

# BIODEGRADABLE GREEN COMPOSITES

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1.1	Introduction	2
1.2	Biodegradable Polymers	2
1.2.1	Starch	2
1.2.2	Cellulose	4
1.2.3	Chitin and Chitosan	4
1.2.4	Proteins	5
1.3	Nanofillers for Composites	5
1.3.1	Cellulose-Based Nanofillers	5
1.3.2	Carbon Nanotube	7
1.3.3	Clay	7
1.3.4	Functional Fillers	7
1.4	Nanocomposites from Renewable Resources	8
1.4.1	Cellulose Nanocomposites	9
1.4.2	CNT Nanocomposites	9
1.4.3	Clay Nanocomposites	10
1.4.4	Functional Nanocomposites	10
1.5	Processing of Green Composites	10
1.6	Applications	11
1.6.1	Packaging	11
1.6.2	Electronics, Sensor, and Energy Applications	11
1.6.3	Medicinal Applications	12
1.7	Conclusion	12
	References	12

## 1.1 INTRODUCTION

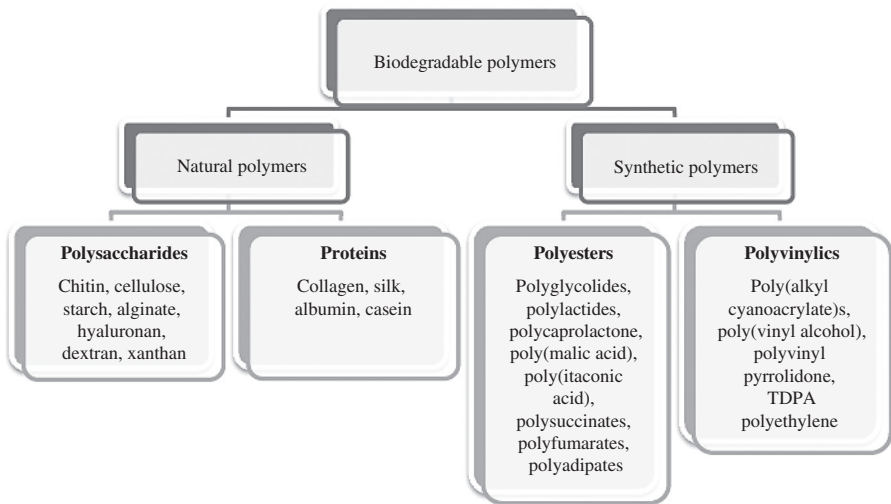
Conventional polymers are usually made from petroleum resources such as polyolefins, and they are ideal for many applications such as packaging, building resources, commodities, and consumer goods. Polyolefin-based plastics have become a foundation of modern civilization and are low cost, durable, resistant to solvents, waterproof, and resistant to physical aging. The resistance of polyolefin materials to degradation by microorganisms is both an advantage and, in the long term, a problem. It was estimated in 2002 that some 41%·w/w of the total global plastic production was used by packaging industries, with 47% of that production being used to package foodstuffs [1]. Most oil-derived packaging is nonrecyclable, or economically impractical to recycle, and quickly becomes landfill, equating to a huge quantity of nondegradable waste. Microorganisms found in landfill soils are unable to degrade conventional plastics [2], and as a result, they remain in the environment for a very long time [3]. This in itself has not been a huge concern until recently. Landfills are unattractive to residents living near them, and new ones are costly and difficult to establish. Landfills are becoming filled to capacity with more waste generated every day due to continued expansion of human urban areas and population increases. Recycling plastics is one possible solution, and since the early 1990s, more and more plastic waste is subject to recycling across developed nations [4, 5]. Australia recycled 18.5% (282,032 t) of the total plastics collected in 2008, and 58.2% of that amount was recycled here with the remainder exported for reprocessing [6]. Despite this admirable effort, it still leaves a phenomenal amount of waste plastics. Recycling is not without its problems since often recycled polymers are contaminated, resulting in inferior mechanical properties to feedstock created ones [7]. This reduces recycled feedstock desirability and hence the economic benefit to recycling. Polymer waste can also be disposed of by incineration, but given the current political climate on greenhouse emissions, this is becoming unfeasible. Incineration also produces harmful gasses and emissions, for example, burning poly(vinyl chloride) (PVC) produces furans and dioxins [8]. In this context, green composites gain their importance.

Figure 1.1 shows a classification of biodegradable polymers mainly in two families. A large number of these biodegradable polymers (biopolymers) are commercially available. They show a large range of properties, and they can compete with nonbiodegradable polymers in different industrial fields (e.g., packaging).

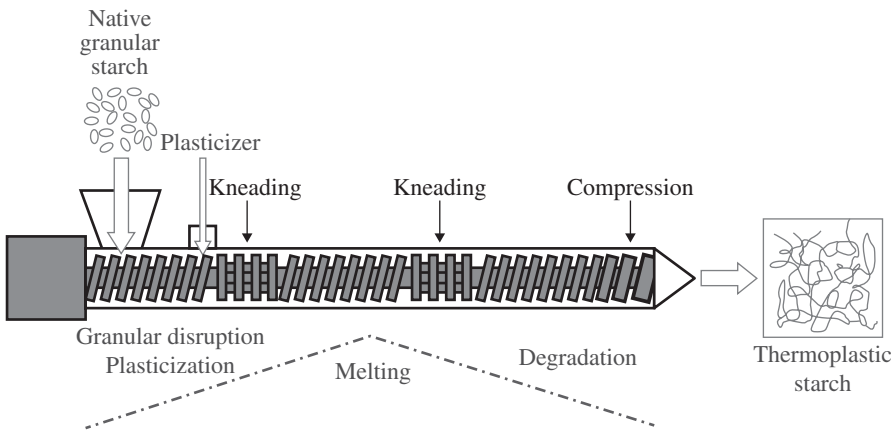
## 1.2 BIODEGRADABLE POLYMERS

### 1.2.1 Starch

Starch is a widely used bioplastic that is actually a storage polysaccharide in plants. It is composed of both linear and branched polysaccharides known as amylose and amylopectin, respectively. The ratio of these polysaccharides varies with their botanical origin, and generally, native starches contain around 85–70% amylopectin and 15–30% amylose. Starch softening temperature is higher than its degradation



**FIGURE 1.1** Classification of biodegradable polymers in four families. (See insert for color representation of the figure.)



**FIGURE 1.2** Thermoplastic starch formation. Source: Xie et al. [11], figure 37. Reproduced with permission from Elsevier. Copyright 2015. (See insert for color representation of the figure.)

temperature due to the presence of many intermolecular hydrogen bonds [9], which affects its processing. Plasticizers like water, glycerol, and sorbitol will help in increasing the free volume and thereby decreasing the glass transition and softening temperatures [10]. The schematic showing the process of obtaining TPS is shown in Figure 1.2. Traditional extrusion, injection molding, and compression molding can be used to process thermoplastic starch. The melt processing technique of obtaining thermoplastic starch is a complex operation that involves plasticization, devolatilization, melt–melt mixing, and morphology control. The final morphology of TPS depends on

composition, mixing time, temperature, shear, and elongation rate of the operation. Although it is possible to make useful products from TPS alone, extreme moisture sensitivity of starch leads to limited practical application. Therefore, the reality in commercialization of starch-based plastics involves blending of TPS with other polymers and additives. Thermoplastic starch formation [11] is shown in Figure 1.2.

### 1.2.2 Cellulose

Cellulose is an abundant and ubiquitous natural polymer. It is the major structural component of plant cells and is found throughout nature. It is widely used in industrial applications in different forms. Cellulose is mostly obtained from wood and cotton at present for many applications; on the other hand, cellulose pulp is also being extracted from agricultural by-products such as bagasse, stalks, and crop straws. Currently, cellulose-based materials are used in two forms on an industrial scale [12]:

1. Regenerated cellulose is used for fiber and film production and cannot be melt processed.
2. Cellulose esters are used in a broad array of applications including coatings, biomedical uses, and other usual plastic applications.

Nonplant resources can also be used to produce cellulose, especially bacteria and tunicates. There is a considerable interest in obtaining cellulose from bacteria, popularly known as bacterial cellulose. *Acetobacter xylinum* produces this cellulose under unique culturing conditions to form a fibrous network [13]. *A. xylinum* produces cellulose with good mechanical strength and biodegradability. “Nanocellulose” comprises of fibrous or crystalline units of cellulose between 5 and 500 nm in diameter with a length of several micrometers. Nanocellulose is available in two forms, that is, microfibrils and nanowhiskers [14].

### 1.2.3 Chitin and Chitosan

Interest in these polymers is driven by their unique properties such as renewable, biocompatible, biodegradable, and nontoxic with excellent adsorption properties [15]. Chitin is an abundantly available natural polysaccharide and is the supporting material in many invertebrate animals such as insects and crustaceans. The monomers in chitin are 2-acetamido-2-deoxy- $\beta$ -D-glucoses, which are attached to (1 $\rightarrow$ 4) linkages, and this polymer degrades by chitinase. The deacetylated chitin is known as chitosan; this deacetylation is more than 50% [16]. Chitosan is a semicrystalline polymer, and its crystallinity depends on the extent of deacetylation [17]. Chitosan is receiving more attention as a possible polysaccharide resource for biomedical applications [17].

The process of obtaining chitin from the shells of crab or shrimp starts with the extraction of proteins followed by treatment with calcium carbonate for dissolution of shells. The chitin obtained from this process is then deacetylated with 40% sodium hydroxide for 1–3 h at 120°C. This yields a 70% deacetylated

chitosan [18]. The molecular weight of chitosan depends on the source, and it varies from 100 to 1100 kDa [19]. Commercial chitosan has around 50–90% deacetylation degree [17]. Chitosan has been extensively explored for films and fibers [16]. Fibers from these polymers are very useful, as wound dressing materials and absorbable sutures [19, 20]. They have generated interest in biomedical applications [17].

#### 1.2.4 Proteins

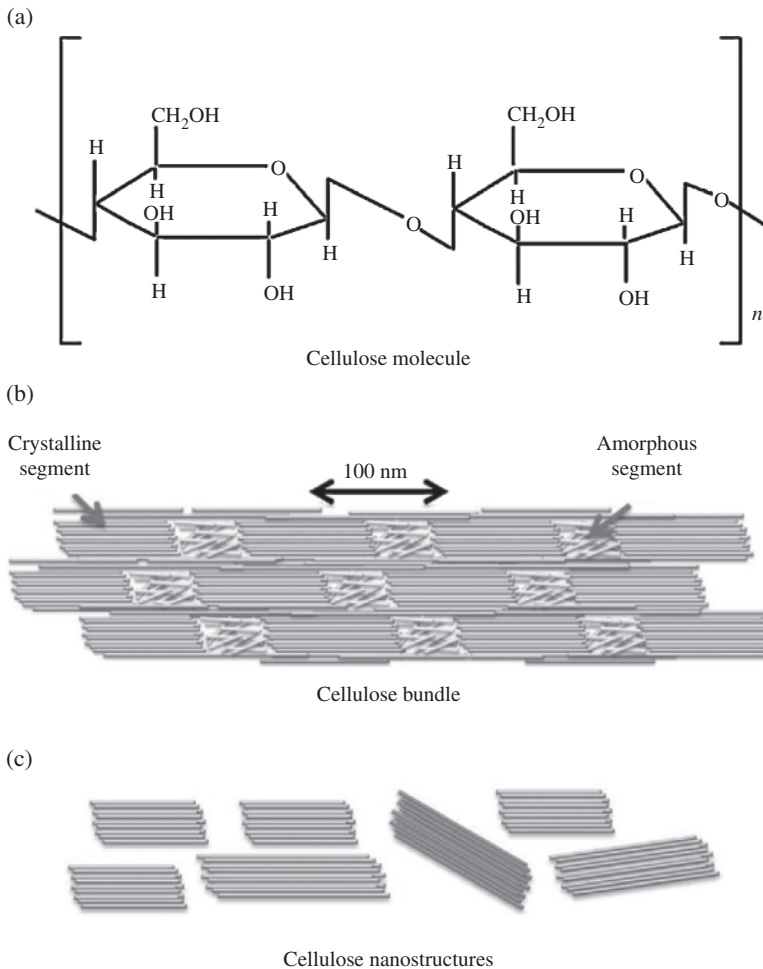
A protein is a random copolymer of different amino acids. Based on the origin, proteins can be classified as plant proteins (e.g., soy, pea, canola, and wheat) and animal proteins (e.g., gelatin, whey, casein, and keratin). Generally, proteinaceous biomaterial can be defined as a stable 3D polymeric network that is strengthened by hydrophobic interactions and hydrogen bonding [21]. Unfolding and realigning of the proteins are necessary to produce useful biomaterials. Hydrophilic compounds and lipid compounds are used for plasticization of proteins. Water, glycerols, fatty acids, and oils are commonly used plasticizers for proteins. Plasticizers reduce the interactions between functional units and improve the polymeric chain mobility and intermolecular spacing. This also results in reduction in glass transition temperature of the proteins. Wet processing and dry processing are used to obtain biomaterials from proteins [22]. Wet processing involves solubilization and dispersion of proteins in solvent. The dissolved protein is casted to obtain films by drying the solvent. Dry processing is the more conventional method in which proteins are mixed with suitable additives followed by thermomechanical processing by conventional techniques such as extrusion and/or molding.

### 1.3 NANOFILLERS FOR COMPOSITES

Bionanocomposites are obtained from 100% biobased materials, in which the fillers and the matrix both are obtained from renewable resources. Nanofillers that are extensively used for the preparation of nanocomposites are listed below.

#### 1.3.1 Cellulose-Based Nanofillers

Cellulose microfibrils and nanocrystalline celluloses or cellulose nanowhiskers (CNW) are the two types of nanoreinforcements obtained from cellulose [14]. Cellulose microfibrils consist of bundles of molecules that are elongated and stabilized through hydrogen bonding [14, 23]. The typical dimensions of these nanofibrils are 2–20 nm in diameters, while the lengths are in micrometer range. Also, these fibrils consist of both amorphous and crystalline regions. This is shown in Figure 1.3. The crystalline regions can be isolated by various techniques, and resultant material is known as whiskers. These whiskers are also known as nanorods and nanocrystals. The lengths of these whiskers typically



**FIGURE 1.3** Schematics of (a) single cellulose chain repeat unit, showing the directionality of the 1–4 linkage and intrachain hydrogen bonding (dotted line), (b) idealized cellulose microfibril showing one of the suggested configurations of the crystalline and amorphous regions, and (c) cellulose nanocrystals after acid hydrolysis dissolved the disordered regions. *Source:* Reddy et al. [24], figure 6. Reproduced with permission from Elsevier. Copyright 2015. (See insert for color representation of the figure.)

range from 500 nm to 1–21  $\mu\text{m}$  in length and diameter in the range of 8–20 nm [25]. Also, it was found that cellulose crystals have a modulus of around 150 GPa and a strength of 10 GPa [26]. This is a very interesting data as it suggests that cellulose can replace single-walled carbon nanotubes (SWCNTs) in many applications. Acid hydrolysis is the most widely used method for extracting CNW, which removes the amorphous regions while crystalline regions remain intact [27].

### 1.3.2 Carbon Nanotube

Carbon nanostructures including fullerene (buckyballs), carbon nanotubes (CNTs) (single walled and multiwalled), carbon nanofibers, carbon nanoparticles, and graphene nanosheets have been widely investigated due to their excellent physicochemical, mechanical, and electrical properties [28–30]. The allotropic behavior of carbon arises from different bonding states representing  $sp^3$ ,  $sp^2$ , and  $sp$  hybridization. In general, the degree of carbon bond hybridization- $n$  ( $sp^n$ ) determines the structure of carbon nanomaterials and their functional properties [28]. CNTs have been synthesized using many methods; among them, (i) arc discharge, (ii) ablation using laser, (iii) chemical vapor deposition, and (iv) high pressure of carbon monoxide are found to be the most popular [31]. Especially for polymeric composites, CNTs impart several advantages:

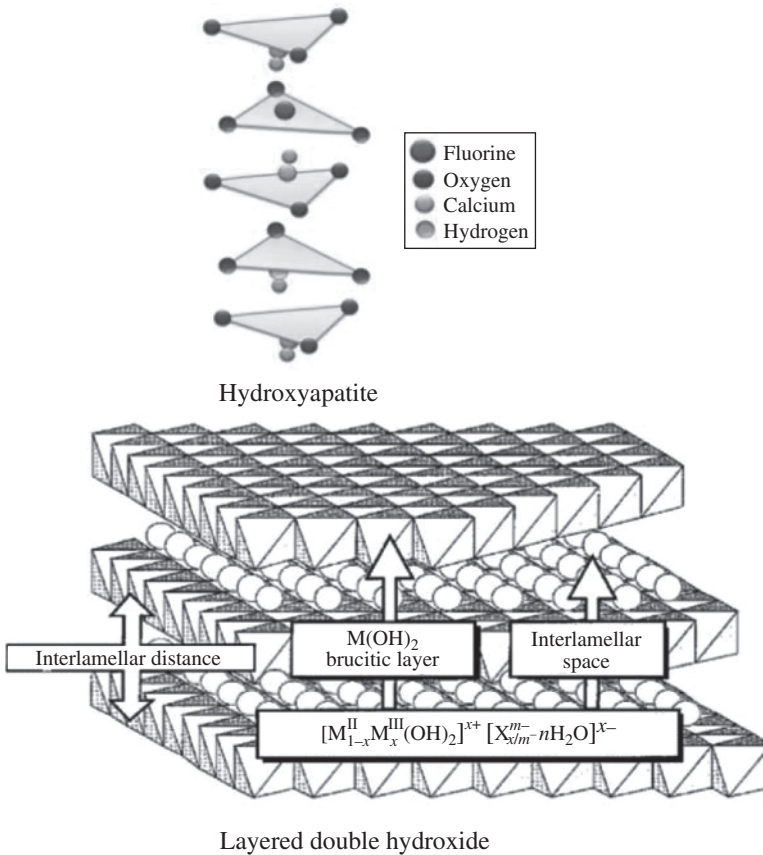
1. Versatility as reinforcement in both thermoplastic and thermoset regimes [32]
2. Extremely high theoretical/experimental tensile strength (150–180 GPa) and modulus (640 GPa to 1 TPa) [32]
3. One-dimensional electronic structure, which enables significantly nonscattering electron transport [33]
4. Their compatibility with other chemical compounds, metal/metal oxide/chalcogenide nanoparticles, and polymeric materials [34] (reinforcement of CNTs into various polymer systems not only provides improvement in mechanical and thermal properties but also creates additional functional properties)

### 1.3.3 Clay

Layered silicates, also known as nanoclays, are most commonly utilized nanofillers in the synthesis of polymer layered silicate nanocomposites. Among these layered silicates, phyllosilicates (2:1) are extensively used in preparing clay-based nanocomposites. The crystal arrangement in the silicate layers is made up of two tetrahedrally coordinated atoms amalgamated to edge-shared octahedral sheets. The dispersibility of layered silicates into individual layers is governed by its own ability for surface modification via ion exchange reactions that can replace interlayer inorganic ions with organic cations. Renewable polyesters are mostly organophilic compounds, while the pristine silicate layers are miscible only with hydrophilic polymers. The silicate layers can be made miscible with hydrophobic polymer by introducing/exchanging interlayer cation galleries ( $Na^+$ ,  $Ca^{2+}$ , etc.) of layered silicates with organic compounds.

### 1.3.4 Functional Fillers

Nowadays, medical implants are very common in practice that utilizes a wide range of biocompatible materials such as metals, alloys, ceramics, polymers, and composites [35]. Among them, bionanocomposites that are fabricated using the combination of biopolymers and various nanostructured inorganic/organic functional fillers receive extensive attention due to their diversified biomedical as well as biotechnological



**FIGURE 1.4** Schematic representation of hydroxyapatite and layered double hydroxide chemical structure. *Source:* Leroux and Besse [38], figure 13. Reprinted with permission from American Chemical Society. Copyright 2015. (See insert for color representation of the figure.)

application [36]. Nanostructured fillers play an important role in biocomposite fabrication, since they bring various desired functionalities to the composites [36]. Functional nanofillers such as cellulose nanofibers, hydroxyapatite (HAp), layered double hydroxides (LDH), silica nanoparticles, and polyhedral oligomeric silsesquioxanes (POSS) are mostly investigated for this proposes [36, 37]. Recently, HAp and LDH have received more attention due to their versatility in the fabrication of various nanocomposites for biomedical application [36] (Fig. 1.4).

## 1.4 NANOCOMPOSITES FROM RENEWABLE RESOURCES

Expansion of nanotechnology in recent years has influenced the scientific, technical, and economical competitiveness of renewable resource-based polymers in developing a range of high-performance engineering/consumer products [39]. Recently,



scientists/engineers from academia and industries are investigating the use of nanostructures (cellulose nanostructures, CNTs, and nanoclays) as reinforcements in order to produce a new class of bionanocomposites [40, 41]. The inherent properties of these nanoparticles in enhancing the thermal, mechanical, dimensional stability, and other types of functional properties (electrical/electromagnetic shielding/barrier/fire retardant/triggered biodegradability/solvent resistance) of the composite materials with the added advantages of eco-friendliness were effectively utilized to create a new class of materials. They also provide additional advantages like ease to process, transparent, low density, and recyclable [14, 39].

#### 1.4.1 Cellulose Nanocomposites

Cellulose-based nanostructures have been utilized for improving PLA's. Microcrystalline cellulose (MCC) is the best source for CNW; however, dispersion of MCC into individual fibers is difficult especially in melt processing. Mathew et al. reported that the reinforcement of MCC in PLA processed through twin-screw extrusion resulted in the retention of MCC as bundles and reduced in the mechanical properties [42]. It was found that the mechanical properties were not increased compared to virgin PLA, which is due to the presence of additives and unsuitable processing temperatures. Reinforcement of cellulose nanostructure into PLA creates a diversified impact that includes improvement in barrier properties, nucleation effects, and foam formation. Sanchez-Garcia and Lagaron [43] reported the barrier properties of PLA/CNW composites. Their research ensured that the addition of 3 wt% CNW into PLA was able to reduce the water and oxygen permeability by 82 and 90%, respectively. CNW acted as shield in PLA and caused the crystallinity development, which resulted in high barrier properties [25]. The effects of microfibrillated cellulose reinforcement in PLA on crystallization were studied by Suryanegara et al. [44]. They found that the microfibril acted as a nucleating agent and altered the crystallization behavior of PLA, which resulted in the enhancement of storage modulus up to 1 GPa [44].

#### 1.4.2 CNT Nanocomposites

In starch-based plastic materials, utilization of CNTs as nanoreinforcement is limited by their effective distribution. One of the successful methods of dispersing CNTs into a starch matrix is functionalization. Fama et al. investigated the fabrication of starch/multiwalled CNT composites and reported their improved mechanical properties. They were successful in dispersing MWCNTs into a starch matrix by adopting new strategies to wrap the CNT surfaces with a starch-iodine complex. This also created a strong adhesion between nanotubes and starch matrix, which caused an effective load transfer that improved their mechanical properties [45]. They were able to achieve a 70% increment in the stiffness with the MWCNT reinforcement of only 0.055 wt%. Another investigation of Fama et al. on starch-based nanocomposites using MWCNT modified with starch-iodine complex resulted in lower water permeability with high storage modulus [46]. These enhanced properties

were obtained due to the uniform dispersion of MWCNT caused by the coating of same material that has been used for matrix.

### 1.4.3 Clay Nanocomposites

Bioplastic–clay nanocomposites have been receiving extensive attention due to their improved thermal, mechanical, and barrier properties as well as reduced flammability compared to their respective virgin polymers [47]. Other positive aspects of nanoclay reinforcement are that it does not hamper the biodegradation of biodegradable polymers [48]. These clay materials were classified into many types based on their chemical nature, structure, and unique properties of swelling as well as exfoliation [49]. In composite fabrication, montmorillonite, hectorite, and saponite are the three most commonly used nanoclay minerals, which belong to the smectites family [48]. Montmorillonite, saponite, and hectorite are the three most commonly used nanoclays in the synthesis of polymer nanocomposites; these nanoclays belong to smectites family [50]. Enhancement of polymer properties by individual clay layers can be obtained through their high aspect ratio and interfacial interactions with polymer networks.

### 1.4.4 Functional Nanocomposites

Biobased polymers with functional fillers such as HAp and LDH found a wide range of applications especially toward tissue engineering, drug deliver and gene therapy due to their compatibility and also noncytotoxic and noninflammatory toward with biological. Chen et al. [51] also demonstrated the precipitation technique for the fabrication of chitosan/HAp nanocomposites for the biomedical applications. Similarly, a wide range of literature available for the fabrication and characterization of HAp reinforced collagen nanocomposites for biomedical applications. Chang and Tanaka [52] reported the simultaneous titration method for the fabrication of HAp/collagen nanocomposites with glutaraldehyde cross-linking. Rhee and Tanaka [53] reported the precipitation method for the fabrication of HAp/collagen/chondroitin sulfate nanocomposites with the possible shaping and consolidation with mechanical pressing. Dagnon et al. [54] reported the solution casting fabrication of PLA/LDH nanocomposites and reported the increment of overall crystallinity. Chiang and Wu [55] investigated the fabrication of biodegradable PLA/LDH nanocomposites by solution mixing process and reported the significant increment of mechanical properties with 1.2% LDH reinforcement.

## 1.5 PROCESSING OF GREEN COMPOSITES

It is important to obtain uniform dispersion for two reasons: for effective stress transfer from matrix to the filler and also for the obtain network structure that can help in thermal and electrical conductivities. According to Thostenson et al. [56], uniform dispersion [57–59], wetting and orientation in the matrix [59, 60], and

functionalization to improve the compatibility are the important issues that influence the processing of CNT polymer nanocomposites. Also, due to difference in size followed by larger surface found in SWCNTs leads to their aggregation compared to the MWCNTs in the polymer matrix. Among various approaches used in dispersion CNTs in polymer matrices include surface modification of nanotubes [61–63], polymer coating on the surface of CNTs [64], *in situ* polymerization technique to obtain CNT nanocomposite [65, 66], dispersion of CNT in polymer solutions using ultrasonic [67, 68], melt processing [69–71], surfactant chemistry [72, 73], electrospraying [74], electrode chemistry [75], and crystallization [76] as well as plasma treatment and/or chemical oxidation to attach functional group.

## 1.6 APPLICATIONS

### 1.6.1 Packaging

Narrow processing window, poor gas and water barrier properties, unbalanced mechanical properties, low softening temperature, and weak resistivity of the plastics have limited their use in a wide range of applications. As discussed in the previous sections, nanotechnology helps in overcoming these problems. Nanofillers help in improving the previously discussed properties of the bioplastics. Bionanocomposites exhibit remarkable improvement compared to the neat matrix and conventional composites due to nanoreinforcements. Polymers provide excellent balance in properties including mechanical, thermal, and barrier properties. It is well recognized that the incorporation of nanofillers especially nanoclay into the polymeric matrix can lead to significant enhancement in the barrier properties [47]. This improved barrier property in nanocomposites is explained on the basis of increased path length due to the presence of nanofillers that the same molecules need to traverse while diffusing through the matrix. Cellulose nanofibers were found to have the same reducing effect on barrier properties of TPS; this effect is attributed to the increase of the tortuosity induced by the presence of the nanofibers [77]. However, cellulose nanofibers are not as effective as that of nanoclay probably due to their shape that limits the increment in tortuous path.

### 1.6.2 Electronics, Sensor, and Energy Applications

Polymers reinforced with engineered/functional nanostructures provide additional electrical, optical, electromagnetic shielding, and magnetic properties and lead to the development of various advanced devices including light-emitting diodes, sensors, solar cells, display panels, and other medical devices [78, 79]. As the global demand for flexible electronic devices increases, polymer nanocomposites receive extensive attention in developing various devices [80]. Besides, ever-increasing uses of electrical and electronic equipment create environmental issues at the end of their life span and generate enormous waste products (e-waste) [81]. As a result, applications of bioplastics and their composites in electronic products are increasing due to their biodegradability and renewability with less environmental impact/carbon footprint [82]. Cellulose-based composite films (which are scientifically known as active paper) with active nanomaterials such as gold, silver,

and CNTs have been used to construct strain, chemical, and biosensors. In recent years, a number of polymer composites reinforced with high conductive fillers have been reported as EMI shielding materials [83, 84]. Such materials found applications in high-performance shielded connectors, scientific/medical/consumer electronic devices, and military/security products.

### 1.6.3 Medicinal Applications

The versatility and adaptability of bionanocomposites enable these materials to be utilized for biomedical applications. An essential characteristic of medical biomaterials is biocompatibility, the ability to function appropriately in the human body to produce the desired clinical outcome, without causing adverse effects [85]. Bionanocomposites are an intuitive choice for medical applications, given that such materials are constructed from biodegraded polymers, and such materials possess tunable mechanical properties. Biobased polymers are increasingly being recognized as biocompatible materials for clinical use. For example, plastics and films made from corn-derived PDO have been shown to be noncytotoxic and noninflammatory to clinically relevant cell lines [86]. Moreover, soy-derived polymers have been demonstrated to be useful as bone fillers [87].

## 1.7 CONCLUSION

Biodegradable green polymers are an emerging class of polymers that have many potential applications to replace the synthetic polymers. There is an immense opportunity in developing new biobased products, but the real challenge is to design sustainable biobased products. The major limitations of the present biodegradable polymers are their high cost. New environmental regulations and societal concerns have triggered the search for new products and processes that are compatible with the environment. Their unique balance of properties would open up new market development opportunities for biocomposites in the twenty-first-century green materials world. It can be concluded that biodegradable green composites are an essential guide for agricultural government, agricultural departments, automotive companies, composite producers and material scientists, and crop producers, all dedicated to the promotion and practice of eco-friendly materials and production methods. The biodegradable green composites can be effectively used as a material for structural, medical, automotive, and electronic applications. Nowadays, green composites are emerging as a viable alternative to glass fiber-reinforced composites especially in automotive and building product applications.

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