic natural fiber. Reproduced with permission from Ref. [51]. © 2013 Elsevier.

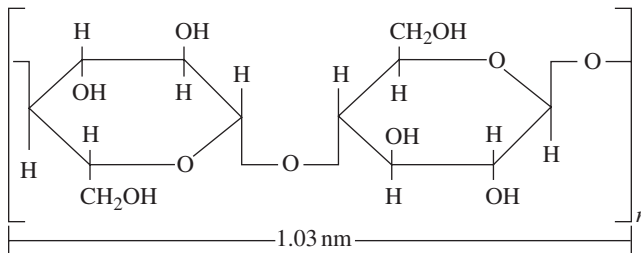


FIGURE 1.2 Structure of cellulose. Reproduced with permission from Refs. [48–50]. © Elsevier.

ships to biomedical in the present time [48–50]. Depending on their extraction as well as on the part of the plant from which they are taken, their properties vary considerably [50]. Figure 1.1 shows the schematic representation of natural fibers [51].

Natural cellulosic fibers primarily contain cellulose, hemicellulose, and lignin as their primary constituent and have been well researched as well as documented in the existing literature [48]. Figure 1.2 shows the structure of cellulose found in natural fibers. Cellulose (a nonbranched polysaccharide) is the prime constituent of all lignocellulosic natural fibers and has been found to exist in two crystalline forms, namely, cellulose I and II [48–51]. Cellulose is a linear condensation polysaccharide that comprises a D-anhydro glucopyranose units joined by β -1,4-glycosidic bonds. On the other hand, hemicelluloses are composed of a combination of 5- and 6-ring carbon ring sugars and have been found to remain associated with cellulose even after the removal of lignin [49, 50]. As opposed to the structure of cellulose, hemicelluloses exhibit a branched structure and consist of mixtures of polysaccharides with much lower molecular weight compared to cellulose [48–50].

Among different constituents of natural cellulosic fibers, lignin is one of the highly branched components. It is a complex chemical compound present in huge quantities in the cell walls of plants. It is the main binding agent for components of the plants and serves as a matrix to the embedded cellulose fibers along with hemicellulose. The structure of lignin is highly branched that consists of phenyl propane units. These units are organized in a complex three-dimensional structure linked together through numerous types of carbon-carbon and ether bonds.

1.2.2 Chitosan

Chitosan is another most significant biopolymer that is derived from chitin (produced by many living organisms) [1, 3, 52]. Chitin is the second most abundant natural polymer available on earth after cellulose and is found in a number of organisms from crustaceans such as lobsters, crabs, shrimp, and prawns along with insects to some types of fungi [31, 34, 52]. Chitin is a nitrogen-rich polysaccharide and a high-molecular-weight linear polymer composed of *N*-acetyl-D-glucosamine (*N*-acetyl-2-amino-2-deoxy-D-glucopyranose) units linked by β -D-(1 \rightarrow 4) bonds. Figure 1.3 shows the comparative chemical structure of chitin, chitosan, and cellulose [49, 52].

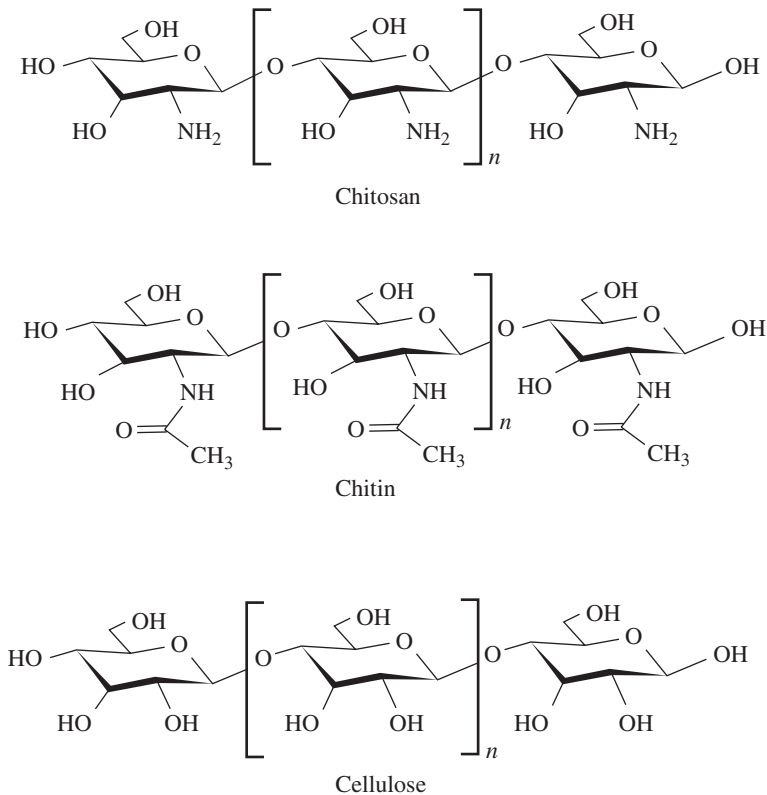


FIGURE 1.3 Structure of chitosan, chitin, and cellulose. Reproduced with permission from Ref. [52]. © 2013 Elsevier.

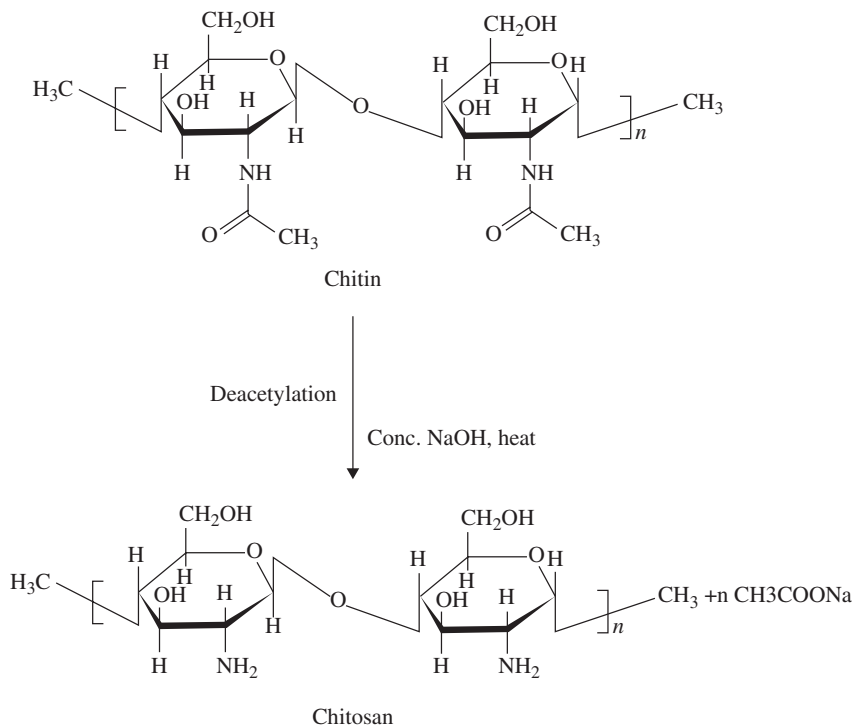


FIGURE 1.4 Deacetylation of chitin to chitosan. Reproduced with permission from Ref. [52]. © 2013 Elsevier.

Chitosan is most frequently produced from chitin by deacetylation process [31, 34, 49, 52]. Figure 1.4 shows the scheme for the extraction of chitosan from chitin.

Chitosan has been found to exhibit a basic character and is one of the highly basic polysaccharides compared to other natural polysaccharides that are acidic such as cellulose, agar, pectin, dextrin, and agarose [24, 29–53]. The degree of deacetylation and the charge neutralization of $-\text{NH}_2$ groups along with ionic strength have been found to control the intrinsic pK_a value of chitosan. Figure 1.5 shows the schematic illustration of the versatility of chitosan.

Along with physical modification, chitosan is most commonly modified by a number of chemical techniques including traditional chemical modification techniques such as photochemical, enzymatic, radiation, and plasma-induced graft copolymerization. Figure 1.6 summarizes some of the commercially used modification techniques for surface modification of chitosans.

1.2.3 Agar

Agar has been commonly recognized as a hydrophilic colloid that is most frequently extracted from certain marine algae and is accumulated in the cell walls [2]. Due to its significant biological activities such as antioxidative, anticancer, anticoagulant, antiviral,

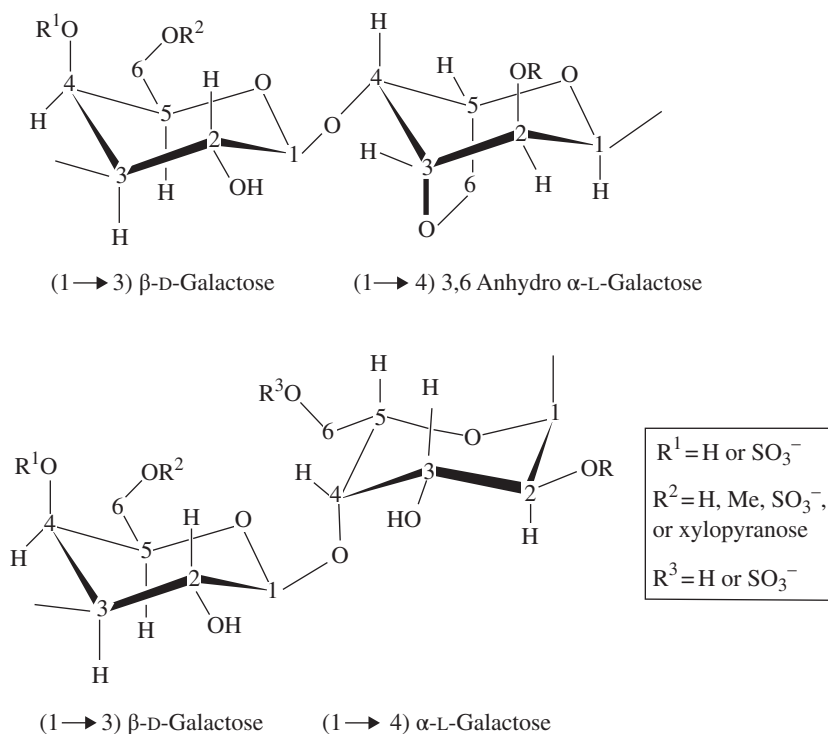


FIGURE 1.7 Structural motifs of agar polysaccharides showing carbon numbering (C_1 – C_6). Reproduced with permission from Ref. [53]. © 2013 Elsevier.

and immunomodulating activities, it is extensively used as a gelling/stabilizing agent in a number of industries starting from food to pharmaceutical. Figure 1.7 shows the structural motifs of agar polysaccharides showing carbon numbering (C_1 – C_6).

Agar is represented by the structural formula $(C_{12}H_{18}O_9)_n$ and is built on a disaccharide-repeating unit of 3-linked β -D-galactose (G) and 4-linked 3,6-anhydro- α -L-galactose (AG) residues. Depending on the source of the agar, there is possible occurrence of different substituents such as sulfate, methoxyl, and/or pyruvate at various positions in the polysaccharide chain. Agar is extracted from macroalgae by a number of conventional techniques, and recently great efforts are being made to extract it rapidly using a microwave-assisted methodology [32, 43, 44, 53]. Depending on the targeted applications, agar is surface modified accordingly [43, 44]. For example, agar is extracted after the alkali treatment to be used as catalysts supports and templates for the preparation of metal oxides using the same methodology and has been characterized by a number of techniques such as X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), nuclear magnetic resonance spectroscopy (CP-MAS ^{13}C NMR and diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS)) [53]. Figure 1.8 shows the SEM images of the alkali treated and untreated agar. These images clearly illustrate the structural changes taking place as a result of alkali treatment.

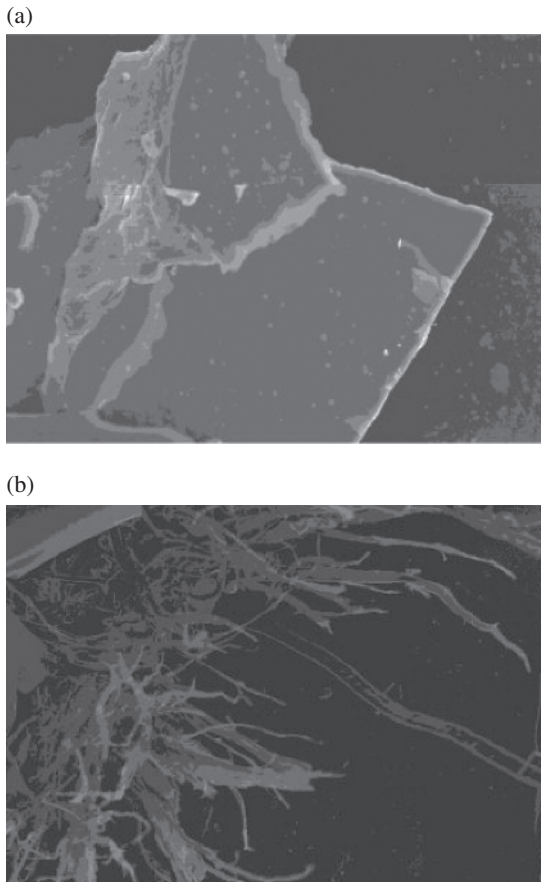


FIGURE 1.8 SEM micrographs of nontreated (a) and alkali-treated (b) mesoporous agar materials. Reproduced with permission from Ref. [53]. © 2013 Elsevier.

The results obtained from the SEM images were further confirmed by DRIFTS and NMR. Figure 1.9 shows the presence of different functional groups on both the treated and untreated agar.

Figure 1.10 also confirms the agarose structure of the extracted material after the alkali treatment. The structures of both the raw and alkali-treated agar show significant changes in their peaks.

1.4 POLY(3-HYDROXYALKANOATES)

PHAs are one of the unique families of polymers that are gaining significant attention during the past few years [49, 54, 55]. PHAs are linear, biodegradable polyesters that are synthesized by a wide variety of bacteria through the fermentation of sugars, lipids, among others [49, 54, 55]. Due to their biodegradable, renewable, and biocompatible

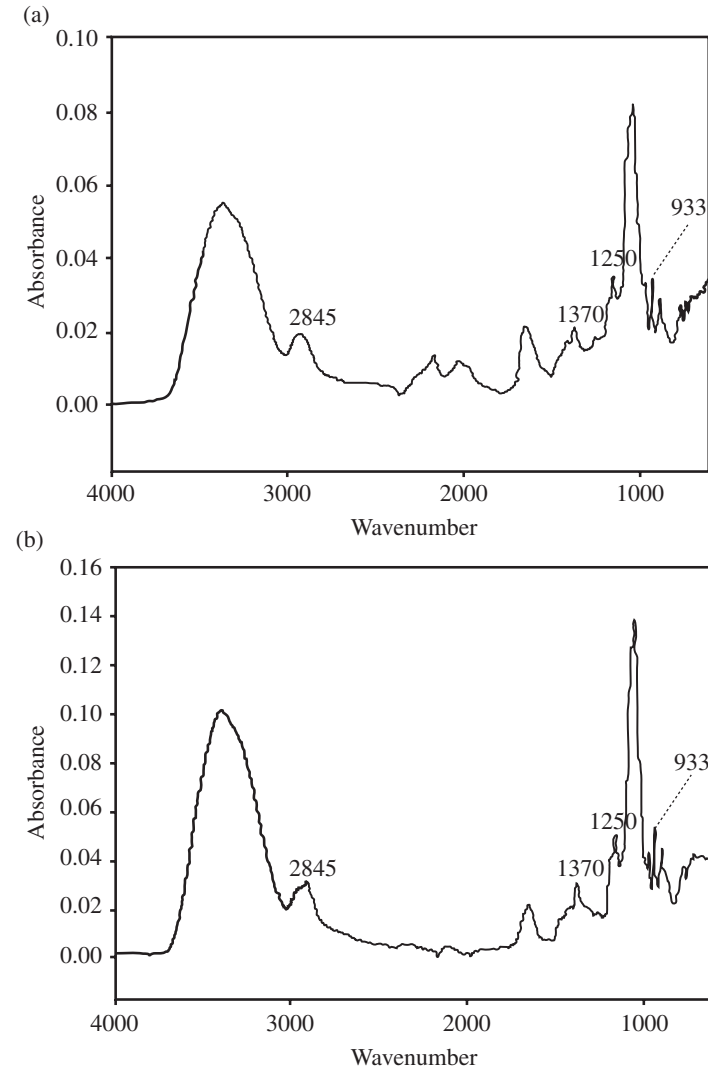


FIGURE 1.9 Attenuated total reflectance infrared (FTIR-ATR) spectra of nontreated (a) and alkali-treated (b) agar extracted from *Gracilaria gracilis*. Reproduced with permission from Ref. [53]. © 2013 Elsevier.

nature, PHAs are emerging as one of the most promising materials for biomedical applications [49, 54, 55]. The structure and different applications of PHAs have been discussed in some of the recent reviews. Similar to other previously discussed polymers, PHAs also suffer from few drawbacks. Figure 1.11 shows the structural representation for different kinds of PHAs [54]. Some of the disadvantages of the PHAs include the brittleness and poor mechanical properties that restrict its successful applications [49, 54, 55]. Therefore to get the desired properties, it is most of the time modified with suitable materials/techniques.

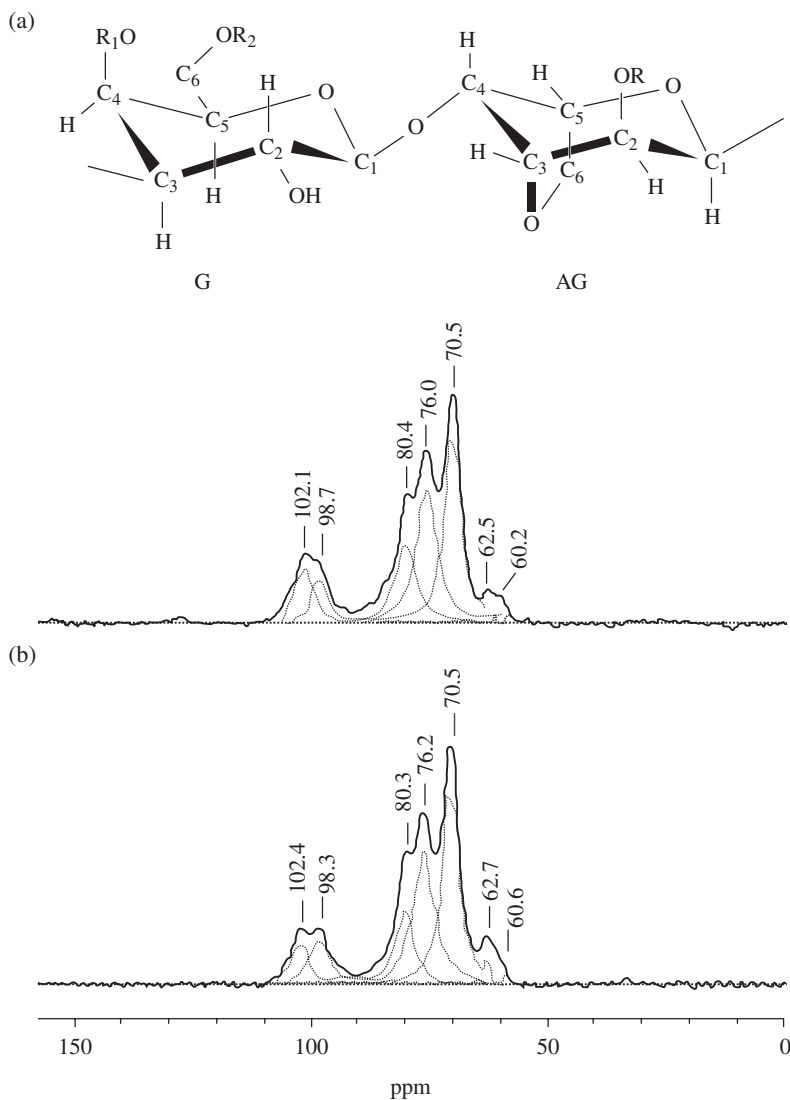
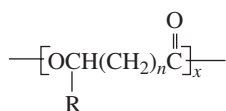


FIGURE 1.10 CP-MAS ^{13}C NMR spectra of native agar (a) extracted at 100°C and alkali-treated agar (b) extracted at 140°C from *Gracilaria*. Top structure depicts the various carbons (C_1 – C_6 from G and AG) associated with the different NMR peaks. Reproduced with permission from Ref. [53]. © 2013 Elsevier.

The effect of microstructure and composition of PHAs, along with the influence of compositional distribution and blending on mechanical properties, has been reported in detail by a number of researchers [49, 54, 55]. Figure 1.12 schematically shows the biochemistry and crystallinity of the PHAs, as these control most of the properties of the resulting material [55].



(PHA)

$x = 100 - 30000$

PHA

$n = 1$	R = H	Poly(3-hydroxypropionate)	(P3HP)
	R = methyl	Poly(3-hydroxybutyrate)	(P3HB)
	R = ethyl	Poly(3-hydroxyvalerate)	(P3HV)
	R = propyl	Poly(3-hydroxyhexanoate)	(P3HHx)
	R = pentyl	Poly(3-hydroxyoctanoate)	(P3HO)
	R = nonyl	Poly(3-hydroxydodecanoate)	(P3HDD)
$n = 2$	R = H	Poly(4-hydroxybutyrate)	(P4HB)
$n = 3$	R = H	Poly(5-hydroxyvalerate)	(P5HV)

FIGURE 1.11 Chemical structure of PHAs. Reproduced with permission from Ref. [54]. © 2013 Elsevier.

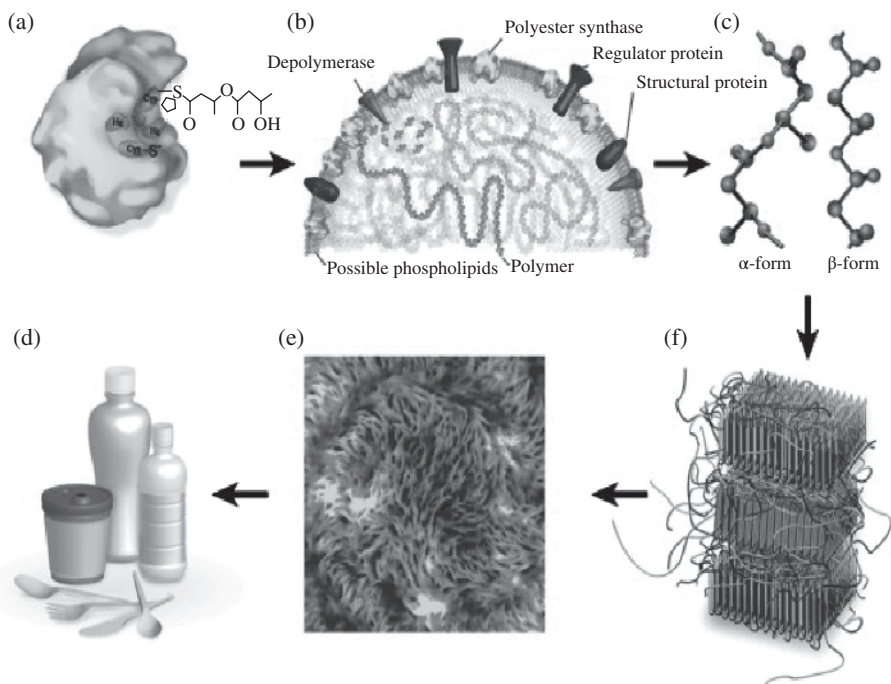


FIGURE 1.12 Overview of PHA synthesis: schematic depiction of (a) chain polymerization catalyzed by enzymes, (b) a PHA granule with granule-associated proteins, (c) different forms of the PHB polymer chain, and (d) semicrystalline polymer structure. (e) AFM image of PHBV film; (f) final plastic products. Reproduced with permission from Ref. [55]. © 2013 Elsevier. (See insert for color representation of the figure.)

A number of mechanisms have been proposed for the synthesis of PHAs from different precursors (Figure 1.13; [55]).

As it is evident from the existing literature that PHAs alone cannot satisfy the strict requirements for certain applications, most of the time it is blended with other materials. It has been reported that such blends exhibit a number of properties ranging from complete cocrystallization through partial segregation. Figure 1.14 shows the variation in phase structure of some of the blends.

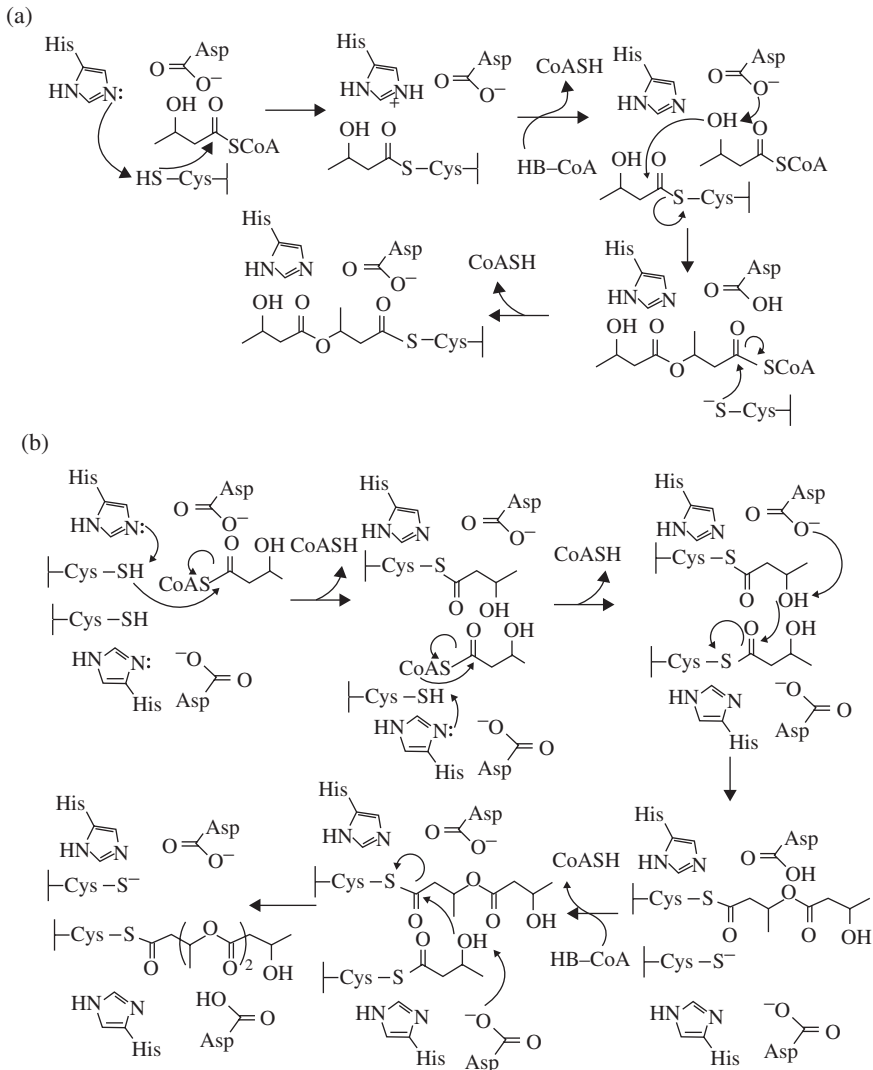


FIGURE 1.13 Proposed polymerization mechanism for the synthesis of PHA. Reproduced with permission from Ref. [55]. © 2013 Elsevier.

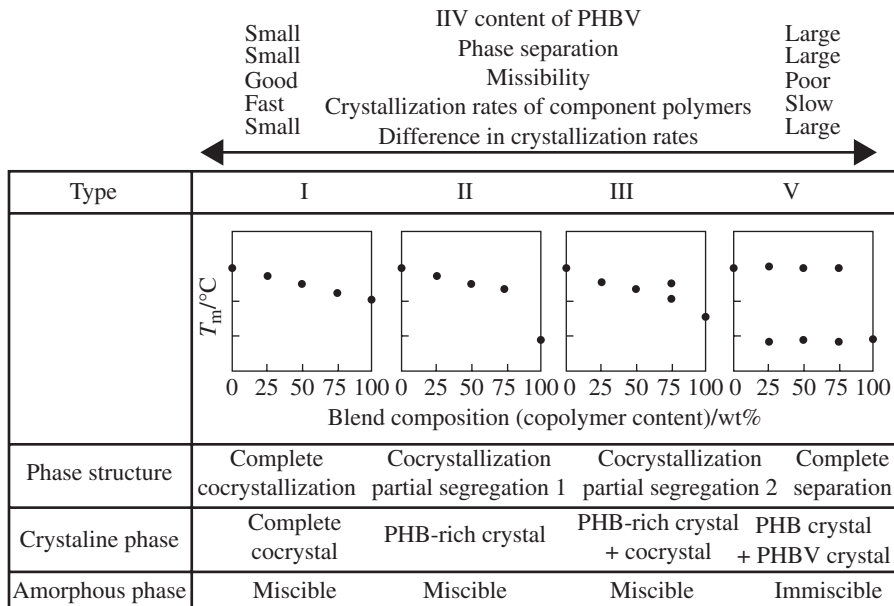


FIGURE 1.14 Variation of phase structures in PHB/PHB-HV blends. Reproduced with permission from Ref. [55]. © 2013 Elsevier.

Although these polymers have some disadvantages, they are promising candidates as novel material for petroleum-based materials with the advantages of being biodegradable.

1.5 STARCH

Among various polysaccharides, starch is an industrially important biopolymer frequently used in food industry as well as in other industries. Depending on the targeted applications, starch has been used as a colloid stabilizer, thickener, and bulking/gelling agent [56]. Due to its enormous advantages, nearly 60 million tons of production has been reported all over the world [56]. Figure 1.15 shows the common structure sketches of starch granules. Starch has been found to be composed of different kinds of glucoses (primarily amylose (AM) and amylopectin (AP)) and occurs in the form of granules.

Starch is classified into normal, wx, and high AM depending upon the amount/ratio of amylose/amylopectin. Although starch is available in large quantity and offers numerous advantages, it has also some shortcomings similar to other biopolymers and has limited applications in its native form. A number of surface modification techniques are being used to alter the surface properties of starch and has been described in detail in the extensive reviews by Pei-Ling as well as in Chapter 7 in this book. Among these, one of the most promising is high hydrostatic pressure (HHP),

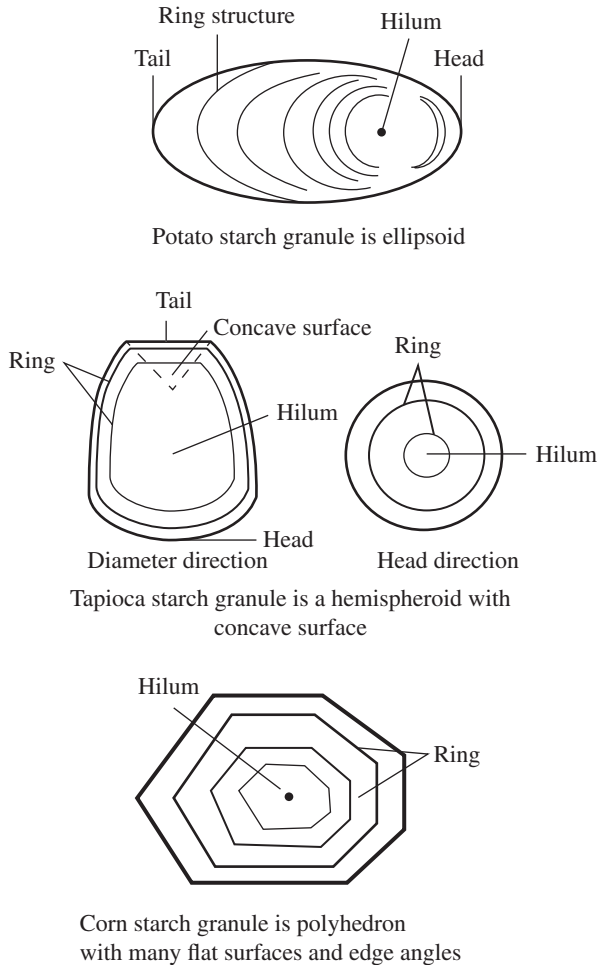


FIGURE 1.15 Structure sketches of starch granules. Reprinted with permission from Ref. [56]. © 2010 Wiley-VCH.

which is a well-established nonthermal processing technology. Figure 1.16 shows the A- and B-type polymorphic structure of amylose as a result of HHP processing [56].

As a result of HHP processing, the structure of starch has also been found to be affected. Figure 1.17 shows the morphological images of the starch processed under high pressure. It is obvious from the micrographs that the outer surface of the starch granule is quite resistant to the HHP, and at the same time, the inner part is filled with structure having the shape of gel.

From the above discussion, it is quite clear that each biopolymer has certain limitation that restricts its use for a number of applications. The main obstacles include the lack of desired physicochemical/mechanical and biological properties. The only way to effectively utilize them is to alter their properties by surface modification

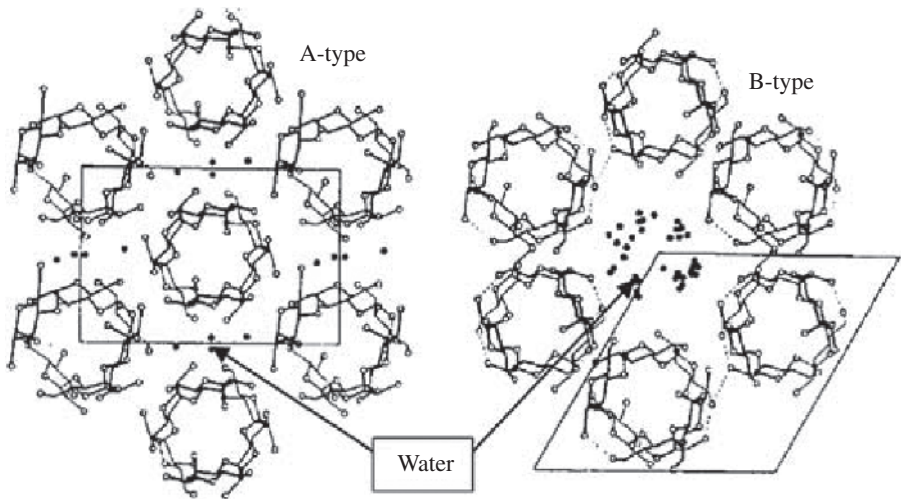


FIGURE 1.16 A- and B-type polymorphs of amylose. Reprinted with permission from Ref. [56]. © 2010 Wiley-VCH.

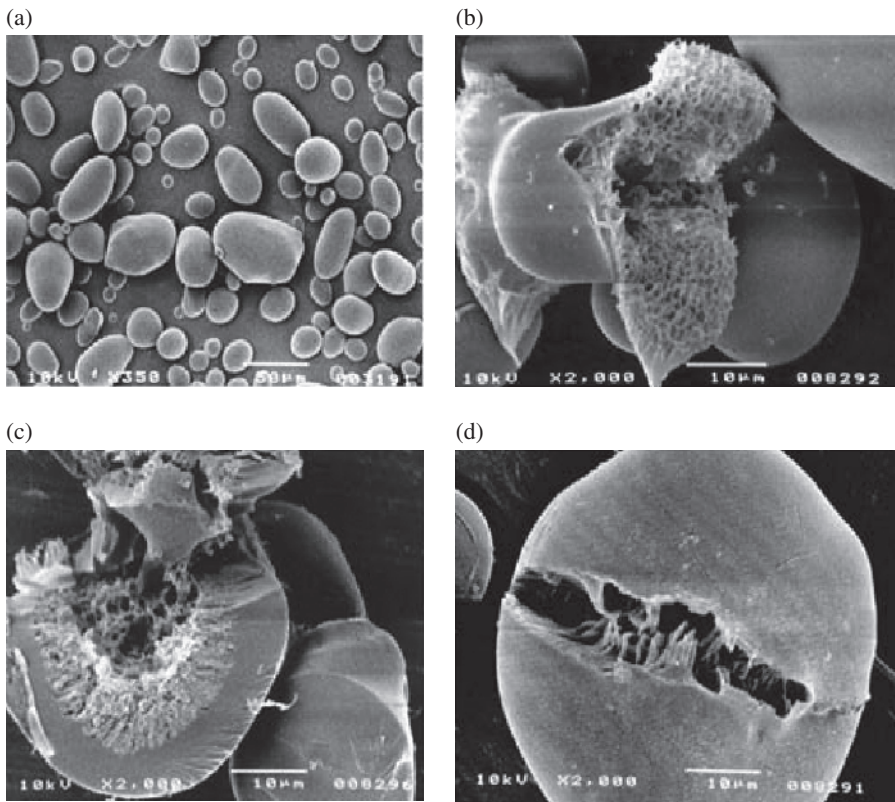


FIGURE 1.17 SEM microstructure of potato starch with details of outer and inner part of starch structure: native (a); treated with high pressure at 600 MPa 3 min (b–d). Reprinted with permission from Ref. [56]. © 2010 Wiley-VCH.

techniques. By utilizing different surface modifications, most of the times, the specific application properties of different biopolymers can be easily obtained. For a particular application, the analysis of the structure–property relationship of a biopolymer under investigation is of utmost importance. At present, a number of biopolymers are being tested for their commercial applications and some of the thrust areas include biomedical, packaging, food production, and automotive. Some biopolymers can directly replace synthetically derived materials in traditional applications, whereas others possess unique properties that could open up a good range of new commercial opportunities. In this book, best efforts have been made to incorporate sufficient information on different surface modification techniques to alter their specific properties for targeted applications.

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