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Chapter 3

Biopolymers – Application in Nanoscience and Nanotechnology

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Abstract

In order to reduce the use of non-renewable resources and to minimize the environmental pollution caused by synthetic materials, the quest for utilizing biomaterials is on a rise. Biopolymers in nature are produced by a range of microorganisms and plants. Biopolymers produced by microorganisms require specific nutrients and controlled environmental conditions. This chapter discusses the recent developments and trends of biopolymers especially in the field of nanotechnology. A basic introduction regarding biopolymers is included at the beginning of the chapter. A detailed discussion on various characterization techniques used for characterizing biopolymers and various frequently used biopolymers is also included. Applications of biopolymers in various fields, especially in the field related to nanoscience and nanotechnology, is elaborated at the end of the chapter. Biopolymers together with nanotechnology have already found many applications in various fields including water treatment, biomedical application, energy sector, and food industry. This chapter is intended to give an overview on the importance of biopolymers in nanotechnology-based applications.

Keywords: Application, Characterization, Biodegradable, Biopolymers, Nanotechnology

1. Introduction

Biopolymers are polymeric biomolecules which contain monomeric units that are covalently bonded to form larger molecules. The prefix 'bio' means they are biodegradable materials produced by living organisms. A wide variety of materials usually derived from biological sources such as microorganisms, plants, or trees can be described using the term "biopolymer". Materials produced by synthetic chemistry from biological sources such as vegetable oils, sugars, fats, resins, proteins, amino acids, and so on can also be described as biopolymer [1].

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As compared to synthetic polymers which have a simpler and more random structure, biopolymers are complex molecular assemblies that adopt precise and defined 3D shapes and structures. This is one important property which makes biopolymers active molecules *in vivo*. Their defined shape and structure are indeed keys to their function. For example, hemoglobin would not be able to carry oxygen in the blood if it was not folded in a quaternary structure.

The main property that distinguishes biopolymers from fossil-fuel-derived polymers is their sustainability, especially when combined with biodegradability. Biodegradable biopolymers from renewable resources have been synthesized to provide alternatives to fossil-fuel-based polymers. They are often synthesized from starch, sugar, natural fibers, or other organic biodegradable components in varying compositions. The biopolymers are degraded by exposure to bacteria in soil, compost, or marine sediment. Furthermore, subjecting biodegradable biopolymers to waste disposal by utilizing their characteristic of being degradable by the bacteria in the ground significantly reduces emission of CO_2 compared with conventional incineration. Therefore, attention is drawn to the use of biodegradable biopolymers from the viewpoint of global warming prevention. In recent years, with the critical situation of the global environment worsening due to global warming, the construction of systems with sustainable use of materials has been accelerated from the viewpoint of effectively using limited carbon resources and conserving limited energy resources. Furthermore, the cost of petroleum feedstocks has risen dramatically and there is a rising consumer interest in using "green" (or renewable resources) as the basis for consumer products.

One of the fastest-growing materials sectors in the past several years has been the production of polymers from renewable resources. Their development is fueled by the potential these polymers hold to replace fossil-fuel-based polymers. The main reasons for this drive can be summarized as follows: (1) inadequate fossil-fuel resources; (2) pricing instability of fossil fuel; (3) contribution of fossil fuel as a feedstock to climate change; (4) its occasional role as a political weapon; and (5) its association with the waste disposal problem created by the fossil-fuel-derived polymers.

The main objectives of this chapter are to give a basic introduction of biopolymers, its classification and different sources, and method of preparation. This chapter also describes various physical and morphological characterization techniques used for biopolymers. Some widely used biopolymers are discussed in detail followed by applications of biopolymers in various fields especially in the field of nanotechnology.

2. Different classes of biopolymers

Biopolymers are classified into different ways based on different scales. Based on their degradability, biopolymers can be divided into two broad groups, namely biodegradable and non-biodegradable, and alternatively, into bio-based and non-bio-based biopolymers (Fig. 1). On the basis of their polymer backbone, biopolymers can be classified roughly into the

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following groups: polyesters, polysaccharides, polycarbonates, polyamides, and vinyl polymers. These groups are again classified into several subgroups based on their origin.

Biopolymers can be classified, depending on the nature of the repeating unit they are made of, into three groups: (i) polysaccharides are made of sugars (e.g. cellulose found in plants), (ii) proteins are made of amino acids (e.g. myoglobin found in muscle tissues), and (iii) nucleic acids are made of nucleotides (DNA, genetic material of a given organism). Based on application, biopolymers can be classified as bioplastics, biosurfactant, biodetergent, bioadhesive, biofloculant, and so on.

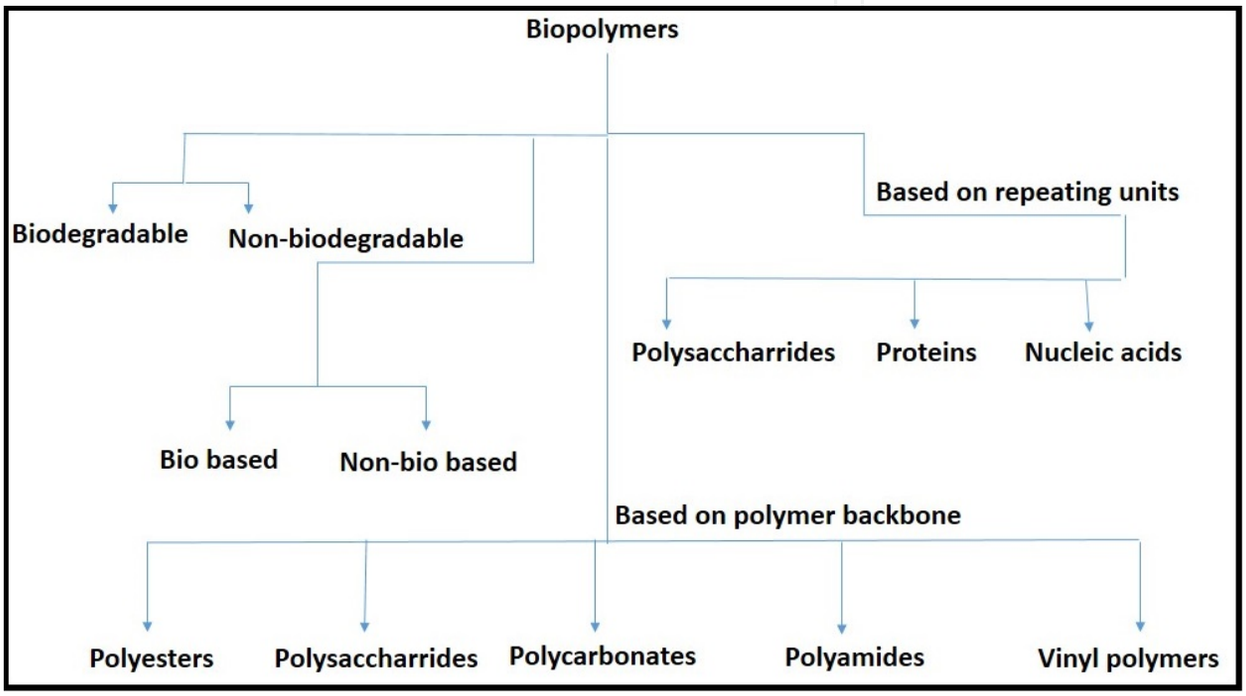


Figure 1. Different class of biopolymers

3. Sources and preparation of biopolymers

Polymeric biomaterials are synthetically derived or modified polymers designed for various applications. Engineering the production of novel biopolymers in plants provides a truly biorenewable avenue for their synthesis. Like all polymer industries, these polymers are also produced in bulk and then shaped for a specific end use. Microorganisms also play an important role in producing a huge variety of biopolymers, such as polysaccharides, polyesters, and polyamides which range from viscous solutions to plastics (Table 1). Their physical properties are dependent on the composition and molecular weight of the polymer [2]. The properties of various biopolymers synthesized by the aid of microorganisms can be tailored by the genetic manipulation of microorganisms, thereby making it suitable for high-value medical application such as tissue engineering and drug delivery.

Biopolymers which are produced with the help of microorganisms require specific nutrients and controlled environmental conditions. They are produced either directly via fermentation or by chemical polymerization of monomers, which are in turn produced through fermentation. Most biopolymers are biocompatible with no adverse effects on biological systems. The mechanism of synthesis of biopolymers from bacterial origin is believed to be either as a result of their defense mechanism or as storage material [3]. They can be degraded by natural processes, microorganisms, and enzymes so that it can be finally reabsorbed in the environment. Biopolymers or organic plastics are a form of plastics derived from renewable biomass sources such as vegetable oil, corn starch, pea starch, and so on (Fig.2). By shifting the focus more into the biopolymers, the conservation of fossil resources and reduction in CO_2 emissions can be achieved thereby promoting sustainable development [4]. Among the microorganisms, algae serve as an excellent feedstock for plastic production because of their high yield and the ability to grow in a range of environments. The use of algae opens up the possibility of utilizing carbon and neutralizing greenhouse gas emissions from factories or power plants. Algae-based plastics have been a recent trend in the era of bioplastics compared to traditional methods of utilizing feedstocks of corn and potatoes as plastics. While algae-based plastics are in their infancy, once they are into commercialization they are likely to find applications in a wide range of industries. Currently, microbial plastics are considered as an important source of polymeric material that have a great potential for commercialization. They can modify the flow characteristics of fluids, stabilize suspensions, flocculate particles, encapsulate materials, and produce emulsions [5].

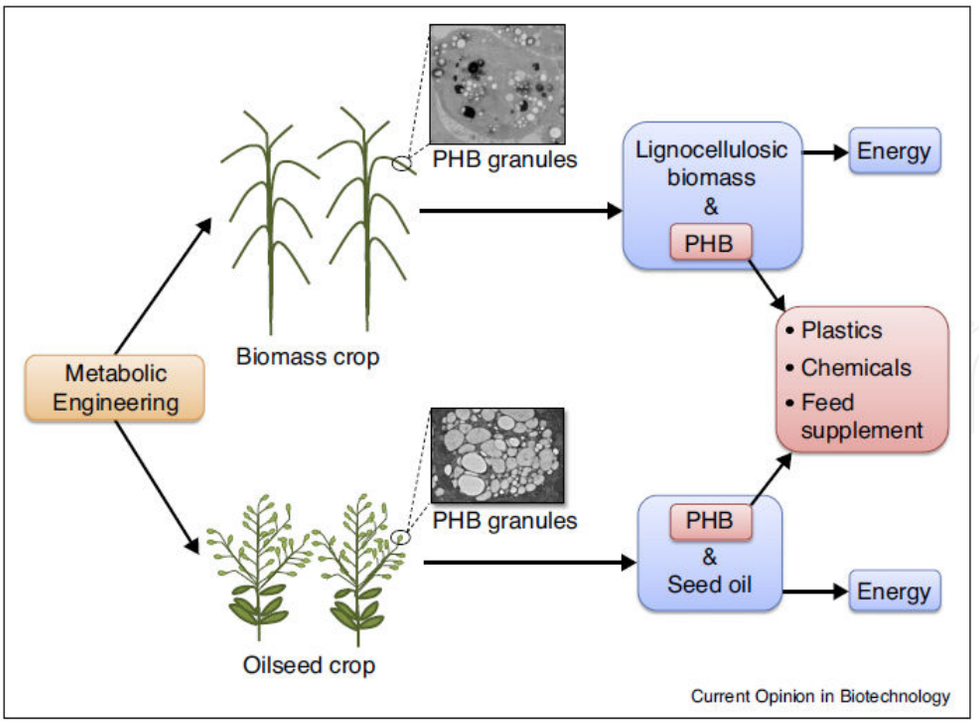


Figure 2. Schematic representation of the production of polyhydroxybutyrate (PHB) in both biomass and oilseed crops [6].

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Polymer	Method/ Source	Example of bacteria used for synthesis
Hybrid plastics	Adding denatured algae biomass to petroleum-based plastics like polyurethane and polyethylene as fillers	Filamentous green algae, Cladophorales
Cellulose-based plastics	Biopolymer of glucose	30 % of the biomass produced after extraction of algal oil is known to contain cellulose
Poly-lactic acid (PLA)	Polymerization of lactic acid lactic acid	Bacterial fermentation of algal biomass
Bio-polyethylene	Ethylene produced from ethanol, by a chemical reaction called cracking. Ethanol derived from natural gas or petroleum	Bacterial fermentation of algal biomass
Poly esters	Biomass	Bacteria like Akaligenes eurrophus, E. coli, etc.

Table 1. Some biopolymers, their sources, and preparation

4. Structure of biopolymers

The structure of biopolymers has been a subject of investigation ever since they were discovered. So far, the most accurate methods for structure determination have been X-ray diffraction techniques. These techniques are, however, restricted to crystallizable molecules, and it has not been established if the molecular structure in a crystal is identical to that in solution. Many methods have been developed or adopted to probe biopolymer properties in solution [7]. The composition and sequence of the monomer units of biopolymers determine their so-called primary structure. Conformation, that is, one or another spatial form of the biopolymer molecules, is determined by their primary structure. Depending on the chemical structure and external conditions, the molecules may be in one or more preferred conformations.

Specific form and structure provide functionality to biological elements microscopically and macroscopically. The combination of cell and cell tissues results in the outward appearance of biological organisms. The causes for the shape of these building blocks of life are manifold. Biopolymers are important for the organization and functionality of cells. Prominent examples are the DNA as the carrier of the genetic code and the cytoskeletal filaments building the scaffold of the cell. The unique property of DNA depends on its equilibrium polymer conformations based on its internal characteristics like flexibility, topology and filament diameter and external constraints such as confinement. Any variation in these properties will alter the genetic characteristics of that living system which shows the significance of structure of biopolymers in living systems.

5. Different characterization techniques

Most of the techniques used for the characterization of polymers can be utilized for the characterization of biopolymers. Characterization of biopolymers has two purposes:

1. Development of parameters for processing;
2. Determination of end-use performance characteristics.

Through characterization, the most important properties of interest are molecular mass, polydispersity, size, degree of association, conformation, interaction, and so on. Some of the characterization techniques which are used for the analysis of biopolymers are listed in the following.

5.1. Fourier Transform Infrared Spectroscopy (FTIR)

FTIR can be used to study the various functional groups and interactions present in biopolymers. Interactions like hydrogen bonding, amide linkage, etc., can be easily detected by analyzing the spectra [8]. Among various techniques, attenuated total reflection (ATR) sampling device-based Fourier transform infrared (ATR-FTIR) spectroscopy is considered as a potential one. It requires minimal sample preparation, permits routine analysis at both laboratory and on-field environments, and is easy to operate. Visible and near-infrared (VIS–NIR) spectroscopy is a well-established alternative for measuring constituents of biological materials. The NIR spectrum is influenced by the different vibrational modes of the molecules, which are caused by their interaction with electromagnetic radiation absorbed at specific wavelengths. This technique can be used for the identification of several complex components such as proteins and carbohydrates in biological materials. Chemometrics allows the extraction of relevant information contained in the spectra for the development of calibration models that allow the classification and prediction of organic sample's composition. The thermotropic phase behavior of a suite of newly developed self-forming synthetic biopolymers has been investigated by variable-temperature Fourier transform infrared (FT–IR) absorption spectroscopy [9].

Various studies have extensively used the FTIR technique to explore the physical and mechanical properties of biopolymers. Two-dimensional (2D) correlation analysis was applied to characterize the ATR spectral intensity fluctuations of immature and mature cotton fibers [10]. FTIR analysis can also be used to verify the interactions between various biopolymers in its composites [11].

Figure 3 shows FTIR spectra of chitosan-starch films, keratin, and the composites synthesized with 20 %. Figure 3A (a) shows the band at 3400 cm^{-1} which is assigned to the hydrogen-bonded hydroxyl groups due to the presence of starch in chitosan-starch film. Fig. 3A (b) shows that the main vibrations attributed to the keratin structure were identified in the region around 3300 cm^{-1} and correspond to a range of amide bands. Furthermore, the peak at 2945 cm^{-1} is assigned to the asymmetric vibration of the CH of the methyl group. In Figure 3B (a) the main peaks related to chitosan-starch films are seen at 700–770 cm^{-1} which correspond to the

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saccharide structure, and the three-characteristic peaks between 995 and 1150 cm^{-1} are attributed to C–O bond stretching.

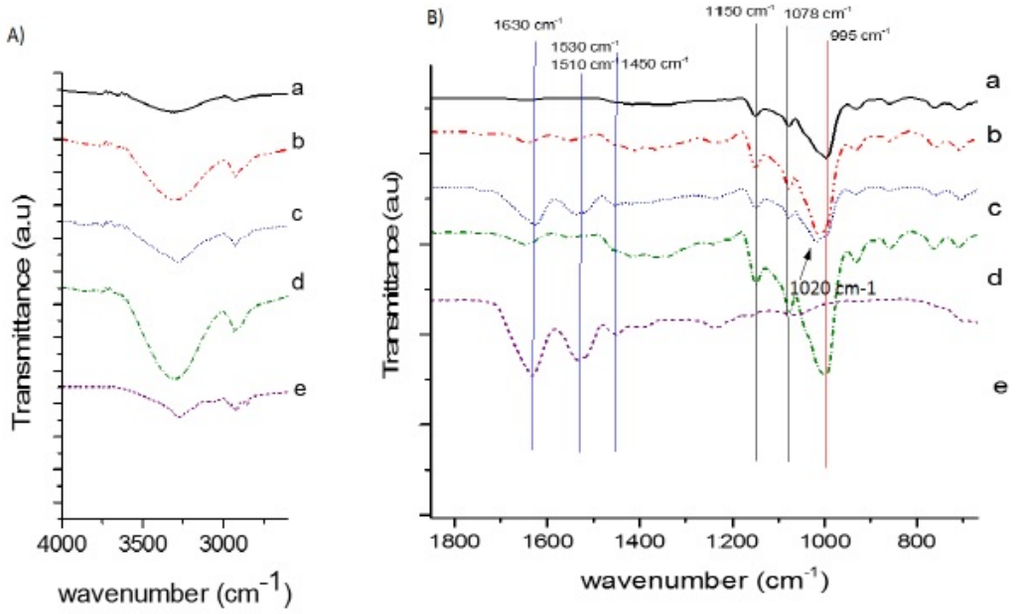


Figure 3. IR spectra of the composite films: A) from 4000–2500 cm^{-1}; B) from 1800–700 cm^{-1}. (a) chitosan-starch film; (b) chitosan-starch-short biofiber 20%; (c) chitosan-starch-long biofiber 20 %; (d) chitosan-starch-ground quill 20 %; (e) keratin [11].

In Fig 3A(e) the band at 1630 cm^{-1} is assigned to the C=O group and the peaks at 1530 cm^{-1} and 1510 cm^{-1} are attributed to the in plane bending of NH group, while the signal at 1,430 cm^{-1} is related to bending of the CH_3 group for keratin. FTIR results correlate to the thermomechanical properties and the morphological features of the composite. The spectrum indicates that a better storage modulus is obtained for composites with short and large fibers than the composite with ground quill. Also better distribution is obtained in these composites.

5.2. X-ray diffraction analysis

X-ray diffraction techniques can be successfully used to study the crystallinity of the biopolymers. Figure 4 represents the X-ray diffraction studies of native wheat starch, compressed starch foam, and compressed starch/fiber foam [12]. The native wheat starch had a semi-crystalline structure with peaks typical of A-type crystals. The gelatinization/compression processes during the composite preparation cause decrease of crystallinity resulting in diffractograms exhibiting a broad amorphous peak with no significant residual A-type crystallinity. The starch granule structure was disrupted by the processes of gelatinization and high compression which is clearly visible from the spectrum. Small peaks were found around 2Θ 12.0, 17.3, and 19.5, which is characteristic for crystallographic parameters of VH-type crystals for destructured starch prepared from solution. For the starch/fiber sample, the spectrum obtained indicates that the crystallinity of the fiber overlaps with the gelatinized starch.

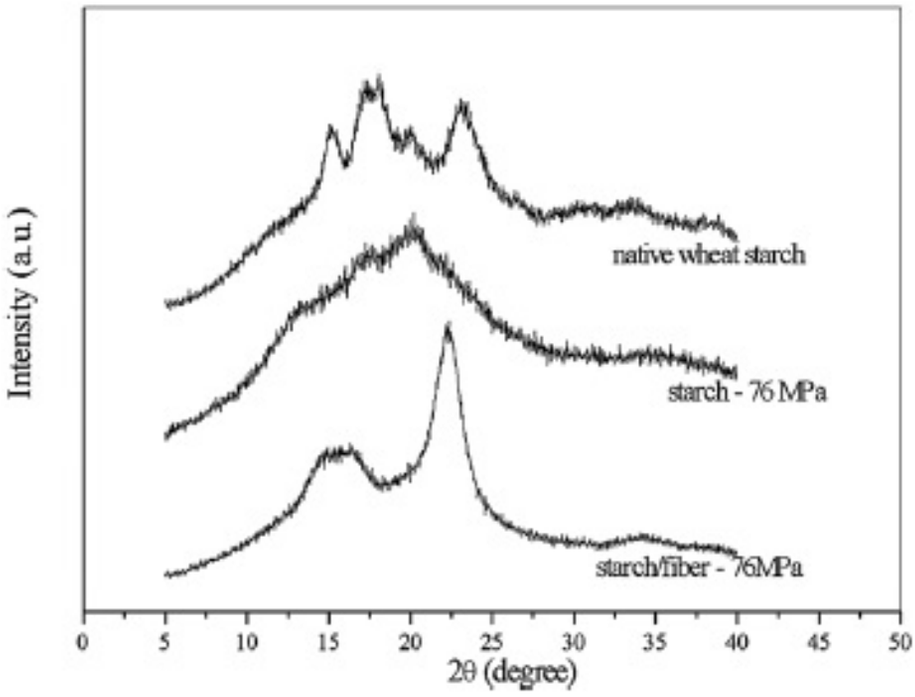


Figure 4. X-ray diffraction profile for native starch, starch (76 MPa) and starch/fiber (76 MPa) [11].

5.3. NMR spectroscopy

The molecular dynamics of water adsorbed on biopolymer surfaces and functional groups of biopolymers can easily be determined by using the NMR technique [13]. NMR spectroscopic technique relaxation times and their dependence on temperature and magnetic field have proved to be a useful source of information for molecular structure, phase change, conformational exchange, solubility, and diffusion of biopolymers. Many studies of spin–lattice relaxation time (T_1), spin–spin relaxation time (T_2), and spin–lattice relaxation time in the rotating frame (T_{1q}) of different biopolymers have been already reported [14]. The molecular origin of nuclear spin relaxation has been examined in cellulose and its derivatives [15]. In order to understand the behavior of main functional groups, the effect of temperature on nuclear-spin relaxation has been probed extensively in biopolymers in cell walls [16, 17]. The temperature dependence of relaxation times of starch chain has been studied in order to investigate structure–hydration relationships in the biopolymer [18].

5.4. Thermal analysis

Thermal analysis (TA) method has become an indispensable analytical technique for the characterization of polymers. The characterization technique provides relevant information about thermal and chemical stability, phase transition temperatures and kinetics, rheology and molecular relaxation times of the polymers. It provides information regarding the relation between the polymers chemical structure and their physical properties. The properties of

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processed polymer depend on morphology and molecular chain orientation of the polymer backbone. In conventional thermal analysis techniques, the method usually involves the monitoring of material properties as a function of temperature. Differential scanning calorimetry (DSC) is one important method used to study the thermal behavior of biopolymers.

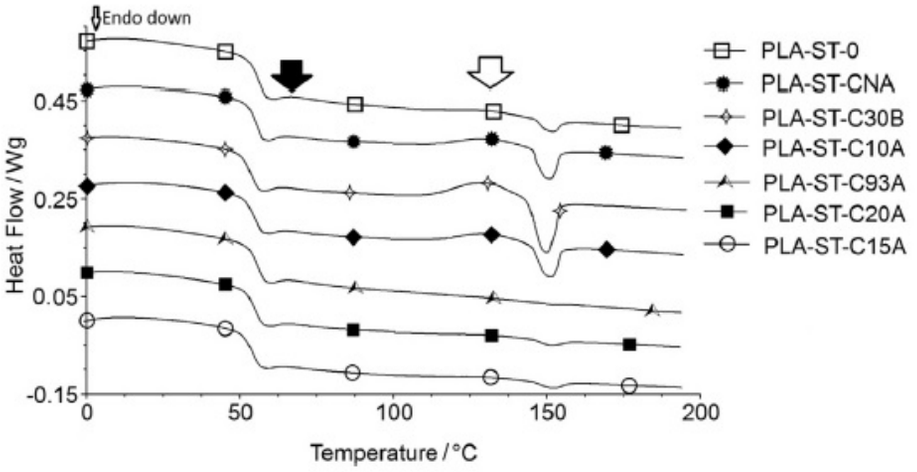


Figure 5. DSC thermograms of PLA/butylated starch blend and blend/MMT composites with MMTclays of different hydrophobicity. The samples had a clay and starch content of 4.5 wt % and 25.5 wt % of the total composite weight, respectively. The control sample PLA-ST-0 had no clay [19].

Figure 5 shows the standard/conventional DSC curves of the neat blend and blend/clay composites. All of the samples showed a glass transition with enthalpy relaxation at approximately 55 °C. There was some apparent cold crystallization for the samples that could not be clearly separated from the melting endotherm [19]. The melting endotherms appeared at approximately 150 °C, and the values could not be accurately determined because of the apparent influence of the cold crystallization exotherms. It was clear that the area under the cold crystallization and melting peaks (enthalpy of cold crystallization and melting, respectively) was higher for the control sample and the samples with less to moderate hydrophobic clays when compared with that of the composites with hydrophobic to extremely hydrophobic clays. This indicated the tendency of the more hydrophobic clays to hinder the re-arrangement of the PLA molecules into organized crystalline structures. Such a hindrance was highest in the case of the PLA-ST-C93A composite because of the high level of compatibility between two phases.

5.5. VIS–NIR spectroscopy

There is an increasing interest in the use of polysaccharides and proteins for the production of biodegradable films. VIS–NIR spectroscopy is a reliable analytical tool for objective analyses of biological sample attributes. It can be used to investigate the compositional characterization of biodegradable materials and correlation of their mechanical properties [20]. Partial least square regression can be used to investigate the correlation between spectral information and mechanical properties. Large-scale production of films requires fast and non-invasive analyt-

ical methods in order to assess film composition and mechanical properties. VIS–NIR spectroscopy is a well-established alternative as a non-destructive process analytical technology for measuring constituents of biological materials. The NIR spectrum is influenced by the different vibrational modes of the molecules, which are caused by their interaction with electromagnetic radiation absorbed at specific wavelengths. This technique has been used for the identification of several complex components such as proteins and carbohydrates in biological materials. Chemometrics allows the extraction of relevant information contained in the spectra for the development of calibration models that allow the classification and prediction of the composition of organic samples [21].

5.6. Scanning Kelvin Probe Microscopy (SKPM)

SKPM has become a very strong tool in material science [22], giving up a surface mapping of electrostatic potential [23]. Electrical properties have an important role in the rejection of charged species in membrane applications such as water softening and heavy metal removal. Increasing membrane charge may improve ion rejection for nanofiltration (NF) and reverse osmosis (RO) processes. If membrane is electrically charged, electrostatic interaction becomes significant for ion removal. Nanocomposites which presented the best flows were characterized by SKPM for getting information about their electrical potential.

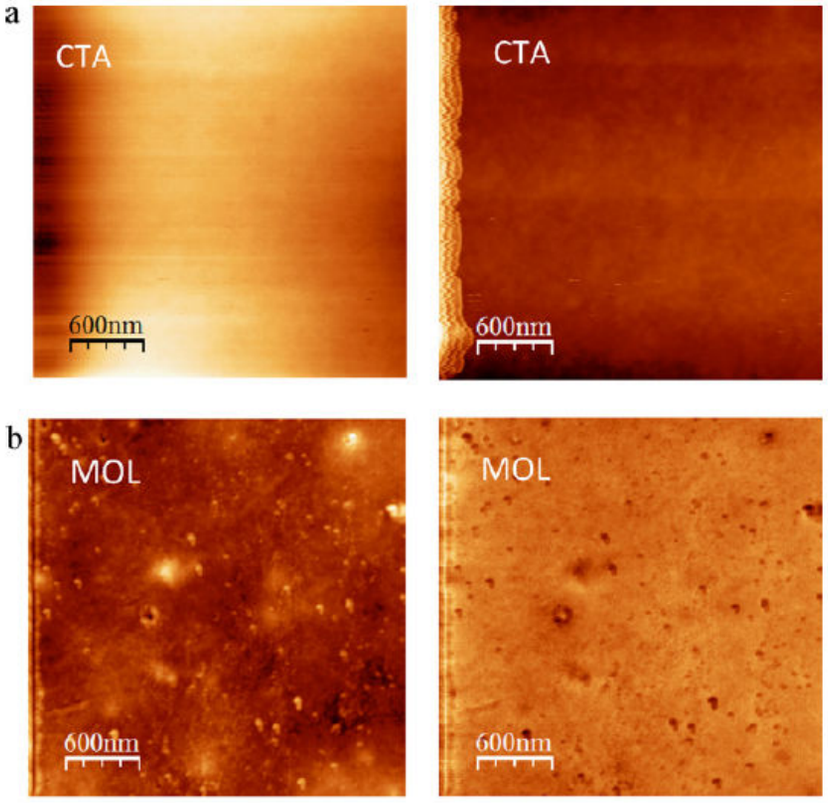


Figure 6. SKPM views of CTA (cellulose triacetate) and nanofiltration composites MOL (Lignin). Topography and surface potential mapping are shown at the left and at the right side of the figure, respectively [23].

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Figure 6 shows SKPM image of cellulose triacetate and lignin. The dark zones in the images correspond to a potential difference between surface and AFM tip, whereas no difference corresponds to bright zones. For neat CTA (cellulose triacetate) membranes, no indication of electrical potential at the surface of the material was found. When lignin is incorporated into the polymer membrane, the resulting nanofiltration membranes showed a surface electrical potential.

6. Frequently studied biopolymers

6.1. Gelatin

Gelatin is a protein made from animal products. It is produced by the partial hydrolysis of collagen obtained from skin, bones, and tissues of animals. They are mostly derived from type I collagen containing no cysteine. There are mainly two types of gelatin based on their synthesis procedure and composition. Type A, which is obtained by acid hydrolysis of collagen, has 18.5 % of nitrogen and type B obtained by the alkaline hydrolysis of collagen has 18 % of nitrogen as they do not contain amide groups [24]. At elevated temperatures, it melts and exists as coils and on lowering the temperature, it undergoes coil to helix transformation. Collagen is resistant to proteases, whereas gelatin is susceptible to these enzymes. Due to the presence of many functional groups like $–NH_2$, –SH, and –COOH, gelatin can be modified with biomolecules and nanoparticles for various applications [25].

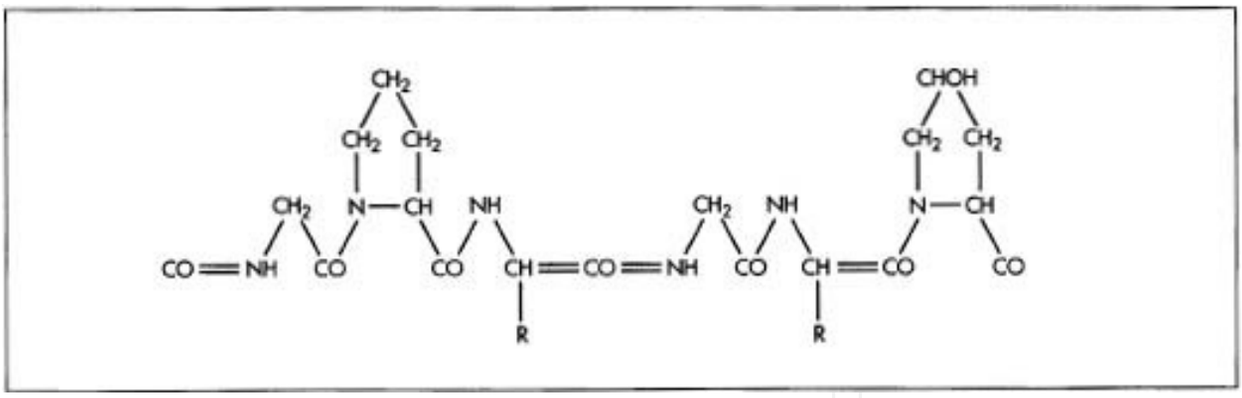


Figure 7. Structure of gelatin

It is hemostatic, pro-angiogenic, non-immunogenic, biodegradable, and biocompatible [26] and can be cross-linked to form hydrogels [27]. It is an ECM protein with wide number of applications in bone tissue engineering [28], wound dressing [29], drug delivery [30], and gene transfection [31]. Gelatin is used for weight loss and for treating osteoarthritis, rheumatoid arthritis, and brittle bones (osteoporosis). Gelatin is also used for improving hair quality and to shorten recovery after exercise and sports-related injury. In manufacturing, gelatin is used for preparation of foods, cosmetics, and medicines.

6.2. Starch

Starch is a semi-crystalline polymer composed of amylose and amylopectin molecules [32]. The primary carbohydrate used for energy storage in plants is starch, the equivalent of glycogen in animals. Both starch and glycogen are polymers of glucose, with different glycosidic linkages between glucose monomers and different degrees of branching. Amylose is a linear polymer composed of (1–4)-linked a-D-glucopyranosyl units while amylopectin is a very large molecule made up of (1–4)-linked a-D-glucopyranose chains with a-(1–6) branches. Starch is one of the most abundant natural polymers and it is cheap and degradable [33]. Properly processed starch can be made into various commercial products [34]. Due to their sensitivity to moisture and poor mechanical properties, they have only found use in various niche markets. Studies have shown that by incorporating fibers, the mechanical and barrier properties of starch products can be improved [35]. Nano and micro structured fibers when dispersed in the polymer matrix while preparing the composite, will improve its tensile strength and flexibility [36].

The significance of starch in plants and humans are undeniable. While plants consider it as a storage of energy, humans need it as a vital part of their diet and also for various commercial products. Starch and its derivatives have already been explored in various applications like in the manufacture of paper, textiles and adhesives. Their biodegradable and renewable nature make them an environmental friendly alternative to the use of synthetic additives in many other products, including plastics, detergents, pharmaceutical tablets, pesticides, cosmetics, and even oil-drilling fluids.

6.3. Cellulose

The monomer unit in cellulose is β-1, 4 linked glucan chains with hydrogen bonds formed between hydroxyl groups and oxygen atoms both within a single glucose chain and between neighboring chains. Hydrogen bonding and van der Waals forces aggregate glucan chains together side by side to form cellulose microfibrils. These cellulose microfibrils are then stacked together to form crystalline cellulose [37]. The polar –OH groups present in the cellulose chain form many hydrogen bonds with OH groups on adjacent chains, bundling the chains together. The stacking of chains is so regular that it forms hard, stable crystalline regions, and this gives the bundled chains more stability and strength. The length of the chain varies greatly from a few hundred sugar units in wood pulp to over 6000 for cotton. It is the most common natural organic polymer which is considered as an almost inexhaustible source of raw material for the increasing demand for environment friendly and biocompatible products. Due to the strong hydrogen bonding, it is insoluble in common solvents. As a result, it is chemically modified into ether, ester, and acetal derivatives.

Cellulose, the most abundant biological material on Earth, is also composed of glucose monomers but joined by beta glycosidic bonds, giving it a straighter shape that packs closely and provides mechanical strength in wood [38].

The remarkable strength of wood is due to cellulose which is a long chain of linked sugar molecules. Plant cell walls, which are the basic building block for textiles and paper, also have

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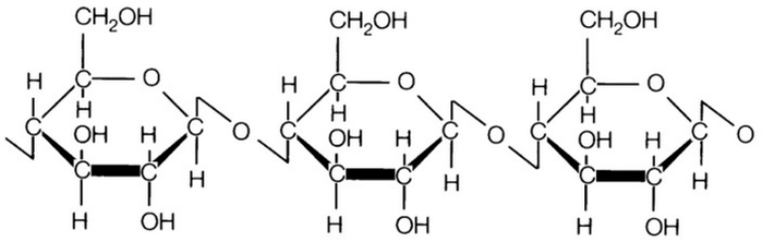


Figure 8. The structural representation of cellulose

cellulose as main component. The purest natural form of cellulose is cotton which is used in many textile applications.

Recently, cellulose has been excessively used in the form of nanofibrils. Cellulose nanofibrils (CNF) or nanocellulose is typically generated by mechanical grinding or high-pressure fluidization of cellulose to remove its lignin content. CNF consists of very thin (5–20 nm) and long (several μm) fibrils with high aspect ratio. At low concentrations, it forms a transparent gel-like material which can be used for producing biodegradable and environmentally safe, homogeneous, and dense films for various applications, especially in biomedical field. Extraction of CNF has been reported from various sources like coir, banana, sugar beet, hemp, softwood, and hardwood pulps. After using various plasticizers, various thermal, mechanical, barrier, and physical properties of the cellulose can be improved so that it can be used in various commercial applications. Plasticizing improves properties like grease proofness, and high barrier against oxygen transmission especially at dry conditions. All cellulose-synthesizing organisms including bacteria, algae, tunicates, and higher plants have cellulose synthase proteins, which catalyze the polymerization of glucan chains.

6.4. Chitin and chitosan

Chitin is a nitrogen-containing polysaccharide, related chemically to cellulose that forms a semitransparent horny substance, and is a principal constituent of the exoskeleton, or outer covering, of insects, crustaceans, and arachnids [39]. The structure of chitin is comparable to the polysaccharide cellulose, which consists of β-(1 → 4) linked nacetylglucosamine, forming crystalline nanofibrils or whiskers. Chitin is the second most abundant naturally occurring polysaccharide found in the outer shell of crustaceans and insect exoskeleton. Chitin is insoluble in most of the organic and inorganic solvents. Chitosan, the de-acetylated derivative of chitin, is a cationic polysaccharide that can form polyelectrolyte complexes with other polysaccharides and is the second most abundant natural biopolymer after cellulose (Fig. 9). It consists of β-(1 → 4)-linked D-glucosamine and N-acetyl-D-glucosamine. Due to easy applicability, water sorptivity, oxygen permeability, blood coagulating property, and cytokine induction (interleukin-8), which activate the fibroblast migration and proliferation, it is used as wound dressing material.

Chitosan, due to its good film forming property, has been widely used for casting free-standing films. It can be applied as a coating on various surfaces to improve the permeability of the

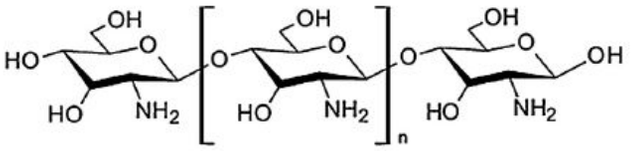


Figure 9. The structure of (a) chitosan biopolymer

surface against moisture and various gases. The water vapor permeability of the paper increased as a result of the chitosan coating. Chitosan coatings can be made on to NH_3- or CO_2-plasma activated polypropylene films, thereby making the film surfaces hydrophilic and prevent oxygen, carbon dioxide, and ethylene transmission. Barrier properties can be further improved by using nanoclays incorporated into chitosan.

6.5. Polylactic Acid (PLA)

Polylactic acid or polylactide (PLA, Poly) is a biodegradable thermoplastic aliphatic polyester derived from renewable resources, such as corn starch, tapioca roots, chips, starch, or sugarcane. PLA is obtainable primarily by the ionic polymerization of lactide, a ring closure of two lactic acid molecules. At temperatures between 140 and 180 °C and under the action of catalytic tin compounds (such as tin oxide), a ring-opening polymerization takes place. Lactide itself can be made through lactic acid fermentation from renewable resources such as starch by means of various bacteria. PLA can also be produced directly from lactic acid by polycondensation. However, this process yields low molecular weight polymers, and the disposal of the solvent is a problem in the industrial production. The properties of PLA primarily depend on the molecular mass, the degree of crystallinity, and possibly the proportion of co-monomers. A higher molecular mass raises T_g, as well as T_m, tensile strength, elastic modulus, and lowers the strain after fracture. Due to the CH_3 side group, the material has water-repellent or hydrophobic behavior. PLA is soluble in many organic solvents, such as dichloromethane or the like. PLA has higher transparency than other biodegradable polymers, and is superior in weather resistance and workability.

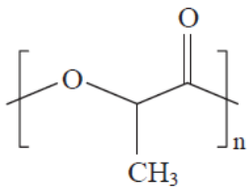


Figure 10. Structural formula of PLA

6.6. Poly(e-Caprolactone) (PCL)

Poly(e-caprolactone) (PCL) is a biodegradable polyester which is commonly used for preparing scaffolds for various tissue engineering applications. It has a low melting point of around

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60 °C and a glass transition temperature of about −60 °C. It is used in the manufacture of specialty polyurethanes with good water, oil, solvent, and chlorine resistance. PCL can be used as an additive for resins to improve its impact resistance and their processing characteristics. PCL is compatible with a range of other materials which enable it to be mixed with other biodegradable polymers to lower its cost and increase biodegradability. It can also be used as a polymeric plasticizer to other polymers like PVC. Polycaprolactone is also used for splinting, modeling, and as a feedstock for prototyping systems such as a 3D printer. PCL is biocompatible, biodegradable polymer which has shown to be capable of supporting a wide variety of cell types. PCL is also a well-known FDA-approved biomaterial which is most widely used in biomedical field [40]. The PCL is intrinsic hydrophobic in nature. Its poor surface wetting and interaction with the biological fluids avoid cells adhesion and proliferation [41]. PCL is prepared by ring opening polymerization of ε-caprolactone in the presence of a catalyst. The significance of PCL in various tissue engineering applications increased because it is degraded by hydrolysis of its ester linkages in physiological conditions. This property makes it useful for various implantable biomaterials. Since its degradation rate is lower than that of polylactide, it is proposed to be used as long-term implantable devices.

6.7. Poly-(Vinyl Alcohol) (PVA)

Poly(vinyl alcohol) (PVOH or PVA) is a white, colorless and odorless, water-soluble synthetic polymer with molecular formula $[CH_2\ CH(OH)]_n$. It is commercially available as beads or as solutions in water. It is used as thickener in glues, paper-making, sizing agent in textiles, water-soluble films useful for packing, and a variety of coatings. Polyvinyl alcohol is used as an emulsion polymerization aid, as protective colloid, to make polyvinyl acetate dispersions. PVA is prepared by first polymerizing vinyl acetate, and the resulting polyvinyl acetate is converted to the PVA. PVA has a wide range of potential applications in optical, pharmaceutical, medical, and membrane fields. It is a water-soluble polymer and allows the development of environment-friendly material processes [42].

6.8. Polyvinyl Acetate (PVAc)

Polyvinyl acetate (PVAc) belongs to polyvinyl ester family and is a thermoplastic resin produced by the polymerization of vinyl acetate monomer. Its general formula is $[CH_3COOCHCH_2]_n$ with a solids content of 50–55 % in water [43]. Most polyvinyl acetate emulsions available in market contain various co-monomers such as n-butyl acrylate, 2-ethyl hexyl acrylate, ethylene, dibutyl maleate, and dibutyl fumarate. Polymerization of vinyl acetate with ethylene can also be used to produce solid vinyl acetate/ethylene copolymers with more than 50 % vinyl acetate content. Polyvinyl alcohol (PVOH) is produced by methanolysis or hydrolysis of polyvinyl acetates. The reaction can be controlled to produce any degree of replacement of acetate groups. Polyvinyl acetate has immense applications in various fields like biomedical, synthesis of metal nanoparticles, sensing activity, and so on [44].

6.9. Collagen

Collagen is the most abundant protein in human. It is found in the bones, muscles, skin, and tendons, where it forms a scaffold to provide strength and structure. Endogenously produced,

collagen plays numerous important roles in health, with the breakdown and depletion of the body's natural collagen associated with a number of health problems [45]. Exogenous collagen is supplied to the body for medical and cosmetic purposes, including helping with healing and repairing of the body's tissues. Around 30 % of the protein in the human body is collagen and 80–90 % of the collagen in the body consists of types I, II, and III. Among this, type I collagen fibrils are stronger than steel hence is the substance that holds the whole body together. Collagen gives the skin its strength and structure, and also plays a role in the replacement of dead skin cells. Collagen in medical products can be derived from human, bovine, porcine, and ovine sources. Collagen dressings attract new skin cells to wound sites [46]. Controllable factors that damage the production of collagen include sunlight, smoking, and high sugar consumption.

6.10. Poly(3-hydroxybutyrate-co-3-hydroxyvalerate) PHBV

Poly(3-hydroxybutyrate-co-3-hydroxyvalerate) PHBV, is a polyhydroxyl- alkanoate- type thermoplastic linear aliphatic polyester. PHBV (Fig. 11) is synthesized by bacteria as an intercellular carbon and energy storage compounds under growth limiting conditions. It is biodegradable, nontoxic, and biocompatible plastic which can be produced from glucose and propionate by the recombinant *Escherichia coli* strains [47]. PHBV is a copolymer of 3-hydroxybutanoic acid and 3-hydroxypentanoic acid and can also be synthesized from butyrolacone and valerolactone in presence of oligomeric aluminoxane as catalyst. PHBV has many applications especially for the development of implanted medical devices for dental, orthopedic, hernioplastic, and skin surgery. Various potential medical devices like bioresorbable surgical sutures, biodegradable screws and plates for cartilage and bone fixation, biodegradable membranes for periodontal treatment, surgical meshes with PHBV coating for hernioplastic surgery, wound coverings, and the like have been developed using this biopolymer [48].

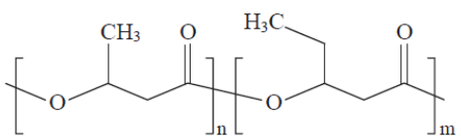


Figure 11. Structural formula of PHBV

7. Applications of biopolymers

Biopolymers, due to its biocompatible and biodegradable nature, can be used to improve the performances of other biologically active molecules in a product. They can also be modified to suite various potential applications which include the following.

7.1. Synthesis of nanomaterials

Nanotechnology is the science of nanomaterials which deals with its synthesis, characterization, and applications. Researchers are currently focusing on developing more eco-friendly

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processes for the synthesis of nanoparticles. The main focus for the synthesis protocol has shifted from physical and chemical processes towards "green" chemistry and bioprocesses. Metal nanoparticles, due to their quantum size effects, possess various novel properties. However, most of their synthesis protocol imposes a major threat to the environment [49]. In common synthetic methods, the reducing agents used which include organic solvents and toxic-reducing agents like hydrazine, N-dimethylformamide, and sodium borohydride are considered to be highly toxic for the environment [50]. All these chemicals are highly reactive and pose potential environmental and biological risks. With the increasing interest in minimization/elimination of waste and adoption of sustainable processes, the development of green chemistry approaches is desirable. Biopolymers have been extensively used as capping and reducing agent for the synthesis of various nanoparticles. Biopolymers like chitosan, heparin, soluble starch, cellulose, gelatin, PVA, PVP, and so on can be used to replace various toxic regents in synthesizing different nanoparticles [51–53].

7.2. Biomedical applications

In recent years, biopolymer materials have aroused great interest because of their biomedical applications, such as those in tissue engineering, pharmaceutical carriers, and medical devices [54, 55]. A common biopolymer, gelatin, was widely applied in medicine for dressing wounds, as an adhesive, and so on. Porous gelatin scaffolds and films were produced with the help of solvents or gases as simple porogens, which enable the scaffolds to hold drug or nutrients to be supplied to the wound for healing [56]. Electrospun PLGA-based scaffolds have been applied extensively in biomedical engineering, such as tissue engineering and drug-delivery system [57]. MWCNT-incorporated electrospun nanofibers with high surface area-to-volume ratio and porous characteristics have also shown potential applications in many aspects of tissue engineering [58, 59].

Biomaterials made from proteins, polysaccharides, and synthetic biopolymers are preferred but lack the mechanical properties and stability in aqueous environments necessary for medical applications. Cross-linking improves the properties of the biomaterials, but most cross-linkers either cause undesirable changes to the functionality of the biopolymers or result in cytotoxicity. Glutaraldehyde, the most widely used cross-linking agent, is difficult to handle and contradictory views have been presented on the cytotoxicity of glutaraldehyde-cross-linked materials [60].

7.3. Food industry

Replacing the oil-based packaging materials with biobased films and containers might give not only a competitive advantage due to more sustainable and greener image but also some improved technical properties. Biopolymers are currently used in food coatings, food packaging materials, and encapsulation matrices for functional foods. They provide unique solutions to enhance product shelf life while also reducing the overall carbon footprint related to food packaging [61]. Within food-related applications, these biobased materials are particularly useful in three main areas: food packaging, food coating, and edible films for food and encapsulation. The most commercially viable materials in food packaging are certain biodegradable polyesters and thermoplastics like starch, PLA, PHA, and so on, which can be

processed by conventional equipment. These materials are already used in a number of monolayer and multilayer applications in the food-packaging field. Starch and PLA biopolymers are potentially the most attractive types of biodegradable material. This is due to the balance of their properties and the fact that they have become commercially available. PLA is of particular interest in food packaging, due to its excellent transparency and relatively good water resistance. The challenge for these specific biomaterials is to improve their barrier and thermal properties so that they perform like polyethylene terephthalate (PET). Other materials extracted from biomass resources, such as proteins (e.g., zein), polysaccharides (e.g., chitosan), and lipids (e.g., waxes), also have excellent potential as gas and aroma barriers. The inherent high rigidity and the difficulty of processing them in conventional equipment are the main drawbacks of these types of materials. The hydrophilic nature of most of the biopolymers affects their use as high-end products. The absorption of moisture causes plasticization of these materials thereby deteriorating the barrier properties of these materials.

Renewable polymers have also been used for encapsulation purposes. Encapsulation has previously been described as a technology to protect sensitive substances against the influences of adverse environments. The term "microencapsulation" refers to a defined method of wrapping solids, liquids, or gases in small capsules, which can release their contents under specific circumstances [62]. Such technologies are of significant interest to the pharmaceutical sector. The increasing interest in edible films and coatings using biopolymers is due to their ability to incorporate a variety of functional ingredients. Plasticizers, such as glycerol, acetylated monoglycerides and polyethylene glycol, which are used to modify the mechanical properties of the film or coating, make significant changes to the barrier properties of the film. However, the major advantage of coatings is that they can be used as a vehicle for incorporating natural or chemical active ingredients, such as antioxidants and antimicrobial agents, enzymes, or functional ingredients, like probiotics, minerals, and vitamins. These ingredients can be consumed with the food, thus enhancing safety, nutritional, and sensory attributes. Edible films can be used as flavor or aroma carriers in addition to providing a barrier to aroma loss [63].

Chitosan has shown great potential as an antimicrobial packaging agent to preserve food against a wide variety of microorganisms. Incorporating antimicrobial compounds into edible films or coatings provides a novel way to improve the safety and shelf life of ready-to-eat foods. Lysozyme is one of the most frequently used antimicrobial enzymes in packaging materials, since it is a naturally occurring enzyme. Biopolymers such as amylose, when mixed with plasticizers have excellent potential in forming thin films for various food and packaging applications [64]. Starch has high sensitivity to relative humidity (RH) due to its hydrophilic nature and this can be reduced by introducing plasticizers which enhances the flexibility of the matrix [65,66]. But this technique also has some limitations due to the complex interactions between the hydrophilic plasticizers and the starch. An "anti-plasticization" process takes place with increased stiffness of the matrix if the structure of the plasticizer molecule and the polymer matrix is not compatible [67].

7.4. Packaging applications

Currently, the most commercially viable materials in food packaging are certain biodegradable polyesters, which can be processed by conventional equipment. These materials are already

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used in a number of monolayer and multilayer applications in the food-packaging field. Among the most widely researched thermoplastics, the sustainable biopolymers used in monolayer packaging include starch, PHA, and PLA [68]. Starch and PLA biopolymers are potentially the most attractive types of biodegradable material. This is due to the balance of their properties and the fact that they have become commercially available. The challenge for these specific biomaterials is to improve their barrier and thermal properties so that they perform like polyethylene terephthalate (PET). Other materials extracted from biomass resources, such as proteins (e.g., zein), polysaccharides (e.g., chitosan), and lipids (e.g., waxes), also have excellent potential as gas and aroma barriers. The main drawbacks of these types of materials are their inherently high rigidity and the difficulty of processing them in conventional equipment.

For bio-based food-packaging applications, the most important parameter to be considered is its barrier properties. Hydrophilic polymers usually have poor moisture resistance which cause water vapor transmission through packaging and thus affect the quality of foods. This results in shorter shelf lives, increased costs, and eventually more waste. Another technique to improve the barrier properties of biopolymers is to add various nanofillers like nanoclays, metal oxide nanoparticles, and so on [69]. Among the bioplastics, polyglycolic acid (PGA) has excellent barrier properties thus it's one of the most promising new commercially available barrier polymers. Its precursor, glycolic acid, can now be produced via a natural metabolic route, the glyoxylate cycle.

7.5. Water purification

Safe drinking water is a significant, but simple indicator of development. Nanotechnology has shown promising developments in providing safe drinking water through effective purifying mechanisms. Several nanomaterials have already proved to have antibacterial and antifungal properties. Developing affordable materials which can constantly release these antibacterial materials like silver nanoparticles to water is an effective way of providing microbially safe drinking water for all. Developing various nanocomposites with functional materials which can scavenge various toxic metals like arsenic, lead, etc., from water together with the antibacterial agents can result in affordable water purifiers that can function without electricity. The main challenge in this technology is developing stable materials which can release nanoparticles continuously overcoming the scaling on nanomaterials caused by various complex species present inside water.

A relatively new biopolymer, chitosan, shows superior performance where many conventional polymers fail. It is a versatile polymer with applications in water treatment, biomedical and dietary supplement industries. Chitosan is used as a flocculant in water treatment processes and will biodegrade in the environment over periods of weeks or months rather than years. Compared to chitosan, many aggressive and cheap synthetic flocculants are available but they leave a residual impact on the environment. Chitosan removes metals from water by forming chelates.

Chelation is a process by which multiple binding sites along the polymer chain bind with the metal to form a metal cage like structure, to remove it from a solution. This property of chitosan

together with its biodegradability make it an eminent candidate for treating difficult industrial storm water and waste water, where conventional methods failed to reduce the contaminant levels. Porous GO-biopolymer gels can efficiently remove cationic dyes and heavy metal ions from wastewater [70]. Nanocrystalline metal oxyhydroxide-chitosan granular composite materials prepared at near room temperature through an aqueous route was also efficient in water purification [71]. Nanofiber membranes can improve the water-filtration process without adversely affecting environment. Combining various nanomaterials together with biopolymers can effectively restrict the formation of biofilms on the polymer surface.

8. Conclusions

Increasing awareness towards the sustainable development has caused the researchers to think about natural and biodegradable polymers for replacing synthetic polymers for various applications. Nanotechnology has already emerged as the future technology which can make tremendous changes to the current existing technology. Various biopolymers are produced by the bacteria under limiting conditions to store carbon and energy resources. Incorporation of various nanofillers to these biopolymers will improve its mechanical and barrier properties which will improve its various applications. The biocompatibility together with the biodegradability of these materials encourages the use of these materials in day-to-day applications.

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