Food Packaging Technology

Food Packaging Technology provides a comprehensive foundation in food packaging concepts, materials, and innovations critical for preserving food quality and ensuring consumer safety. Designed to bridge academic knowledge and industry application, the book explores conventional and modern packaging methods, the science behind modified atmosphere and active packaging, and the rising role of biopolymers in sustainable packaging. It serves as a core resource for students, researchers, and professionals involved in food science, food technology, and packaging industries.

Key Features

- Explains core packaging principles and their importance in food safety and shelf-life extension
- Covers modern advancements including modified atmosphere, active, and intelligent packaging
- Details sustainable packaging with a focus on biopolymers and ecofriendly solutions
- Explores packaging design, machinery, testing protocols, and safety standards
- Includes real-world insights into regulatory, functional, and industrial perspectives

Structured to align with academic curricula and industrial requirements, this book blends theoretical knowledge with practical relevance. It is an ideal reference for food technology students, packaging professionals, researchers, and quality assurance personnel looking to enhance their understanding of packaging's critical role in the food supply chain.

Food Packaging Technology

Edited by

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CRC Press
Taylor & Francis Group
Boca Raton London New York

CRC Press is an imprint of the
Taylor & Francis Group, an **informa** business

Designed cover image: M. Sukumar

First edition published 2026
by CRC Press
2385 NW Executive Center Drive, Suite 320, Boca Raton FL 33431

and by CRC Press
4 Park Square, Milton Park, Abingdon, Oxon, OX14 4RN

CRC Press is an imprint of Taylor & Francis Group, LLC

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ISBN: 978-1-041-13098-7 (hbk)
ISBN: 978-1-041-13097-0 (pbk)
ISBN: 978-1-003-66803-9 (ebk)

DOI: 10.1201/9781003668039

Typeset in Times
by SPi Technologies India Pvt Ltd (Straive)

Contents

6 Biopolymer for Food Packaging

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6.1 OVERVIEW OF BIOPOLYMERS: DEMAND, RESOURCES, AND VARIOUS APPLICATIONS

In recent times the market price of petroleum products and oils has increased. These facts have helped to raise interest in biopolymers and in particular biodegradable biopolymers. Biodegradable plastics and polymers were first introduced in the 1980s. There are many sources of biodegradable polymers, from synthetic to natural polymers. Natural polymers are available in large quantities from renewable sources, while synthetic polymers are produced from nonrenewable petroleum resources (Vroman & Tighzert, 2009).

These biopolymers are large macromolecules composed of single, repeating monomer units. They are of high molecular weight, and their material characteristics vary according to the nature of their monomer chemistry.

Agriculture offers a broad range of commodities including forest, plant/crop, and farm and marine animals, which have many uses. Plant-based materials have been used traditionally for food and feed and are increasingly being used in pharmaceuticals and nutraceuticals.

Figure 6.1 shows the production of biopolymers in three categories: polysaccharides from direct extract of plant biomass, polylactides (PLA) and poly(ϵ-caprolactone) (PCL) from the lactic acid fermentation of micro-organisms, and poly(β-hydroxyalkanoates) (PHA) and polyhydroxybutyrsyte (PHB) from the reduction of suitable substrates by genetically modified microorganisms.

Biopolymers are applied in food packaging, biomedical, and bioplastic industries as an alternative to petrochemical and synthetic polymers. Agricultural resources of starch and cellulose serve as the best biopolymers for solid packaging materials. These are very weak when they come in contact with water and they get diluted. This problem is resolved by adding composites such as starch-blended products to the packaging material. Adding cellulose and chitosan to the starch films gives partial resistance to water and increases the mechanical properties; these starch-blended films are completely biodegradable within 3 months.

Acetylation of the starch or cellulose gives more resistance to water and increases oxygen barrier and mechanical properties. However, in the acetylation procedure usage of chemicals such as pyridine and acetic acid may increase the biodegradability time.

DOI: 10.1201/9781003668039-6

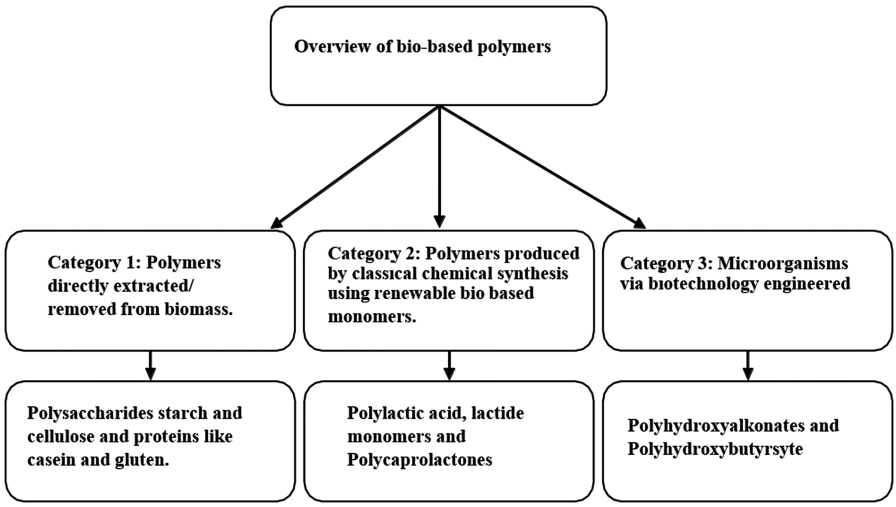

FIGURE 6.1 The overview of biopolymers and its resources.

The antibacterial activity of blend films (starch/chitosan) is enhanced by increasing the content of chitosan in blend systems (Zhai et al., 2004).

6.2 WHY THERE IS A NEED FOR BIOPOLYMER IN FOOD PACKAGING SYSTEMS

The food industry has witnessed a spate in the manufacturing of new food packaging materials. Most of them are colorful and aesthetic and cause increasing environmental concerns due to their nonbiodegradable nature. Thrown-out plastic causes pollution to land as well as the ocean. According to a new report by the Ellen MacArthur Foundation (Goncalves, 2020), there will be more waste plastic in the sea than fish by 2050 unless the industry cleans up its act. The new plastics will consume 20% of all oil production within 35 years, up from an estimated 5% today.

Plastic production has increased 20-fold since 1964, reaching 311 million tons in 2014, the report says. It is expected to double again in the next 20 years and almost quadruple by 2050.

Despite the growing demand, just 5% of plastics are recycled effectively, while 40% end up in landfill and one-third in fragile ecosystems such as oceans, as shown in Figure 6.2.

Much of the remainder is burned, generating energy but causing more fossil fuels to be consumed in order to make new plastic bags, cups, tubs, and consumer devices demanded by the economy. Nevertheless, food packaging is a noteworthy contributor to municipal solid waste (MSW) because food is the only product class typically consumed three times per day by virtually every person. Accordingly, food packaging

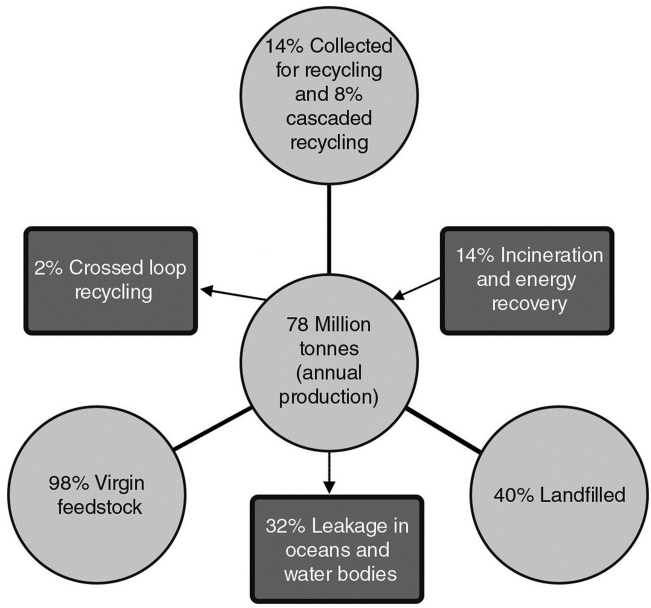

FIGURE 6.2 Global plastic packaging material flow.

accounts for almost two-thirds of total packaging waste by volume (Hunt et al., 1990). Moreover, food packaging is approximately 50% (by weight) of total packaging sales.

The principal roles of food packaging are to protect food products from outside influences and distribution damage, to contain the food, and to provide consumers with ingredient and nutrition information. Traceability, convenience, and tamper indications are secondary functions of increasing importance. The goal of food packaging is to contain food in a cost-effective way that satisfies industry requirements and consumer desires, maintains food safety, and minimizes environmental impact. Package design and construction play significant roles in determining the shelf life of a food product. The right selection of packaging materials and technologies maintains product quality and freshness during distribution and storage. Materials that have traditionally been used in food packaging include glass, metals (aluminum, foils and laminates, tinplate, and tin-free steel), paper and paperboards, and plastics. Today's food packages often combine several materials to exploit each material's functional or aesthetic properties (Marsh & Bugusu, 2007).

6.3 WASTE MANAGEMENT APPROACH TO BIOPLASTICS/ BIOPOLYMERS IN FOOD PACKAGING

Proper waste management is important to protect human health and the environment and to preserve natural resources. Integrated management approach involves source reduction, recycling, composting, combustion, and landfilling.

Source reduction involves the toxicity reduction of the waste, and it encompasses using less packaging, designing products to last longer, and reusing products and materials, according to the Environmental Protection Agency (EPA). Specific ways to achieve source reduction include using thinner gauges of packaging materials (i.e., light weighting), purchasing durable goods, purchasing larger sizes (which use less packaging per unit volume) or refillable containers, and selecting nontoxic products (Leverenz, 2002).

Recycling diverts materials from the waste stream to material recovery. Unlike reuse, which involves using a returned product in its original form, recycling involves reprocessing material into new products, such that food packaging materials can also be recyclable.

Composting, considered by the EPA as a form of recycling, is the controlled aerobic or biological degradation of organic materials. Composting of any biodegradable matter first involves arranging organic materials into piles and providing sufficient moisture for aerobic decomposition by microorganisms. Composting is a valuable alternative to waste disposal.

Combustion, the controlled burning of waste in a designated facility, is an increasingly attractive alternative for waste that cannot be recycled or composted. Reducing MSW volume by 70–90%, combustion incinerators can be equipped to produce steam that can either provide heat or generate electricity (Marsh & Bugusu, 2007).

The essential prerequisites of a good packaging film (Kader, 1989) are the following:

- Allow for a slow and controlled respiration with reduced oxygen absorption of the commodity
- Allow for a selective barrier to gas and water vapor
- Create a modified atmosphere with respect to internal gas composition, thus regulating the ripening process and leading to shelf life extension
- Maintain structural integrity and improve mechanical handling
- Serve as a vehicle to incorporate food additives and prevent microbial spoilage during extended storage

6.4 PLANT-BASED BIOPOLYMERS

The three major plant-based biopolymers are proteins, oils, and carbohydrates. Starch and cellulose, also called polysaccharides, are the main naturally occurring polymers in the large carbohydrate family. Natural fibers such as flax, hemp, paddy straw, kenaf, and jute mainly consist of cellulose, hemicelluloses, and lignin, but they are usually listed as a raw material used as a fiber in composites.

Corn, soybean, wheat, and sorghum are the four major crops grown in the United States with total annual production of about 400 million metric tons. About 10–15% of these grains are used for food, 40–50% for feeds, and the rest for various industrial uses. According to US Department of Agriculture statistics, the total land used for crops is about 455 million acres, which is about 20% of total usable land (Ebnesajjad, 2013).

In general, seeds make about 45–52% of the dry mass of a plant. This implies that there is a potential to produce about 400 million metric dry tons of cellulosic sugar-based biomass in the United States alone.

6.4.1 Starch and Cellulosic Biopolymers for Packaging Applications

Starch is a hydrocolloid biopolymer. It is a low-cost polysaccharide, one of the cheapest and most abundantly available biodegradable polymers. Starch is produced by agricultural plants in the form of granules, which are hydrophilic. Starch is mainly extracted from potatoes, corn, wheat, and rice. It is composed of amylose (poly-α-1,4-D-glucopyranoside), a linear and crystalline polymer and amylopectine (poly-α-1,4-D-glucopyranoside and α-1,6-D-glucopyranoside), a branched and amorphous polymer. The relative amounts and molar masses of amylose and amylopectin vary with the starch source, yielding materials of different mechanical properties and biodegradability (Fredriksson et al., 1998; Ratnayake et al., 2001). As the amylose content of starch increases, the elongation and strength also increase.

The stability of starch under stress is not high. The glucoside links start to break at 150°C, and above 250°C the granules collapse. Retrogradation, that is, reorganization of hydrogen bonds, is observed at low temperatures during cooling. In its applications starch can be mixed, kept intact, and used in various resins as a filler or melt for blending compounds. In the former form, fillers are starch whiskers used with polymer resins. Starch nanocrystals can be obtained by partial acid hydrolysis of the amorphous regions of granules. They are then incorporated into natural polymers as PHA natural rubber or starch itself (Dubief et al., 1999; Angellier et al., 2005, 2006). In the latter form, the molecular order inside the granules must be destroyed to improve starch processability. Granules are gelatinized in water at 130°C. Starch is usually used as a thermoplastic. It is plasticized through destructuration in the presence of specific amounts of water or plasticizers and heat, and then it is extruded (Martin et al., 2001). The most common plasticizers are polyols such as glycerol (Weber, 2000). When used, polyols may induce a recrystallization reaction called retrogradation.

The properties of the extruded starch depend on the water content and the relative humidity (Imam et al., 1995). Thermoplastic starch (TPS) has a high sensitivity to humidity. Thermal properties of TPS have been shown to be more influenced by the water content than the molecular weight (Van Soest et al., 1996). TPS thus obtained is almost amorphous. A new crystalline form induced by the process can remain in the thermoplasticized product. The plasticizer content is another important parameter. The interactions between the plasticizer and starch are weak if the plasticizer content is below 10 wt%. The material is then fragile and is difficult to work with it. When the plasticizer content is higher than 20 wt%, flexibility and elongation properties improve (Myllarinen et al., 2002).

Starch is renewable and biodegradable polysaccharides (Lenz, 1993). Usually native starch from plant contains about 30% amylose, 70% amylopectin-tin, and less than 1% lipids and proteins. Biodegradable starch-based plastics, such as starch/cellulose, starch/PVA (poly-vinyl alcohol), and so on, have recently been investigated

due to great potential markets in agricultural foils, garbage or composting bags, food packaging, the fast food industry, as well as biomedical fields (Funke et al., 1998).

Starch is totally biodegradable; it can be hydrolyzed into glucose by microorganism or enzymes and then metabolized into carbon dioxide and water. It is worth noting that carbon dioxide will recycle into starch again via plants and sunlight. Starch itself is poor in processability, and its end products are also poor in thir dimensional stability and mechanical properties. Therefore, native starch is not used directly (Choi et al., 1999; Primarini & Ohta, 2000).

6.4.2 Starch Blend with Synthetic Degradable Polymers

In the beginning, starch was used as a filler of polyolefin by Griffin, and its concentration is as low as 6–15%. Adding starch to vinyl polymers will enhance biodegradability.

To prepare completely biodegradable starch-based composites by this strategy, biodegradable polymers are assumed. Usually, the components to blend with starch are aliphatic polyesters, PVA, and biopolymers. The commonly used polyesters are PHA, obtained by microbial synthesis, and PLA or PCL, derived from chemical polymerization. The goal of blending low-cost starch with completely degradable polyester is to improve its cost competitiveness while maintaining other properties at an acceptable level (Lu et al., 2009).

To improve the compatibility between PLA and starch, a suitable compatibilizer should be added. Besides, gelatinization of starch is also a good method to enhance the interfacial affinity. Starch is gelatinized to disintegrate granules and overcome the strong interaction of starch molecules in the presence of water and other plasticizers, which leads to good dispersion (Martin et al., 2001; Park et al., 2000). The glass transition temperature and mechanical properties of the TPS/PLA blend depend on the composition and the content of plasticizer, indicating the compatibility between PLA and TPS is low but some degree of interaction is formed. PCL is another important member of the synthetic biodegradable polymer family. It is linear, hydrophobic, partially crystalline polyester and can be slowly degraded by microbes (Scott & Gilead, 1995). Blends between starch and PCL have been well documented in the literature (Vikman et al., 1999). The weakness of pure starch materials including low resilience, high moisture sensitivity, and high shrinkage has been overcome by adding PCL to the starch matrix even at low PCL concentration.

6.4.3 Starch Blend with Microbial Biopolymers

Natural polymers such as chitosan and cellulose and their derivatives are inherently biodegradable and exhibit unique properties. A number of investigations have been devoted to studying its blend with starch. Starch and chitosan are abundant naturally occurring polysaccharides. Both of them are cheap, renewable, nontoxic, and biodegradable. The starch/chitosan blend exhibits good film-forming properties, which is attributed to the inter- and intramolecular hydrogen bonding formed between amino groups and hydroxyl groups on the backbone of the two components. The mechanical

properties, water barrier properties, and miscibility of biodegradable blend films are affected by the ratio of starch to chitosan.

Extrusion of the mixture of corn starch and microcrystalline cellulose in the presence or absence of plasticizers is used to produce edible films. By increasing the content of the cellulose component, the rupture strength is increased, whereas the elongation at break and the permeability of films for water vapor are decreased. Starch can form thermodynamically compatible blend films with water-soluble carboxymethylcellulose when the starch content is below 25 mass%. Such films are biodegradable in the presence of microorganisms. Starch-based nanocomposite film is obtained by casting the mixture of plasticized starch and flax cellulose nanocrystals (CNC). The mechanical and water barrier properties are greatly improved. The tensile strengths of nanocomposite and unreinforced films are 498.2 and 11.9 MPa, respectively (Cao et al., 2008).

6.4.4 Cellulose Extraction and Processing Methodology for Biopolymer Packaging

The properties of cellulose like good tensile strength, low density, biodegradability, and so on have led to rising research interest. Cellulose has a highly organized hierarchical structure resulting in high crystallinity (~90%) and high Young's modulus (114 GPa) (Hsieh et al., 2008). Cellulose is the structural material of the fibrous cells with a high level of strength and stiffness per unit weight and has a straight carbohydrate polymer chain consisting of β-1-4 glucopyranose units and a degree of polymerization of about 10,000 (Lu et al., 2009). The molecules aggregate and are present in the form of microfibrils. The hydroxyl (–OH) groups in the cellulose structure play a major role in governing the reactivity and physical property of the cellulose.

6.4.5 Methodology in Processing and Extracting Cellulose from Raw Agricultural Resources

The preprocessing requires more physical methods than chemical extraction methods. Physical treatment includes pressing and drying of the agricultural source such as paddy straw, husk, and sugarcane bagasse (Figure 6.3).

6.4.5.1 Mechanical Properties of Tamarind Starch Films

Film formation was found be improper when cast with only 12% tamarind seed starch (w/v) mixed with 2.5% glycerol(v/v) as a plasticizer and 1.5% acetic acid (v/v) as anion-exchange polymerizer. Good interfacial adhesion between starch and cellulose was expected because both contained hydroxyl groups that can form hydrogen bonds between interfaces. Thus, the mixture of 12% tamarind seed starch (w/v) mixed with 2.5% glycerol (v/v) and 1.5% acetic acid (v/v) was reinforced and homogenized with 4% cellulose (w/v) for preparation of films and also to improve the mechanical properties of the film. These cellulose-reinforced tamarind (CRT) starch films were analyzed for their mechanical properties (tensile strength and

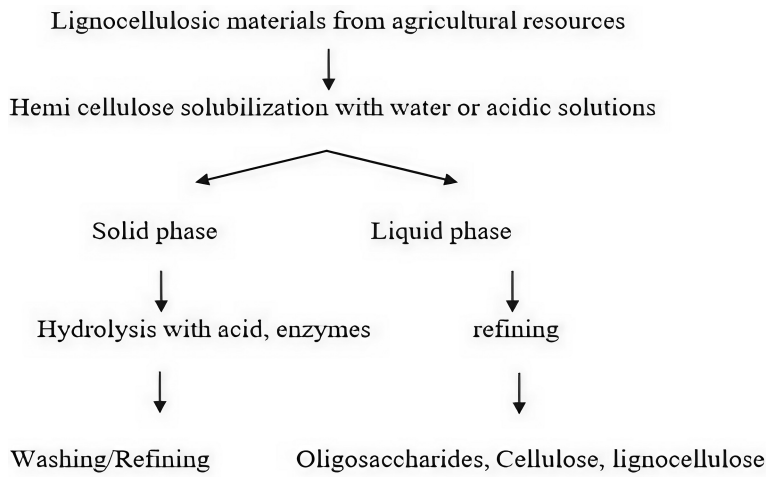

FIGURE 6.3 Preprocessing of lignocellulosic materials.

elongation at break). The tensile strength and elongation at break of CRT starch films were found to be 4.05 MPa and 354.47%, respectively (Sudharsan et al., 2016). Thus, the composite material cellulose gives better mechanical properties as well as showing high thermostability.

Cellulose-reinforced starch shows improvement in tensile strength; this may be due to increased concentration of cellulose powder. Oxygen transfer rate (OTR) of optimized CRT film was found to be 1034.45 ± 2.57, 682.76 ± 3.41, and 395.23 ± 3.75 cc m^{-1} day^{-1} for film thicknesses of 0.25, 0.38, and 0.47 mm, respectively. Water vapor permeability (WVP) of optimized CRT film was found to be 0.91, 0.73, and 0.65 g s^{-1} m^{-1} Pa^{-1} for film thicknesses of 0.25, 0.38, and 0.47 mm, respectively. Increase in thickness of CRT film was found to reduce its OTR and WVP properties. The low WVP of optimized CRT film may be due to the rich amylose content of tamarind seed starch. Increase in amylose content of starch tends to reduce the WVP of starch-based films. The reason for such behavior may be that during recrystallization, amylose forms a B-type crystalline structure, whereas amylopectin has an amorphous structure. Diffusion of moisture is easier in amorphous systems than in crystalline ones.

The empty fruit bunch (EPF) of palm also serves as a good source for cellulose production. EPF is composed of 40.37% cellulose, 20.06% hemicellulose, and 23.89% lignin. Having high cellulose content, EFB has high potential as a source for cellulosic derived products such as cellulose fiber, nanocellulose, glucose, xylose, and ethanol. Cellulose also has other potential uses as a source for bioplastic production. Cellulose has no plasticity feature.

Uses of cellulose in bioplastic production need some modification. Derivates of cellulose that have been used in bioplastic synthesis include CNC, nanofiber cellulose (NFC), cellulose acetate butyrate, cellulose acetate, and bio-PE. Cellulose derivate was mixed with other biopolymers, such as starch and PLA, in a matrix in

order to increase physical properties or as a filler. The demand for bioplastic increases along with the rising concern about environmental problems caused by petroleum-based plastic. Global production capacity of bioplastic increased by 38% per year during 2003–2007 and is predicted to reach 3.45 million tons in 2020. Cellulose and cellulose derivate are about 11% of the global capacity.

Cellulose from EFB could be used as a bioplastic composite source. Potential cellulose from EFB is 11.5 million tons in Indonesia, making EFB a good source for bioplastic. Cellulose is produced using sodium hydroxide and sodium hypochlorite. Cellulose obtained from EFB is modified in order to increase physical properties of the bioplastic.

Bioplastics are made from corn starch, potato starch, or banana starch, which is used by humans and animals for their living. Instead of using starches that are extracted from edible things, we should use waste newspaper, which is mainly made up of cellulose, and these newspapers are dumped into oceans for disposal.

Cellulose is converted to glucose in a two-stage process in which cellobiose is produced from a cellulosic feedstock under the influence of *Trichoderma reesei* in the first stage, and cellobiose from the first stage is converted to glucose in the second stage by the action of purified cellobiose derived from *Aspergillus terreus*. Cellobiose from *A. terreus* is purified by contacting a crude aqueous extract of the cellobiose with an ion exchange resin and an anion exchange resin. The purified cellobiose may be immobilized on a suitable substrate. The present invention relates to a process for the production of glucose from cellulose. In one of its more specific aspects, this invention relates to a process for the conversion of cellulose to glucose wherein cellulose is converted to cellobiose under the influence of *T. reesei*, and cellobiose is converted to glucose by a purified cellobiose derived from *A. terreus*. In another of its more specific aspects, this invention relates to a process for the production of a purified enzyme having a very high activity for the production of glucose from cellobiose.

6.4.6 Chitosan-Blended Starch Composite Bioplastic

Chitin is a white, hard, inelastic, nitrogenous polysaccharide and is the major source of surface pollution in coastal areas. Chitin consists of 2-acetamido 2-deoxy-b-D-glucose through a β (1–4) linkage. Chitin is usually isolated from the exoskeletons of crustaceans and more particularly from shrimps and crabs (Austin et al., 1989; Minke & Blackwell, 1978). Squid is another important source of chitin in which it exists in the β form, which was found to be more amenable for deacetylation. It also shows higher solubility, higher reactivity, and higher affinity toward solvents and swelling than α-chitin due to much weaker intermolecular hydrogen bonding ascribable to the parallel arrangement of the main chains.

The production of chitosan from crustacean shells obtained as a food waste is economically feasible, especially if it includes the recovery of carotenoids. The shells contain a considerable amount of astaxanthin, a carotenoid that has so far not been synthesized and that is marked as a fish food additive in aquaculture. The major procedure for obtaining chitosan is based on the alkaline deacetylation of chitin with strong alkaline solution. Isolation of chitin itself from different sources is

affected by the source. Generally, the raw material is crushed, washed with water or detergent, and cut into small pieces. The mineral content of the exoskeleton of the different crustaceans is not the same, and consequently different treatments may be used. The potential of chitosan is to act as a natural food preservative. The incorporation of natural antimicrobial substances in the packaging film is an alternative way to reduce the chemical substances used in food preservation (Cissé et al., 2013).

The mechanical properties of the films showed slight enhancement due to the incorporation of the enzyme system; however, the WVP, which is a key parameter to ensure the organoleptic qualities of food and the film's capability to fight against dehydration or rehydration, was not improved with this modification. The chitosan films obtained containing different amounts of the peroxidase system were used for mango packaging and coating to protect them against pathogens. Their use can help prevent the loss of mango due to fungi and bacteria during storage and transport. A comprehensive review dealing with the application of chitosan in food protection applications has been published by No et al. (2007). The application of chitosan in the food industry is mainly due to its film-forming ability and its antimicrobial activity against a wide range of food-borne filamentous fungi, yeasts, and bacteria. Three mechanisms were proposed to explain the antimicrobial mechanism of chitosan, albeit not being very exclusive. The first hypothesis attributes the antimicrobial property of chitosan to a change in cell permeability due to interactions between the positively charged chitosan molecules and the negatively charged microbial cell membranes. This interaction leads to the leakage of proteinaceous and other intracellular constituents. Other mechanisms are the interaction of diffused hydrolysis products with microbial DNA, which leads to the inhibition of the mRNA and protein synthesis. Finally, a chelation of metals and spore elements with chitosan results in depriving the cells of their essential nutrients, leading to their starvation and death. This research (No et al., 2007) discussed the effect of chitosan on several food items.

De Moura et al. (2008) proposed nanocomposites using chitosan as nanofiller in hydroxypropyl methylcellulose (HPMC) to improve mechanical and film barrier properties. Different concentrations of CS nanoparticles (NPs) were incorporated in HPMC to evaluate changes in mechanical properties, WVP, and oxygen permeability. Incorporation of chitosan NPs in the films improved tensile strength (30.7–66.9 MPa) and film barrier properties.

6.5 MICROBIAL SEMI-SYNTHETIC POLYMER PRODUCTION AND ITS APPLICATION AS BIOPLASTICS

The fermentation of sugars produces different monomers, which are converted to polymers. A new range of PLA was first manufactured by Cargill Dow Polymers (Marshall, 1998). PLA is produced from the ring open polymerization of the produced lactic acid via fermentation of sugar. The lactic acid prepared by this biotechnological method is almost exclusively l-lactic acid. PLA is completely degraded under compost conditions. PLA is not soluble in water; nevertheless, microorganisms in marine environments can degrade it. PLA is a hard material. Its hardness is similar to acrylic plastic (Vroman & Tighzert, 2009).

Any starch and even cellulosic compounds converted into sugar can be used to produce lactic acid by fermenting with biotechnically engineered bacterial strains, so the produced lactic acid is further converted chemically and purified and stored as PLA bioplastic material.

6.5.1 PLA: Another Biodegradable Polymer

PLA has been explored extensively. Lactic acid, which is the main precursor in PLA synthesis, is produced in large amounts by the bacterial fermentation of the hexoses (carbon source) using lactic acid bacteria. PLA is used in biomedical applications such as implants, sutures, drug delivery, tissue engineering, and stent development due to its biocompatibility properties. PLA can be processed using various techniques and is commercially available in the market in different grades. It is reasonably priced and target only the biomedical market.

Lactic acid is produced by the bacterial fermentation of carbohydrates. The large-scale production of lactic acid has been carried out using a range of feedstocks including corn, sugar beet, molasses, whey, spent grain, sugarcane, and wastepaper as a cellulosic feedstock. Lactic acid contains an asymmetric carbon atom and hence two different configurations, the l and d isomers. Both the isomers can be produced using bacterial systems. Fermentation processes involved in the lactic acid production differ based on the kind of bacteria used. Two different methods used in lactic acid production include (1) the homo-fermentative and (2) the hetero-fermentative method. The homo-fermentative method involves the conversion of each molecule of glucose into two molecules of lactic acid. This method is prevalent in most industrial processes due to high yields of lactic acid. The hetero-fermentative method is a type of fermentation in which the lactic acid yield is surpassed by the production of significant amounts of byproducts such as ethanol, acetic acid, and carbon dioxide. Hence, its use is not widespread due to the low yields of lactic acid. Maximum yields have been achieved by using glucose feedstock as the main carbon source. *Lactobacilli* species are the most commonly used microorganisms for the production of lactic acid. The most commonly used lactic acid bacteria include *Lactobacillus rhamnosus*, *L. delbrueckii*, *L. amylophilus*, *L. bavaricus*, and *L. casei*. Lactic acid can be produced by various other bacteria and fungi, as well as yeast. The production media contains 5% sugar and a nitrogen-containing nutrient. Both batch and continuous processes can be used for lactic acid production. Various parameters such as pH, temperature, and impeller speed are considered important during lactic acid fermentation. About 90–99% of lactic acid conversion occurs within two days of fermentation.

Continuous fermentation produces higher yield compared to batch fermentation. Lactic acid fermentations have also been carried out by repeated batch production of the immobilized lactic acid bacteria. After the fermentation is complete, lactic acid has to be separated from the fermentation broth and purified to be used for the polymerization process. A traditional method to obtain highly pure lactic acid involves neutralization with a base accompanied by filtration, concentration, and acidification.

A liquid/liquid extraction process is one method used for the recovery of lactic acid. Another process for lactic acid recovery is based on the esterification with

alcohols accompanied by distillation and hydrolysis. Various separation techniques such as ultrafiltration, nanofiltration, electrodialysis, and ion exchange can be used in combination with the aforementioned recovery processes for the purification of lactic acid (Basnett & Roy, 2010). Reduction in the cost of production resulting in a competitive price of the biodegradable polymers will broaden their range of application. The key properties of these biopolymers such as biodegradability and biocompatibility have made it feasible to envisage the extensive use of these biopolymers in the biomedical field. Their role in cardiac stent development is significant. It is impossible to predict the future with certainty, but the data revealed from the studies so far have been very promising. Hence, biopolymers have emerged as one of the most promising candidates for use in coronary stent development.

6.5.2 Polyhydroxyalkanoate

Bio-based materials such as polynucleotides, polyamides, polysaccharides, polyoxoesters, polythioesters, polyanhydrides, polyisoprenoids, and polyphenols are potential candidates for the substitution of synthetic plastics. Among these, PHA, which belongs to the group of polyoxoesters, has received intensive attention because it possesses biodegradable thermoplastic properties. PHA is synthesized by bacteria under unbalanced growth conditions. Some bacteria have been reported capable to produce PHA at as much as 90% (w/w) of dry cells during depletion of essential nutrients such as nitrogen, phosphorus, or magnesium. PHA serves as a storage compound of carbon, an energy source, and also as a sink for reducing equivalents for some microorganisms. PHA acts as an ideal storage compound due to its insolubility inside bacterial cytoplasm, which exerts negligible increase in osmotic pressure. It was shown that the bacteria containing PHA storage materials would be able to survive during a starvation period compared to those without PHA as this energy-reserve material slows down the cell autolysis and subsequently mortality.

6.5.2.1 Biosynthesis of PHA

PHA is produced using natural isolates and recombinant bacteria from renewable carbon sources. Among the more than 250 different natural PHA producers, only a few bacteria have been employed for the biosynthesis of PHA. These include *Alcaligenes latus*, *Bacillus megaterium*, *Cupriavidus necator*, and *Pseudomonas oleovorans*, which are capable of utilizing various carbon sources including plant oils or wastes to produce PHA. *C. necator* has been the most extensively studied and commonly used bacterium for PHA production. In the 1980s, a glucose-utilizing mutant of *C. necator* was employed by Imperial Chemical Industries (UK) for the industrial production of poly (3-hydroxybutyrate-co-3-hydroxyvalerate) [P(3HB-co-3HV)], which was sold under the trade name of Biopol. However, there are some limitations associated with the use of natural PHA producers. Natural PHA-producing bacteria usually harbor native machinery for polymer degradation and are often hard to lyse, making the recovery of PHA difficult. For industrial production of PHA, it is desirable to develop strains that can reach high final cell density in a relatively short period of time and produce high PHA content from simple, inexpensive substrates. Thus, genetic engineering serves as a powerful tool in the development of strains that can efficiently produce PHA from inexpensive renewable resources. Genetically engineered bacteria

such as recombinant strains of *Escherichia coli*, which produce PHA containing 3HB, 3HHx, and 3HO monomers from soybean oil, and a recombinant strain of *C. necator* harboring the *Aeromonas caviae* PHA synthase gene, which produces P (3HB-co-3HHx) from palm oil, have been developed.

Microorganisms that produce PHA can be classified into two types. The first group of bacteria requires limitation of essential nutrients such as nitrogen and oxygen, and the presence of an excess carbon source for the efficient synthesis of PHA. The representative bacteria belonging to this group include *C. necator*, *Protomonas extorquens*, and *Protomonas oleovorans*. On the other hand, the second group of bacteria does not require nutrient limitation for PHA synthesis and can accumulate PHA during its exponential growth phase. Some of the bacteria included in this group are *A. latus*, a mutant strain of *Azotobacter vinelandii*, and recombinant *E. coli* harboring the PHA biosynthetic operon of *C. necator*. Therefore, the simplest approach is to choose renewable, inexpensive, and readily available carbon substrates that could support both the microbial growth and PHA production efficiently (Chee et al., 2010).

6.5.3 Poly (Hydroxybutyrate)

Polyester was produced biotechnologically in 1925; PHB was attentively studied as a biodegradable polyester. PHB is highly crystalline with crystallinity above 50%. Its melting temperature is 180°C. The pure homopolymer is a brittle material. Its glass transition temperature is approximately 55°C. It has some mechanical properties comparable to synthetic degradable polyesters such as PLA. During storage time at room temperature, a secondary crystallization of the amorphous phase occurs. As a result, stress and elongation modulus increase ($E = 1.7$ GPa), while the polymer becomes more brittle and harder. Elongation at break is then much lower (10%). Compared to conventional plastics, it suffers from a narrow processability window (Vroman & Tighzert, 2009).

PHB is susceptible to thermal degradation at temperatures in the region of the melting point. To make the process easier, PHB can be plasticized with citrate ester. PHB is degraded by numerous microorganisms (bacteria, fungi, and algae) in various environments. The hydrolytic degradation yields 3-hydroxy butyric acid, a normal constituent of blood, nevertheless with a relatively low rate. Different monomers have been grafted onto PHB to prepare biodegradable polymers to be used for wastewater treatments. The grafted monomers were either hydrophilic, such as acrylic acid or sodium-p-styrene sulphonate, or hydrophobic, such as styrene or methyl acrylate. The degree of grafting was different according to the monomers, increasing in the following order: styrene, sodium-p-styrene sulfonate, methyl acrylate, and acrylic acid. Multicomponent polymeric systems containing PHB have been obtained in two ways. The first is by radical polymerization of an acrylic polymer in the presence of PHB. The second is by melt mixing PCL with PHB. Peroxide is used in both processes to form intergrafted species responsible for compatibilization. These methods have been considered as reactive blending. It should be noted that apart from the bacterial synthetic method, other chemical ways have been developed for the production of PHB. The ring opening polymerization of β-butyrolactone yields PHB.

PHB serves as an energy storage molecule and accumulates intracellularly as storage granules in microbes. Bacterial samples known for bioplastic producers are *Ralstonia*, *Bacillus*, and *Pseudomonas*. These species were identified by 16S rRNA sequencing. Conditions were extensively optimized by varying the temperature, carbon, nitrogen, and substrate sources for maximal PHB production. Accumulation of PHB in these strains was confirmed by microscopic staining. The phenotypic profiles of these species were subsequently studied using phenotype microarray panels, which allowed the testing of the effect of more than 90 different carbon, nitrogen, sulfur, and phosphorus sources as well as pH on the growth characteristics of these strains (Singh & Parmar, 2011).

6.5.4 Polycaprolactone

Poly-ϵ-caprolactone is a relatively cheap cyclic monomer. A semi-crystalline linear polymer is obtained from ring opening polymerization of ϵ-caprolactone in the presence of tin octoate catalyst (Mochizuki & Hirami, 1997). PCL is soluble in a wide range of solvents. Its glass transition temperature is low, around –60°C, and its melting point is 60–65°C. PCL is a semi-rigid material at room temperature, has a modulus in the range of low-density polyethylene and high-density polyethylene, a low tensile strength of 23 MPa, and a high elongation to break (more than 700%). Thanks to its low Tg, PCL is often used as a compatibilizer or as a soft block in polyurethane formulations. To improve the degradation rate, several copolymers with lactide or glycoside have been prepared (Nair & Laurencin, 2007). PCL is commercially available under the trade names CAPA® (Solvay, Belgium), Tone® (Union Carbide, USA), or Celgreen® (Daicel, Japan) and many others. Possible applications in packaging have been investigated.

6.6 NANOCOMPOSITES FOR ACTIVE FOOD PACKAGING MATERIAL

Silver NPs have been synthesized using starch as a reducing agent (Ayala Valencia et al., 2013). The design and development of nanostructured materials with metallic NPs, such as silver NPs (Ag-NPs), is highly useful to minimize the growth of contaminants by microorganisms. Therefore, there is a rising interest in developing bio-based polymers with antimicrobial activity. SAg-NPs are known to have inhibitory and antimicrobial properties and low toxicity, receiving special attention from the industry. Ag-NPs can also be employed as absorbent pads in food packaging to absorb moisture and fluids exuded from meat and fish, keeping the products looking fresh and creating an aesthetically attractive packaging.

6.7 BIODEGRADATION OF BIOPLASTICS

A large variety of wheat gluten-based bioplastics, which were plasticized with glycerol, were subjected to biodegradation. The biodegradability tests were performed in a liquid medium (modified Sturm test) and in farmland soil. All gluten materials were

fully degraded after 36 days in aerobic fermentation and within 50 days in farmland soil. No significant differences were observed between the samples. The mineralization half-life time of 3.8 days in the modified Sturm test situated gluten materials among the fast-degrading polymers. The tests of microbial inhibition experiments revealed no toxic effects of the modified gluten or of its metabolites. Thus, the protein bulk of wheat gluten materials is nontoxic and fully biodegradable, whatever the technological process applied (Domenek et al., 2004).

Biodegradability tests are of two types: One is screening tests with enzymatic and aquatic versions of aerobic and anaerobic tests on the selected samples. The second one is the real-life test of soil burial, in which composting field testing applies. Bioplastics are degraded by many kinds of microorganisms in nature, and the bioplastics are converted into water and carbon dioxide by microbial metabolism. Nonbiodegradable petrochemical plastics such as PA66, polypropylene, and polyethylene remain in the environment for a long time because the plastics are resistant to the invasion of microorganisms. To analyze the biodegradability of each plastic in nature, three kinds of commercial bioplastics (PBS, PBS-starch, and PLA) and a nonbiodegradable petrochemical plastic (PA66) were buried in an agricultural soil (initial bacterial biomass: 1×109 cells/g soil), and the weight reductions of plastics were analyzed after 28 days, and samples were tested for their biodegradability. The powdered bioplastics were added in soil, and the rate of decrease in soil TC was measured after 28 days. The degradation ratios of PBS-starch, PBS, and PLA after 28 days were 24.4%, 16.8%, and 13.8%, respectively. These bioplastics were degraded faster than the commercial bioplastics. The enhancement of biodegradability of powdered bioplastics in the soil seemed to be caused by the increase in the surface area. The relative biodegradability of each powdered bioplastic was similar to those of the commercial bioplastics.

Therefore, for PLA degradation, microbial attack at a high temperature (such as by thermophilic bacteria under a composting process) might be needed. For the treatment of waste bioplastics in the soil, the biodegradability of each bioplastic should be considered. The degradation rates of bioplastics were proportionate to the bacterial biomass in the soil. Many kinds of bioplastic-degrading bacteria might exist in the soil environments, and a higher number of bioplastic-degrading bacteria seem to exist in soil rich in total bacterial biomass. Since fertile soil is rich in bacterial biomass, bioplastics seemed to be efficiently degraded in fertile soil environments. When bioplastics were buried in soils for 28 days and 2 years, bacterial biomass and diversity were not influenced by the degradation of bioplastics. In the case of using powdered bioplastics, the bacterial biomass did not change either. However, the bacterial biomass decreased when PA66 was buried in soil for two years. The presence of PA66 in the soil might lead to the inhibition of aeration for the well-functioning of microorganisms. Utilization of bioplastics in agricultural fields was expected to increase in the future; thus the influence of bioplastic degradation on material circulation in the agricultural soil should be understood (Adhikari et al., 2016). Nitrogen is an essential nutrient for plant growth; therefore, nitrogen circulation is one of the most important activities for both conventional and organic agriculture. In this study, nitrogen circulation activity in the bioplastic-buried soil

was measured, and a negative effect of PLA degradation on the activity was observed. In addition, the fungal biomass was not increased by the degradation of bioplastics in this experiment; however, studies on the effects of large amounts of buried bioplastics in agricultural fields on the growth of phytopathogens would be necessary for the safe usage of bioplastics. Although the degradation of bioplastics in this study did not affect the bacterial diversity in the soil environment, the degradation rate in the soil was low. New bioplastics having high degradation rates in soil, which are safer and greener for the environmental microorganisms, should be developed in the near future (De Wolf & Isard, 2007).

6.7.1 Biodegradation of Plant-Based Plastics

Starch is composed of two distinct macromolecules: (1) amylose, a linear α-D-glucopyranosyl unit linked with α-1,4 bonds, and (2) amylopectin, a highly branched fraction of α-1,4-linked glucan chains connected by α-1,6 linkages, and it is considered as a major energy reserve for a large variety of green plants (Miao et al., 2015). Starch-based bioplastic is one of the most economic, abundant, and renewable biomaterials widely used for biomedical and disposal purposes. Chemically or physically modified starch-based materials are frequently studied to understand degradation kinetics and drug delivery. In vitro enzymatic degradation by fungal amylase is used to hydrolyze starch films with different molecular, crystalline, and granular types in order to understand the effect of different structures on enzymatic degradation (Li et al., 2015). Degradation of cassava starch-based composite films is investigated using the indoor soil burial method. Increased water sorption promotes the entry of soil microorganisms, and the starch films are utilized as a source of energy for their growth. The loss of matrix components of the films is monitored by the reduction in weight, and the morphology is studied through scanning electron microscopy.

6.8 BIODEGRADATION OF GELATIN

Gelatin is derived from the fibrous insoluble protein called collagen by chemical denaturation and is comprised of three polypeptide chains having a repeating Gly–X–Y sequence (glycine–proline–hydroxyproline) arranged in a triple helix, stabilized through hydrogen and hydrophobic bonds. Changes in pH and temperature or the presence of denaturing chemicals can cause a disruption of the gelatin structure arising from the loss of the triple helix conformation. The processing of gelatin needs to be well controlled to achieve high gelling strength, avoiding the extensive degradation of the peptide structure. The degradiation of gelatin and its composite with MMT by lysozyme and proteinase K has a much faster rate in CPX–gel (ciprofloxacin loaded) as compared to CPX–MMT–gel, or MMT–gel, mainly due to their 3D structures. The CPX–gel degrades rapidly because of the large number of hydrophilic amino and carboxyl groups and the physical structure of the CPX–gel scaffold has a higher porosity and leaner pore walls. Thus, the gelation and biodegradation are the two key factors that affect the cellular behavior and tissue regeneration and ultimately control the in vivo drug delivery.

6.8.1 Biodegradation of Alginate

Alginate, a water-soluble linear polymer obtained from brown algae, is composed of (1-4)-β-D-mannuronic acid (M) and (1-4)-α-L-guluronic acid (G) units in the form of homopolymeric (MM- or GG-blocks) and heteropolymeric sequences (MG- or GM-blocks). The degradation kinetics of alginate are controlled by varying the molecular weight, chemical structure, and crosslinking. The modulation of the degradation rate of alginate gels is done with an oxidation reaction using uronic acid residues by inducing hydrolytically labile acetal-like groups within the alginates. The oxidation of alginate leads to the cleavage of the carbon–carbon bond of the *cis*-diol groups. However, the oxidation makes the gel more malleable, leading to an inverse relation between degradation rate and gel stiffness.

6.9 BIODEGRADATION OF CHITOSON

Chitosan is one of the most important biodegradable and biocompatible polymers, made up of β-(1,4) linked 2-deoxy-2-amino-D-glucopyranose and partially of β-(1,4) linked 2-deoxy-2-acetamido-D-glucopyranose, and is obtained by the alkaline deacetylation of chitin, which is the major component of the exoskeleton in crustaceans. Chitosan is hydrolyzed (chitosanolysis) by specific enzymes (chitinase/chitosanase) and nonspecific enzymes (cellulases, pectinases, papains, lipases). Research isolated the chitinase-producing actinomycete *Streptomyces rimosus* for the biodegradation of chitinous substances. The lysozyme-loaded chitosan films exhibited a ~21% mass loss after 4 weeks of implantation in rats compared to the control that suffered only a 7% mass loss. The degradation products of monomers and oligomers of glucosamine and *N*-acetyl-glucosamine have been detected using capillary electrophoresis–mass spectroscopy.

Guar gum is a polygalactomannan obtained from the seeds of *Cyamopsis tetragonalobus*, found in the northwestern region of India. Guar gum (GG) is a nonionic, water soluble, and biodegradable heteropolysaccharide made up of a β-(1 → 4) D-mannose backbone randomly linked with α-(1 → 6) D-galactose units. The enzymatic hydrolysis of guar gum significantly affects its physico-chemical and rheological characteristics, which become useful for its incorporation in food products as dietary fiber.

Agar is a mixture of heterogeneous galactans, mainly composed of 3,6-anhydro-L-galactoses (or L-galactose-6-sulfates), D-galactoses, and L-galac toses alternately linked by β-(1,4) and α-(1,3) linkages. Many microorganisms that can hydrolyze and metabolize agar as a carbon and energy source have been identified in seawater and marine sediments. Agarolytic microorganisms such as *Saccharophagus degradans* and *Streptomyces coelicolor* commonly produce α-agarase, β-agarase, and β-porphyranase enzymes, which catalyze the hydrolysis of agar. During the photodegradation process, temperature and humidity variations promote a decrease in agar's mechanical properties caused by a reduction in molecular size and a decrease in the number of sulfate groups. These variations alter agar's crystallinity and lead to the formation of microfractures and embrittlement and promote microbial attack (Kumar & Maiti, 2016).

6.10 FOOD PACKAGING COMPOSITES DEGRADATION

Currently, nonbiodegradable plastics are commercially used for the packaging of beverages, biscuits, food, and medicines and in agricultural sectors and are being disposed of without recycling. Therefore, substantial research efforts have been focused on the use of biodegradable plastics to reduce the environmental pollution. PLA has been approved for its intended use in food packaging by the Food and Drug Administration (FDA). PLA-based packaging products for items like water, juice, and yogurt are widely used in the supermarkets of Europe and North America and meet the food standards, maintain aroma and freshness after processing, and are also resistant to microbial stains. Therefore, PLA is gradually moving toward becoming a "green" food packaging material for goods under different trade names such as Biota, Noble, Dannon, and so on (Ahmed & Varshney, 2011). Kale et al. (2006) showed the biodegradation of a PLA bottle in compost media after 30 days of treatment. Danone is the first company in Europe to replace packaging made from polystyrene with PLA for yogurt products. Food-borne diseases have become an increasingly relevant health and safety concern in the food industry. In order to inhibit the growth of unwanted microbes on foods, antimicrobial packaging offers a means to potentially extend the shelf life of perishable foods to maintain quality. Incorporating antimicrobial substances like cinnamaldehyde in poly(lactic acid)/poly (tri-methylene carbonate) (PLA/PTMC) films is to find out better ways to extend the shelf life of foods. Biocompatible and biodegradable ϵ-poly-L-lysine (EPL)/ PCL copolymers are made to self-assemble into monodispersed NPs, which show a broad spectrum of antibacterial activity against *E. coli*, *Staphylococcus aureus*, and *Bacillus subtilis*.

The self-assembled NPs induce changes in the bacterial osmotic pressure, thereby resulting in cell invagination to form holes and create a leakage of cytoplasm. The organically modified MMT (Cloisite 30B) exhibited antimicrobial activity against gram-positive bacteria (*Listeria monocytogenes* and *S. aureus*), presumably due to the quaternary ammonium group present in the modified organoclay, while the natural MMT did not show any such antimicrobial activity. Antimicrobial PCL-based bionanocomposites using quaternary ammonium modified montmorillonites (OMMTs) have been prepared for packaging.

The performance of the composite films against *S. aureus* (gram positive) and *E. coli* (gram negative) has been evaluated from the number density of bacteria in the sample. When 7.5 log cells of *E. coli* O157:H7 were inoculated in orange juice, a significant reduction of 3.5 log units in the *E. coli* cell population was observed after 72 hours when PLA/nisin was used, whereas the control had decreased to about 6 log units. This suggests that nisin incorporation into PLA films was an effective inhibitor of *E. coli* O157:H7 in orange juice at a ratio of 2.08 mL of liquid per square centimeter of exposed polymer surface. An agar diffusion test was investigated to monitor the antimicrobial activity of PLA/nisin films for solid food packaging. The antimicrobial activity of the film was expressed in terms of the inhibition zone. The formation of an inhibition zone around the PLA/nisin film showed its potential for antimicrobial packaging in food applications (Kumar & Maiti, 2016).

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