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Preface

Biodegradable polymers play an essential role in innovative food packaging while causing no harm to the environment. Unfortunately, conventional food packaging necessitates petrochemical-derived polymer as a packaging material, which endangers both the environment and human health. The significant limitations of conventional packaging materials are their non-biodegradability and the release of harmful gases such as dioxin and HCN during disposal. The application of biodegradable packaging material for food products is more prevalent in the European countries, and the USA is owing to its similarity in physicochemical properties with polypropylene-based plastic. However, despite its biodegradability and similarity in physicochemical properties with plastic, bioplastic's rapid usage is restricted due to its high production cost and complex production strategies. Certain biobased polymers are currently being tested for packaging applications in various food commodities. The mechanical and chemical properties of biobased plastic vary depending on its source. The moisture barrier properties, gas permeability, tensile strength, and heat stability of such plastic material determine its commercial acceptability in food packaging industries.

Based on the current scenario, the book *Novel Approaches for the Manufacture of Biodegradable Polymer-Based Food Packaging Materials* is a much-required effort in this series. The book is divided into 16 chapters that focus on novel approaches to the production of biodegradable polymers. Scope and importance of biodegradable polymers, animal, plant, and microbially derived biopolymers, nanocomposite biopolymers, polyhydroxyalkanoates, polylactide in food packaging, enzymes and metabolic engineering involved in biopolymer synthesis, downstream processing strategies, functionality test methods, application of biopolymers in packaging, standards for testing the biodegradability, and future prospects are presented and discussed in detail. The book proposes a new perspective with advancement and long-term solutions to existing gaps in the nanocomposite biopolymer production process and active packaging. This book will also provide a thorough understanding of the factors influencing the stability of biodegradable polymer films. Finally, the book predicted that microbially derived biodegradable polymers would play an

essential role in food packaging in the near future. Hence, this book will serve as an asset for the researcher working in the relevant area, including researchers, scientists, teachers, and students.

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I am grateful to my co-editors, Prof. Dinesh Chandra Rai, Professor and Head, Department of Dairy Science and Food Technology, Institute of Agricultural Sciences, Banaras Hindu University, India, Prof. Kianoush Khosravi Darani, National Nutrition and Food Technology Research Institute of Iran and Ms. Veena Paul, Department of Dairy Science and Food Technology, Institute of Agricultural Sciences, Banaras Hindu University, India, for providing the immense support in compilation of this book. I am thankful to all my authors from India and Iran who contributed different chapters for this book as per their expertise. I am grateful to Springer Nature group for selecting our book proposal and permitting us to complete this task. I am thankful to external reviewers who approved the book proposal after thorough evaluation. I pay my sincere gratitude to our Director and Esteemed Dean for their constant encouragement. I am grateful to my Head of the Department Prof. Dinesh Chandra Rai, Department of Dairy Science and Food Technology, Institute of Agricultural Sciences, Banaras Hindu University, India, for his immense motivation and providing necessary facilities required for compilation of this book. I would like to pay my sincere thanks to my parents Shri Vishnu Dutt Tripathi and Mrs. Urmila Tripathi for their encouragement and support. I would like to pay my sincere thanks to my beloved wife Mrs. Priyanka Upadhyay and my kids Master Ojas and Baby Prajul for their kind support and cooperation. Lastly, I am thankful to almighty who blessed me to complete this task.

Contents

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Introduction: Scope and Importance of Biodegradable Polymers

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Veena Paul, Abhishek Dutt Tripathi, Kamlesh Kumar Maurya, Pankaj, Dinesh, and Chandra Rai

Abstract

In today's world, the interest in biodegradable polymers has grown significantly. The demand for these polymers has skyrocketed, making them broadly utilized polymers with a range of several applications. Plant, animal, and microbially derived biopolymers have piqued the interest of researchers. Because of their inherent properties like biodegradability, biocompatibility, inexhaustibility, and economic availability, the need for biodegradable polymers has been enhanced. Recent trends in the food packaging industry have shown the employment of biodegradable polymers with improved characteristics. This chapter emphasizes biodegradable polymers' development, classification, application, challenges, and market opportunities. The application of these polymers in active and intelligent packaging are summarized. This chapter also highlights the application of biodegradable polymers as an assuring green technique for assuring the quality and safety of food.

Keywords

Biodegradable polymers · Food packaging · PHA · PLA · Bacterial cellulose · Biocomposites

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1.1 Introduction

Excessive use of plastics and their aggregation in the natural environment as a stubborn source of pollution have put life on earth in jeopardy (Geyer et al. 2017). About 30% of plastics are consumed as packages, and about 47% are biodegradable polymers. Remarkably, about 75% of biodegradable polymers are employed as packaging material in the food sector (European bio-plastics 2020). The crucial role of these polymers is to protect the product from harmful effects caused by microbiological contamination, chemical damage, and mechanical impact. The packaging material serves many benefits. It acts as a barrier against physical damage and environmental contamination, and it protects the food commodity from damage by any other external factors. It ensures quality and safe food with enhanced shelf-life (Cazón and Vázquez 2020). Food packaging is used in the manufacturing, preservation, storage, distribution, and preparation of food. Thus, to maintain the characteristics of food products, the choice of packaging material is essential (Ivonkovic et al. 2017).

According to current research studies, the European Union used 1,130,000 million food packaging materials in 2018. Consumption of packaging material has resulted in the generation of waste in a large amount. In 2013, data showed that the European Union generated 156.9 kg of waste from the packaging industry per inhabitant. It is likely to rise at a 4.2% annual rate in the coming years. The most common packages used in the food sector are polypropylene, high, low, and very-low-density polyethylene, polyvinyl chloride, polystyrene, and polyethylene terephthalate. These packages contribute to roughly 90% of total plastic production. These packages are economical with exceptional characteristics. However, they are nonbiodegradable and have numerous constraints. The waste management of synthetic polymers poses a severe environmental threat (Cazón and Vázquez 2020).

Presently, the need for biodegradable polymers has been extended worldwide as a potential packaging material. Nevertheless, biodegradable polymers in the food packaging sector are limited because of expensive production costs. This can be overcome by employing the production of naturally derived polymers. These are either plant-based, animal-based, or microorganism-based. Biodegradable polymers derived from natural resources can be used as novel packaging material in the food sector. Eco-friendly biodegradable packaging is expected to impact food product quality and market in the future significantly. Polysaccharides and proteins are the most diverse biopolymers used as films in the food packaging sector. These are naturally derived from renewable sources like plants, animals, or microorganisms. The commonly used polysaccharides in biodegradable packaging are alginate, carrageenan, chitosan, cellulose, and its derivatives, pullulan, and starch. Casein, gelatin, gluten, whey, soybean proteins, zein, and keratin are all proteins. Presently, biodegradable polymers of renewable origins cannot entirely substitute synthetic polymer from the food packaging market. However, they may partly serve as a significant stress factor. These polymers enable humidity control, exchanges of gases (internally and externally), compound migration, and undesirable aromas.

Furthermore, they can sustain and deliver antimicrobial or antioxidant agents into the food matrix (Cazón and Vázquez 2020).

This chapter aims to discuss the development and classification of biodegradable polymers for packaging in harmony with nature. Further, their application in the food industry and challenges and market opportunities are discussed.

1.2 Development of Biodegradable Polymers

Today, at the dawn of the twenty-first century, products derived from renewable sources are valued for environmental friendliness. In general, consumers worldwide are becoming more aware of biodegradable polymers. Due to the continuous buildup of synthetic polymers, there is a decline in arable lands, oil wells, and the gases released while burning waste has urged the fabrication of biodegradable polymers to be used as a packaging material (Ivonkovic et al. 2017).

1.3 Classification of Biodegradable Polymers

Based on different criteria, biodegradable polymers are classified (Fig. 1.1). As described by European Bioplastics, biodegradable polymers are either biologically derived or biodegradable or both (Rai et al. 2021). They can be categorized as biodegradable and nonbiodegradable. Despite being derived from natural sources, not all biodegradable polymers are biodegradable. Their pathway and rate of degradation determine the biodegradability of polymers. Biodegradable polymers such as polyhydroxyalkanoate (PHA), starch, cellulose, polylactic acid (PLA), and their derivatives are used to make biodegradable polymers. Biodegradable biopolymers, like traditional fossil-based polymers, can be recycled. Instead, they can be degraded by microorganisms, thus, creating a zero-waste model (Rai et al. 2021).

Under natural or stimulated conditions, biodegradable polymers decompose from microbial enzymatic action into CO_2, H_2O, and inorganic compounds. However, comparing biodegradability is challenging because of the various standards, degradation processes, and circumstances used to evaluate polymer's degradation rate. The test duration is an essential parameter in these standard methods for determining biodegradation. In wastewater, the biodegradation tests are for not more than half of a year, but on the contrary, in marine water, the biodegradation tests require about 2 years (Sanchez-Salvador et al. 2021).

At present, out of the total plastic production (335 million tonnes), not more than 0.3% (0.91 million tonnes) are biodegradable plastics. PLA, polybutylene adipate terephthalate (PBAT), and starch blends are commonly fabricated biopolymers, accounting for 24%, 42%, and 17% of total production (European Bio-plastics 2020). Based on origin, biodegradable polymers can be categorized into four parts (Fig. 1.2).

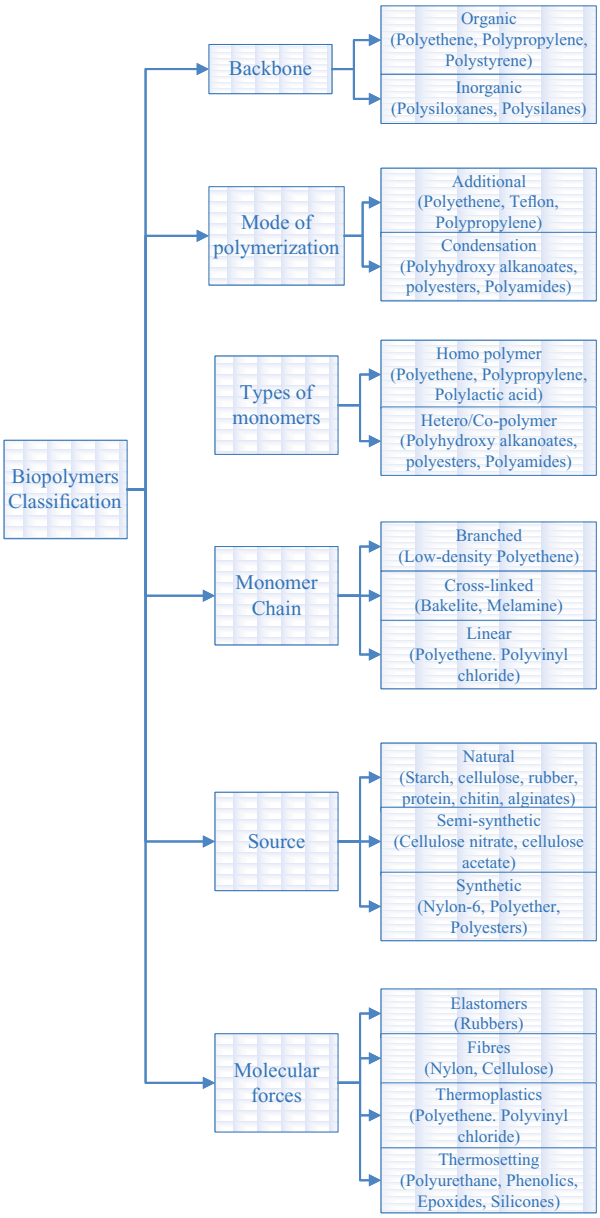

Fig. 1.1 Different criteria for the classification of Biodegradable polymers

1.3.1 Agro-based Biopolymers

The agro-waste like sugarcane bagasse, banana peels, corn stalks, wheat straw, and jute can be valorized to produce biodegradable polymers (Fig. 1.2). Initially, the

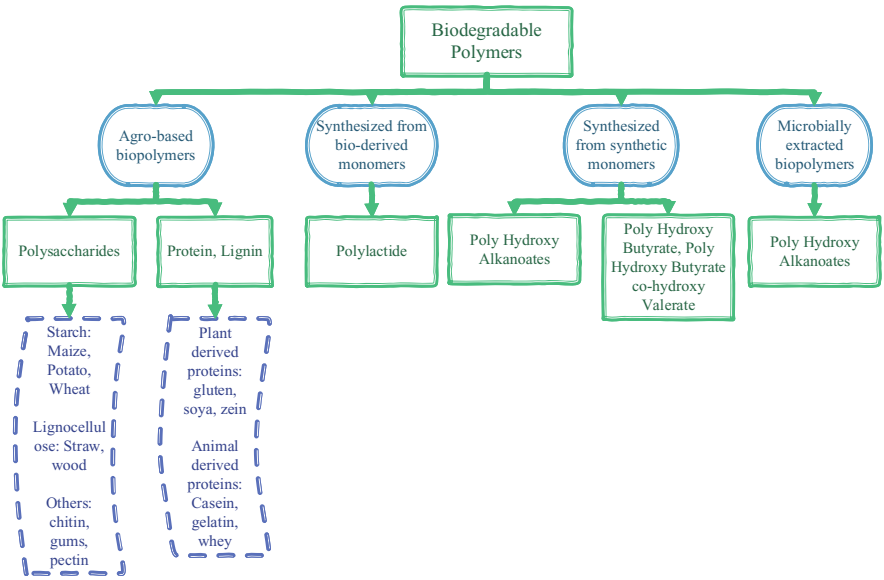

Fig. 1.2 Classification of biopolymers (origin-based)

substrate (agro-waste) conversion into functional biopolymer occurs via microbial breakdown of the substrate under favorable growth conditions (Rai et al. 2021).

Biopolymers derived from agro-waste consist of polysaccharides and proteins. Polysaccharides, also known as complex carbohydrates, are found in the essential structural parts of a plant or animal's exoskeleton, such as cellulose and chitin, generated by glycosidic linkages. On the other hand, protein macromolecules are fabricated of amino acids associated with peptide bonds. Each type of protein is distinguished by its amino acid composition (Sanchez-Salvador et al. 2021).

Starch, a natural ingredient that consists of amylopectin and amylose. The amylopectin ratio to amylose impacts the functionality and other properties of starch-based products. A high level of amylose increases film strength; nevertheless, amylopectin forms a film with low strength due to branched structure. The strength of polymers can be enhanced by employing plasticizers (Rai et al. 2021). Commercially starch is abundantly obtained from potatoes, rice, etc. (Amulya et al. 2021). Starch-based biopolymers are a suitable substitute for commercial packaging applications as they are obtained from renewable sources and have higher biodegradability and oxygen barrier property. Mater-Bi (MB™), a Novamont product, is comprised of starch and starch mixes (60%) and hydrophilic (40%) blends. About 26% of MB™ degrades under aerobic conditions within 3 months. This biodegradable polymer degrades completely in aerobic sludge in 100 days. MB™ produces methane and CO_2 under anaerobic conditions (Mohee et al. 2008). Table 1.1 shows the biodegradability rate of various biodegradable polymers.

Gómez and Michel Jr (2013) studied the blend of starch and PLA. They observed the conversion rate of starch-PLA bled under aerobic and anaerobic conditions.

Table 1.1 Biodegradability rate of various biopolymers

Types of biopolymers	It can be degraded in	Biodegradability rate		References
		(Days)	(%)	
Mater-Bi™	Marine water	236	68.9	Tosin et al. (2012)
Cellulose acetate	Municipal wastewater	12	44	Mostafa et al. (2018)
Polylactic acid	Municipal wastewater	28	39	Lambert and Wagner (2017)
Polyhydroxyalkanoate	Soil	60	35	Torres et al. (2019)
Polyhydroxybutyrate	Sea water	14	80	Rai et al. (2021)

Under aerobic conditions, the blend with 65% moisture composted to 51% in 4 months, whereas under the anaerobic situation, the same blend composted to 50% in 85 days (Gómez and Michel Jr 2013). These studies show that biopolymeric blends will likely replace synthetic polymers and can be a low-waste-generating alternative in the future.

Agro-waste, a cheaper substrate for industrial-scale production of polymers. Cellulose is obtained naturally in cotton linter, corn, wheat, paddy, and barley husk and stalk as a by-product (Rai et al. 2021). Due to its partial solubility in water, it cannot be used directly. However, it can be blended with plasticizers to suit various applications (Amulya et al. 2021). Cellulose has been used to make cellophane films widely used in packaging (Rai et al. 2021).

1.3.2 Bio-derived Monomer-Synthesized Biopolymers

Bio-derived monomers are derived from renewable sources. These monomers lessen carbon emissions. PLA, derived from lactic acid monomer from starch/sugar fermentation, is commercially used. It has improved mechanical properties and is broadly used for packaging with a short shelf life (Sanchez-Salvador et al. 2021). PLA is a viable choice in the packaging market (Amulya et al. 2021). PLA is created by polymerizing the enantiomers D-lactic Acid (PDLA) and L-lactic acid (PLLA). PLA can be made from both natural and synthetic processes. The natural renewable process is favored because it has less influence on the environment. The physical properties of PLA can be determined by the PDLA/PLLA ratio used during polymerization (Rai et al. 2021).

Because of its transparency, PLA has gained widespread acceptance in the packaging industry. Techniques like block polymerization/grafting and physical blending improve the physical properties of PLA. PLA biopolymers, both in their pure form and with additives such as starch, softwood, and sisal fibers, have been able to degrade (>50%) within 3 months when composted (Table 1.1). Due to their low carbon footprint and compatibility, such polymers are useful in the agricultural sector (Rai et al. 2021).

Poly(glycolic acid) (PGA) derived from sugar cane have a similar chemical structure as PLA, but their degradation rate is higher. Moreover, the copolymerization of PGA and PLA results in a linear poly(lactic-co-glycolic) acid (PLGA) polymer fabrication with improved physical and mechanical properties (Sanchez-Salvador et al. 2021). However, PGA has only been manufactured on a small scale and for medical use because of the expensive production process.

1.3.3 Biopolymers Synthesized from Synthetic Monomers

Polymers derived from synthetic monomers, like petroleum resources, have hydrolyzable groups such as esters, amides, urethanes, or biodegradable backbones such as polyesters and polyamides polyurethanes, polyanhydrides, or polycarbonates (Sanchez-Salvador et al. 2021). Table 1.2 illustrates the properties of commercially used biopolymers.

Poly(butylene adipate-co-terephthalate) (PBAT) is made from a synthetic monomer formed by polycondensing 1,4-butanediol with adipic and terephthalic acids. Because of its biodegradability, thermal, and mechanical properties, PBAT is regarded as one of the most appealing biodegradable polymers (Ferreira et al. 2019).

1.3.4 Microbially Extracted Biopolymers

Natural polyesters such as PLA, PHA, and PHB have been isolated by microbial degradation (Rai et al. 2021). Two types of biopolymers are derived from microorganisms. The first type consists of a class of natural biodegradable polyesters known as polyhydroxyalkanoates (PHAs). Microbially synthesized PHAs are highly crystalline and optically active compounds. PHAs have several applications due to improved physical and mechanical properties. At the same time, its application is restricted due to limited thermal property (Sanchez-Salvador et al. 2021). There is a majority of commercial PHAs. Poly-3-hydroxybutyrate (PHB) was the first commercial PHA discovered in 1925. Following PHB, poly(3-hydroxybutyrate-co-3-

Table 1.2 General properties of biodegradable polymers commercially used

Biodegradable polymers	Properties				
	Elongation at break (%)	Glass transition temperature (°C)	Melting temperature (°C)	Tensile strength (GPa)	Young's modulus (GPa)
PHB	5	–	177	43	–
PLA	<5	64	173–178	50	350–3500
PCL	–	−60	58–63	–	–
PBAT	>600	−30	110–120	32–36	20–60
PBS	230	−32	114	42	690
BC	–	–	–	200–300	2000

hydroxyvalerate) (PHBV) demonstrated reduced crystallinity with improved flexibility. Novel PHA polymers, such as poly(3-hydroxybutyrate-co-4-hydroxybutyrate) (P3HB4HB), poly(3-hydroxy octanoate) (PHO), and poly (3-hydroxybutyrate-co-3-hydroxyhexanoate) (PHBHHx), have recently been developed using novel fermentation technology in association with metabolic engineering (Ke et al. 2017).

PHAs produced from bacterial fermentation have elastomeric properties (Mor et al. 2021). PHAs, as microbial-produced biopolymers, can be used in the packaging sector because of their high gas permeability and water barrier properties (Tripathi et al. 2021). Many microorganisms produce PHAs by utilizing lipids or sugars extracted from various agro-waste (Mor et al. 2021). After interfusing within this family, no less than 100 monomers are identified, resulting in materials with a wide range of properties. PHA polymer is classified into three types based on its properties and applications: pure PHA, PHB, and PHBV. Agricultural products obtained from oilseed crops and sugar crops aid PHA production. PHA typically accumulate intracellularly in granules accounting for approximately 90% of the cellular mass (Kabasci 2020). As a result, the production of pure PHA is restricted. PHA fabrication is typically 20–80% more expensive than conventional polymers because of increased production costs. The lack of transparency and low production volumes of PHA polymers are disadvantages. Inorganic nanofillers (like montmorillonite) may enhance the thermal stability of PHA (Khosravi-Darani and Bucci 2015). PHA exhibits good thermo-mechanical properties, similar to plastics; thus, it may replace PE and PP. PHAs are used as bio-additives. Recently, PHAs has been used as mulched films.

PHA microbial production using glucose generally produces PHB and PHV. PHB polymer is mainly biodegradable and biocompatible, ideal for various industrial, medical, and agricultural applications (Amulya et al. 2021). PHB differs from other biodegradable polymers based on their physical properties (water insolubility and hydrolytic degradation resistance), thermal stability, and biodegradability with no residue (Adeleye et al. 2020).

PHB is fabricated by bacteria like *Alcaligenes eutrophus*, *Cupriavidus necator*, and *Bacillus megaterium* (Yaradoddi et al. 2019). During the PHB extraction, initially, two molecules of acetyl-CoA condense and form acetoacetyl-CoA. Further, this molecule reduces and forms hydroxybutyryl-CoA. Then, this reduced molecule generates PHB. The produced PHB possess increased crystallinity and thermal properties than PHA. PHB-PLA blends possess improved properties than PLA polymers. A study on PHB-PLA blends was reported to have enhanced barrier properties. Nanoclay and PHB increase the thermo-mechanical properties (Helanto et al. 2019).

The bacterial cellulose (BC), produced through the microbial fermentation of *Achromobacter*, *Aerobacter*, *Agrobacterium*, *Alcaligen*, *Azotobacter*, *Escherichia*, *Komagataeibacter*, *Zoogloea*, *Pseudomonas*, *Rhizobium*, *Salmonella*, and *Sarcina*. BC is a gel-like, swollen, flexible membrane produced through biosynthesis. BC has gained interest as an excellent antibacterial agent because of its purity, exemplary nanofibrils network, and improved tensile strength and water holding capacity

(Sanchez-Salvador et al. 2021). During BC production, additional pretreatments are not necessary for removing lignin, pectin, and hemicellulose compared to other plant-based polymers requiring chemical pretreatments to expel the abovementioned substances. The BC is extracted through the bottom-up method. These polymers are biocompatible and possess high molecular weight, high water retaining capacity (>90%), and high crystallinity (80–90%) compared to plant-based polymers (Zinge and Kandasubramanian 2020).

Algal polymers have recently become popular due to their improved photosynthetic efficiency. The algal biomass is a sustainable source for biopolymer extraction. The algal polymers can be obtained as algal biomass and plasticizer blends. Chlorella has been primarily used in blends (Rai et al. 2021). *Spirulina* sp. has also been used to make blended polymers. The blending properties of *Spirulina*-based polymers differ from those of *Chlorella*-based polymers due to differences in their amino acid content (Cinar et al. 2020).

1.4 Biocomposites

Aside from the methods mentioned above, producing biocomposites using natural fibers has improved their physicochemical properties (Wu et al. 2020). Biocomposites are typically created by blending a natural ingredient with a biopolymer to fabricate a hybrid polymer that combines both individual component properties. Their applications can explain the increasing trend in the biopolymer market. Biocomposites are made up of a stiff and high-strength polymer matrix that serves as reinforcement. It protects the reinforcement from environmental degradation.

Synthetic polymers (like PE, PP, and polyethylene) are commonly used as matrix materials. Moreover, with the increased requirement of biopolymers, studies have been directed towards more renewable sources (Amulya et al. 2021). As a result, natural fibers and biological particles are widely used to reinforce composite preparation (Wu et al. 2020). The polymers with improved stiffness and thermal stability have been selected for reinforcement.

1.5 Biodegradable Polymer Application in the Food Sector

Biopolymers have been used as a food packaging material as cutleries, wrap, containers, and films in the food industry. Recently, polymers acquired from inexhaustible assets that can be reused and treated the soil have earned expanding consideration. The properties of biopolymers can be improved by employing polymer engineering to replace the synthetic packages used in the food industry. Polymers like PHBV have been used as a food wrap. The production cost of PHBV wrap is higher, but it degrades in active microbiological conditions in 5–6 weeks. Auras et al. (2006) created a polyethylene terephthalate and polystyrene blend for new food packaging applications.

1.6 Challenges and Market Opportunities

With the rise of ready-to-eat food, food packaging has become a significant portion of the packaging market, with global sales expected to reach USD 411.3 billion by 2025 (Grand View Research 2020). Despite the research and development approach for biopolymers, only a few biopolymers can match the market demand for food packaging material. Likewise, the market drifts show that the Asia-Pacific region is relied upon to have the quickest development because of the simple accessibility and minimal expense of crude material needed to produce bioplastics.

In 2020, 1.2 million tonnes of biopolymers were produced globally, out of which approximately 18.7% of biopolymers were PLA and starch blends. Packaging industries utilized almost 47% of the produced biopolymers. Novamont's Mater-Bi (MB™), Bio-on's Minerv-PHA™, and Mitsubishi Chemica's GS PLA® produce biopolymers for food packaging and other applications (Rai et al. 2021).

1.7 Conclusion and Future Prospective

All around the world, plastic reusing is quantitatively insufficient for ecological manageability. The waste valorization and biopolymer fabrication using agro-waste will be a step toward sustainable development to reduce carbon footprint.

Biopolymers with improved physical and thermomechanical properties are a sustainable and green approach to replace plastics. Bioplastics are ideal and are more liked over conventional petro inferred plastics than their eco-accommodating nature. The present significant concern is the contamination caused to nature by these nondegradable plastics. They have wide application in the clinical, horticultural, and packaging industry fields. Unlike manufactured plastics, they produce no profluent to the encompassing nature and are henceforth more secure to utilize. The fundamental issue in synthetic plastic is the absence of a waste administration framework that has been an incredible danger to humankind since a long time ago. These all perspectives lead to innovative work in the area of bioplastics.

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Plant-Derived Biopolymers in Food Packaging: Current Status and Market Potential

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Abstract

Plant-based biopolymers show many advantages as biofilms and coatings for food packaging purposes; however, the current commercial technologies mostly employ synthetic polymers and plastics to achieve proper mechanical and barrier properties, which have been proved to have a negative impact on packaging sustainability, lack of biocompatibility and biodegradability, and poor recyclability. Therefore, attempts to employ natural and plant-based biopolymers as packaging materials have increased considerably. In order to meet the requirements, plant-based biopolymers must be functionalized and/or incorporate into a matrix as an additive to improve the ultimate physical and chemical properties of the packaging matrix. Here, we reviewed essential information about biomaterials extracted from plant sources, such as starch, cellulose, gums, pectin, wheat gluten, soy protein, and zein, regarding the use of such biopolymers in the food packaging area.

Keywords

Plant-based biopolymers · Starch · Cellulose · Gums · Pectin · Wheat gluten · Soy protein · Zein

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2.1 Introduction

The food packaging industry has been associated with plastic materials due to their excellent barrier and low cost. However, there are ecological concerns on their detrimental effects such as emission of greenhouse gases, generation of high amounts of wastes deposited in landfills, and using up valuable nonrenewable petroleum products (Kumar et al. 2017). Biopolymeric materials could be a potential alternative to conventional packaging materials due to their excellent capabilities to reduce environmental problems, as well as inhibiting moisture loss, oxygen penetration, water absorption, solute transport, and also showing excellent biocompatibility and biodegradability (Aider 2010; Siracusa et al. 2008). Therefore, developing biopolymer films has been exploited increasingly over the last two decades. Based on various sources of extraction, biopolymers can be classified into plant- and animal-derived compounds. The increased demand for food quality and safety in the food industry has resulted in films formed by plant-based polymers (Kanmani and Rhim 2014). Plant-based biopolymers possess antioxidant and antimicrobial properties and usually result in modified physicochemical and mechanical characteristics of packaging material. Therefore, they can promote shelf life and durability of the packaged product. Plant-derived biopolymers can be extracted from different sources including seeds, leaves, and fruits (Mir et al. 2018). Due to the abundant plant species (approximately 300,000) and the growing reliance of human civilizations on plant extracts, the available plant-based polymers for food applications have rapidly increased throughout the centuries (Joppa et al. 2011; Alvarez 2014).

Plant polysaccharide-based polymers such as starch (Nogueira et al. 2018), cellulose (Zhao et al. 2019), gums (Cao and Bin Song 2020), pectin (Brito et al. 2019; Vaziri et al. 2019), and plant protein-based polymers such as wheat gluten (Sartori et al. 2018), soy protein (Zhao et al. 2016), and zein (Padua and Wang 2002) are promising plant-derived biopolymers for food packaging industry. Starch is one of the most favorable biopolymers due to its high availability and low cost and has been extensively used for food bio-packaging applications. Starch and its derivatives exhibit attractive properties such as moisture and air barrier, edibility, biodegradability, heat-sealing capacity, and safety (Shah et al. 2015). There are several kinds of sources for starch extraction like potato, corn, rice, cassava, and tapioca. It can be utilized as a thermoplastic matrix or a co-constituents with other commercial thermoplastics by destruction of its granular structure in the presence of chemical agents, heat, or pressure (Rouilly and Rigal 2002). Furthermore, starch has been used as a filler in small amounts (6–30%) to increase the biodegradability of the synthetic product (Bagheri 1999). Cellulose is the amplest natural polymer mainly found in wood. As cellulose is highly fibrous, crystalline, and insoluble in water, it cannot be used in its native form (Nechita and Iana-Roman 2020). Alternatively, cellulose derivatives such as cellulose acetate, ethylcellulose, methylcellulose, and hydroxyethyl cellulose are able to form edible films and are commercially available (Tang et al. 2012). Several researches resulted in higher biodegradability of synthetic plastics with cellulose fibers (Mwaikambo 2006). Gums are another group of

polysaccharides, naturally produced by some trees, seeds, shrubs, and tubers, that can be used as film forming agents in food packaging industry (Nejatian et al. 2020). Pectin is an anionic heterogeneous branched polysaccharide that mainly composed of methoxy esterified α, d-1, 4-galacturonic acid units (Lochhead 2017). Pectin is able to form biodegradable edible films and also generate matrixes in the presence of calcium ions. As pectin is widely accessible from agro-waste materials and can easily be modified by demethylation, it is considerably attended in the food packaging industry (Krochta and De Mulder-Johnston 1997).

Wheat gluten is a complex water-insoluble protein obtained from wheat flour. The major components of wheat gluten are gliadins (soluble prolamins) and glutenins (glutelins) with incorporation of small amounts of starch, wheat oils, and insoluble hemicellulose (Pallos et al. 2006). Gluten-based films represent low oxygen permeability level and high carbon oxide permeability level, so they could be advantageously used for improving the shelf life of food products (Giacalone and Chiabrando 2013; Muratore et al. 2005). Soy proteins are mainly consisting of two globulin fractions, β-conglycinin (7S, ~35%) and glycinin (11S, ~52%). Among plant-based protein sources, soy proteins are the most widespread ones, and due to their low oxygen permeability, they are suitable for packaging applications (Rouilly and Rigal 2002). Zein films have lower water vapor permeability and higher oxygen permeability compared to wheat gluten. However, their tensile strength is comparative to that of wheat gluten matrixes (Tang et al. 2012). Corn zein represent unique solubility in alcohol and form film matrixes by involving four steps, including dissolving into ethanol or isopropanol solutions, heating, cooling, and casting on a petri dish (Tang et al. 2012). Many strategies such as utilization of cross-linkers and incorporation of lipids have been used to reinforce zein-based films. Plant-based biopolymers have gained interest due to their potential influence on the functional properties of biofilms.

In this chapter we cover essential information about plant-derived biopolymers as green sources of biopolymers for food packaging industry, notably their origin, structural, and physical, functional, mechanical, antioxidant, and antimicrobial properties. Furthermore, the present status and future market about the potential of plant-based biofilms and bio-coatings in food packaging industry will be discussed.

2.2 Plant-Based Biopolymers in Food Packaging Industry

Plastics, as common traditional packaging materials, have been applied in the food packaging industry from a long time ago. Although they may provide several desirable characteristics like transparency, stiffness, good mechanical performance, heat sealability, good barrier to carbon dioxide, oxygen, and aroma compounds, several ecological and waste disposal challenges have restricted their use in recent years. The process of recycling of these materials is also expensive and impractical, due to the presence of various contaminants and their nondegradability properties (Siracusa et al. 2008). According to the global ecological awareness, reducing conventional packaging materials, including plastics, metal, glass, paper, and

paperboard, is needed. Accordingly, development of bio-based polymers, as a major alternative to produce bioactive and biodegradable films, has become a central focus of food packaging efforts. Plant-derived biopolymers, which include polysaccharides and proteins, are potentially applied to fabricate environmentally sustainable coatings and films to extend the shelf life of ingredients and food products. In addition, they can promote the value of these products by offering antibacterial, antioxidant, and discoloration properties (Brito et al. 2019). Besides, the substantial volume of food wastes produced mainly from fruits and vegetables during the manufacturing of beverages and other processed foods can be used to produce different compounds. These residues are mainly fruit layers and vegetable ends, which are often discarded during processing stages. However, valuable bioactive compounds and biopolymers can be extracted from these residues (Ayala-Zavala et al. 2010; Andrade et al. 2014). The scientific community has been focused on retrieving the bioactive molecule contents from food residues and developing new and sustainable strategies to minimize the waste, as well as to extend the shelf life of the packaged food products. Therefore, exploring valuable sources of biomaterials from plant residues and potential strategies to extract them is of paramount importance (Fai et al. 2016). Various polysaccharides and proteins derived from plant sources have been reported as low-cost and widely available biopolymers, which exhibit desirable biocompatibility, biodegradability, emulsifying capabilities, and film-forming capacities (Dehghani et al. 2018). It is also becoming increasingly important to utilized these biopolymers to contribute in synthetic packaging materials such as petrochemical-based plastics, namely, polyvinylchloride (PVC), polyethylene terephthalate (PET), polyamide (PA), polystyrene (PS), and polypropylene (PP), to improve the functional properties of the final product and to obtain biodegradable and eco-friendly compounds (Siracusa et al. 2008). Bioplastics with the highest proportion of renewable biopolymers and additives are gaining much attention in the field of food packaging. The performance of these biopolymer-based compounds strictly depends on their physical and functional properties during their interaction with the food for maintaining their quality and safety. In this regard, obvious understanding and recognition of physical, mechanical, and barrier properties and compatibility with the food is important for their potential incorporation. In particular, plant extracts present as one of the most promising natural biopolymers, as they not only modify physicochemical properties of packaging materials but also act as an antioxidant and antimicrobial agent to enhance their overall functions (Bifani et al. 2007). The plant-based biopolymers are extracted from various sources such as leaves, fruits, and seeds. The incorporation of grape fruit seed extract into carrageenan films (Kanmani and Rhim 2014), tea extract into chitosan films (Peng et al. 2013), beetroot and carrot extract into hydroxypropyl methylcellulose films (Akhtar et al. 2012), and raspberry extract into soy protein films (Wang et al. 2012) is one of the examples of plant-based film enrichment. The incorporation of plant-based materials to food packaging films has led to generous desirable properties. The properties of films are influenced by the individual compounds that made them, so the type and concentration of each compound affect the ultimate techno-functional properties. Basically, the physical and chemical

interactions within these compounds determine the structural and functional characteristics of the film (Silva-Weiss et al. 2013). These characteristics include thickness, color, mechanical and tensile strength, solubility, water vapor and oxygen permeability, and antimicrobial and antioxidant properties. Thickness is a vital parameter in techno-functional modification of biodegradable films, which influences the shelf life of the packaged food. Several studies have exploited the positive impact of plant extracts incorporation into biofilms on their thickness. The addition of tea extracts has been purported to increase the thickness of film by the formation of strong interaction occurring in the composite film matrix (Peng et al. 2013). Blend of mango kernel extracts within edible films has been enquired, and the results showed an increased thickness in film compared to the control one (Maryam Adilah et al. 2018). Grape fruit seed extract has been utilized for thickness improvement of agarose-based films due to their high phenolic constituents that form linkages with hydrogen bonds (Lim et al. 2010). In another study, incorporation of grape fruit seed extract in carrageenan-based films resulted in thickness increase with increasing the concentration of extract (Kanmani and Rhim 2014). The presence of phenolic compounds in plant extracts can also modify the original color of films. This alteration strongly depends on the concentration and origin of extracts. Another study revealed that the incorporation of thyme extract in chitosan-starch biocomposite films increased more reddish color due to the formation of strong interactions between amine groups of chitosan molecules and hydroxyl groups of polyphenols (Talón et al. 2017). The effect of murta fruit extract and mango peels extract incorporation into methyl cellulose film and fish gelatin film were investigated and resulted in yellowish increasing (Maryam Adilah et al. 2018; López de Dicastillo et al. 2016). Transparency of films is another essential parameter for food packaging material in order to fulfill the consumer's willingness to observe the product through packaging. At the same time, they should provide an adequate barrier to light to protect the light and UV-sensitive compounds from degradation. Plant extracts offer protection against adverse effects of UV radiations by their intrinsic opacity properties, and thus the addition of plant extracts in packaging films results in less degradability rates. As an example, films of tuna gelatin containing the murta ecotypes leaves extracts revealed better light protection properties (Gómez-Guillén et al. 2007). Chitosan and polyvinyl alcohol films enriched with extracts of mint/pomegranate peel displayed lower transmittance and better barrier properties to UV light compared to the control ones. The incorporation of plant extracts reduced the transparency, whereas, in films with greater contents of polyvinyl alcohol, the opacity values further reduced and film was more transparent (Kanatt et al. 2012). Similar results were observed in carrageenan-grape fruit seed extract composite. The absorption at wavelength of 270–280 nm and transmittance at wavelength of 280 nm in the UV region and 660 nm in the visible light region was measured. Carrageenan film supplemented with grape fruit seed extract exhibited absorption peaks, while the control film without plant extract did not show any absorption peak. This could be attributed to the high content of polyphenolic compounds which are present in most natural extracts. Polyphenolic compounds involve in the light absorption at lower wavelengths. In contrast, the transmittance

value of the control film was substantially higher than the composite film, and it decreased by the addition of plant extract content. Therefore, the carrageenan/fruit seed extract composite film can be applied as a potent biocomposite packaging material with excellent UV barrier and high transparency properties (Kanmani and Rhim 2014). Another study incorporated ginseng extract into alginate films to investigate the effect of plant extract treated films on the transparency and protection against UV light. At 280 nm, the blended film showed very low transmission in UV light compared to the control film (Norajit et al. 2010), which could delay in lipid oxidation caused by UV light exposure. Gingko leaf extract was blended with gelatin to form a plant-based biofilm. Similar results were obtained after spectroscopic scanning of the samples. Light transmission decreased by the addition of gingko leaf extract, mainly due to the presence of flavonoids and ginkgo lactone contents in the gingko leaf extract. In case of incorporating green tea extract, grape seed extract, and gingko leaf extract into gelatin film, an increase in opacity occurred, which showed higher light barrier properties (Wang et al. 2014).

Natural polymers consisting of plant extracts usually lack adequate mechanical and tensile strength. In order to prevent failure, mechanical behavior of the composite film should be precisely determined. The type and nature of plant-based polymers have significant influences on mechanical properties of the biocomposite films. Elongation at break and tensile strength are the two important properties that are related to film chemical composition, storage time, temperature, and film's resistance properties (Gurgel et al. 2011). Generally, plant extracts have been shown to improve the mechanical properties of the films due to the presence of polyphenols, which interact with natural polymer chains such as starch, protein, and lipid and act as a cross-linking agent. Table 2.1 reveals some of the recent studies on plant extracts incorporation into biopolymers and their effects on the resultant biofilm with regard to water vapor permeability (WVP), tensile strength (TS), thickness (T), and elongation at break (EB). The interactions between plant extracts and biopolymers modify the structure and techno-functional properties of biofilms such as color, thickness, solubility, water and oxygen permeability, mechanical properties, antioxidant, and antimicrobial properties.

The mechanical properties of soy protein isolate and fish gelatin films significantly increased when mango kernel extracts were added to the film (Adilah et al. 2018). The effect of fish gelatin incorporation on cross-linking degree was superior as compared to soy protein, because the linear structure of fish gelatin is more suitable to interact with phenolic compounds than the globular structure of soy protein. Besides, fish gelatin is capable to form a stronger network after solubility, simply by reassembling triple helix structures (Tulamandi et al. 2016). On the other hand, several studies revealed lower mechanical properties of plant-based films, especially those based on fruit residues (Il Park and Zhao 2006; Martelli et al. 2013). Accordingly, it is necessary to explore new reinforcing materials and potential strategies to extract and prepare these materials to feasibly overcome this obstacle.

Despite the wide application of plasticizers in commercial purposes, they are not able to fully adhere to other matrix components, thus resulting in poor integration. Bionanocomposites are a new category of materials that are considered as a

Table 2.1 Recent studies for biopolymers modifications based the incorporation of plant extracts for food packaging applications

Plant extract	Biopolymer	WVP	TS (MPa)	T (μm)	EB (%)	References
Mango kemel	Soy protein isolate	7.93–8.78	1.82–3.06	56–55	49.92–148.92	Maryam Adilah et al. (2018)
Thyme	Starch	6.9–8.3	7.3–9.8	–	29–30	Talón et al. (2017)
Murta leaf	Methyl cellulose	–	11.1–13.9	51–64.7	164–205	Hauser et al. (2016)
Murta fruit	Methyl cellulose	–	5.15–14.20	–	12–51.50	López de Dicastillo et al. (2016)
Cinnamon leaf oil	Bombacaceae gum	3.93–3.64	8.71–6.47	–	17.42–17.39	Cao and Bin Song (2020)
Fruit and vegetable residues	Pectin	–	2.9–1.8	12–24	16–30	Brito et al. (2019)
Grapefruit seed	Carrageenan	1.22–1.64	3.21–43.38	38.3–43.3	18.14–27.27	Kanmani and Rhim (2014)
Onion peel	Funoran	4.86–5.64	16.93–24.58	77–95	20.49–35.77	Ju and Bin Song (2020)
Betalains from red pitaya peel	Starch/polyvinyl alcohol	2.48–2.88	30.77–35.02	115–119	39.61–41.99	Qin et al. (2020)
Pomegranate peel	Zein	–	21–28	–	1.2–4.1	Cui et al. (2020)
Grapefruit seed	Gelatin	0.66–0.87	55.2–63.4	62.1–66.3	9.6–13.3	Riahi et al. (2021)
Olive leaf	Carrageenan	6.61–7.43	8.51–11.83	32–48	29.21–36.58	Martiny et al. (2020)
Caraway seed	Chitosan	11.9–13.5	20.54–32.21	10.5–11.8	13.33–17.91	Homayounpour et al. (2021)

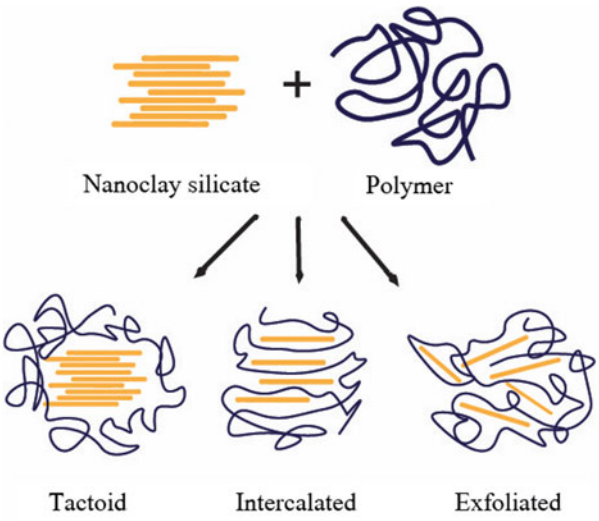

Fig. 2.1 Possible polymer clay structures

promising approach for improving mechanical, barrier, and thermal properties of the packaging films and coatings. Bionanocomposites are mainly consist of a biopolymer matrix and nanoparticles in three different dimensions, including isodimensional nanoparticles such as silica and metal nanoparticles, the ones with two dimension in nanometer range such as carbon nanotubes and cellulose nanowhiskers and the ones with one dimension in nanometer range such as layered crystals and layered silicate clays (Rhim and Kim 2014). Among these, layered silicate clays are widely employed as nanocomposite fillers due to their low cost, simple processability, and significant improvements. They consist of two coordinated tetrahedral silicone atoms that are fused to a octahedral sheet with a thickness of approximately 1 nm, and the lateral dimensions differ from tens of nanometers to several micrometers, depending on the source and the preparation method (Pavlidou and Papaspyrides 2008). For the formation of these bionanocomposites, layered silicate clays-polymer blends are commonly formed in three types, based on the type of clays and the processing conditions, consisting of immiscible tactoid, intercalated, and exfoliated, as shown in Fig. 2.1. In immiscible tactoid condition, clay particles are dispersed into the clay matrix, and the polymer cannot intercalate into the clay layers. Intercalation occurs when a polymer chain is inserted into the layers and a well-oriented multilayer morphology stacking is achieved. Exfoliation nanocomposite is a condition when the silicate layers are fully delaminated and dispersed and thus exhibit enormous improvements in performance properties, due to the higher interfacial area between polymer chains and layered clays (Rhim and Kim 2014).

Vegetable residues are another reinforcing materials that are known to add nutritional values to the biodegradable films, as well as enhancing flexibility and homogeneity of the film (Andrade et al. 2016). The addition of high methoxylated pectin with various granulometry fractions provided better mechanical properties by

increasing film elongation and tensile strength at break and decreasing elasticity. It has been reported that the stiffness of the film depends strongly on the Young's modulus measurement. The larger the Young's modulus, the greater the stress required to undergo deformation, and thus the higher the strength and stiffness; and therefore, the greater the stress required to undergo deformation (Brito et al. 2019). The water sorption isotherms, which revealed thermodynamic equilibrium information between the water vapor and the film at the interface, proved to have lower accessible polar groups capable to provide water sorption sites. Water vapor permeability is one of the most important properties for food packaging purposes. Water vapor permeability depends on the chemical composition and morphology of the polymers and the environmental conditions, which influence solubility and diffusivity of water molecules within the matrix (Siripatrawan and Harte 2010). Murta extract-carboxymethyl cellulose biocomposite film resulted in lower water vapor permeability due to the leaf extracts incorporation (Bifani et al. 2007). The addition of green tea extracts had a significant positive effect on the water barrier properties of gelatin-based films. The abundant polyphenolic compounds, which are able to interact with polar groups of polypeptides found in gelatin, inhibit the formation of hydrophilic bonding of hydrogen groups with water (Siripatrawan and Harte 2010). Other researchers have noted the effect of plant-based extracts and biopolymers on barrier properties. The shelf life of the packaged food can be predicted based on the barrier properties of the biocomposite matrix (Wang et al. 2014). The solubility and moisture content of biodegradable films are important parameters affected by the nature of compounds. By the addition of hydrophilic polymers, more water molecules can bind to available hydroxyl groups, and thus, more water retains in the film. The amount of moisture content has been reported to be in the range of 16.43–35.75% in carrageenan-based films. Greater moisture values were observed with increasing carrageenan concentration. In another study, ginger extract-gelatin composite film resulted in higher moisture content as compared to gelatin film without ginger extract incorporation (Wang et al. 2014). It has been shown that plant extracts incorporation increases the solubility of films, mainly due to the presence of hydroxyl groups and their hydrophilic properties. The swelling behavior of the films is varied and strongly depends on the polymer structure and its thickness and concentration. The functional properties of food packages are enormously affected by the arrangement of various components in the biofilm composite, including plant-based extracts and polymers. The microstructure and morphology of the biofilm determine the homogeneity of the surface and porosity and thus could be responsible for water vapor permeability variations. It has been reported that the surface of gelatin-based films with plant extracts was less homogeneous and more brittle as compared to the films without any plant extract (Wang et al. 2014). This could be due to the denser cross-section microstructure of the composite film and the interaction of polyphenolic chains with hydrophobic molecules of gelatin. A similar result was observed in the soy protein-raspberry extract biofilm. The entanglement of soy protein side chains within plant extract molecules resulted in a more compact structure and subsequently affected the properties of the packaged product (Wang et al. 2012). The inclusion of

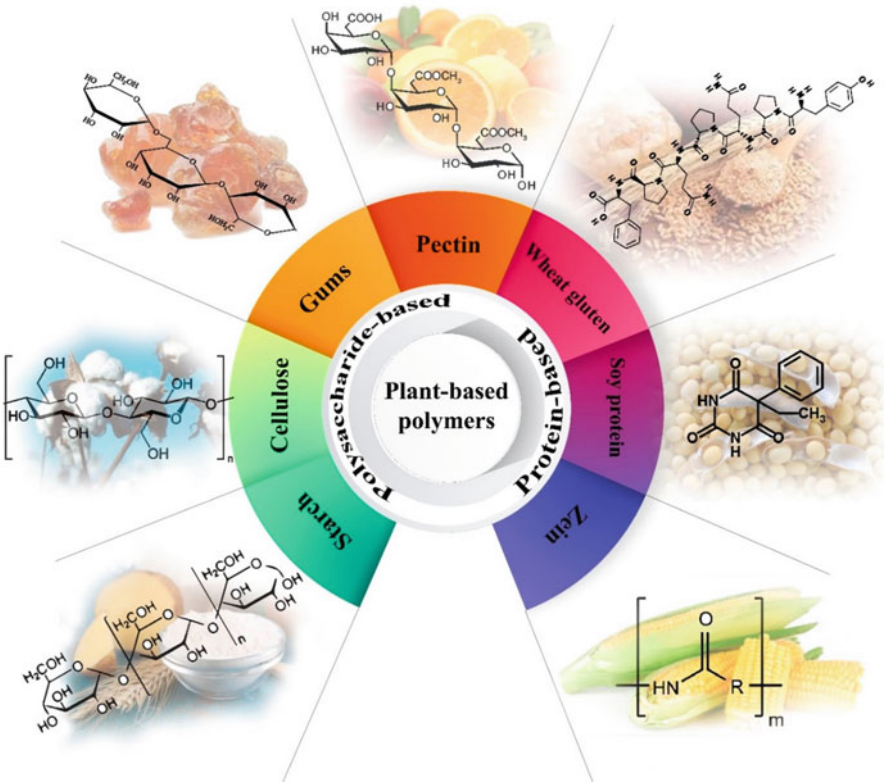

Fig. 2.2 The main types of plant-based biopolymers including starch, cellulose, arabic gum, pectin, wheat gluten, soy protein isolate, and zein; their structure and the origin of extraction

plant-based polymers and extracts may also provide a natural and potential source of antioxidants. The antioxidant property is a promising strategy to reduce oxidative degradation of the packaged food product during the storage period and thus maintain the nutritional quality and increase the shelf life of food (Mir et al. 2018). Antimicrobial property is another important barrier to extend the shelf life by inhibiting or reducing the growth of foodborne pathogens and microorganisms in foods. Natural antimicrobial agents can be found in plant extracts due to the presence of active compounds like catechin, epigallocatechin, epicatechin, eugenol, thymol, and carvacrol (Peng et al. 2013). Antioxidant and antimicrobial properties of the packaging systems can prolong the shelf life of food by controlling and minimizing pathogen contamination, enzymatic browning, oxidation, and nutritional losses. The main types of biopolymers that are commonly be obtained from plant-based sources, as well as their structure and origin is depicted in Fig. 2.2. They can be divided into two main groups: polysaccharides and proteins.

2.3 Plant Polysaccharide-Based Packaging Polymers

Polysaccharides are abundant carbohydrate biopolymers that exist naturally in higher photosynthetic plants and contain hundreds and thousands of repeating units of monosaccharides linked by glycosidic bonds. They can also originate from bacteria, fungi, and marine biomass. The biocompatibility, biodegradability, and non-toxicity properties make them famous and suitable candidates for broad applications, especially in the food packaging industry. Edible coatings, biofilms, and bioactive and intelligent packaging containing plant-based polysaccharides have been reported as some of the most attractive research topics of polysaccharides in food packaging. Besides, polysaccharides are eco-friendly biomaterials with desirable properties toward living microorganisms. Thus, combining one or more of these polymers with other materials makes it a promising approach to prepare and develop novel formulations for the best packaging systems (Majid et al. 2018; Hussain et al. 2017).

2.3.1 Starch

Starch is a widely available and low-cost polysaccharide naturally present in agricultural raw materials such as potato, rice, corn, tapioca, and wheat (Gabor (Naiaretti and Tita 2012; Shen et al. 2014). Starch is one of the most promising carbohydrates that mainly consists of two α-glucose polymers, linear amylose (ploy-α-1,4-D-glucopyranoside), and highly branched amylopectin (poly-α-1,4-D-glucopyranoside and α-1,6-D-glucopyranoside). Amylose molecules form helix structure by the association of bond angles within 200–20,000 glucose units. Amylopectin molecules are highly branched amorphous polymers composed of short-chain glucose units attached along with glucose units. The ratio of amylose and amylopectin is varied based on the source of starch, modified starch, and high amylose starch (Tang et al. 2012; Rastogi and Samyn 2015). Various sources of starch can be used to synthesize biodegradable and edible films due to their excellent barrier properties. However, as the semicrystalline nature of starch is brittle, it can be modified physically, chemically, or enzymatically to improve its mechanical properties for packaging applications. Hybrid combinations of starch and other materials such as synthetic polymers and plasticizers are alternative solutions to enhance starch-based biofilms. Xylitol, sorbitol, and glycerol are typical examples of plasticizers used with starch to form a flexible thermoplastic biofilm with adequate stability. The effect of gelatin on the mechanical properties of starch films was also investigated. The results showed remarkable enhancement in solubility, water vapor migration rate, moisture absorption, and structural stability of the film (Kumar et al. 2019).

2.3.2 Cellulose

Cellulose is one of the abundant biopolymers on the earth and has many industrial applications, including the food industry (Cash and Caputo 2009). Microfibrillated cellulose (MFC), nanocrystalline cellulose (NCC), cellulose nanofibers (CNF), and bacterial cellulose (BC) are three main types of cellulose that have been used for food packaging (Klemm et al. 2009, 2011). In recent years, there was an increase in the use of cellulose for packaging. Cellulose derivates, including methyl cellulose (MC), ethyl cellulose (EC), carboxymethyl cellulose (CMC), hydroxyethyl cellulose (HEC), hydroxypropyl cellulose (HPC), and cellulose acetate (CA), have been produced on a large scale. NCC and MFC are also used for making biocomposites to enhance rheological, thermal, and mechanical properties (Zhu et al. 2016).

Barrier properties of packaging play a vital role in selecting the materials (Heydari et al. 2014). Cellulose hydrogen bands with itself and also with other molecules could reduce the permeability of packages (Jin et al. 2021). Moreover, cellulosic materials have high crystallinity, which makes the material more impermeable to gases (Moon et al. 2011). Material impermeability could be improved by making multilayer composites. TEMPO-oxidized CNF coating with polyethylene was fabricated as a barrier layer packaging films, and the membrane showed excellent oxygen barrier properties to store dry food (Vähä-Nissi et al. 2017). CNCs' crystallinity is the highest among all cellulose type and provided better barrier properties. CNCs have been using as a worthy oxygen barrier when used to make composites with polypropylene carbonate, polylactic acid, polyethylene glycol, and polyethylene terephthalate (Cash and Caputo 2009). Water vapor permeability is one of the main concerns for designing food packages (Yu et al. 2020). Besides polymer selection, factors like pressure, relative humidity, crystallinity, film thickness, density, and hydrophilicity contribute to water vapor permeability. Due to cellulose high crystallinity and hydrophobicity, cellulose can reduce permeability. The barrier properties of cellulose are excellent for water. However, unmodified cellulose is gas permeable (Vartiainen et al. 2016). Extrusion is another method for producing cellulosic packages. NC has been employed as a filer to enhance the mechanical strength of polymers and adhesives. Also, modification CNSs and using various grafting may improve their incorporations with other polymers and heighten compatibility between polymers (Vartiainen et al. 2016).

Radical scavenging and antioxidant properties are some of the most critical aspects of food packaging materials that can increase shelf life. Pure cellulose is transparent in the range of 400–800 nm and poor UV shield (Farooq et al. 2020). An antibacterial effect is another important feature of food packaging and has an essential effect on self-life. Due to cellulose's high surface area, cellulosic materials could be loaded with decent amounts of antibacterial agents (Pirsa et al. 2020). Also, cellulose can heighten the stability of packaging in water and be functionalized with different nanoparticles, introducing antibacterial materials. Also, loading antibacterial agents into the materials could be an option since cellulose materials showed perfect control release properties. Inorganic materials are more resistant to intense processes and could be used to make composites. Silver nanoparticles are

Table 2.2 A summary of cellulose modification investigations for food packaging applications

Additive material	Modified properties	References
Shikonin	Functional color indicator depending on the pH	Roy and Rhim (2021)
Gelatin/polyvinyl alcohol	Enhanced mechanical, optical, and water barrier properties	Haghighi et al. (2021)
Zein	Antimicrobial	Zhou and Wang (2021)
Gelatin	Enhanced mechanical and water barrier properties	Leite et al. (2021)
Chitosan	Antimicrobial and UV blocking	Zhang et al. (2021)
Chitosan	Enhanced mechanical properties	Wang et al. (2021)
Carboxymethyl cellulose and silver nanoparticles	Antimicrobial and barrier properties	He et al. (2021)
Nano-ZnO and GQDs	Antimicrobial and barrier properties	Li et al. (2021)
Nisin	Antimicrobial	Gedarawatte et al. (2021)
Polylactic acid	Enhanced oxygen barrier properties	Jung et al. (2020)
Chitosan and polypyrrole	Active food packaging, antimicrobial, mechanical and barrier properties	Gao et al. (2020)
Vinyl alcohol and RGO	Barrier properties	Wang et al. (2020)

one of the most used antibacterial agents and are more chemically and thermally stable than other agents. Cellulose/silver nanoparticle composites have many applications as active packaging in the food industry (Pirsa et al. 2020; Van Hai et al. 2020). For example, cellulose modification using TEMPO oxidation to add carboxylate groups may be a proper method to enhance cellulose/silver nanoparticle composites (Luan et al. 2018).

Mechanical strength is one of the most essentials properties of food packaging materials (Heydari et al. 2013). Blending cellulose with other biopolymers may improve composite properties. Adding a low amount of cellulose may enhance mechanical properties. However, adding more cellulose may result in a matrix's segregation and reduce mechanical strength and barrier properties. Also, Increasing the concentration of cellulose decreases thermal stability of a composite (Nagarajan et al. 2021). Table 2.2 provides a summary of some additive materials to enhanced cellulose-based food packaging films.

2.3.3 Gums

Gums are another group of plant-based polysaccharides which are can be produced by seeds, trees, tubers, and shrubs and made up of sugars such as rhamnose,

dextrose, xylose, galactose, arabinose, arabinose, mannose, and uronic acid (except glucose). These natural biocompatible materials can form a viscous suspension, a gel, dispersion, or a colloidal solution and have been utilized as emulsifiers, thickeners, and gelling agents for centuries in different ways. The chemical structure can be varied based on its molecular weight, the length of the main chain, moieties and branches, and the interaction of hydroxyl groups, polar groups, and hydrogen bonds (Mohammadinejad et al. 2019). These renewable and biocompatible materials are low-cost and widely available and, in most cases, present appropriate film-forming capabilities, which makes them great candidates for the food packaging industry (Cao and Bin Song 2020). Arabic gum, guar gum, gellan gum, karaya, locust bean, cashew gum, and tragacanth gum are some of the potential examples for applying in food packaging due to their long shelf life, good thermal and mechanical stability, and relatively high water-solubility. Gum arabic is a tree gum exudate and is the most commercially employed gum due to its unique emulsification and film-forming properties (Ali et al. 2013). The structure is chemically composed of galactose, arabinose, rhamnose, and glucuronic acid residues. Gum arabic fibers were fabricated by electrospinning and treated by methane plasma and γ-ray irradiation to improve their physicochemical, thermal, and mechanical properties. The results of this study showed significant improvements in the thermal and tensile properties, as well as the surface roughness and crystallinity, when treated with both plasma etching and γ-ray irradiation (Padil et al. 2019). Tragacanth gum (TG)-based biofilms have been shown to possess excellent properties such as nontoxicity, colorless, odorless, biodegradability, and oxygen barrier. In a study, ZnO nanoparticles were incorporated in TG-based bionanocomposite films and provided antimicrobial defense toward a variety of bacteria during 24 h incubation. The presence of ascorbic acid in biofilms showed lipid oxidation prevention (Janani et al. 2020). Generally, the use of antimicrobial and antioxidant agents in biofilms has proved to be a promising approach for extending the shelf life and improving the food quality by eliminating the microbial load and lipid oxidation. Guar gum, a nonionic heteropolysaccharide derived from cluster beans, is composed of galactomannan and repeated units of mannose [(1,4)-linked β-D-mannopyranose] and galactose [(1,6)-linked α-D-galactopyranose] (Oliveira et al. 2011). Although guar gum could be a potential candidate for its high molecular weight and water solubility, it showed insufficient thermomechanical and barrier properties. To improve biofilms characteristics, the incorporation of nanoparticles has been introduced because of their high specific surface area and interfacial interactions on branches. Besides, it has been proved that metal nanoparticles such as silver, copper, and gold nanoparticles offer significant antimicrobial activities. In a study, different levels of bimetallic nanoparticles consist of silver-copper (Ag-Cu) incorporated into guar gum to develop a nanobiocomposite film-forming matrix. The results of this study demonstrated significant improvement in the thermal, mechanical, and barrier properties, as well as the excellent antimicrobial activities of guar gum films reinforced by silver-copper nanoparticles (Arfat et al. 2017). In another study, guar gum and oxidized guar gum have been applied in gelatin-based biofilms, and the results showed that the gelatin-oxidized gum could successfully

enhance thermal stability, water solubility, and tensile strength, due to the formation of covalent cross-linking through the Schiff-base reaction (Yavari Maroufi et al. 2020). Cashew gum is another plant-based gum widely derived from the cashew tree (*Anacardium occidentale L.*), mainly found in Brazil. This gum could be a possible alternative to gum arabic and bring socio-economic value to cashew-producing countries; however, more investigations are needed to precisely determine its emulsifying properties. These compounds are byproducts of the cashew industry, consisting of D-galactopyranose, D-glucopyranose, L-arabinofuranose, L-rhamnopyranoside, and D-galacturonic acid. They have an anionic character and can interact with polycations; however, they are brittle and inflexible. Research has been carried out on blending cashew gum with other biopolymeric materials to enhance their mechanical properties. For example, the blend of cashew gum and gelatin has been reported to offer higher elongation and tensile strength (Oliveira et al. 2018).

2.3.4 Pectin

Pectin is a key plant-based biopolymer that constitutes plant cell walls and is extracted primarily from citrus and apple byproducts. This eco-friendly and biodegradable polysaccharide comprises variably methylated D-galacturonic acid (GalA) units and their methyl esters, joined by α-(1,4) glycosidic linkages. Based on the esterification degree, pectin can be classified into high methoxylated (HM) pectin and low methoxylated (LM) pectin. The esterification degree of HM and LM pectins strongly influences gelling properties of pectin and lies in the ranges of 60–75% and 20–40%, respectively. The acid groups in HM pectin are insufficient for gel formation; thus, de-esterification is required for decreasing esterified carboxyl groups. There are four different techniques for producing LM pectin from HM pectin: acid, alkali, enzyme, and ammonia demethylation and amidation. The effects of various treatments with acid, alkali, and ammonia on the physical properties of an apple-based pectin have been evaluated, and the results showed that the acidic treatment had higher impact on increasing the average molecular weight and the intrinsic viscosity of the pectin during de-esterification, which is more desirable for gel thickening and gel formation (Table 2.3) (Alemzadeh 2010). The gelation mechanism of LM pectin is based on the electrostatic bonding of carboxylic groups and ionic cross-linking by divalent cations (usually Ca^{2+} ions). The gelling ability can also be improved by amidation of pectin, in which amide groups allow the

Table 2.3 The effect of various de-esterification methods on molecular weight and intrinsic viscosity on apple pectin (Alemzadeh 2010)

Type of treatment	Average molecular weight	Intrinsic viscosity (mL/g)
Acidic	32,000	186
Alkali	28,300	170
Ammonia	27,400	166

association of pectin chains through hydrogen bonding (Jantrawut et al. 2013)–(Kiaei Pour et al. 2020).

At pH higher than pectin's pK_a, anionic carboxyl groups interact electrostatically with cationic groups such as chitosan and hence resulting in polyelectrolyte complexes (Öztürk et al. 2016). In the case of HM pectin, hydrogen bonding and hydrophobic interactions induce chain aggregation, and insufficient carboxyl groups prevent the formation of a continuous network. In an acidic medium, the reduced negative charge density and pectin hydration lead to hydrogel formation (Pilgrim et al. 1991). Alternatively, chemical cross-linking of pectin by the reaction of hydroxyl, carboxyl, and methoxyl groups of pectin with bifunctional groups such as glutaraldehyde can be achieved (Pourjavadi and Barzegar 2009). This irreversible hydrogel represents improved mechanical strength compared to physically cross-linked ones. Pectin films and coatings possess high Young's modulus and tensile strength. However, high water vapor permeability and hydrophilicity limit its application in food packaging. Therefore, several kinds of research have been conducted on the combination of pectin with other biodegradable biopolymers to overcome undesirable water barrier properties and high hydrophilicity and enhance their mechanical properties. Blended pectin/gluten films exhibited significantly higher tensile strength, light/UV, and water vapor barrier properties compared to the gluten and pectin films, which could be related to the electrostatic interaction between both polymers. In addition, this blended film had the advantage of being more transparent and less yellowish, which is an essential factor to attract consumers (Sartori et al. 2018). The enrichment of fruit and vegetable residues as raw material with HM pectin resulted in homogenous and high soluble biodegradable films. The presence of pectin in this film increased Young's modulus and provided greater mechanical strength and stiffness and notably lower hygroscopicity and elasticity (Brito et al. 2019). Generally, pectin is used in various food applications such as gelling agent, emulsifier, stabilizer, and texturizer. In food packaging, pectin-based materials can be used in different types of biofilms, bionanocomposites, nanofibers, multilayered nano/microemulsions, hydrogels, and aerogels in association with other materials and additives to meet the essential demands for food preservations and coatings. Table 2.4 represents some of the recent pectin-based biomaterials for food packaging applications.

2.4 Plant Protein-Based Packaging Polymers

Protein-based biofilms derived from plant resources such as soy, zein, gliadin, and lectins have been developed for food packaging applications due to their availability, renewability, biodegradability, and good film-forming properties. Due to the hydrophilic nature of most protein-based films, they have offered high water vapor permeability and also water-holding capacity. However, their oxygen permeability is low. Compared to animal-derived proteins, plant-derived ones are more preferable because they have lower extraction costs and are able to mitigate immunogenicity and viral transfer. Moreover, they readily undergo physical or covalently coupling to

Table 2.4 Some of the recent pectin-based matrixes used for food packaging applications

Type of matrix	Additive	Application	References
Pectin-alginate nanoparticles	Laponite	Barrier and antimicrobial properties	Vishnuvarthanan and Rajeswari (2019)
Pectin-pullulan biofilm	Silver nanoparticles	Antimicrobial properties	Lee et al. (2019)
Pectin-chitosan-starch biofilm	Mint and rosemary oils Nisin	Antioxidant and antimicrobial properties	Akhter et al. (2019)
Pectin-fish gelatin	Hydroxytyrosol, dihydroxyphenylglycol	Oxygen barrier and antioxidant properties for meat preservation	Bermúdez-Oria et al. (2019)
Pectin-chitosan multilayered emulsion	Astaxanthin	Release of hydrophobic carotenoids	Liu et al. (2019)
Pectin-polyethylene oxide	–	Reinforcement	McCune et al. (2018)
Pectin-gluconaman	Tea extract	Antimicrobial and antioxidant activities	Lei et al. (2019)
Pectin-citric-starch	Acca sellowiana	Antimicrobial, antioxidant, and bioactivity properties	Sganzerla et al. (2020)
Pectin films	Copaiba oil nanoemulsions	Improving physico-mechanical and antimicrobial properties, proper biodegradability	Norcino et al. (2020)
Pectin-pullulan films	–	Increase thermal stability and surface hydrophobicity	Priyadarshi et al. (2021)
Pectin-gellan	Nisin	Antimicrobial activity and release of nisin	Rivera-Hernández et al. (2021)
Pectin	Oregano essential oil and resveratrol emulsion	Fresh meat preservation	Xiong et al. (2020)

the various molecules, thanks to their functional groups. Wheat gluten, soy protein, corn zein are among the most common examples of plant protein-based biofilms, which will be elaborated in the following sections.

2.4.1 Wheat Gluten

Wheat gluten is an enriched protein complex, and it contains water-insoluble and ethanol-soluble prolamins (gliadins) and water and ethanol insoluble glutelins (glutenins) with small amounts of starch, oil wheat, and insoluble hemicellulose. The gliadins components are mainly monomeric single chain polypeptides, and the components of glutenins are polymeric chains with disulfide linkages. It has been demonstrated that gluten-based films possess satisfactory oxygen barrier properties, while their permeability to carbon oxide is high, which makes them suitable for modified atmosphere packaging. One of the main drawbacks of gluten-based processes is the lack of research associated with the gluten structure. Therefore, more research is needed to comprehend the tertiary and quaternary structure of it more deeply (Tang et al. 2012).

2.4.2 Soy Protein

Soy protein is a globulin containing acidic and basic polar and nonpolar amino acids. Twenty different amino acids are reported to contribute to soy protein structure, namely, lysine, tyrosine, phenylalanine, leucine, aspartic, and glutamic acid (Félix et al. 2014). The two main components of soy protein are β-conglycinin (7S, approximately 35%) and glycinin (11s, approximately 52%). Three classes of soy protein that are commercially available are as follows: soy flour comprises 56% protein and 34% carbohydrate, soy concentrate comprises 65% protein and 18% carbohydrate, and lastly, soy isolate contains 90% protein and 2% carbohydrates (Swain et al. 2004). Soy protein can be a suitable substitute for plastics and synthetic polymers due to its several advantages, including good film-forming ability, biodegradability, good tensile strength, and elongation, as well as high availability for large scale production. However, due to their brittleness and poor water resistance, various physical and chemical treatments have been proposed to improve soy protein film properties. Incorporation of plasticizers such as glycerol, ethylene glycol, hydramine, galactose, sucrose, fructose, sorbitol, and propylene glycol with protein isolate leads to more flexibility but, at the same time, decreases their tensile strength. Chemical treatments such as sulfonating hydroxyl groups, diazotizing amine groups, transforming hydroxyl groups to carboxyl groups, transforming amine groups into quaternary ammonium salts can modify the soy protein and increase their water solubility; however, they require toxic chemical agents during the reaction, resulting in toxicity and poor mechanical properties of the films. It has been demonstrated that the transferring reaction of hydroxyl groups on benzene rings and aliphatic chains into sulfo groups and the presence of strong acids such as sulfur trioxide or chlorosulfonic acid is needed (Badvel et al. 2015). Diazotization of amine groups and hydroxyl transforming reactions also occurred under strong acidic and alkali conditions, respectively, which destroy protein polymers (Gandhi et al. 2014). Graft polymerization of soy proteins can occur under mild conditions while improving their mechanical properties and water solubility. In a study, the effect of acrylic acid

graft modification of soy protein films on various properties such as biodegradability, transparency, water solubility, tensile, and mechanical properties was investigated. The results indicated that grafted soy protein films had substantially better performance than the ingrafted ones (Zhao et al. 2016). Nano-reinforcement by incorporating biomaterials into the film precursors is a potential option to improve film properties more effectively compared to conventional modifications and micro-compounds, without destroying polymer structure, transparency, and film formation. This type of reinforcement can be classified into lamellar, fibrillar, and particulates, based on their dimension. Nanocrystalline polysaccharides such as starch, cellulose, and chitin are ideal candidates to be used as reinforcing materials. They are capable of promoting mechanical properties, miscibility, interfacial adhesion, and prolonging shelf life and quality of the packaged food by absorbing or releasing specific compounds.

2.4.3 Zein

Zein is the main protein of the corn that is a virtual hydrophobic polyamine and commercially utilized to formulate different types of thermoplastic products in the industry. Zein films are potentially useful for biodegradable packaging because they are shiny, antimicrobial, antioxidant, oxygen-barrier, and adhesive, but in lieu, zein films are brittle. The water vapor permeability of zein films is lower than other protein films. Oxygen and carbon dioxide permeability of zein films are higher than wheat gluten films but lower than other polysaccharides and biocomposite polysaccharide/lipid films. Cross-linking agents and plasticizers incorporation such as glycerol or glycerol blends with polypropylene glycol (PPG) or PEG are reported to affect their mechanical and barrier properties. Zein-based biofilms possess Young's modulus value of 267 MPa at 25 °C and 50% humidity.

A new type of composite starch corn-based films was developed by incorporating zein nanoparticles loaded with orange-peel oil, a natural antimicrobial and high degradable and value-added compound containing essential oils, fermentable sugars, carbohydrates, and polyphenols flavonoids (Esteban and Ladero 2018). The results of this study showed that encapsulating orange-peel oil into zein emulsion-based nanoparticles not only controlled the release of oil and eliminated its oxidative degradation but also improved the mechanical and barrier properties of the composite film. In another study, cellulose nanocrystal-corn zein biocomposite film cross-linked with 1,2,3,4,-butane tetracarboxylic acid was prepared to examine its performance as an oxygen and water vapor barrier (Ben Shalom et al. 2021). The results proved the positive effect of corn zein on flexibility, toughness, and thermal stability of biocomposite films. Moreover, cross-linked films exhibited excellent barrier ability, film flexibility, and water absorption capacity. In contrast, non-cross-linked films showed poor performance, which might be due to the role of cross-linker in the formation of chemical linkages between protein chains and nanoparticles, preventing the protein swelling in moisture.

2.5 Current Status and Market Potential

Trends in the emergence of plant-based biopolymers gave rise to innovative packaging approaches that are resulted in the enhancement of food safety, feasibility, and bioactivity of functional materials. According to the findings of a recent survey of 6000 consumers from various countries regarding consumers' views related to different types of packaging materials, more than half of them mentioned that they would pay more for sustainable and eco-friendly products with plant-based packages (Long 2019). Another report released by the Plant Based Products Council (PBPC) showed an increasing appetite for consumer desire in the USA to support plant-based products by purchasing them, and the market size is estimated to be more than 136 million people (Barrett 2019). A market study published by Markets&Markets declared that the global market for plant-based polymers is estimated to increase from $ 10.5 billion in 2020 to $ 27.9 billion by 2025 at a CAGR of 21.7%, and packaging is one of the growing end-use industries that dominates this market, and demands to replace conventional plastics and reduce the dependency on fossil fuels to address environmental issues is growing rapidly. Focus of governments on related regulations and policies such as banning or implementing extra surcharges on the plastic-based packaging's usage can support and propel the demand for plant-based biopolymers in food packaging applications (MarketsandMarkets 2020). Although there are still some limitations in the development of plant-based food packages, they will make their way into the global market in the near future due to their attractive environmentally friendly properties.

2.6 Conclusion

In this current chapter, we demonstrated that biodegradable, biocompatible, and sustainable films and coatings made from plant-based ingredients are attractive to substitute synthetic polymers due to their availability and eco-friendly properties. It is an important issue due to their promising performance in extending shelf life and lowering health risks. These plant-based polymers are generally divided into polysaccharides and proteins. Each polymer from individual specific plant sources has its own characteristics and provides specific film properties such as water vapor permeability, color, flexibility, water solubility, barrier properties towards lipid, gasses, and moisture, mechanical strength, thermal stability, and antioxidant and antimicrobial activities. The main limitation of plant-based polymers is their sensitivity to moisture and heat that inhibit their large-scale utilization in biofilm formation. The challenge is to fulfill the consumer demands and requirements for desirable and high-quality film properties. Employing novel processing techniques to integrate ingredients, plasticizers, nanofillers, and gelling cross-linkers, as well as chemical modification of these polymers to improve their barrier and rheological properties, is a helpful rout to resolve the difficulties in the practical application and development of plant-based polymers as sustainable alternatives instead of conventional plastic-based polymers for safe and fully protective food packaging.

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3 Plant- and Animal-Derived Enzymes and Their Potential Application in Food Processing and Preservation

Mahmoud Aminlari

Abstract

Enzymes are biological catalysts which increase the rate of biochemical reactions in living cells. It is important that enzymologist understand the specific action of particular enzyme in a plant or animal tissue and apply these properties in vitro and in a food product. Most enzymes can be used as processing aids and as protection agents against microbial and deteriorative processes. Although the advancements made in recombinant DNA technology and in food applications of microorganisms have resulted in a more practical and economic enzyme production, some of these enzymes are sufficiently abundant in their natural sources to make them amenable to large-scale production (e.g., egg white lysozyme and plant proteases). In this chapter several plant and animal enzymes and their occurrence and potential applications in food industry will be presented. Emphasis will be made on enzyme working on carbohydrates, proteins, and lipids. A section is devoted to miscellaneous enzymes used in food industry, such as phenylalanine ammonia lyase of wheat seedling which metabolizes Phe, thereby rendering foods suitable for PKU patients. In the final section of this chapter, examples of chemical modification of enzymes to improve their properties will be discussed and examples of the studies on chicken egg white lysozyme to enhance its functional and antimicrobial activities, performed in the laboratory of this author, will be presented.

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Keywords

Plant enzymes · Animal enzymes · Food application · Antimicrobial · Bioactive peptides · Chemical modification

3.1 Introduction

Enzymes perform many biochemical functions in living cells. They participate in multitude of biochemical reactions which are vital for cell well being, growth, and production of various biochemical products. As such, enzymes are indispensible in any living system. Some enzymes are unique to particular cell type while others are present in many different types of cells. It is the responsibility of the food enzymologist to determine and adapt the functionality of a particular enzyme in a plant or animal tissue to a functional property in food systems.

Enzymes of plant and animal origin have been used in the food industry for centuries and production of alcohol from sugar by yeast through fermentation is the oldest example of production in biotechnology. Enzymes present in various raw materials have been used to produce traditional foods such as cheese, yoghurt, and bread and fermented beverages such as wine, beer, and vinegar for many thousands years (Poulsen and Buchholz 2003). In the second half of eighteenth century, in vitro digestion of meat by pepsin from gastric secretions was reported. The first industrial application of enzymes involved using crude protease mixture from animal pancreas as laundry detergents in the beginning of twentieth century. Historically, abundance of raw starting materials resulted in obtaining most of the pure intracellular enzymes from skeletal muscle or through fermentation by yeast. Starting in the late 1940s, significant improvements in purification techniques such as chromatography applied to proteins resulted in preparation of enzyme in preparation of large quantities of industrial important enzymes (Aehle 2007). The advancements made in recombinant DNA technology made it possible to achieve microbial production of the enzymes of interest on an industrial scale. At present, scientists use molecular biology and genetic engineering techniques to search for novel enzymes and to optimize production of the majority of industrial enzymes.

The grade or degree of purity of enzyme preparation depends on its application. Partially purified, low-cost enzyme preparations can be used for many industrial applications such as laundry or large-scale food processing operations that do not need highly purified enzymes. They are commonly produced in large scale worldwide and are mostly obtained from animal or plant sources with few purification steps. Examples include proteases and enzymes working on carbohydrates. Enzyme destined for analytical purposes must be pure and do not contain contaminations that can interfere with enzymatic procedure. Examples of these types of enzymes are glucose oxidase and restriction endonucleases. Finally, clinically important enzyme which must be highly purified usually sold in crystalline form and must be devoid of any contaminating activity. A very famous example of this group of enzymes is asparaginase which is used for treatment of childhood leukemia (Chahardahcherik

et al. 2020). The last two types of enzyme are produced from microbes, plants, or animals. These enzymes are produced in mg-g quantities worldwide using sophisticated purification procedures.

Applications of enzymes in foods and food products include broad and highly diverse industries such as dairy, meat, baking, fruits and fruits juice, and vegetable processing. Several factors must be taken into consideration when one attempts to employ an enzyme in foods. These include reaction specificity, requirement for mild conditions, possibility of formation of unacceptable by-products by a chemical process, and relative cost-benefit. Exogenous enzymes are used in the production of many commodities such as glucose, high-fructose corn syrup, invert sugar, and other sweeteners as well as food ingredients, protein hydrolysates, and structured lipids. Modification of components within a food matrix (cheese manufacturing, tenderization of meats, beer stabilization, extraction and debittering of citrus juice and softening of crumb) and improvement and achievement of more efficient processes (such as oil extraction from seeds, cheese ripening, beverage filtration, clarification of juices, faster dough mixing, leavening, and stabilization of baked foods) are among the goals achieved by application of exogenous enzymes. Enzymes are also used to control processes to reach certain goals, such as online biosensors and component analysis, reduced use of raw materials, quality control, omitting or replacing chemical food additives and preventing formation of potential hazardous products in the food, and improvements of nutritional attributes. There are some regulations in food industry which allow adding certain chemical agents to foods to achieve particular goals, such as oxidizing and reducing agents (cysteine, bisulfites, and potassium bromide) in baking industry and preservatives such as benzoate and sorbates in different foods. However, in recent years, due to the increased awareness of consumer, food producers and processors have witnessed an increase in demand for foods perceived as "natural." Therefore, identification and development and application of natural ingredients and development of products without chemical additives are a common practice among food scientists. In many cases the beneficial effect of enzymes to replace chemical agents can be demonstrated.

This chapter aims to address and review recent developments in identification of novel plant and animal enzymes with potential application in the food industry. It is hoped that the materials presented in this chapter will provide basis and interest for developing new enzyme technologies which will meet new and changing needs of the food industry. The activities of many endogenous enzymes continue postharvest and postmortem and in most cases contribute to the food quality deterioration, such as excessive ripening of fruits by pectic enzymes, hydrolytic rancidity of milk lipids due to lipase activation, and extra meat tenderization by calpain system. However, the aim of this chapter is to exclusively address the application of exogenously added enzymes of plant and animal origin for their beneficial effects. Because of space limitation, this chapter focuses on enzymes working on major food constituents (i.e., carbohydrates, proteins, and lipids). Few enzymes with specific action in foods will be briefly described under the heading "miscellaneous enzymes." A section is devoted to demonstrate the role of plant and animal proteases in producing bioactive

peptides. In the final section of this chapter, examples of chemical modification of enzymes to improve their properties will be discussed and some of the studies done on lysozyme in the laboratory of this author will be presented. Table 3.1 summarizes the use and suggested use of enzymes in food industry.

3.2 Enzyme Working on Carbohydrates

Most of the enzymes working on food carbohydrates are hydrolase, i.e., use water as one of the substrates. These enzymes are also referred to as glycosyl hydrolases or glycosidases. These enzymes catalyze the hydrolysis of different glycosidic linkages in polysaccharides. In nature, their role is to participate in degradation of biomass such as starch, cellulose, and hemicellulose and in antibacterial defense strategies, in pathogenesis mechanisms, and in normal cellular function (e.g., trimming mannosidases involved in N-linked glycoprotein biosynthesis). Glycosidases and glycosyltransferases are the major enzymes for the synthesis and breakage of glycosidic linkages in carbohydrates (Bourne and Henrissat 2001). Glycosidases are classified either as "retaining" or "inverting" types, based on the fate of the anomeric configuration (α or β) of the hydrolyzed glycosidic bond. Another general distinction among glycosidases is whether they are "endo" or "exo" splitting. Exo-splitting types mostly act on the nonreducing end of the substrate, whereas endo-splitting types randomly attack interior glycosidic bonds of the substrate. The "α" and "β" nomenclature, as in amylases and glucosidases, refers to the anomeric configuration of the liberated reducing group as being axial and equatorial, respectively (Whitaker 1994). Different glycosidases act on different parts of starch molecule. α- Amylases act randomly on the interior α,1–4 glycosidic bond while isoamylases and pollulanases hydrolyse α,1–6 bonds at the branch points (Wong and Robertson 2007; Parkin 2017). Glucoamylases are exo-splitting and start hydarolysing α,1–4 bond from the nonreducing end of amylose and amylopectin to produce β-glucose as product. β-Amylase is also exo-splitting and breaks every other α,1–4 bonds from the nonreducing end of amylose and amylopectin toproduce β-maltose.

Applications for various glycosidases in food technology are widely spread. These enzymes account for about half of enzyme used in the food industry, exclusively for the production of low molecular weight sweetener, dextrin as bulking or thickening, and for carbohydrate modification in baking and fruit products (such as cellulases and pectic enzymes) (Saini et al. 2017). Most of these enzymes are commercially available. Classification and properties of glycosidases important in food industry is shown in Table 3.2.

Table 3.1 Some uses and suggested uses of enzymes in food industries (adapted from Whitaker 1994)

Enzyme	Food	Purpose or action
Amylases	Baked goods	Increase in maltose content for food fermentation
	Brewing	Conversion of starch to maltose for fermentation, removal of starch turbidity
	Cereals	Conversion of starch to dextrins and maltose, increase water absorption
	Confectionary	Recovery of sugar from candy scraps
	Fruit juices	Removal of starch to increase sparkling properties
	Jellies	Removal of starch to increase sparkling properties
	Pectin	Aid in preparation of pectin from apple pomace
	Syrup	Conversion of starch to low molecular weight dextrins (corn syrup)
	Vegetables	Hydrolysis of starch as in tenderization of pease
Cellulase	Brewing	Hydrolysis of complex carbohydrates cell walls
	Coffee	Hydrolysis of cellulose during drying of beans
	Fruits	Removal of graininess of pears, peeling of apricot, tomatoes
Invertase	Artificial honey	Conversion of sucrose to glucose and fructose
	Candy	Manufacture of chocolate-coated soft-cream candies
Lactase	Ice cream	Prevention of crystallization of which results in grainy, sandy texture
	Milk	Stabilization of milk proteins in frozen milk by removal of lactose.
		Hydrolysis of lactose, permitting use by adults deficient in lactase in intestinal and infants with congenital lactase deficiency.
Tannase	Brewing	Removal of polyphenolic compounds
Pentosanase	Milling	Recovery of starch from wheat flour
Naranginase	Citrus	Debittering citrus juice by hydrolysis of the glucoside naringin
Pectic enzymes	Chocolate, coca	Hydrolytic activity during fermentation of cocao
	Coffee	Hydrolysis of gelatinous coating during fermentation of beans
	Fruits	Softening
	Fruit juice	Improving yield of press juice, prevention of cloudiness, improving concentration process
	Olive	Extracting oil
	Wines	Clarification
Proteases	Baked goods	Softening action in dough, cut mixing time, increase extensibility of Dough, improvement in grain, texture, loaf volume, liberate β-amylase.
	Brewing	Body, flavor and nutrient development during fermentation, aid in liberation and clarification, chill-proofing
	Cereals	Modification of proteins to increase drying rate, improve product handling characteristics, manufacture of misu and tofu
	Cheese	Casein coagulation, characteristic flavor during aging

(continued)

Table 3.1 (continued)

Enzyme	Food	Purpose or action
	Chocolate, coca	Action on beans during fermentation
	Eggs	Improve drying properties
	Meats, fish	Tenderization, recovery of proteins from bones and trash fish, liberation of oils
	Milk	In preparation of soy-milk
	Protein hydrlysate	Condiments such as soy sauce, specific diets, dehydrated soups, gravy powder, processed meats, production of bioactive peptides, aids in digest ion of proteinous foods
	Wines	Clarification
Lipase	Cheese	Aging, ripening, and general favor characteristics
	Oils	Conversion of lipids to glycerol, fatty acids and monoglycerides
	Milk	Production of milk with slightly cured flavor for use in milk choclates

3.2.1 Amylases

3.2.1.1 α-Amylases

The amylases are used to hydrolyze starch into smaller dextrins and thereby "thin" starch suspensions. α-Amylase is an endo-splitting glycosidase that hydrolyses α-1 → 4 glycoside bond, with retained configuration of the producthe of hydrolysis. The initial product is dextrin, and the final major products are maltose and maltotriose. The hydrolytic activity of the enzyme starts to decline as the enzyme approaches the α-1,6 branches since the enzyme is specific for α-1 → 4 bonds. "α-Limited dextrin" is the product of the extensive hydrolysis of amylopectins with α-amylases. α-Amylase is an important contributor in carbohydrate metabolism of microorganisms, plants, and animals. The active site requires an oligosaccharide substrate of at least three glucose units in length. Branched α-limit dextrin and maltooligosaccharides of up to 12 glucose units are the typical end products of α-amylase action on starch molecules. The action of the enzyme results in rapidly decreasing the average molecular weight of starch polymers and reducing the starch solutions viscosity because of the random nature of hydrolysis. α-Amylases require Ca^{2+} for activity. The optimum pH for pancreatic α-amylase is 6–7 in the absence of Ca^{2+}, but in the presence of Ca^{2+}, the enzyme is fully active int pH range of 6–11. These ions bind at multiple sites, especially the site close to the active site cleft, thereby stabilizing secondary and tertiary structure. Ca^{2+} binds tightly and serves to broaden the pH stability of the enzyme to between pH 6 and 10. Also the presene of NaCl enhances α-amylase activity in the pH range of 6–9. The thermal stability of the α-amylase is within the ranges of 30–130 °C (Pandey et al. 2000). Microbial α-amylases are the major industrial source of the enzyme, although malt (barley or wheat) amylases are also available. The α-amylase routinely is purified from barley using different purification steps, including salt precipitation, centrifugation, ion

Table 3.2 Catalytic properties of some glycolytic enzymes important in food technology (adapted from Whitaker 1994; Wong and Robertson 2007)

Enzyme	Bond selectivity	Product selectivity	Products
α-Amylase (endo)	α-1→4 Glucose	Retaining α→α	Initial major product dextins, final product maltose, maltotriose
β-Amylase (exo)	α-1→4 Glucose	Inverting α→β	β maltose
Pullulanase (endo)	α-1→6 Glucose	Retaining α→α	Acts on pullulan to give maltotriose and on starch to give linear dextrins
Glucoamylase	α-1→4 (α-1→6) Glucose	Inverting α→β	β-Glucose
Cyclomaltodextrin transferase	α-1→4 Glucose	Retaining α→α	Acts on cyclodextrins and linear dextrins to give maltose and maltotriose
Cellulase	β-1→4 glucose	1,4 β -dextrins, mixed 1,3-1,4-β-dextrins	
Invertase	β-1→2 Fructose	Retaining β→β	Glucose and fructose
β-Galactosidase	β-1→4 Galactose	Retaining β→β	Galactose and glucose
β-Gluctosidase	β-1→4 Aglycan, β-1 Glucose	Retaining β→β	Aglycan and Glucose
Polygalactourinase	α-1→4 Galactouronic acid	Inverting α→β	
Xylanase	α-1→4 Xylose	Retaining β→β	
Lysozyme	α-1→4, NAM-NAG	Retaining α→α	

exchange, and affinity column chromatographic methods such as CM sepharose CL-6B column and cyclohexaamylose (CHA)-sepharose affinity column. The enzyme can be also expressed in yeast and then purified from yeast extract as described above (MacGregor and Morgan 1992).

Food Application of α-Amylases

Starch Hydrolysis

α-Amylase is used industrially for production of dextrose, alcohol, beer, and bakery products as well as preparation of starch syrup and liquefaction of starch to produce dextrins which are further hydrolyzed by glucoamylase to yield glucose for production of corn syrup, fuel ethanol, or alcoholic beverage production. A thermostable α-amylase is used in industrial starch transformation. The process uses α-amylase

and Ca^{2+} to a 30–40% solid starch slurry, at pH 4.5, and heating to 105 °C. The mixture of linear and branched dextrins (maltodextrins) thus produced show a degree of hydrolysis ranging from 8 to 15 DE (DE: dextrose equivalence which can then be further hydrolyzed to produce a 15–40 DE maltodextrins (used as corn syrups, thickening, bulking, and increasing viscosity), sweetener production, and a 95–98% glucose syrup (95 DE) with the help of other enzymes such immobilized glucoamylase which can be subsequently converted to high-fructose corn syrup of 42% fructose (52% glucose) by an immobilized glucose isomerase column (Parkin 2017; Van der Maarel et al. 2002).

Future trends in starch industry will focus on extending pH stability (to pH 4–5), heat stability, and reducing Ca^{2+} requirement of α-amylases, thereby improving starch processing and transformation. Furthermore, enhancing the thermal stability will result in better process efficiency as well creating opportunity for single-step processing. A major priority in use of amylases in starch industry might include enhancement of selectivity of reactions to obtain preferred products or product distributions.

Baking and Baked Goods Industries

Enzymes have always played an important role throughout the history of bread making. The ancient Egyptians made use of enzymes present endogenously in the flour, although they may not have been aware of the effect. The first application of enzymes in baked goods, a trend which is practiced today as well, was supplementation of α-amylase by addition of malt to correct the concentration of endogenous α-amylase in the flour, thereby compensating the suboptimal concentrations of endogenous flour enzymes. Virtually all of the glycosidase presented in Table 3.2 have been added for some benefit in baking applications. The most widely used enzyme in baking industry in terms of amount and value is α-amylase. Initially amylases were believed to function primarily by mobilizing fermentable carbohydrate for yeast. The primary effect of amylase supplementation is securing adequate gassing power by degradation of damaged starch granules in the dough, which facilitates maltose production by endogenous β-amylase (Christophersen et al. 1998). The most widely used α-amylase in baking industry is the so-called fungal α-amylase or Taka-amylase from *Aspergillus oryzae*. The most common alternatives, malt amylases from barley or wheat malt, have higher protease side activities and higher thermo stability, and this makes them more prone to negative side effects when overdosed.

Another important goal of using amylases in baking industry is ant staling. Staling is a highly complex phenomenon. Retrogradation of amylopectins is believed to be the main contributor to bread staling (Morgan et al. 1997). This happens during the first hour of cooling, when a gelation network of amylose molecules is formed within which gelatinized starch granules are embedded. Amylopectin side chains recrystalize leading to rigidification of the starch granules and firmness of the crumb structure. Inter- and intragranular amylose recrystallization is also involved in the staling process. It is estimates that in the United States, the value of disposed baked goods as a result of staling in 1990 was about Us S$1 billion. The

emergence of maltogenic types of α-amylases and β-amylase in recent years have brought about production of shorter maltooligosaccharides (DP 7–9) with less tendency to stale (Hebeda et al. 1991).

Brewery and Fermentations

Brewing is one of the oldest food processes done by mankind. Brewing is defined as the process of beer production in which the sugars in starch are fermented to ethyl alcohol through the action of yeast. The endogenous enzyme in the kernel itself or the exogenous enzymes added from external sources participate in the fermentation process. Nowadays, brewing is one of the lead food industries in the world, and utilization of enzymes is one of the main aspects of brewing industry (Gomaa 2018).

The most common enzymes used in brewing industry are α-amylase, β-amylase, β-glucanase, and protease. The main reaction in the brewing of beer is conversion of starch into alcohol. In the first stage α-amylase, β-amylase hydrolyzes starch into fermentable sugars. In the second stage, these sugars are converted to alcohol and carbon dioxide by yeast enzymes. In the traditional process, the endogenous of enzymes of malted barley is a key ingredient in brewing. However, the endogenous amylases are insufficient to metabolize all of the fermentable carbohydrate because of low concentration, lack of thermal stability, or presence of endogenous inhibitors in the grains. Therefore, it is mandatory to use α- and β-amylases from external commercial sources which also bring extra quality attributes such as clarification, color, texture, or flavor to the product (Bamforth 2009). Auxiliary enzymes such as glucoamylase, pullulanase, glucanases, xylanases, and cell wall hydrolyzing are added to completely degrade starch to α- and β-limit dextrins, to render, limit dextrins fermentable, and hydrolyze glucans (similar to cellulose, but with β-1,3 and β-1,4 linkages) and xylans. The remaining limit dextrins provide body to the final product.

3.2.1.2 β-Amylases

β-Amylase is an exoglucanase that hydrolyses 1,4-α-D-glucosidic bonds in polysaccharides and successively releases maltose units from the nonreducing end starch and glycogen. A very good source of β amylase is sweet potato which contains about 5% of the total soluble proteins in the tuber. The action of this endogenous enzyme results in production of maltose which is responsible for sweetness of sweet potato (Thacker et al. 1992).

Properties and Applications

There are several similarities and differences between β amylase and α-amylase. Both enzymes cleave α-1,4 glycosidic bonds in amylose and amylopectin. β Amylase cleaves successively maltose units from the nonreducing end. Both have an average molecular weight of about 50 kDa. While α-amylase is widely distributed in nature, β amylase is only found in plants. β-Amylase is responsible for the sweetness of ripened fruit because it hydrolysis starch into maltose during ripening of fruits. Optimum pH for the hydrolytic activity of β-amylase is 4.0–5.5. The configuration of product units in α-amylase reaction is mainly α oligosaccharides and in β-amylase

is β maltose. α-Amylase is an endo-splitting glycosidase while β-amylase is exo-splitting. α-Amylase does bypass the branch point (i.e., α-1,6 glycosidic bonds), and β-amylase cannot bypass. Both enzymes cause reduction in viscosity as demonstrated in Fig. 2d and e, α-amylase more rapidly than β-amylase (Das and Kayastha 2019).

The amino acid sequences of β-amylases from different plants, including sweet potato, soybean, barley, wheat, maize, rye, cowpea, alfalfa, and several species of bacteria have been deduced from their respective gene sequences. The sequences between plant and bacterial β-amylases show only 30% homology (Thalmann et al. 2019).

β-Amylase has been purified form a variety of plant sources including germinated barley, sweet potato, and soybean. Purification follows several fractionation steps including acetone, ethanol, or ammonium sulfate precipitation followed by cation/anion exchange chromatography, gel filtration, and the affinity chromatography using cyclodextrin sepharose 6B column. β-Amylase is employed by the starch industry in the production of high-maltose syrup which has a higher viscosity and lower hygroscopicity, fewer tendencies to crystallize, and more resistance to browning than glucose syrup, the characteristics that are suitable in the confectionery and baking industry (Aiyer 2005).

3.2.2 Pectic Enzymes

3.2.2.1 Introduction

Pectins or pectic substances are a group of polysaccharides made of polymers of α-d-galactopyranosyluronic acids with various degrees of methylation on the carboxyl group of the galactouronic acids at O^6 position through ester bond. Pectins are commonly obtained from citrus peel and apple pomace. In food technology pectins are primarily used to prepare spreadable gels in the presence of sugar, acid, and/or calcium ions. When more than 50% of the carboxyl groups are in the methyl ester form, pectins are classified as high-methoxyl (HM) pectins; the remainder of the carboxyl groups will be present as a mixture of free carboxyl group and their sodium salt. Low-methoxyl (LM) pectins are preparations in which less than 50% of the carboxyl groups are esterified. The percentage of carboxyl groups is the degree of esterification (DE) or degree of methylation (DM) (Benen et al. 2003; Schols and Voragen 2003; Yapo 2011).

The pectin-degrading enzymes or pectic enzymes are a diverse group of enzymes and are classified into three general types, polygalacturonase, pectate and pectin lyases, and pectin methyl esterase. Polygalacturonases and pectic lyases belong to the hydrolase and layse classes, respectively, and are essentially depolymerizing enzymes. The methylesteraseases hydrolyze the methylester at O6 of a galacturonic acid. These enzymes are typically found in plants and microorganisms (especially fungi such as *A. niger*) and have been purified and extensively characterized (Benen et al. 2003).

Pectic enzymes do occur naturally in higher plants as endogenous enzymes and are endo- and exo-splitting. They are assumed to play important roles in plant development and during ripening. In food technology they are also added as processing aids as exogenous enzymes. The modern genomic approach will enable us to better understand their presence in plants in numerous isoforms and their roles in plant developments. Considering that pectic enzymes alone account for about one quarter of the world's food enzyme production, one can safely conclude that we are dealing with a huge market that could benefit immensely from the application of technological innovations designed to reduce economical costs and increase the productivity of the system (Alkorta et al. 1998; Whitaker 1990).

3.2.2.2 Polygalacturonases

Polygalacturonases are widely distributed in fruits such as pears, peaches, and avocado and are responsible for softening of these fruits. They catalyze the hydrolysis of the α-1,4-D-galacturonosidic linkage. Whereas endo-polygalacturonases hydrolyze the pectin polymers randomly, the exo-polygalacturonases only cleave off galacturonic acid monomers or digalacturonides from the nonreducing end. The enzymes, as found for the pectate lyases, use both polygalacturonic acid and low to moderate degree of esterification of galactouronic acids as their substarte (Benen et al. 2003). Polygalacturonases are widely applied in industrial processes such as fruit juice extraction, degumming of plant fiber, waste water treatment, oil extraction, coffee and tea fermentation, paper and pulp industry, and animal feed production. A mixture of amylases and pectinases is used for clarifying fruit juices. Polygalacturonases activities are abundant in tomatoes. The decrease in viscosity of the homogenates upon aging is a problem in tomato juice industry and is attributed to the continued action of endogenous polygalacturonases. These enzymes are instantaneously heat inactivated to obtain a viscous tomato juice and the high-consistency tomato paste (the so called "hot break" process). "Cold break process" is practiced when tomatoes are used for color and flavor only, and in such cases, consistency is provided by other ingredients such as starch. Breakdown of the pectins by combined pectin methylesteraseases/polygalacturonase action occurs during holding time between crushing and heat treatment (Benen et al. 2003; Javed et al. 2018).

3.2.2.3 Pectin Methylesteraseases

Wine and fruit juice industry has commercially utilized pectin methylesteraseases as early as 1930. The activity of these enzymes has been detected in various plants which confirms their wide distribution (Gupta et al. 2015; Dixit et al. 2013). Pectin methyl esterases are of major importance for the preparation of pectins for specific applications. These enzymes along with polygalacturonases are used in clarification of juices in fruit juice industry and for liquefaction of fruit mashes. In such an application, for the complete disruption of the cell walls, the pectinases are combined with cellulases and hemicellulases. Pectin methylesteraseases from *Datura stramonium* in combination with polygalacturonase increased clarity of orange, apple,

pomegranate, and pineapple juices by 2.9-, 2.6-, 2.3-, and 3.6=fold, respectively (Dixit et al. 2013).

3.2.2.4 Pectate Lyases

Figure 3b shows that pectate lyases cleave the α-1,4-D-galacturonosidic linkage through a β-elimination reaction resulting in the formation of a Δ4,5-unsaturated newly formed nonreducing end. Pectin lyases perform the same reaction except that pectin lyases require methylesterified galacturonic acid residues adjacent to the scissile bond. Pectate lyases have been identified in plants (Uluisik and Seymour 2020). The first clear cut demonstration of plant pectate lyase activity was reported in the plant zinnia eleganse (*Zinnia elegans*) (Domingo et al. 1998). These enzymes are involved in remodeling the cell wall during cell elongation and differentiation and in the ripening of strawberries and bananas. Because of high-pH optima, which generally are above pH 8.0, and calcium requirement, pectate lyases have not found any application in the food industry. However, pectate lyases and pectin lyase may well be present in commercial pectic enzyme preparations used in the food industry (Semenova et al. 2006).

3.2.3 Cellulases

Cellulose is the most abundant biopolymer on nature. It is mainly produced in higher plants in which it forms the rigid skeleton of the plant. Cellulose is a homopolymer consisting of up to 1000 β-1,4-linked anhydroglucopyranoside units. Single glucose polymers are packed onto each other to form a highly crystalline fibrillar material in which the individual cellulose chains are held together by hydrogen bonds. Cellulose microfibrils also contain some amorphous regions, the amount of which depends on the source. The most crystalline cellulose is produced by algae and the least crystalline by plants (Klemm et al. 2005).

Cellulases belong to the group of β-glucan hydrolases that have the ability to degrade cellulose. Several microorganisms such yeast, filamentous fungi, and bacteria existing in the intestine and colon of monogastric animals are hydrolyze cellulose to oligosaccharides and eventually to glucose. The wide spectrum of microorganisms present in the digestive tract of ruminants is able to fully degrade cellulose. Like many depolymerizing enzymes, cellulases are classified into two distinct groups, end-splitting, or exo-splitting glucanases which act in the middle of the cellulose chain or at either end of the cellulose chain, respectively (Tenkanen et al. 2003). There are reports on the presence of cellulases in plants; however, only the endoglucanases (1,4-β -D-glucan-4-glucanohydrolase) have been found This enzyme catalyses random cuts in cellulose chains, thereby producing shorter cello-oligomers, which can be further degraded by exoglucanases. The generation of microbial cellulases in transgenic plants such as sugarcane and corn has been reported. These advances can offer one possible use of plant biomass in the form of biofuel crops or residual agricultural crop waste as renewable energy sources (Hefferon 2017).

Cellulase has a wide range of applications in industrial biotechnology and is the second most used industrial enzyme after protease. However, cellulases are not widely used in the food industry but can be added to help the action of other enzymes pectinases and hemicellulases to disrupt the plant cell wall and enhance the extraction of the targeted molecules in processing of cereal-based beverages and foods such as beer and bread. In addition, the application of enzyme cocktails containing cellulases results in improving the extraction yield and the overall process efficiency. In addition, added cocktails enzymes containing cellulases is used increasingly for improved processing and product quality and to improve dough structure, thereby providing a more even flavor distribution and a better rise of dough and improved the dough strength, elasticity, and crumb structure of the baked goods. Cellulases are used in rather large amounts in animal feed for improving digestibility (Zhang and Zhang 2013). Other application of cellulases include processing of natural textile fibers composed of cellulose (Zhang and Zhang 2013; Autio et al. 1996) and extraction nutraceuticals and compounds from natural sources with additional health benefits, besides the nutrition role from plants (Fernandes 2018).

In general, cellulases alone or in combination with other cell wall degrading enzymes are applied in all processes involving extraction of valuable compounds such as polysaccharides, oil, and protein, from the plant material (Laurikainen et al. 1998).

3.2.4 Other Glycosidases

3.2.4.1 β-Glucosidases

β-Glucosidases are large group of enzymes with many important functional properties in biological systems. Based on their catalytic and sequence characteristics, β-glucosidases are categorized in several glycoside hydrolase families (Singh et al. 2016). Certain glycosidases release important flavor compounds from glycosylated nonvolatile and flavorless glycoconjugates precurses present fruit and plant tissues. These precurses, mostly aryl and alkyl β-glycosides, disaccharides, and short chain oligosaccharides, can be metabolized by β-glucosidases which results in the liberation of multitude of flavoring compounds. Glycosidases are important in wine industry for releasing flavor compounds from glycosidic precursors. β-Glucosidases are widely distributed in nature and are present bacteria, fungi, plants, and animals (Romero-Segura et al. 2009).

Another aspect of glucosidases important to food processing and quality is the presence of cyanogenic glycoside in many plant sources which can produce toxic hydrogen cyanide (HCN) when tissue is macerated during preparation or by chewing. The examples include the cyanogenic glucoside linamarin in cassava roots and leaves (vastly consumed as food staple in tropical regions of Africa, Asia, and South America), lima beans, bitter almonds, and flax seeds. There are approximately 25 cyanogenic glycosides known, such as linamarin in cassava and lima beans; dhurrin in sorghum; and amygdaline in almonds, peaches, and apricot pits (Hughes 1999).

The enzyme rhodanese is a ubiquitous enzyme the activity of which has been detected in all living organisms from bacteria to man. It is believed that this enzyme function to detoxify cyanide in animal tissues. This enzyme is also widely distributed in plants (Chaudhary and Gupta 2012). The main source of this enzyme was regarded to be the liver of animals. However, extensive studies on the distribution pattern of rhodanese in our laboratory have demonstrated that other organs, in particular the digestive tract, indeed contain greater amounts of rhodanese, which indicate that cyanide produced from cyanogenic glycosides is principally detoxified in the GI tract before being absorbed (see (Aminlari and Vaseghi 2006) for a review).

3.2.4.2 Xylanases

Like cellulose, xylan is a polysaccharide abundantly found in nature and is a major hemicellulose component of the plant cell wall. Xylanases are β-retaining glycosidases that catalyze the hydrolysis of linear β-1,4-linked in xylose polymers. These enzymes can be endo- or exo-splitting. The xylanases are ubiquitous in nature, and their presence is reported in a wide range of organisms (Biely 2003). They are present in plants (especially in cereals), bacteria, and fungi with molecular mass of 16–40 kDa. The endogenous plants xylanolytic enzymes participate in many physiological and morphological reactions involving cell wall. During germination hydrolysis of xylan polysaccharides by these enzymes disrupts the physical barrier imposed by the walls and allows free diffusion of starch and storage protein-degrading enzymes. Enzymes degrading hemicellulose polysaccharides are also reported to be present in wheat grain and wheat flour (Kumar et al. 2017).

Xylanase enzymes are used as processing aid in food industry to depolymerize pentosans which have high water-holding capacity. These enzymes cause increases in dough viscosity leading to increased elasticity, gluten strength, and final loaf volume. The combination xylanases are particularly important in the formulation of frozen dough. Endo xylanases are one of the hemicellulases that are used in fruit and vegetable processing. Xylanases are also used in brewing to reduce viscosity of the wort in brewing, allowing ease in separation/filtration steps, reduced haze formation, and slightly improved process yields (Kumar et al. 2017; Bhardwaj et al. 2019).

3.2.4.3 Glucoamylase

Glucoamylase catalyses the hydrolysis of glycosidic bonds from nonreducing end of starch-derived substrates to produce glucose. It attacks α-(1,4), α,β-(1,1), α-(1,6), α-(1,3), and α-(1,2) glycosidic bonds between adjacent glucosyl residues, in order of decreasing rate. Glucoamylase plays a major role in food processing to saccharify starch in cereals and produce glucose syrups from maltodextrins after the action of α-amylase. Glucoamylase is produced by some eubacteria, a few Achaea, a number of yeasts, and many filamentous fungi. Although there are reports of animal and plant glucoamylase, these appear to be fundamentally different enzymes with kinetic properties that overlap those of true glucoamylase. For this reason, and in spite of wide application of this enzyme in food industry, this enzyme will not be further discussed in this chapter.

3.3 Enzymes Working on Proteins

Proteolytic enzymes also referred to as proteinases or proteases are enzymes that catalyze the hydrolyze peptide bonds in proteins and peptides, according to the following equation:

$$-\mathrm{NH}-\mathrm{CHR_1}-\mathbf{CO}-\mathbf{NH}-\mathrm{CHR_2}-\mathrm{CO}-+\mathrm{H_2O}-\mathrm{NH}-\mathrm{HR_1}$$
$$-\mathrm{COOH}+{}^{+}\mathrm{NH_3}-\mathrm{CHR_2}-\mathrm{CO}-$$

Proteases are found in all living organisms (animals, plants, and microorganisms). They are essential for breaking down of proteins to peptides and amino acids. In the human gastrointestinal tract, the proteolytic enzyme pepsin (stomach) and a large group of small-intestinal proteolytic enzymes (trypsin, chymotrypsin, carboxypeptidases, leucine aminopeptidases, tripeptidases, and dipeptidases) convert the proteins of ingested foods to amino acids.

Proteases are some of the best-characterized enzymes in terms of their vital role in the human digestive system and early commercialization (the first standardized calf rennet for cheese making was marketed in 1874) (Wong and Robertson 2007). Peptidases transform food proteins in situ or are added exogenously to cause protein transformation.

3.3.1 Specificity

The study of protease specificity provides information on active-site structure and function, protein-protein interaction, regulation of intracellular and extracellular pathways, and evolution of protease and substrate genes (Diamond 2007). Proteolytic enzymes are either endo-proteases or exo-proteases. The endo-proteases hydrolyze peptide bonds in the interior of the polypeptide chains (trypsin, chymotrypsin, chymosin) while the exo-proteases act on peptide bonds at the N-terminal (aminopeptidases) or the C-terminal (carboxypeptidases) of the protein molecule. Some proteases are said to have broad specificity, i.e., they can hydrolyze peptide bonds irrespective of the side chain group adjacent to the scissile peptide bond. Examples include pepsin and bacterial subtilisin from various *Bacillus* spp. Majority of proteolytic enzymes, however, have absolute specificity for one or few of the amino acid residues at the scissile peptide bond. The scissile bond of the peptide substrates is the bond linking residues R1 and R2 in above equation. For example, trypsin hydrolyzes the peptide bonds on the C-terminal side of lysine and arginine residues. The corresponding residues for chymotrypsin and elastase are aromatic amino acids, namely, phenylalanine, tyrosine, or tryptophan, and small hydrophobic groups such as alanine, respectively (Wong and Robertson 2007; Grahn et al. 1999).

The specificity for the substrate is defined as the properties of the binding sites of protease reflected in the sequence of amino acids in the active site which is complementary to the sequence of amino acid adjacent to scissile bond of the respective protein substrate. This complementarity provides a chemical and spatial

arrangement for favorable binding interaction between the substrate amino acid side chains with residues that form the binding site of the protease, as shown below:

$$\begin{array}{c} S3-S2-S1-S1'-S2'-S3' \\ ------NH-CHR-\mathbf{CO}-\mathbf{NH}-CHR-CO------ \\ P3-P2-P1-P1'-P2'-P3' \end{array}$$

In the the protease active site, S1, S1', . . . refer to the amino acids that provide the chemical and spatial environment that complements the substrate amino acids referred to as P1, P1', . . .). The arrow shows the scissile peptide bond. These sites have been mapped and characterized for many proteases (Wong and Robertson 2007; Vizovišek et al. 2018).

3.3.2 Classification

Proteases are classified into four different types according to the nature of specific group of enzymes involved in the hydrolytic catalysis of peptide bond, i.e., the nucleophilic attack at the carbonyl carbon of the scissile peptide bond of the substrate. These types of proteases are described below (Whitaker 2003).

3.3.2.1 Serine Proteases

Serine proteases have in common the presence of the side chain of a serine residue in the active site which participates in the catalytic activity. Among the serine proteases, the most well known are trypsin, chymotrypsin, and elastase. Other serine proteases include collagenase, the nine proteases involved in blood coagulation and subtilisin is from *B. subtilus*. The molecular masses of most serine proteases are 25–35 kDa, and they are characterized by an active site compromising a surface groove involved in binding the substrate. The pH optimum of this enzyme is around 8 (Whitaker 2003; Hedstrom 2002; Di Cera 2009).

3.3.2.2 Aspartic (Acid) Proteases

Aspartic proteases are characterized by two highly conserved aspartic acid residues which participate in the catalytic activity of the enzyme which act as general acid/base (Whitaker 2003; Nair and Jayachandran 2019). Aspartic proteases are endopeptidases and have optimum pH near 3–4. Pepsin, chymosin (also called "rennin" or "rennet," used in cheese-making), cathepsin (involved in postmortem meat tenderization), and the chymosin-substitute peptidases from Mucor spp. are among the most well-known aspartic proteases. The molecular mass of these enzymes is 34–40 kDa (Nair and Jayachandran 2019).

The very important enzymes in cheese making are chymosin and the *Mucor* proteases. The gene for calf chymosin has been cloned and expressed in microorganism such as *Aspergillus ridulans*, *Escherichia coli*, *A. awamori*, and *Saccharomyces cerevisiae*. FDA has approved recombinant calf chymosin for use in cheese

making. While the optimal pH o for these enzymes is 3–4, the optimum pH for hydrolyzing the Phe105-Met106 bond of kappa-casein and coagulation of the caseins is at pH 5 (Kawaguchi et al. 1987; Ulusu et al. 2016).

3.3.2.3 Cysteine (Sulfhydryl) Proteases

There are over 130 known cysteine proteases present in plants, animals, and microorganisms. Most members of this group belong to the papain family; other members include chymopapain (multiple isoforms) papain from tropical tree, *Carica papaya* (papaya), actinidin from kiwi fruit, ficin from fig latex, bromelain from pineapple, and lysosomal cathepsins from animal tissues. Among them papain, bromelain, and ficin represent 5% of the global sales of proteases (Illanes 2008; Verma et al. 2016). Papain is the best-studied cysteine protease, which has major uses in the food industry for meat tenderization and other applications as discussed in more detail later in this chapter. Calpains are unique cysteine proteases of muscle which cause postmortem tenderization of muscle.

The molecular mass of these enzymes is in the range of 24–35 kDa with optimum pH 6.0–7.5. These enzymes are rather heat stable and can withstand temperatures up to 60–80 °C in part due to the presence of three disulfide bonds (Whitaker 2003; Otto and Schirmeister 1997).

3.3.2.4 Metalloproteases

The major metalloproteases include the carboxypeptidases A and B, carnosinase which acts on β-alanyl-L-histidine and related compounds, glycyl-glycine dipeptidase, amino-acyl-histidine hydrolase, and cytosolic α-amino-acyl-peptide hydrolase. Most of metalloproteases are exopeptidases and require Zn^{2+} as cofactor. Some enzymes of this group require Mn^{2+} (such as prolidase and iminodipeptidase. Other metalloproteases are endo-acting thermolysin (from *Bacillus thermoproteolyticus*) and the neutral endoprotease from *Bacillus amyloliquefaciens* (Tavano et al. 2018).

3.3.3 Application of Proteases in Food Industry

Some of proteases are available commercial with different degrees of purity, and some are mixture of several enzymes. Some of the important commercial applications of proteolytic enzymes are shown in Table 3.3 and are described below (Whitaker 2003).

3.3.3.1 Production of Protein Hydrolysates

Proteases such as papain, chymotrypsin, pepsin, trypsin, and thermolysin are extensively used to hydrolyze food proteins aiming to alter their functional properties such as solubility, foaming, emulsifying, gelling, nutritional, flavor/sensory, and textural attributes as well as reduced allergenicity. Nonspecific proteases, such as papain, extensively hydrolyze proteins resulting in solubilization of poorly soluble proteins. These protein hydrolysates are composed of low-molecular-weight peptides with two to four amino acid residues. However, extensive hydrolysis is not beneficial

Table 3.3 Use of proteolytic enzymes in food processing (adapted from Whitaker 2003)

Food	Purpose of action
Baked goods	Softening action in doughs. Cut mixing time, increase extensibility of doughs. Improve texture, elasticity and loaf volume. Liberate β-amylase
Brewing	Body, flavor, and nutrient development during fermentation
	Aid in filtration and clarification. Chill-proofing
Cereals	Modify proteins to increase drying rate, improve product handling characteristics. Production of miso and tofu
Cheese	Casein coagulation. Characteristic flavor development during aging
Chocolate, cocoa	Action on beans during fermentation
Egg, egg products	Improve drying properties
Feeds	Waste product conversion to feeds. Digestive aids, particularly for pigs
Fish	Solubilization of fish protein concentrate. Recovery of oil and proteins from inedible parts
Legumes	Hydrolyzed protein products. Removal of flavor. Plastein formation
Meats	Tenderization. Recovery of protein from bones
Milk	Coagulation in rennet puddings. Preparation of soybean milk
Protein hydrolysates	Condiments such as soy sauce and tamar sauce. Bouillon
	Dehydrated soups. Gravy powders. Processed meats. Special diets
	Antinutrient factor removal. Specific protein inhibitors of proteolytic enzymes and amylases
	Phytate. Gossypol. Nucleic aci
Wines	Clarification
In vivo processing	Conversion of zymogens to enzymes. Fibrinogen to fibrin. Collagen biosynthesis. Proinsulin to insulin. Macromolecular assembly

because functional properties such as gelation, foaming, and emulsifying properties are adversely affected. Production of protein hydrolysate involves treating a protein isolate by a selected endopeptidase in a batch process for a few hours followed by inactivation of the added enzyme by heat treatment. On the other hand, hydrolysis by exopeptidases converts small oligopeptides to composite amino acids. In order to enhance peptidase access to scissile bond of protein substrate and facilitate hydrolytic attack, the proteins are denatured by pretreatment. Proteins that are commonly used for production of food protein hydrolysate include milk, meat, yeast, fish, legumes, wheat, and vegetables. Protein hydrolysate can improve functional properties such as emulsifying capacity and stability, foaming capacity and foam stability, ant oxidative activities, water absorption capacity, and nutritional properties (Chalamaiah et al. 2012; Thiansilakul et al. 2007; Sinha et al. 2007; Clemente 2000).

Protein hydrolysates can be incorporated into special formulations designed to provide nutritional support for patients with different needs. Protein hydrolysates with defined characteristics can be produced by sequential action of endopeptidases and exoproteases followed by specific post-hydrolysis procedures (Rocha et al.

2009). For production of protein hydrolysates, the level of protein in the source should be maintained at 8–10%, provided there are no limitations on solubility, and depending on purity, the amount of added enzyme is generally ~2% on a protein basis. This allows a sufficiently high protein: enzyme levels such the enzyme approaches its maximum velocity with limited autolysis of the enzyme. The hydrolysates can be characterized by the degree of hydrolysis (DH), sequence of produced peptides, functional properties such solubility, emulsifying properties, etc. DH can be easily evaluated with o-phthaldialdehyde (OPA) method which determines the number of free amino groups (Mirzaei et al. 2016). Typically, a DH value of 3–6% corresponding to peptides of 2–5 kDa is desired for physicofunctional properties, while DH of 8% or more means 1–2 kDa peptides having optimum solubility for use in clinical nutrition and sports products. Extensive hydrolysis (DH as high as 50–70%) yields small peptides and amino acids of <1 kDa which are useful for hypoallergenic foods and infant formulas and as flavoring ingredient in products such as soups, gravies, and sauces. One problem associate with the greater DH is the possibility of production of bitter peptides (small and hydrophobic), thereby necessitating to control this potential flavor defect (Chalamaiah et al. 2012). Proteases can be used to separate and isolate residual muscle protein from bones of fish and land animals as protein hydrolysates (Chalamaiah et al. 2012; Mizani et al. 2005).

3.3.3.2 Application of Proteolytic Enzymes in Dairy Industry

Milk as a very perishable commodity can be preserved by processes such as fermentation, drying, pasteurization/ sterilization, and freezing and modification by enzyme. The fact that milk is a liquid facilitates enzyme addition. Application of exogenous enzymes for cheese production is the oldest and is still the largest mode of use of enzyme in food processing. The principal enzymes used in dairy technology are proteinases, peptidases, lipases, and lactase and oxidoreductases. In this section we will focus on the proteases since they are by far the most widely used enzymes in dairy technology. Applications include cheese manufacturing, alteration of functional properties, production of protein hydrolysate, and nutritional and other applications (Fox 1993; Shah et al. 2014).

Cheese Manufacturing

The principal gastric enzyme of neonatal ruminants is chymosin or rennet. Chymosin has a high milk-clotting activity but low general proteolytic activity. Addition of calf chymosin (rennet) and chymosin substitutes (see below) to milk causes a milk-clotting reaction that leads to cheese manufacture. The rennet coagulation of milk is a two-stage process. In the first (primary) phase, rennet catalyzes the specific hydrolysis of the PHE105-MET106 bond of κ-casein and produces "para-casein" and TCA (trichloroacetic acid)-soluble peptides (glycomacropeptides). In the secondary phase, Ca-induced gelation of para-casein at 30–35 °C occurs. The rate and extent of proteolysis are greater than coagulation, and therefore hydrolysis is essentially complete before the onset of coagulation. Hydrolysis results in the loss of micelle-stabilizing properties of k-casein. The para-k-casein remains in the micelle

but the caseino (glyco) macro peptide which is hydrophilic diffuses into the whey. pH of milk is decreased to 5.8–6.5 by added starter cultures followed by addition of chymosin to start clotting. Some enzyme activity remaining in the curd and sustained proteolysis activity of starter cultures contribute to flavor development during subsequent ripening and aging of cheese.

The recombinant calf chymosin produced in *E. coli* contains no pepsin while some milk clotting activity of calf rennet may be due to the presence of pepsin (Kawaguchi et al. 1987; El-Sohaimy et al. 2010).

Increasing production and consumption of cheese have resulted in shortage of veal rennet, and the supply has been inadequate for many years, which has led to a search for rennet substitutes. During the past four decades, the increasing use of a variety of milk clotting enzymes has become a major technical trend in cheese manufacture. Although many proteinases can coagulate milk, only few have been found to be more or less acceptable as rennet. These include bovine, porcine, and chicken pepsins; rennet (aqueous extracts made from the fourth stomach of calves, kids, lambs, sheep goat and cow); microbial rennet made by *Endotbia parasitical* and *Mucor* species (*Mucor miebei* or *M. pusillus*) and *Cryphonectria parasitica* and plant proteases (Shah et al. 2014; Kim et al. 2004a).

Many commercial calf rennets contain pepsin. Fungal rennets generally yield acceptable cheese, inspite of their different specificity towards αs_1- and β-caseins, compared to chymosin. However, they are replaced with microbial recombinant chymosin, particularly in the United States (Nelson 1977; Green 1977).

Milk Clotting Enzymes from Plants

Although several properties of microbial milk-clotting enzymes exhibits high proteolytic activity and high thermostability. Made them suitable for cheese manufacturing, plant rennets have attracted considerable attention and interest in cheese industry. The reason for this is that they are easily available and their purification processes is simple. Another advantage of plant proteases is the acceptability of the manufactured cheese by the vegetarians which may improve their nutritional intake.

As discussed above, based on the catalytic mechanism used during the hydrolytic step, plant proteases are classified into several groups. The main classes of milk-clotting proteases are aspartic, serine and cysteine proteases (Shah et al. 2014).

Aspartic proteases are widely distributed in plants species. They are involved in multiple metabolic processes such as storage, responses of plants to stress and pathogens, and plant senescence. Most aspartic proteases are heterodimeric proteins with large subunit of 28–35 kDa and small subunit of 11–16 kDa, and only very small number of monomeric proteins with molecular mass of 36–65 kDa. Examples of this type of enzyme include (Shah et al. 2014):

1. Cardosin from flowers of the artichoke thistle (*Cynara cardunculus*)
2. Cynarase from flowers of globe artichoke (*Cynara scolymu*)
3. A cardosin A like enzyme from thistle (*Cynara humilis*)
4. An enzymatic extract from the thistle *Silybum marianum* flowers

5. Oryzasin from seeds of rice (*Oryza sativa*)
6. Enzymatic extract from flowers of moringa (*Moringa oleifera*)
7. Onopordosin from cotton thistle (*Onopordum acanthium*)
8. Cirsin JN703462 from flowers of common thistle (*Cirisum vulgare*)
9. Enzymatic extract from cell suspension of red star-thistle (*Centaurea calcitrapa*)

Serine proteases are also widespread in plants and belong to several taxonomic groups. Their function in plants is almost the same as the aspartic proteases, with some additional features. Serine proteases are extracted, purified, and characterized from several parts of plants, especially fruits. Some of the enzymes in this group are (Di Cera 2009):

1. Dubiumin from seeds of *Solanum dubium* (*Solanum*, also called bittersweet or woody nightshade) (from Wikipedia, the free encyclopedia).
2. Cucumisin from *Cucumis melo* fruits (muskmelon is a species of melon that has been developed into many cultivated varieties). These include honeydew, cantaloupe, and Persian melon (from Wikipedia, the free encyclopedia).
3. Lettucin from leaves of lettuce, Lactuca sativa (from Wikipedia, the free encyclopedia).
4. Religiosin from *Ficus religiosa* (sacred fig is a species of fig native to the Indian subcontinent and Indochina) (from Wikipedia, the free encyclopedia).
5. Streblin from stems latex of Streblus asper (a tree known by several common names, including Siamese rough bush, khoi, serut, and toothbrush tree).

Cysteine proteases or thiol-proteases have a cysteine sulfhydryl group in their active site that participates in the catalytic mechanism. These enzymes have been purified and extensively studied for their potential application as milk coagulants. The following is a list of examples of serine proteases from plants (Amal Ben Amira et al. 2017; Lo Piero et al. 2011):

1. Enzymatic extract from seeds of *Albizia lebbeck* (a species of *Albizia*, native to Indomalaya, New Guinea, and Northern Australia and widely cultivated in tropical and subtropical regions. It is often called lebbek tree siris, frywood, koko, and woman's tongue tree.
2. Enzymatic extract from seeds of sunflower (*Helianthus annuus*).
3. Ficin from branches latex of figs tree *Ficus carica sylvestris* and an enzyme from stem latex of Sideroxylon *obtusifolium* (*Sideroxylon* is a genus of trees in the family *Sapotaceae*. They are collectively known as bully trees.
4. Actinidin from kiwi (*Actinidia chinensis)* fruits.
5. Calotropain from latex of crown flower *Calotropis gigantea*.

Recently, we reported on application of actinidin to the production of cheese from cow's milk. Comparison of actinidin and chymosin indicated that the former could be a potential alternative to the latter in application as milk coagulant (Alirezaei et al. 2011).

Several defects in cheeses made by plant proteases, including development of bitterness and improper texture and differences in sensory properties of cheese, have resulted in drawback of most plant rennets and have limited their industrial use. These defects are caused by excessive proteolytic activities and low ratios of milk-clotting activity/proteolytic activity. Therefore, before selecting appropriate plant rennets, the enzyme activity, different gelation parameters, and comparison with those of commercial rennet (chymosin) must be evaluated.

3.3.3.3 Application of Enzymes in Meat Industry

The palatable quality of meat is influenced by several factors, among which meat tenderness is considered the most important determinant of consumer preferences. The chemical and physical properties of muscle tissue and the associated connective tissue are major contributors to meat quality. The conversion of muscle to meat is a complex process.

Tenderness is a characteristic resulting from the interaction of actomyosin of myofibrillar proteins, the background of connective tissue, sarcomere length, and the bulk density of fat. Another important factor in meat tenderness is the extent of proteolytic degradation of muscles (Arshad et al. 2016; Marques et al. 2010).

Several chemical and physical methods can be used to tenderize meat. The goal is to decrease the amounts of connective tissue without extensively degrading myofibrillar proteins. The breakdown of myofibril starts after the enzymatic activation of system and includes the proteins tropomyosin, troponin T, troponin I, C-protein, connectin, desmin, vinculin, dystrophin, nebulin, and titin. The action of the complex endogenous proteolytic enzymes, calpain-calpastatin, which act in muscle tissue after slaughter, is the first step of meat tenderness. Cathepsins and calpain are among the first enzymes used in meat tenderization. Calpains are calcium-dependent proteases that degrade myofibrillar proteins. The difference in the level of meat tenderization among different breeds or species of animals is due to variation of the concentration of the enzymes resulting in increased or decreased proteolysis of myofibrillar proteins (Lian et al. 2013).

Several factors contribute to meat tenderness such as type of muscle, pre- and post-slaughter factors, and postmortem pH and temperature. Proteolytic enzymes from plant sources have received special attention because they active over a wide range of temperatures and pH. Treatment by proteolytic enzymes is one of the most popular methods of meat tenderization. The use of exogenous proteases for meat tenderization improves meat quality. Plant proteases (papain, bromelain, ficin and actinidin) and proteases from *Aspergillus oryzae* and *Bacillus subtilis* have been approved as generally regarded as safe (GRAS) for use in the meat. Collagen and elastin are connective tissue proteins that cause toughness in meat and are hydrolyzed by these enzymes thereby resulting in tenderness. The endopeptidases papain and bromelain are applied to muscle or meats that do not become sufficiently tenderized during postmortem aging. Papain and bromelain are the most commonly used plant enzymes for meat tenderization. Plant proteases affect the structure of myosin and actin filaments. Several methods are available for assessing tenderness of meat including assaying for activity of enzymes, hydroxyproline content,

myofibrillar fragmentation index, and scanning electron microscopy. A proteolytic enzyme with specificity for collagen and elastin working at the relatively low pH of meat, and either at low storing temperature or at high cooking temperature, would be the ideal meat tenderizer (Arshad et al. 2016; Lian et al. 2013).

Papain

Papain is a nonspecific sulfhydryl protease present in the latex of the tropical plant *Carica papaya*. The crude latex is obtained by scoring the fruit and then allowing the latex to dry. In the food industry, papain is commonly used for meat tenderization, production of protein hydrolysate, and the clarification of juice and beer, in the baking and dairy industries for cheese manufacturing and for the extraction of flavor and color compounds from plants. Papain is purified by reducing contaminating agents and further extraction. The enzyme is heat stable and requires a temperature of 80 °C for 22 min for 95% inactivation. Papain has a tendency to over-tenderize the meat surface, making it "mushy." Papain is used to increase the amount of free amino acids in dry fermented sausages. The three-dimensional structure for papain has been determined. Broad-spectrum enzymatic activity has been shown by papain in the pH range is 5.9–7.5, and the temperature range of activity is at 70–90 °C with optimum of 65–75 °C. Under these conditions papain has excellent activity in hydrolysis of myofibrillar proteins and moderate effect on hydrolysis of collagen (Istrati 2008; Gokoglu et al. 2017).

Papain, bromelain, ficin, and other bacterial and fungal proteases can be used in the fruit juice industry and in beer clarification. The defect referred to as chill-haze in beer is the result of interaction of tannins and proteins, thereby causing formation of complexes that make the solution turbid and hazy. Papain is added after fermentation and prior to final filtering. The enzyme is ultimately destroyed by beer pasteurization. Measurement and controlling proteolytic activity in beer is important, since some residual protein is necessary to maintain specific quality attributes, and excessive action of the enzyme may loss of foam stability (Mosafa et al. 2013).

Bromelain

Bromelain (or bromelin) is the soluble enzyme present in large quantities in many parts of pineapple (*Ananas comosus*). The juice of different parts of the plant contains bromelain. It has a strong proteolytic activity and is commercially available in powdered form. It is widely used in food, detergent, and textile industries. It is estimated that 95% of the enzymes used in the United States are obtained from plant proteases like papain and bromelain, whereas microbial proteases are not widely used as tenderizer. Bromelain is extracted and purified from pineapple by the reverse micelle technique. Bromelain proteolytic activity often results in over tenderization of meat due to extensive degradation of myofibrillar proteins and collagen. Bromelain can be used in tenderization of adult beef at 10 mg/100 g meat after 24 h at 4 °C. Following this time period, enzyme can be inactivated by heating at 70 °C. Bromelain is active in the pH range of 4–7 and optimum is 5–6. The temperature range of activity is at 50–80 °C, and optimal is 65–75 °C. Under these conditions bromelain

has moderate activity in hydrolysis of myofibrillar proteins and excellent effect on hydrolysis of collagen (Arshad et al. 2016; Gokoglu et al. 2017).

Ficin

Ficin is a sulfhydryl or cysteine protease commonly obtained from *Ficus carica* (fig tree). Ficin is a very good example of plant protease and is becoming increasingly popular to replace animal or microbial recombinant proteases. This enzyme can be applied for producing protein hydrolysate, bioactive peptides, in milk coagulations for cheese manufacturing, in meat tenderization, and synthesis of peptides. Ficin does have huge potential and brilliant prospect in the near future (Englund et al. 1968; Morellon-Sterling et al. 2020). Ficin has a molecular weight of 44.5 kDa and shows maximal activity at pH 5.0–9.0 and optimum pH is 7.0. The enzyme is fully active at 45–75 °C with optimum temperature of 60–70 °C. Under these conditions ficin has moderate activity in hydrolysis of myofibrillar proteins and excellent effect on hydrolysis of collagen. These properties make ficin a very useful plant protease in food industry. We used ficin to tenderize beef used for manufacture of sausages. The results indicated that solubility of meat proteins increased and SDS-PAGE results showed the disappearance of several protein bands in ficin-treated meat. Ficin-tenderized meat substantially improved water holding capacity and emulsion stability. The results of this study indicated that some quality attributes of meat products can be improved by enzymatic modification of protein sources in the manufacture of meat products (Ramezani et al. 2003).

Actinidin

Actinidin is a sulfhydryl protease extracted from gooseberry or the kiwi fruit. It has a molecular weight of 32 kDa. Actinidin has many advantages over other plant proteases such as papain and ficin because of its mild tenderizing activity even at high concentrations and low inactivation temperature (60 °C). It is widely used in the food industry. Kiwifruit juice is powerful and easily prepared meat tenderizer, which could contribute efficiently and effectively to the meat tenderization process (Boland 2013; Morton et al. 2009). Actinidin is used commercially for meat tenderization and as aid in the digestive process. The tenderness of lamb can be improved by pre-rigor infusion of kiwifruit juice in carcasses which results in enhanced proteolytic activity, significant degradation of the myofibrillar proteins, production of new peptides, as well as activation of m-calpain during post-mortem ageing (Boland 2013; Morton et al. 2009).

A group in our lab studied the effect of actinidin on beef for use in manufacture of sausage. Actinidin was partially purified from kiwi fruit by salt precipitation followed by DEAE-Sephadex column chromatography. The effect of purified actinidin on the protein solubility (nitrogen solubility index [NSI]), water holding capacity (WHC), texture, and SDS-PAGE pattern of beef was studied, and the quality attributes of a sausage product was evaluated. Actinidin significantly increased NSI and WHC of beef; the highest NSI and WHC (approximately 20% and 8% increase, respectively) were observed when beef was incubated with 0.9 unit enzyme/g beef. Texture analysis indicated increased tenderization (10% decrease in

shear force) when slices of beef were treated with actinidin at 37 °C for 2 h. SDS-PAGE results indicated appearance of several low molecular weight bands (<10 kDa) after treating beef with different levels of actinidin for 30 or 60 min. Slight changes in protein band in the range of 100 to 120 kDa and 13 to 25 kDa were also observed. The use of actinidin-tenderized beef significantly improved emulsion stability, texture, and organoleptic properties of the sausage product (Lewis and Luh 1988). We applied actinidin to tenderize camel meat and beef and used the tenderized meats in the manufacture of emulsion type sausages. The properties of sausages made from the meat of both species were similar. Emulsion satiability, folding, texture taste, and overall quality of sausages produced from actinidin-tenderized meat was superior to untreated samples (Aminlari et al. 2009). Actinidin is still not approved as GRAS by FDA (Lewis and Luh 2007; Toohey et al. 2011).

Conclusion

Meat tenderness is the most important attribute associated with meat quality and consumer satisfaction. Different plant proteases like papain, bromelain, actinidin, and ficin can hydrolyze connective tissue proteins collagen and elastin thereby causing tenderization of meat and meat products. A purified solution of these enzymes can be injected intravenously into animals 2–10 min before slaughter or after stunning, which helps even distribution of the enzyme throughout the muscle tissues (Arshad et al. 2016).

3.3.4 Bioactive Peptides

Bioactive peptides are defined as specific protein fragments that have a positive impact on body functions or conditions and may influence health (Sánchez and Vázquez 2017). In recent years peptides with known sequences have been identified which have been shown to contain biological activities such as antihypertensive, immunomodulatory, antioxidant, antimicrobial, hypocholesterolemic, opiate-like, mineral binding, and antithrombotic actions. These bioactive peptides positively affect the cardiovascular, nervous, gastrointestinal, and immune systems (Choi et al. 2012). Most of the bioactive peptides are inactive in the native protein sequences and become active only when released from the parent proteins in vitro by intentionally added proteases or in vivo by the action of proteolytic enzymes during digestion (Korhonen and Pihlanto 2006). The inherent amino acid composition and sequence determine the activity of these peptides. Bioactive peptides usually have 3–20 amino acid residues per molecule (Bhat et al. 2015) and in some cases may contain more than 20 amino acids. These peptides may be used as components of functional foods or nutraceuticals because of their health-enhancing potential and safety profiles. There is increasing commercial interest in the production of bioactive peptides from various sources. Some of rich sources of bioactive peptides include milk and egg; meat of various species of animals; fish; many plants including soy bean, chickpeas, and rice; and many other food-proteins and nonconventional protein sources (Mazorra-Manzano et al. 2018; Sabbione et al. 2016).

Proteolytic enzymes can be used to moderately hydrolyze proteins and produce peptides or polypeptides or extensively cleave proteins to release free amino acids. These products demonstrate physicochemical properties different from the original protein. Proteolytic enzymes of starters, endogenous proteases of foods, or exogenous enzyme added intentionally (e.g., rennet) differ in their specificity and therefore produce bioactive sequences with different sequences and properties (Korhonen and Pihlanto 2006; Sabbione et al. 2016). Bioactive peptides are produced by using one protease at a time or a combination of two enzymes with different specificity. Enzymes commonly used for release of bioactive peptides are pepsin and trypsin to simulate gastrointestinal digestion and commercial preparations such as alcalase, neutrase, flavourzyme, thermolysin derived from bacteria and fungi (Rui et al. 2012), and ficin (Shahidi et al. 2018).

A group in our laboratory has produced bioactive peptide fragments from goat's milk whey proteins using trypsin and ficin. Goat's milk whey proteins were digested, and peptides were purified by ultrafiltration followed by reverse-phase high-performance liquid chromatography (RP-HPLC). The antibacterial activity of peptides against *Escherichia coli* ranged from 4.67 to 87.46% and against *Bacillus cereus* was 3.03–98.63%. A group of peptides with the molecular mass of ~3 kDa showed maximum inhibition against both Gram-positive and Gram-negative bacteria. This fraction was further purified by HPLC. In total, 14 peptide fractions were collected and evaluated for their antibacterial activities. One peptide had the highest growth inhibitory activity with MIC50's of 383 ± 8 μg/mL and 492 ± 10 μg/mL against *E. coli* and *B. cereus*, respectively. In a similar study, we used trypsin and ficin to generate antibacterial peptides from goat milk caseins. The peptide obtained by ficin with MW of <3 kDa had the highest antimicrobial activity and was selected for further purification by RP-HPLC. In total, 27 peptide fractions were separated. One of the fractions (No. 14) possessed the highest activity against *E. coli* and *B. cereus* (Esmaeilpour et al. 2016, 2017). The authors of both papers suggested these novel antibacterial peptides can potentially replace synthetic food preservatives in food industries.

In another research project, the yeasts *Kluyveromyces marxianus* and *Saccharomyces cerevisiae* protein hydrolysates were prepared by trypsin and chymotrypsin and the peptides purified by RP-HPLC. The antioxidant and ACE (angiotensin-converting enzyme) inhibitory activities of the generated peptides were determined. From *K. marxianus* two new peptides, LL-9, MW 1180 Da, and VL-9, MW 1118 Da, were identified. These peptides were sequenced and their functional properties studied. Both peptides exhibited significant ACE inhibitory activity (IC50 of 22.88 mM for LL-9 and 15.20 mM, for VL-9). Molecular docking studies revealed that the ACE inhibitory activities are due to interaction with the His513, His353, Glu281 and Tyr520, Lys511, and Gln281 pockets of ACE by LL-9 and VL-, respectively. In the case of *S. cerevisiae* a fraction with molecular weight of <3 kDa exhibited the highest activity. RP-HPLC resolved this fraction into five fractions, one of which (fraction F3) with amino acid sequence of Tyr-Gly-Lys-Pro-Val-Ala-Val-Pro-Ala-Arg (MW: 1057.45 Da) had ACE inhibitory ($IC_{50} = 0.42 \pm 0.02$ mg/mL) and antioxidant activities (26.25 ± 0.13 μM TE/μg protein). These peptides

have excellent bioactive properties that can potentially replace the chemically synthesized antioxidant and antihypertensive agents (Mirzaei et al. 2015, 2018).

Plant proteases such papain, ficin, and bromelain can be used to produce bioactive peptides. However, serine proteases such as zingibain, cucumisin, and cysteine proteases actinidin obtained from ginger rhizome, melon, and kiwifruit, respectively, are new emerging plant proteases which have been considered recently (Nafi et al. 2013).

Scientists are continuously searching for novel plant proteolytic enzymes from different sources with specificity towards peptide bonds, hereby producing bioactive peptides having specific functional properties that allow their application in prevention or treatment of disorders such as hypertension, diabetes, obesity, and cancer (Mazorra-Manzano et al. 2018).

3.4 Enzymes Working on Lipids

3.4.1 Lipases

Lipases are enzymes that catalyze hydrolysis of ester bonds in fats and convert triacylglycerols into fatty acids and monoacylglycerols. Most lipases have a basic pH optimum and act only at the oil-water interface (Schmid and Verger 1998).

In foods the activity of endogenous lipases results in acylglycerol hydrolysis and development of hydrolytic rancidity and off-flavor due to oxidative rancidity, as free fatty acids are more prone to oxidation. On the other hand, exogenous lipases are added to develop specific flavors in certain foods. In food industry lipases are obtained from animal forestomach and pancreatic tissues in the forms of purified edible tissue preparations or as aqueous extracts (NAS 1996). The porcine pancreatic lipase has 450 amino acids with a molecular weight of MW of ~50 kDa (Wong 2003). Microbial lipases which are used in industry are produced by *Aspergillus oryzae* var., *Aspergillus niger* var., *Rhizomucor miehei*, and *Candida rugosa* (Wong and Robertson 2007).

New trends in commercial application of lipases involve producing flavoring short-chain acids from lipids and rearrangement of the position of fatty acid groups along the glycerol backbone. These activities result in the formation of highly valued triacylglycerols with novel functional properties from low-value lipids. Typical applications in the food industry include flavor generation in cheese. Using pregastric lipases from goat, lamb, and calf, selective hydrolysis of short-chain (C4−C8) fatty acids from triacylglycerols of milk fat can be achieved (Wong and Robertson 2007). Lipids can be modified by taking advantage of the selectivity of lipases, i.e., spicificity and stereoselectivity toward the fatty acyl group; position of fatty acids along the sn-glycerol backbone, mono-, di-, or triacylated; and interactions among these factors, which confer characteristic. Lipases from over 100 sources have been characterized for different types of selectivity. The possibility of rearranging the fatty acyl groups along sn-glycerol catalyzed by lipases; yield the

so called "structured lipids," novel acylglyserole with new functionalities (Gunstone 1999).

Lipases are used in manufacture of dairy products and confectionery goods, and development of flavor in processed foods. Lipases are used in baking industry and are added to bread dough as dough improvers. This functionality results in increased bread volume, more uniform crumb and air cell size, and lesser tendency to stale. Hydrolysis of lipids produces mono- and diacylglycerolipids which function as emulsifying agents in the dough (Wong and Robertson 2007).

3.4.2 Lipoxygenases

Lipoxygenases are widely distributed in plant and animal cells and are abundantly found in legumes. Lipoxygenase belongs to the oxidoreductases class of enzymes and catalyze many oxidative reactions (Song et al. 2016). While in plants the substrates of lipoxygenase are mainly linoleic acid and linolenic acid, in animal cells arachidonic acid is the primary substrate. Lipoxygenase catalyzes the deoxygenation of polyunsaturated fatty acids (PUFA), converting them to diene hydroperoxy fatty acids which further decompose to different chemicals and volatile compounds (Gigot et al. 2010). Application of lipoxigenase in foods might be associated with some undesirable reactions such as off-color, off-flavor, and nutrient deterioration (Wong and Robertson 2007). The flavor and aroma compounds produced by lipoxygenase activity on fatty acids affect the food flavor. In one aspect, the aroma compounds might improve the desirability of foods, and on the other hand, the oxidized compounds produced might give rise to off-flavor of foods. Continued research for understanding the properties and reaction mechanism of lipoxygenase by food scientists might help to utilize this enzyme as a useful natural food additive (Shi et al. 2020). In the banking industry, lipoxygenase can potentially substitute potassium bromate and benzoyl peroxide, which are commonly used as strengthening and bleaching agents, respectively. Dough strengthening effect is probably through affecting disulfide cross-links within the gluten. Lipoxygenase has been widely used in the food and beverage industries to produce aroma compounds (Wong and Robertson 2007).

3.4.3 Phospholipases

Phospholipases are a large class of enzymes with great diversity (Mansfeld 2009). Phospholipases from mammals, plants, and microbes are continuously being studied for potential use in industry. Some are commercially available at industrial scale for food industry. They are generally classified as acyl hydrolases and phosphodiesterases. These enzymes are further divided into different groups based on the hydrolytic cleavage site within the phospholipid molecule. The acyl hydrolases include the phospholipase A1 which hydrolyzes 1-acyl ester bond of phospholipids to release lyso-phospholipids and free fatty acids, phospholipase A2

which catalyzes the hydrolysis of fatty acids at the sn-2 position of phospholipids releasing lyso- phospholipids and free fatty acids, phospholipase B which does not discriminate between the two positional acyl ester bonds, and lysophospholipase A ½ (partially hydrolyzes phospholipids) (Wong and Robertson 2007). Phospholipase C and D are phosphodiesterases which cleave the phosphorus-oxygen bond between glycerol and phosphate, releasing diacylglycerol and phosphate esters. Except phospholipases A2, most of these phospholipases are not largely available for industrial purposes. The phospholipase A2 which can be obtained from porcine pancreas or snake and bee venoms is traditionally used in industry for modification of phospholipids, such as phospholipids of egg yolk, to produce emulsification in mayonnaise, sauces or salad dressings, baking industry, or refinement of vegetable oils by degumming (Mansfeld 2009).

Phospholipases application of in food industry include edible oils production of, dairy, and baking products or emulsifying agents, in refinement of vegetables oils for removing undesirable compounds, in increasing yield cheese manufacturing and as emulsifier in bread as bakery improvers (Ramrakhiani and Chand 2011; Zhao et al. 2010; Casado et al. 2012).

3.5 Miscellaneous Enzymes

3.5.1 Catalase

Catalase is an oxidoreductase enzyme that catalyzes the breakdown of hydrogen peroxide, often produced as a by-product of aerobic respiration, into oxygen and water. This enzyme plays an important role in quenching the reactive oxygen species (ROS). This enzyme acts as an antioxidant and protects the cell against oxidative stress (Kaushal et al. 2018).

Catalase is widely distributed in nature. It is found in all aerobic microorganisms, and in all plant and animal cells. The highest catalase activity is found in liver and kidney. In food processing, catalase is used to determine the adequacy of blanching of vegetables and fruits, as antimicrobial agent and for enzymes inactivation to preserve organoleptic properties of the products when stored frozen for a long time (Williams et al. 1986; Wong and Whitaker 2003). Contamination of milk by neutrophil granucytes can easily be detected by measuring catalse activity. Catalase is very useful for removing hydrogen peroxide from milk samples for cheese production. H_2O_2 is used in the cold pasteurization process of milk for cheese manufacture. The residual H_2O_2 is converted to water and molecular oxygen by catalase, thereby avoiding its toxicity. Catalase enzymes are typically obtained from bovine livers or microbial sources (Kilcawley et al. 1998).

3.5.2 Amino Oxidases

Biogenic amines and polyamines are organic bases with aliphatic, aromatic, and heterocyclic structures which are present in variety of foods, such as fish, meat, cheese, vegetables, and wines. They are produced by decarboxylation of amino acid substrates catalyzed by enzymes from contaminating bacteria. Histamine, tryptamine, tyramine, spermine, spermidine, putrescine, cadaverine, 2-phenylethylamine, and agmatine are the most common biogenic amines found in foods (Ruiz-Capillas and Herrero 2019). Biogenic amines in foods are responsible for allergic reactions experience by consumers. Several methods for prevention the production or removal of biogenic amine in food have been practiced, including limiting microbial growth by chilling and freezing. However, for many socioeconomic and technological reasons, such approaches are not always practical. One approach to prevent biogenic amine formation in foods or to reduce their levels once formed might be application of enzymes which metabolize these amines (Naila et al. 2010).

Amine oxidase catalyzes the reaction with mono-, di-, or polyamine as substrate (Ito and Ma 2003):

$$RCH_2NH_2 + O_2 + H_2O \rightarrow NH_3 + RCHO + H_2O_2$$

The activity of these enzymes has been detected in bovine plasma and bovine lung, pea seedling, yeast (*Candida boidinii*, *Asp. Niger*, and *Arthrobactor*). The amine oxidase of pea seedling is a copper containing diamine oxidase, catalyzing the oxidative deamination of histamine to imidazole acetaldehyde and concomitant formation hydrogen peroxide. The antihistamine properties of this enzyme make it an attractive candidate in fish industry to combat the allergic responses elicited by consumption of fish. However, the observed variation in the efficacy of the enzyme has been attributed to the diversity and distribution of the enzyme inhibitors present in the variety of fish species (Ebrahimnejad et al. 2013; Stránská et al. 2007).

3.5.3 Phenylalanine Ammonia-Lyase

The genetic deficiency of the hepatic enzyme phenylalanine hydroxylase (PAH) in humans causes development of the disorder phenylketonuria (PKU) which affects about 1–3 Caucasian live births in every 10,000. The enzyme converts phenylalanine to tyrosine using molecular oxygen and tetrahydrobioptrin as necessary cofactor to perform its catalysis (Al Hafid and Christodoulou 2015). PAH deficiency leads to hyperphenylalaninenemia, a dramatic increase in blood phenylalanine concentration and appearance of phenylalanine, phenylpyruvate, and phenylacetone in urine. Several abnormal phenotypes including seizure, growth failure, microcephaly, and mental retardation have been associated high levels of accumulated phenylalanine in PKU patients. Children with severe PKU can have normal cognitive development if blood phenylalanine level is maintained at near normal levels through dietary control

at early infancy (Ding et al. 2004). The basic treatments of PKU include restricting phenylalanine of diet. However, this treatments result in deficiencies of several nutrients and undesirable organoleptic attributes that make long-term compliance a major challenge (Levy 1999).

Phenylalanine ammonia lyase (PAL) is an enzyme that catalyzes conversion of L-phenylalanine to ammonia and *trans*-cinnamic acid (which is excreted as hippurate in urine). PAL is widely distributed in plants. It has a molecular mass in the range of 270–330 kDa. A large number of plant species were screened for PAL activity. The enzyme activity was highest in grain seedlings, with maximal enzyme activity in 7-day-old red spring wheat (Goldson et al. 2008; Camm and Towers 1973). We have studied the stability of wheat seedling PAL during storage at different temperatures and found a first-order kinetic for inactivation of PLA with half life of 30 and 18 days at −18 °C and 4 °C, respectively. Activity of PAL increased while germination occurred at 25 °C up to 8 days. These results can be used to develop appropriate strategies for storing PAL containing materials with retained PAL activities (Aminlari et al. 2010).

In recent years PAL has been studied for its possible therapeutic benefits in patients with PKU. The use of phenylalanine ammonia-lyase (PAL) can be used as an alternative to the dietary treatment of PKU. The use of recombinant PAL for enzyme substitution therapy in a murine PKU model has been reported (Sarkissian et al. 1999). An active recombinant PAL from parsley (*Petroselinum crispum*) has been prepared and chemically modified to render PAL non-immunogenic and stable in the circulation (Kim et al. 2004b). Encapsulation of PAL for oral therapy may provide a potential alternative treatment for patients with PKU (Goldson et al. 2008). One significant challenge in application of PAL for PKU therapy is protecting PAL from proteolysis and/or denaturation and against immunologic responses. Different physical and chemical methods have been investigated to address this problem. These include PAL immobilization such as in semipermeable microcapsules, entrapment in silk fibroin, and modification with PEGylation (Bell et al. 2017; Ikeda et al. 2005).

3.5.4 Lysozyme

In recent years consumer demand for "natural" foods has driven development of products without additives. In order to meet this demand, much attention and interest have been directed towards identification and application of naturally made compounds such as antimicrobial agents, in food and pharmaceuticals (Branen and Davidson 2004). Some naturally occurring proteins such as lactoperoxidase, lactoferrin, and lysozyme have received much attention and are being considered as potential antimicrobial agents to replace the currently used synthetic food preservatives (Demain 2009).

Lysozyme, also known as muramidase or N-acetylmuramide glycanhydrolase, is an antimicrobial enzyme found in many different sources, from viruses to vertebrates, and has been subjected to extensive scrutiny, both as a protein model

and a natural antimicrobial and pharmaceutical agent. It forms part of the innate immune system. Lysozyme is abundant in secretions including tears, saliva, human milk, and mucus. Chicken egg white has the highest content of lysozyme (it constitutes 3.5% of the total egg white proteins), from which this enzyme is purified and is commercially produced (Proctor and Cunningham 1988). Lysozyme is a glycoside hydrolase that catalyzes the hydrolysis of 1,4-beta-linkages between N-acetylmuramic acid and N-acetyl-D-glucosamine residues in peptidoglycan, which is the major component of Gram-positive bacterial cell wall. In general, lysozyme shows in vitro antimicrobial activity against some Gram-positive bacteria such as *Staphylococcus aureus*, *Micrococcus luteus*, *Bacillus stearothermophilus*, and *Clostridium tyrobutyricum* but little action against Gram-negative bacteria (Cunningham et al. 1991). Gram-negative bacteria, including food borne pathogens, resist lysozyme due to steric hindrance posed by the outer LPS layer; hence, lysozyme cannot access the peptidoglycan (Ibrahim et al. 1994). Thus, modification of lysozyme, which can broaden its antibacterial properties against both Gram-negative and Gram-positive bacteria, can also increase the usefulness of lysozyme (Seo et al. 2013).

Lysozyme has received considerable interest as a food preservative (Cegielska-Radziejewska and Szablewski 2013). In many countries, lysozyme is used as a preservative in many types of foods (including vegetables, seafoods, soy bean products, meat products, and semihard cheeses and as a component of pharmaceutical products. In the European Union, its use in specific products such as hard cheeses and in wine making to control infection (E number E 1105 as a food additive) is allowed (Losso et al. 2000). Proctor and Cunningham (1988) and Cunningham and others (1991) have reviewed the use of lysozyme as a food preservative.

During the last two decades, extensive research in the author's laboratory and others have been directed toward modification of lysozyme in order to improve its antimicrobial properties. Several types of these modifications are summarized in Table 3.4. The results of modifications of lysozyme using its conjugation with different small molecule and polysaccharides by application of a Maillard-based reaction, as well as modifications using proteolytic enzymes, have revealed that these types of modifications have not only increased the functional properties (such as solubility and heat stability) but also extended the antimicrobial activity of lysozyme (Aminlari et al. 2014). We have shown that it is possible to broaden the antimicrobial effect of lysozyme by several types of modifications, which consequently make these lysozyme derivatives excellent food preservatives. Table 3.3 summarizes the effect of different types of modifications on lysozyme.

3.6 Conclusions

Nature provides us with remarkably vast array of enzymes with extraordinary catalytic properties. In their natural reservoirs, these so called "endogenous" enzymes perform essentially all biochemical reactions vital to the living organisms. When these enzymes are removed from their natural habitat, they continue to

Table 3.4 Modified lysozymes and their properties (adapted from Aminlari et al. 2014)

Modified lysozymes	Effect on functionality
Palmitic acid	Enhanced antimicrobial against *E. coli* (WT-3301)
Short and middle chain saturated fatty acids	Enhanced antimicrobial against G-positive bacteria
Glucose–stearic acid monoester	Enhanced activity against *E. coli and E. tarda* (G8104)
Perillaldehyde	Enhanced activity against *E. coli K12 and S. aureus*
Cinnamaldehyde	Enhanced activity against *E. coli* and *S. aureus*
Glucosamine	Improved solubility at different pHs and temperatures, increased heat stability, emulsion activity and stability, and foam capacity
Caffeic acid–cinnamic acid	Antimicrobial activity against *E. coli* (ATCC 8739), decreased activity against) *S. aureus* (ATCC 6538)
Dextran	Enhanced activity against *E. coli* and *S. aureus* in cheese
Dextran	Enhanced activity against *E. coli* and *S. aureus* in milk
Dextran	Treatment of bacterial isolates from cows with mastitis
Dextran	Preparation of a lysozyme–dextran nanogel
Dextran	Increased heat stability, higher emulsifying property
Galactomannan	Antibacterial emulsifier
Galactomannan	Emulsifier, antibacterial against G-negative pathogen *E. tarda*
Chitosan	Enhanced bactericidal action against *E. coli K-12*
Chitosan	Lysozyme-composite film with activity against *E. coli*, *L. monocytogenes*, and *S. faecalis*
Cellulose	Preparing a textile with potential barrier to microbial invasion
Gum Arabic	Enhanced activity against *E. coli* and *S. aureus* in mayonnaise
Xanthan gum	Enhanced activity against *E. coli* and *S. aureus*
Dextran sulfate	Enhanced activity against *E.* coli and *S. aureus*
Barley beta-glucan	Enhanced activity against *E.* coli and *S. aureus*
Tragacanth	Enhanced activity against *E. coli, S. typhimyrium, B. cereus,* and *S. aureus*
Inulin	Improved functional properties
Trypsin and ficin digestion of dextran-conjugated lysozyme	Enhanced activity of peptides *E. coli* and *B. cereus*

catalyze same reactions when they have access to their substrate. At this stage, they are indeed "exogenous" enzyme. Food scientists have used these exogenous enzymes as food additives for many years. In this chapter the properties of several enzymes from plant and animal sources were presented, and their application or potential application in food industry was discussed. Over the years it has become clear that despite advances in experimental mutational studies, a quantitative understanding of enzyme catalysis will not be possible without computer modeling approaches (Frushicheva et al. 2014). With advent of new technologies such as information technology, rational molecular design, and DNA enzyme

(deoxyribozyme) technologies (Breaker 1997; Woolcock 2016), it is expected that new doors for application of these technologies will open to food enzymologists in near future. The discussion is by no means complete and with advent of knowledge of enzymology, the endeavor will continue. For those of us who (as Arthur Korenberg, the discoverer of DNA polymerase once said) are in love with enzymes, the challenge has just begun.

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Microbial-Derived Biodegradable Polymers as Food Packaging Tool

4

K. Khosravi-Darani, D. Z. Bucci, and Ramona Massoud

Abstract

Plastic application is one of the crucial concerns due to the global environmental impact, and shifting to biodegradable food packaging would be a favorable option. This review aims to use biodegradable microbial-derived polymers in food packaging. The main criteria in food application are mechanical and thermal characteristics and water vapor gas transfer. Among materials, microbial polymers, polysaccharides, and polyhydroxyalkanoate are desirable in food packaging due to being biodegradable, having better physical properties, and lower O_2 and CO_2 permeability with no catalysts residue. This article focuses on microbial polysaccharides (e.g., bacterial cellulose) and polyhydroxyalkanoate in food packaging. The necessity of using biobased polymers in food packages is expressed in the introduction part. The application of the most common biopolymers is described. The biopolymers production, polyhydroxybutyrate-based nanocomposites, and some microbial polysaccharide (e.g., BC) properties in food packaging are also discussed. Moreover, some improvement issues of polyhydroxybutyrate and microbial polysaccharide (e.g., BC) properties are explained, and the nanotechnology impresses on improving the physical properties. Eventually, the article includes some possible future trends.

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Poly(hydroxybutyrate) · Poly(hydroxyalkanoate) · Food packaging · Properties · Modifications · Nanoparticles · Microbial polisaccharides and bacterial celulose

4.1 Introduction

Polymer-based fossil fuels are among the essential manufacturing industries of the world. There is still a global concern about nonrenewable plastic materials (Weber 2000). Plastic packaging is widely used globally due to its excellent properties, such as being easily shaped, extruded, and molded in different colors and patterns (Petersen et al. 1999a). Food packaging is an integral part of the food chain to provide physical protection, shelf life extension, and easy carriage. Plastics are generally used in food packaging to be convenient, easy to process, and cheap (Bohm et al. 2010; Plastics Europe 2015). The most common food-packaging polymers are PE or polyethylene used in water, milk, and oil packaging; PET or polyethylene terephthalate used in liquid and drinks packaging; PVC or polyvinylchloride and PP or polypropylene for margarine, yogurt, and iced tea packaging; PS or polystyrene for mushroom and egg packaging; and PA or polyamide in perishable food like cheese and meat packaging as they are flexible (Weber 2000).

The main concerns in food packaging issues are toxic ingredients migration into foodstuffs, environmental impacts, and cost (Petersen et al. 1999a). The petrochemical source of polymer is more than 95% of the world's production, and they remain in the environment for many years. Plastic waste after consumption is in a considerable amount (63%) (Petersen et al. 1999a; Rech et al. 2020). The recyclings' purpose is to decrease the annual plastic amount and their reusage (Petersen et al. 1999a). However, recycled substances can only be applied in food packaging if they achieve the food standards despite their time and cost-consuming processes. There are no cohesive recycling programs in many parts of the world (Bohm et al. 2010; Wang et al. 1997).

The food industry spends about 100 billion dollars on food processing annually (McKinsey 2018; Brody et al. 2008). Nearly 0.1 of global food cost goes to food processing and packaging. Food packaging is creatively increasing for the following reasons: decreasing the time for preparing food, increasing materials' bioconversion and consumers' acceptability (Brody et al. 2008). The packaging substances are stabilizers, fillers, and plasticizers. Stabilizers help in improving the mechanical properties of food components (Callister 2006). Fillers are used to making barriers and also developing mechanical properties. Filling polymers with inexpensive materials decreases the cost. Plasticizers are also used to increase the flexibility and firmness of polymers (Hourston 2010). The interaction of plastic food packaging substances with food is still one of the main concerns in the food industry (Birley 1982).

In this sense, today, the pandemic times of Covid-19 have brought tremendous learning and awareness to consumers. It is a transition time with a tendency to review diet and food options demanding natural and healthier food products and sustainable packaging. Consumers and the food market are increasingly interested in the food-health concept. Many companies have concentrated their research around nutraceutical allegations (Brody et al. 2008). According to Guillard et al. (2018), novel tolerable packaging increases food quality and safety by inhibiting food-borne diseases and contamination. In this way, there is a great challenge to scientists and industries to develop healthier foods and less harmful packaging materials. In terms of food packaging materials, the slow degradation of polymers due to having environmental problems represents the importance of searching for renewable packaging materials. The last few decades have led to severe global environmental problems, as their recycling and energy recovery are ineffective and end up in rivers and oceans (Plastics Europe 2015). Ocean care has also been a concern of the UN's global climate commission with the fight against marine litter. Therefore, there is an increasing interest in substituting plastics with biodegradable plastics (Singh et al. 2019). They are a new class of substances from renewable biological sources like biopolymers, particularly food packaging applications. They have excellent protection and easier degradation after usage and are eco-friendly (Khan et al. 2016). The biodegradable packaging is suitable for short-time packagings like disposable dishes, medical devices, and garbage bags (Brody et al. 2008).

Replacing conventional petrochemical-based polymers with microbial biodegradable polymers like PHA's and polysaccharides improved with nanocomposites are among the policies to lessen the environmental influence of petroleum-based plastics to have a better world free of plastic pollution and food losses. According to Guillard et al. (2018), that would be possible by improving packaging properties to decrease food waste, but this can be achieved successfully through a sustainable product packaging design model SPPkDM (Guillard et al. 2018; Khan et al. 2016).

4.2 Biodegradable Polymers in Food Packaging

Biodegradable polymers have been estimated to consume about 50 million kilograms per year in the European region. Nevertheless, the production of biopolymers is still small compared to the annual production of polymers, which is about 1% and is equal to about 100 million tons (Rahman et al. 2021).

About 23 million tons of plastic packaging are manufactured in European countries every year, reaching 92 million tons in 2050. It is estimated that by 2050 the plastic industry will represent 1124 million tons of plastic substances. Unfortunately, there would be more plastics than fish in the oceans (Singh et al. 2019). Developing innovations in the food packaging market and a 50% decrease of food waste till 2050 would help save 100 million tons of food, reducing 250 million tons of CO_2, recovering 18 km^3 water resources, and 100 million hectares of land (Muhr et al. 2013). This achievement is in line with the EU targets.

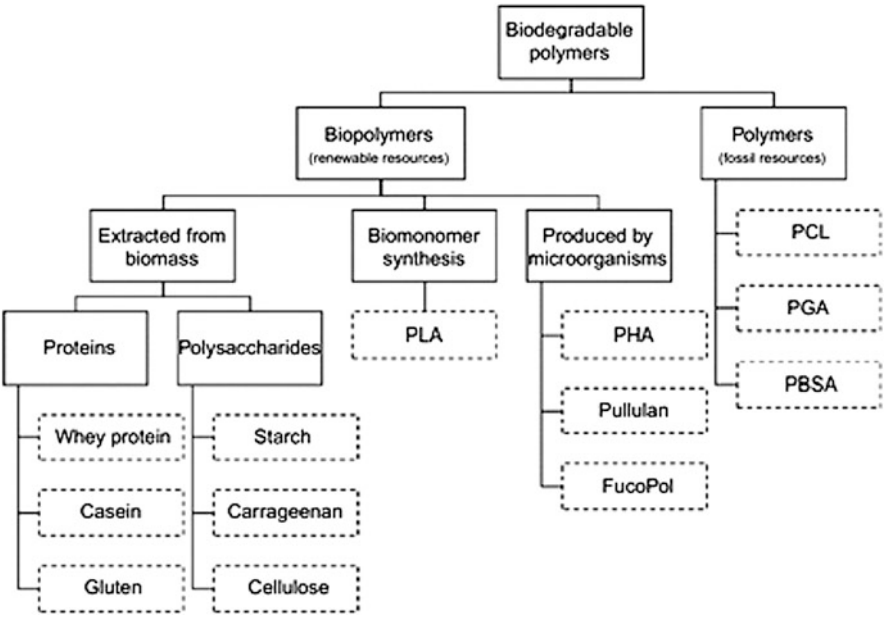

Fig. 4.1 Biopolymer categorization (Carrasco et al. 2011; Bucci et al. 2005)

Nowadays, the common plastic food packaging economy is an iconic linear application (Fig. 6): 98% of plastic packaging in Europe is from virgin oil-based feedstock, and 14% is recycled after usage. The rate of global paper recycling (58%) (Lovera et al. 2007) and steel and iron (70–90%) (Hänggi 1995). More than 40% of plastic packaging is now put in landfills and above 30% leaks into ecosystems and oceans. By 2050 the oil consumption will grow to 20% going through this trend (Lovera et al. 2007). At the moment, about eight million tons of plastics leak into the ocean annually (Fortunati et al. 2010).

According to ASTM Standard D-5488-84, a biodegradable substance is a material that can be decomposed to CO_2, water, methane, inorganic combination, or microorganisms through chemical or enzymatic reactions and can be evaluated by standard tests in specified disposal conditions (Wang et al. 1997). According to Fig. 4.1, biodegradable polymers are classified into two groups: biopolymer arises from renewable resources and polymer derived from fossil resources. It is essential to know that not all bioplastics are biodegradable. Biodegradation characteristics relate to the polymer structure and the final products' combination. So, the biodegradation process does not depend on the resources of the polymer origin, biobased, or fossil (Hourston 2010). Biodegradable materials have unique properties for various applications like packaging, biomedicine like nanocarriers in drugs, and tissue engineering with medicinal coatings (Hourston 2010; Birley 1982).

Specifically, thermoplastic biodegradable polymers like PHA or polyhydroxyalkanoates, PLA or polylactic acid, and PCL or polycaprolactones get

from renewable resources. PCL is made from the conversion of crude oil chemically. It is a low viscosity, chlorine resistance, and low melting point polymer made by melt blending methods used in utensils, pharmaceutical systems and biodegradable packaging (Lovera et al. 2007). PLA is a thermoplastic biopolyester generally made from corn starch fermentation and biodegraded by microorganisms. It is the most commercial biopolymer in food packaging and containers (Arrieta et al. 2014b). Plasticizers would decrease the stiffness and, therefore, less oxygen barriers and transparency. PLA, in contrast to PET, would be processed more efficiently (Fortunati et al. 2010), transparency (Arrieta et al. 2013), and printability (Fortunati et al. 2012a), biodegradability (Fortunati et al. 2012b), but more rigid with low thermal resistance. PLA is limited in food packaging as they are poor mechanically (Mattioli et al. 2013). The stability and degradation in thermal processing should be considered (Carrasco et al. 2011). The PLA blending with some biopolymers would develop the properties and cost (Arrieta et al. 2014a). PLA and PHB have the same melting temperature. The melt blending process would also increase PLA crystallinity (Zhang and Thomas 2011; Park et al. 2002). Nowadays, a combination of PLA-PHB is reported to be desirable for short time industrial food packaging (Arrieta et al. 2014b). There are still some mechanical problems in thermal attributes (Arrieta et al. 2014a, b; Tsuji and Yamada 2003; Jacobsen et al. 1999; Jacobsen and Fritz 1996; Chen et al. 2003; Khosravi-darani and Bucci 2015).

4.2.1 Biopolymer-Based Food Packaging

Naturally occurring substances called biopolymers are the best biodegradable materials. They have been attracting much attention recently due to the unique properties of natural abundance biodegradability and biocompatibility with potential applications (Petersen et al. 1999a; Bohm et al. 2010). They are partially or biodegradable (Arrieta et al. 2014a; Ishrat et al. 2018). Their primary function is food protection with the same quality during storage life (Brody et al. 2008). Due to having different sources and production methods, they can be categorized into three groups according to their source (Callister 2006; Birley 1982; Bucci et al. 2005) (Fig. 4.1):

1. Directly extracted from biomass like soy, casein, whey proteins, and collagen (protein), triglycerides (lipid) and starch, cellulose, and gums (polysaccharides). The quality of these polymers derived from natural sources relates to the season of the year. Consequently, these polymers show outstanding properties over time (Singh et al. 2019; Coelhoso et al. 2015).
2. Made from bio-derived monomers like polylactides.
3. Microorganism-based microbial polymers like some polysaccharides such as gellan gum, pullulan) and PHA, polyamides, and polyphosphates. The biopolymers in this last group are mainly polyhydroxyalkanoates, and still, bacterial cellulose is developing.

In recent decades, there has been an expressive advancement in research for developing microbial polymers such as polysaccharides and polyesters. This results from two combined facts advanced molecular methods and genome sequences. A progressive issue is the vital role of bacterial polymers in pathogenesis and their ability to create bio-based substances. Such renewable, biocompatible, and biodegradable materials have great potential to replace fossil fuel polymers, providing solutions in different areas with high aggregate value materials and principally sustainable food packaging.

4.2.2 Microbial Biopolymers

Microbial polysaccharide is a novel alternative to the traditional ones (Singh et al. 2019). These biopolymers are structurally diverse macromolecules, and environmental concerns attracted considerable interest in these materials. The biopolymers have also been produced for decades by microbial fermentation, but they are still expensive (Birley 1982).

This group of polymers is a recent and innovative field (Rech et al. 2020). They are now being introduced by applying various genetic engineering tools to the microorganisms (Petersen et al. 1999a). The bacterial genetic transformation led to unnatural biopolymers analogs and future polymer modification (Dhall and Alam 2019).

Bacteria can create various types of biopolymers like polysaccharides (sugars by glycosidic linkage), polyesters (fatty acids by ester linkage), polyphosphates (phosphates by anhydride linkage), and polyamides (amino acids by peptide linkage) (Bucci et al. 2005).

The most common classes of microbially produced biopolymers are polyesters (PHAs) and polysaccharides. The bacteria use them as an energy and carbon source, and the composition units relate to the type of microorganisms, carbon source, nitrogen, temperature, and time (Arrieta et al. 2014a; Valentina et al. 2008).

This review is focusing microbially produced biopolymers and their current and future applications from medical to food packaging. There are still some limitations and a need to progress creative processes and products.

4.2.3 Bacterial Polysaccharides in Food Packaging

Polysaccharides are among the large macromolecules worldwide. They can be extracted from different animals like chitosan, plants like starch, and algae-like alginates and produced by microorganisms (Singh et al. 2019; Arrieta et al. 2014b).

Microbial polysaccharides are biodegradable biopolymers that can be intracellular (glycogen), structural, or extracellular such as dextran, xanthan, alginate, hyaluronic acid, and cellulose (Petersen et al. 1999a; de Paula et al. 2017).

The two potent bacterial EPSs are GalactoPol made by *Pseudomonas oleovorans* and FucoPol made by *Enterobacter* (Azeredo et al. 2019).

Scientists have studied and extensively described the molecular structures of polysaccharides (EPSs). The production cost is higher than natural and synthetic polysaccharides, and the high costs go back to substrate and downstream progress (de Paula et al. 2017; Azeredo et al. 2019). Glucose and sucrose are the most common substrates with high productivities and yields. Galactose, lactose, and xylose are less frequent as some microorganisms can not use them (Jarmander et al. 2015).

Many industrial and agricultural wastes and byproducts (de Paula et al. 2017; Jarmander et al. 2015), as glycerol remains from biodiesel, are used as microbial cultivation substrates (de Paula et al. 2017).

Freitas et al. (2014) represented a biodegradable film for food packaging based on EPS. It was based on glycerol byproducts from the biodiesel industry (Freitas et al. 2014). In high purity applications, using wastes and byproducts requires more investment in downstream processes (de Paula et al. 2017).

Remarkably, only a few EPSs have been developed as essential biopolymers with significant commercial value due to the different conditions like bacterial cellulose or levan (de Paula et al. 2017) or as rheology modifiers like gellan and xanthan for their better physical properties (Arrieta et al. 2014b). The bacterial EPSs would replace polysaccharides from plants such as pectin or guar gum and algae-like carrageenan (Freitas et al. 2014).

Polysaccharides are mainly used as hydrocolloids. However, some microbial polysaccharides have a film-forming ability to support the preparation of the thin membrane (de Paula et al. 2017). They would be used in various industries: medical, food, and other industrial processes (Petersen et al. 1999a; Callister 2006; Valentina et al. 2008). Nowadays, not many commercial microbial polysaccharide membranes are developed and being used (de Paula et al. 2017).

However, it is possible to produce tailor-made polysaccharides through genetic engineering of bacterial polysaccharides modified enzymes or developing fermentation situations (Bucci et al. 2005). The design of microbial polysaccharides materials becomes practical by blending with other polymeric components such as citric acid through cross-linking, stearic acid by esterifying, and plasticizers (Bucci et al. 2005). These methods develop the biopolymers' properties like solubility, viscoelasticity, stability, crystallinity, porosity, glass transition temperature, gelation degree, and material strength. The modified properties help them to compete with the natural polysaccharides and synthetic products like polyvinyl alcohol (PVA) (de Paula et al. 2017). So, makes it viable for commercial use in a wide range of areas of biomedicine, cosmetics, and chemical industries to food and packaging (Bucci et al. 2005).

4.2.4 Properties

The constituent sugars or sugar acids evaluate the diversity of bacterial polysaccharides and their properties, the glycosidic linkage-type, the polymer length, the molecular weight, the diversity of side chains: pyruvate, acetyl, and succinate. The principal properties are Aw, ionic strength, stability, extendibility,

elasticity, gelation, crosslinking, modifiability, and biodegradability (Bucci et al. 2005).

4.2.5 Food Packaging Film and Coating Application

Some polysaccharides such as bacterial alginate, GalactoPol, and FucoPol can make chemical and physical intermolecular linkage, leading to a cohesive polymeric compound with film-forming capacity (Bucci et al. 2005).

Application of microbial polysaccharides like pullulan, curdlan, xanthan, gellan-gum, hyaluronan, BC (bacterial cellulose), and bacterial alginates as a food packaging film or edible coatings for food products (de Paula et al. 2017; Jarmander et al. 2015) requires biotechnological methods (Petersen et al. 1999a; Bucci et al. 2005). They are perfect carriers for bioactive components, antioxidants, flavor matrixes, pre- and probiotics (Freitas et al. 2014).

Those films and coatings are suitable barriers against gas like O_2 and CO_2 because of a hydrogen-bonded polymer matrix (Bucci et al. 2005). However, they are limited for moisture barrier application. It is possible to apply a strategy to increase water resistance by cross-linking reactions between polymer chains to serve as barriers of stand-alone films made from microbial polysaccharides, such as gellan, GalactoPol, xanthan, bacterial cellulose, curdlan, and pullulan (de Paula et al. 2017). Pullulan can be formed into compression materials similar to polymers such as polystyrene or polyvinyl chloride in their transparency, gloss, hardness, and strength packaging of vegetable oil in pullulan pouch which result in shelf-life extension and reduced rancidity (Petersen et al. 1999a).

Bacterial cellulose is better established on the market, with several products in different areas and food packaging among all microbial polysaccharides. These applications are better described in section (Mensitieri 2011).

The principal traits and applications of polysaccharides in food and packaging are represented in Table 4.1.

Yang et al. mentioned the gellan film cross-linking in $CaCl_2$ solution that developed the water vapor barrier trait and significantly reduced swelling (Yang et al. 2000).

Freitas et al. reported the crosslinking esterification reaction in hydroxyl and carboxyl in GalactoPol chains in film solution in acidic conditions (Freitas et al. 2014). Lipid addition to the polymeric matrix by the help of oil in water emulsions increases the barrier to water vapor. They reported some researches that produced biodegradable films like kefiran, hyaluronan, and gellan (Krzan et al. 2006) derived from microbial polysaccharides could be replaced by conventional polysaccharides (Jarmander et al. 2015).

Reports by Freitas et al. evidenced an increase in water vapor barriers in films with lipids in the polymer matrix. He mentioned that Tapia et al. reported increasing water vapor resistance in gellan coatings by adding olive oil to fresh papaya. Other examples of water vapor resistance growth were the application of beeswax or rice wax in pullulan films to form multilayer barriers (de Paula et al. 2017).

Table 4.1 Main applications in food of microbial polysaccharides (Ferreira et al. 2016)

Polysaccharide	Microorganism	Composition	Membrane properties	Main food applications
Pullulan	*Aureobasidium pullulans*	Maltotriose (three glucose)	Biodegradable Transparent Edible oil and grease resistant Heat sealable High water solubility Barrier to oxygen	Coating material Wrapping material Blends with other polymers to improvement of mechanical properties Inner package • Seasoning bag of instant noodles • Instant coffee
Gellan gum	*Sphingomonas elodea*	Glucose Rhamnose Glucuronic acid	Biodegradable Edible Lipid barrier Excellent gas barrier Good tensile strength	Edible coatings in breading and batters for chicken, fish, cheese, vegetables and potatoes Encapsulation of flavor and bioactive ingredients
Xanthan gum	*Xanthomonas campestris*	Glucose Mannose Glucuronic acid Acetate pyruvate	Biodegradable Edible	Edible coating • Meet (Prevent moisture migration during frying) • Fruit (Extend shelf-life)
FucoPol	*Enterobacter A47*	Fucose Galactose Glucose Glucuronic acid Acetate Succinate pyruvate	Biodegradable Transparent High gas barrier Poor waste resistance	Possible application as inner layer in multilayer packaging

Nowadays, with the awareness of sustainability and the importance of green technology use, a significant number of different polysaccharide-based materials are found to be used as intelligent biopackaging (Yang et al. 2000).

The polysaccharide/bioactive component indicators principle of work is the same as synthetic ones, and the indicators are incorporated in a polymer matrix. The final material is obtained by lyophilization. Many bioactive components have been used to evaluate their suitability for replacing conventional synthetic/toxic compounds like natural colors and extracts (Krzan et al. 2006).

The most commonly used microbial polysaccharide membranes for food industry applications are gellan gum, xanthan gum, dextran, and pullulan. They are widely applied as emulsifiers, thickeners, stabilizers, texturizers, gelling agents, and film formers (Azeredo et al. 2019). Microbial polysaccharides used as food additives enhance food quality (Bartkowiak 2012), sensory properties, expansion shelf life, and better processing (Jarmander et al. 2015).

The application of microbial polysaccharide membranes in industrial applications is limited (de Paula et al. 2017).

4.2.6 Other Aplications

Natural polysaccharides like sodium alginate and chitosan can pervaporate the dehydration of solvents like isopropanol, ethanol, acetone, and tetrahydrofuran with acceptable separation performance. Microbial polysaccharide membranes are also improved for solvent dehydration by pervaporation. Solvent dehydration is economical and related to food, pharmaceutical, and chemistry industry (de Paula et al. 2017; Bartkowiak 2012).

Some studies on curdlan and bacterial cellulose usage for the **electronic devices component developments** (de Paula et al. 2017). EPSs represented a highly adsorbing capacity for colors, aromatic compounds, and heavy metals in effluent treatment because of their hydrophilic properties (de Paula et al. 2017). Due to their biocompatibility and biodegradability, natural polysaccharides like chitosan and alginate are suitable for many **medical applications**. The same occurs with EPSs because they can make polymeric matrices and shape them like structured materials such as hydrogels, nanoparticles, and scaffolds, for example, coatings of medicines and medical devices, drugs delivering agents and surgical sealants, tissue engineering, and wound dressings (de Paula et al. 2017; Freitas et al. 2014). EPSs like hyaluronan, pullulan, and bacterial alginate are being studied for the mentioned applications (de Paula et al. 2017).

4.2.7 Blends of Polysaccharides

The biodegradable films based on polymer blends, including microbial polysaccharides, have been studied. It allows designing more versatile materials by tailoring the taits like mechanical, viscosity, gelation degree, water affinity, bioactive stabilization, porosity, and material strength. The would-be blended with polymeric or non-polymeric components such as plasticizers, citric acid for cross-linking, and stearic acid for esterifying (Lovera et al. 2007; Bucci et al. 2005).

Trovatti (2013) mentioned, based on some authors, that especially synergistic properties for membranes made from microbial polysaccharides blend with synthetic or natural polymers. She also reported improving the properties of the gellan and chitosan/pullulan membranes in reaction to metal cations like Ca and improving processability and flexibility with glycerol or ethylene glycol. The problem is that they affect their hydrophilicity and often enhance oxygen permeability. The inclusion of lipids in the formulations (e.g., sunflower oil) helps enhance the oxygen and water vapor permeability (Trovatti 2013). Moradi et al. (2019) also reported the mechanical properties of pullulan films blended with other polymers like gelatin and chitosan (Moradi et al. 2019).

Curdlan blended with konjac glucomanan and chitosan improved the film's traits with better moisture barrier and antibacterial activity (Bucci et al. 2005).

Xanthan gum, as mentioned before, is applied as a thickening agent in the foodstuffs. However, it can be blended with gellan and chitosan/pullulan to develop the properties of the membrane (Jarmander et al. 2015).

Blending also allows such materials suitable for 3D bioprinting with medical and engineering usage like drug delivery and tissue engineering (Bucci et al. 2005).

4.2.8 Nanocomposites

According to microbial polysaccharides, the nanocomposites improved as well as the petrochemical-based polymers (Callister 2006). The incorporation of nanotechnology improves the functionality of food packaging, especially in fresh vegetables and fruits (Callister 2006). They are a growing interest in the scientific and industrial fields (Khan et al. 2016). These polymers are particles with at least one dimension in the nanometer area, and the nanoparticle incorporation into the polymer matrix creates some unique properties (Bucci et al. 2005).

Different sized nanoparticles ranging from 1 to 100 nm are applied in the food industry's nanotechnologies to produce safer and healthier food products (da Gama and Dourado 2018). It is essential to point out that nanoparticles in food packaging are less harmful than their use as food ingredients (Tarrahi et al. 2020). This is also the perception of consumers based on studies that nanotechnology packaging is more beneficial than using nanotechnology in foods (Bucci et al. 2005; da Gama and Dourado 2018). Anyway, it needs better regulation, consumer awareness, and methods of nanotechnology risk assessment (Khosravi-darani and Bucci 2015).

The nanoparticles in food packaging represent antimicrobial activity, acting as antimicrobial polypeptides carriage and protecting microbial spoilage. These carriers develop the food shelf life with the help of serving enzymes, antioxidants agents, and some bioactive substances. Some metal ions and inorganic metal nanoparticles like Fe, Ag, Zn, C, Mg, and silicon dioxide nanoparticles are used for their antimicrobial activity in food. Nile et al. (2020) summarized some nanomaterial-based biosensors with their usage in food packaging nanotechnology. In this report it was not possible to identify monomicrobial polymers in food packaging applications. The only one listed was PLA (Nile et al. 2020), and it is biodegradable but not a microbial polymer (Wang et al. 2012).

As a microbial polysaccharide, bacterial cellulose is introduced as a unique environmentally friendly substance for nanocomposites. It is essential to highlight those natural nanomaterials have microporous 3D network structures like cellulose nanofibrils (Lovera et al. 2007; Fortunati et al. 2010).

Pullulan films with starch nanocrystals or nano/microfibrils of bacterial cellulose are valuable nanocomposites. They can make nanostructures like nanoparticles, hydrogels, elastomers, microcapsules, foams and sponges, and fibers (Bucci et al. 2005).

Introzzi et al. represented the improvement of a new nanocomposite coating with high oxygen barrier having pullulan clay. Applying on PET, oxygen permeability in the double layer was considerably lower than the original PET layer. This was reported in high humidity as the polysaccharide matrix lost its barrier traits. The results showed a promising alternative to replace synthetic oxygen barrier polymer coating in food packaging (de Paula et al. 2017).

4.2.9 Bacterial Cellulose (BC)

The nanomaterial, microfibrillar tridimensional of continuous nanocellulose fibers 20–100 nm wide%) (Valentina et al. 2008) with a high specific surface, better biocompatibility, crystallinity, tensile strength, and water content (Fortunati et al. 2010). The aspect of dried BC membranes is similar to that of a sheet of paper, with a discrete surface gloss (Lovera et al. 2007). BC is also the only nonvegetable nanocellulose originating from microorganism fermentation in static or agitated cultures (Lovera et al. 2007; Bucci et al. 2005). The cellulose formation can be explained as a defensive method to protect bacteria from UV light side effects or help bacteria have the oxygen supply. BC synthesis can be divided into two intermediary steps: (I) the intracellular formation of 1,4-β-glucan chains and (II) the assembly and crystallization of cellulose chains. In this last step, the cellulose chains are extruded to the external environment (Arrieta et al. 2013). They are deposited over the bacterial colonies as a protective membrane to ensure their survival in their natural habitat (Lovera et al. 2007). BC is preferred over plant cellulose because it does not contain any impurities in plant sources like pectin, hemicellulose, and lignin and show a better degree of crystallinity and polymerization (Petersen et al. 1999a; Arrieta et al. 2013). It is similar to plant celluloses ($C_6H_{10}O_5$) in molecular formula (Arrieta et al. 2013). BC is the production of many species of bacteria like *Komagataeibacter* (former *Gluconacetobacter* or *Acetobacter*) (Valentina et al. 2008), *Achromobacter*, *Rhizobium*, *Salmonella*, *Alcaligenes*, *Agrobacterium*, *Aerobacter*, *Pseudomonas*, *Sarcina*, *Azotobacter*, *Dickeya*, and *Rhodobacter* (Petersen et al. 1999a; Arrieta et al. 2013). *Komagataeibacter* is usually the choice for food research and applications due to its higher BC purity and yield. It can produce cellulose (1.0–4.0%) at commercial levels (Petersen et al. 1999a).

Cellulose-producing microorganisms are easily found mainly in a high-volume residue of the coconut processing industry, the coconut water. Coconut water is rich in sugar and other nutrients sufficient to support the growth and reproduction of microorganisms, which secrete cellulose as their main by-product, known as "Nata de Coco" (NC). The edible Nata de Coco is the only established industry of BC that provides consolidated data on its production and market and offers products at accessible costs (Lovera et al. 2007).

BC is produced in undisclosed, but certainly modest, amounts by a few companies, like Dermafill in the USA and Bionext in Brazil, which commercialize BC dressing in the form of sterilized sheets in several dimensions. BC is also produced for biomedical application by Jenpolymers, Germany (Lovera et al. 2007).

4.2.10 Properties

BC shows better mechanical properties than plants cellulose: higher tensile strength, water holding capacity, solubility, ion interaction and strength, antibacterial properties, cross-linking, gelation, extendibility, and stability on a broader range of pH and temperatures, as well as being more economical (Sukara and Meliawati 2016).

It presents biocompatibility and hydroexpansivity (approximately 200 times its weight) (Lovera et al. 2007; Arrieta et al. 2013). This last property makes it an attractive material for surgical implants and its versatility to be molded in various sizes and shapes (Lovera et al. 2007). Its fibrillar structure makes it a uniform and ultrafine highly porous material with a soft texture and gas permeability (Gustavo and Regina 2006). These unique traits encouraged many researchers to work on the new applications of bacterial cellulose in medical and food technologies (Lovera et al. 2007).

BC is unique due to having antibacterial properties and being cheap (Arrieta et al. 2014a). Applying antibacterial packaging would significantly diminish the application of preservatives in food products. This new material meets the consumer's longings for sustainability in searching for natural food products and environmentally friendly packaging (Khosravi-darani and Bucci 2015).

4.2.11 BC Applications from Medical to Food Packaging

Bacterial cellulose is accepted as a desirable versatile biomaterial. It is applied in an expanded range of scientific fields, especially food and biomedical**.** BC membranes are produced under controlled conditions. Synthetic culture media are used in their dried form to cure second and third degrees of skin burns, chronic wound healing, treatment pads, tissue/organs drape, and burn bandages (Arrieta et al. 2013, 2014a). Bacterial cellulose is an attractive issue these days due to the enhanced interest in **tissue-engineered** products for injuries and wounds and the regeneration of damaged body organs (Fortunati et al. 2010). As an example, mentioned by that a BC-based composite has been designed with suitable shape for implantation as a replacement material for damaged tissues such as the meniscus and the cartilage (Bodin et al. 2007).

Scientists for certificate wound healing studied the time to close a wound and reduce pain and and ease its use. The results showed that the healing time was equivalent to the commercial controls, with an advantage for pain relief and ease of use, leading to greater satisfaction for the patient and nurse (Lovera et al. 2007; Valentina et al. 2008). Some trademark products like Dermafi ll and Bionext are available on the market (Arrieta et al. 2014a). BC extensively protects the wounds by transferring antibiotics/medicines into them and preventing external infection while covering the wounds (Petersen et al. 1999a; Arrieta et al. 2013).

BC is a promising material for **pharmaceutical excipient** according to Kulkarni et al. (2012) that used bacterial cellulose in the drug formulation. The showed that

bacterial cellulose is a great pharmaceutical aid in tablet formulation and gives tablets better consistency (Kulkarni et al. 2012).

BC is used for facial beauty masks and skincare treatment in the cosmetic field. BC membranes impregnated with cosmetic emulsion compositions (whitening or antiaging formulations) or anticellulite wraps are used directly on the skin. In both wound dressing and cosmetic masks, the performance of the membranous form of BC is fundamentally essential (Valentina et al. 2008).

In food processing, BC produced by *Acetobacter xylinum* is so common as it has better properties than cellulose, like higher tensile strength, water holding capacity, soft texture, and more fiber (Arrieta et al. 2014a). Conversely, BC gel from Nata de Coco has become very popular, and it is a traditional dessert in Southeast Asia. It is now readily available on the market and spreads worldwide at low costs (Khan et al. 2016; Lovera et al. 2007). Has a simple manufacturing process with well-documented production price ad information (Singh et al. 2019).

Furthermore, nata de coco products exploitation occurred. It has sophisticated molecular gastronomy with better organoleptic and health traits (Lovera et al. 2007; Arrieta et al. 2013). It has a remarkable ability of gelling, thickening, water binding, and stabilizing. It is used in desserts, salads, ice cream, and other foodstuffs. Bacterial cellulose is also a common ingredient in low cholesterol and calorie food products. Paste-like cellulose material in chocolate drink's formulation in 0.5% stopped the cocoa powder precipitation by trapping it in the microfibrillar mesh, improving the viscosity of the drinks (Ferreira et al. 2016).

Adding alginate during the process improves the texture, and this property is so desirable in various food products. Bacterial cellulose was more impressive when added to heated oil-free foods. One crucial feature of BC is that it develops the food's rheology to prevent flavor exchange and increase food stability in different temperature pH and freezing conditions (Fortunati et al. 2010).

4.2.12 BC Bio-based Films and Coatings for Packaging

Food grade BC would apply in food films and coatings. Also, it can produce bacterial cellulose nanocrystals (Lovera et al. 2007). Azevedo et al. studied the process condition for BC production and its applications as food ingredients, packaging like coatings, and films (Azeredo et al. 2019). Otoni et al. (2017) pointed out that food films and coatings are better for external packaging due to hygiene reasons. Some flavor components like fruits may be added to various food products (Otoni et al. 2017).

BC fibers in combination with PVA resulted in biomaterials for packaging with biodegradability and strength but sensitivity to moisture. There were few reports about the use of BC/PVA for food packaging due to its high water absorption capacity (Arrieta et al. 2014a).

4.2.13 BC Active Packaging Materials

Another vital application of BC is in active food packagings, and it is used as a carrier for antimicrobial agents into food and increases microbial food stability. Santos et al. (2018) reported the antimicrobial BC membranes by saturating BC sheets in nisin, and it increases the shelf life and confirms product safety. Active food packaging with biocellulose may integrate oxygen and ethylene scavengers, antimicrobial agents, moisture removers (Santos et al. 2018).

Films of BC with PVC and the antimicrobial agent sorbic acid can be prepared by dispersing a BC powder in a PVA solution under vigorous stirring and then drying at room temperature in plastic Petri dishes. These biobased polymeric films have a potential application in food packaging with antimicrobial activity (Lovera et al. 2007).

4.2.14 Other Applications for BC

BC is also used in paints, acoustics, mining, textile, oil gas recovery, paper, nonwoven cloth, films, fiber coating, adhesives, fire retardant, etc. (Fortunati et al. 2012a). Bacterial cellulose **biofabric** is applicable **in the textile** industry (Fortunati et al. 2010).

Sony Corporation developed the first high technological application of BC and has already commercially been available on the market for several years. They used dried BC fibers in a composite material for **acoustic diaphragms** in speaker systems in several products as earphones, headphones, and loudspeakers (Fortunati et al. 2012a). **The acoustic diaphragms produced were reported** to have superior physical properties like Young's modulus and tensile strength compared to conventional materials. They also reported that the production of such material might be very profitable (Fortunati et al. 2012a; de Paula et al. 2017).

In the following, several promising pieces of the research reported by Freitas et al. (2014) on BC in **the development of electronic components** will be highlighted: organic LED fabricated with BC-acrylic resin composite; the electrically conducting BC with multiwalled carbon nanotubes; an electro-active LiCl-impregnated BC composite; and a BC electric paper embedded in an electrochromic color (de Paula et al. 2017).

4.2.15 Application of BC-Based Composites

Table 4.2 exhibits the basic compositions and characteristics of the selection of such materials (Arrieta et al. 2014a).

According to the examples listed above (Table 4.2), BC-based products are high-value-added, which is not relevant for this application because the production costs are low compared to the product profit and the low amounts of BC required. Nevertheless, BC is still a high-cost raw material, produced by a biotechnological

Table 4.2 BC-based composites

Modification	Properties/Applications
PLA	Reinforcement of PLA matrix with acetylated BC
PHA	Biocompatible and biodegradable reinforced PHAs
Chitosan	Reinforcement of the polymeric matrix for packaging and biomedical applications
Pullulan	Reinforcement of the polymeric matrix for food industry
Alginate	Composite with improved mechanical properties and good miscibility between the components
CMC	The incorporation of CMC into the culture medium during the BC synthesis interfered with the formation of BC fibers, leading to composites with low mechanical strength and low crystallinity
PVA	Biodegradable composite materials for application in the packaging industry
Starch	Composite prepared by incorporating starch in the culture medium during the BC synthesis showed no significant improvement of mechanical properties
Acrylic acid	Improved mechanical properties

process, which needs a long period to be synthesized, besides its purification and sterilization, i.e., different processes that increase costs and time to deliver the end product. As for any other raw material, low amounts of BC can be used in high-value-added products or high amounts of low-cost products (Arrieta et al. 2014a).

Chiulan et al. (2018) reported nanocomposite films in food packaging by bacterial cellulose (BC) nanofibers in polyvinyl alcohol/starch substrate. The results improve mechanical properties by adding 1% BC nanofibers into polyvinyl alcohol/starch. In 2% BC, the water vapor permeability would increase. They were obtained for only 2 wt % BC nanofibers in the composite film. So, polyvinyl alcohol/starch/2BC seemed desirable in food packagings (Chiulan et al. 2018).

4.2.16 Future of BC

BC is a material with outstanding properties and hence numerous potential applications. The growing number of patents and scientific publications related to BC points to an increasing demand, which requires a severe scale-up in its production, as well as a decrease in its cost, which however should, in principle, be a consequence of the scale-up, at least in part (Arrieta et al. 2014a).

It is on its way to making BC biopolymer become an important raw material for new developments. However, BC's commercialization is still very incipient, and its commercialization is focused on high-value niche markets. There are still various issues for mass production of BC due to not having sufficient fermentation systems and high process costs (Arrieta et al. 2013).

The next type of microbially produced polymers to be described are biopolyester (PHA) polyhydroxyalkanoates. They pose hydrophobic nature rather than the polysaccharide-derived substances to produce a good moisture barrier material with poor gas barrier properties (Brody et al. 2008).

4.3 (PHAs)

Polyhydroxyalkanoates (PHAs) are commonly used and produced by using bacterial fermentation in a wide variety of microorganisms, from the sugars or lipids, which accumulate the intracellular granules and supply energy for the microbes (Bohm et al. 2010). It commonly takes place in limiting elements like S, P, N, O, Ca, Fe, and Mg (Halami 2008). They made over 90% of cells dry weigh (Petersen et al. 1999a). The polymer extraction happened with the help of some solvents such as chloroform, propylene chloride, and methylene chloride (Ishrat et al. 2018). The structure of PHA comprises more than 100 types of alkanoate monomers. Three types exist based on their long-, short-, and medium-chain length (Azeredo et al. 2019). PHA would drive from hydroxy fatty acids with 3 to 14 or more than 15 carbons. The short-chain PHA is produced by *Alcaligenes latus* and *Ralstonia eutropha*. The medium-chain PHA is produced by *Pseudomonas putida* (Hofer et al. 2011). There are only four types of PHA that achieved a large scale of production, and they are poly[(R)-3-hydroxybutyrate-co-(R)-3-hydroxyhexanoate], poly[(R)-3-hydroxybutyrate], poly[(R)-3-hydroxybutyrate-co-4-hydroxybutyrate], and poly [(R)-3- hydroxybutyrate-co-(R)-3-hydroxyvalerate] (Fortunati et al. 2012b; Valentina et al. 2008). The production of PHA begins with fermentation, followed by separation of biomass, drying, and extraction, and ending with PHA packaging (Arrieta et al. 2014a).

PHAs would be used in packaging materials like boxes, films, coatings, foam and fibers, biofuels, and drug carriers. There are some concerns in large-scale applications: PHA properties and costs (Fortunati et al. 2012b). Over the past years, recombinant PHA production strains have been developed to produce PHA with better mechanical and thermal properties (Halami 2008).

4.4 PHB

PHB or Poly 3-hydroxybutyrate is a well-known biodegradable PHA produced by various bacteria (Petersen et al. 1999a; Bohm et al. 2010; Plastics Europe 2015). It is renewable, biocompatible, and thermoplastic (Wang et al. 1997; Brody et al. 2008). It is the most studied and used among the PHA family. It accumulates in the membrane of bacteria in more than 80% of the cell's weight (Guillard et al. 2018).

PHBV or polyhydroxybutyrate-co-hydroxyvalerate is stronger than PHB. It is piezoelectric trait makes it more useful (Kabilan et al. 2012; Nair and Laurencin 2007). PHB can be changed into D3-HB (hydroxybutyrate), a component of human blood. It can be used in tissue engineering, as a drug carrier (Zinn et al. 2001; Philips et al. 2007) and in disposable supplies and packings (Rosa et al. 2004). Bucci et al. (2005) reported PHB usage in food packaging compared to PP (Bucci et al. 2005). The PHB deformation was nearly 50% lower than PP, which is more complex than PP. PHB performed better than PP in warmer conditions. The PHB production expense depends on the substrate, strain, cultivation method, and production process. It uses cheap substrates (Khosravi-Darani et al. 2013; Mokhtari-Hosseini et al.

2009a; Titz et al. 2012; Muhr et al. 2013), modeling (Shah-Hosseini et al. 2003a), suitable experimental design (Khosravi-Darani et al. 2004), and a new recovery method (Khosravi-Darani and Vasheghani-Farahani 2005a; Tripathi et al. 2012). Besides the various application of PHB (Bourbonnais and Marchessault 2010), it is used in food packaging (Park et al. 2002). The effect of different carbon and nitrogen sources and culture variations on biomass production and PHA (Khosravi-Darani et al. 2004) and *Pseudomonas aeruginosa* (Tripathi et al. 2012) is also significant. In batch fermentation, the PHA yield in sugar cane refinery waste and urea was acceptable. The maximum PHA amount (70%) was produced by *Alcaligenes* sp. in palmitic acid and the maximum PHB amount (78%) in flask cultivation of bioreactor. It is reported that *Alcaligenes eutrophus* is the most common bacterial PHB producer. Proliferating and accumulating in significant levels of PHB (more than 80%, dry cell weight) is its advantage (Bucci et al. 2005). PHA monomers are also produced from long-chain fatty acid biotransformations (Bourbonnais and Marchessault 2010). It is shown that plants oil produced polysaccharides (Srivastava and Tripathi 2013) and medium-chain PHA (Huisman et al. 1989).

4.4.1 PHB Properties

As mentioned above, PHB has a crystalline structure with a high crystallinity degree and melting temperature. It is biodegradable and non-water-soluble with piezoelectricity. PHB has attractive barrier properties with low water and oxygen permeability (Bucci et al. 2005) and is very similar to conventional polyesters (Rech et al. 2020). These properties make it more desirable for food packagings (Wang et al. 1997; Park et al. 2002).

PHB's strength and Young's modulus are the same as PP, but the break elongation (at $5 \pm 10\%$) is significantly less (Kulkarni et al. 2012). The PHB stiffness in the PHB spherulites forms in non-externally stress conditions (Otoni et al. 2017; Santos et al. 2018; Chiulan et al. 2018; Halami 2008). Long storing at room temperature makes it more brittle. PHB does not pose catalysts residues as the production sources are microorganisms. It does not have chains, so it remarkably flows in processes (Santos et al. 2018; Chiulan et al. 2018; Halami 2008).

4.4.2 Molecular Weight of PHA

The molecular mass is one of the main properties in evaluating PHB, and it affects this polymer's physical properties like permeability, viscosity-temperature of glass transition, and solubility. This property relates to the microorganism sp., substrate, culture extraction method, and polymer purification (Razali et al. 2020a).

4.4.3 Physiological Characteristics of Microorganisms

Microorganisms can produce various polymers with different molecular masses. *Ralstonia* sp. produces the polymers with high molecular weight, whereas the methylotrophic bacteria produce PHB with low molecular weight in a downstream process (Al-Battashi et al. 2019).

4.4.4 PHA Synthase Expression Levels

Increasing the PHA synthase activity reduces the molecular mass of PHB in *Ralstonia eutropha* and *Escherichia coli* (Arcos-Hernández et al. 2013). It was reported that the PHB molecular mass was evaluated by the PHA synthase gene activity in *Pseudomonas*, and by enhancing the number of PHA synthase gene copies, the molecular mass was reduced (Bugnicourt et al. 2014). In *Commonas acidurans*, an increase in PHB production from 4-hydroxybutyric acid is observed by a continuous increase in PHA synthase activity. The PHB molecular mass-produced by *Ralstonia eutropha* relates to the PHA synthase activity (Nath et al. 2008).

4.4.5 Carbon Source

The carbon source may affect the PHB molecular mass. Methylobacterium extroquence growth on methanol and succinate as carbon sources leads to the production of PHB with a molecular weight of 1.7×10^6 Da and 0.6×10^6 Da (Razali et al. 2020a). Miyazaki et al. (2000) studied the simple and complex carbon source effect on PHB molecular weight made by *Azotobacter crococcum* (Miyazaki et al. 2000). The PHB molecular mass was not changed by changing the glucose amount as a carbon source (from 400 to 500 kDa), whereas the change in sugarcane molasses enhances the molecular mass from 300 to 640 kDa (Mokhtari-Hosseini et al. 2009b).

4.4.6 Cultivation Conditions

Also, the bacterial culture, like pH, culture age, and nutrients, would significantly affect the PHB molecular mass (Nath et al. 2008).

4.4.7 Nutrient Restriction

The nutrient restriction affects the PHB production and affects its molecular mass. Bustamante et al. (2019) produced PHB from *Pseudomonas* and restricted Mg^{2+}, NH_4^+, and PO_4^{-3} with molecular masses of 3.7×10^5, 2.5×10^5, and 3.1×10^5 Mg,

respectively (Bustamante et al. 2019). Ghoddosi et al. (2019) evaluated the effects of phosphate and magnesium on PHB molecular mass from *Ralstonia eutropha*. This study showed that more glucose and less nitrogen limitation reduced the PHB molecular mass, whereas phosphate modification had a negligible effect (Ghoddosi et al. 2019).

4.4.8 Culture pH

The PHB affects the molecular weight by pH. Tripathi et al. (2013) claimed that rising pH would increase the PHB molecular mass in *Alcaligenes* sp. (Tripathi et al. 2013).

4.4.9 Cultivation Age

The polymer molecular mass may diminish during fermentation because of the depolymerase enzyme (Mokhtari-Hosseini et al. 2009c). Miyazaki et al. (2000) evaluated the effect of culture age on PHB molecular mass from *Azotobacter chromium*. They were applying sugarcane molasses (5% w/w) as a carbon source increases PHB molecular mass (30%) during 72 h. Applying glucose as a carbon source, the molecular mass reached the maximum level during 48 h (Miyazaki et al. 2000). Applying sugar beet molasses as a carbon source enhances the PHB molecular mass (2000–4000 kDa) in *Azotobacter vanilladi*, increasing 24 h (Chen 2010).

4.4.10 Temperature

Temperature affects PHB from Methylobacterium extroque on methanol as substrate, but PHB molecular weight was stable around 100KDa (Bustamante et al. 2019).

4.5 Polyhydroxybutyrate Purification and Extraction Methods

PHB molecular weight also relates to the purification and separation process. PHB molecular mass was reduced during the extraction methods (Bustamante et al. 2019). The extraction elements like solvent amount and type and used temperature significantly affect the degradation of PHB. In the sodium hypochlorite digestion method, there is a high polymer degradation rate. Berger et al. (1989) showed a reduction (50%) of PHB molecular mass applying the sodium hypochlorite process (Berger et al. 1989). Pretreating with SDS and Triton-x100 before using sodium hypochlorite developed the polymer's molecular quality and mass. It is reported that antioxidant addition like sodium bisulfate developed the PHB molecular mass (Chen 2010).

4.5.1 Production Costs

Many factors influence the PHB producing cost. The most important ones are substrate price, polymer accumulation yield, and yield of the substrate unit. Some agricultural by-products used as substrates (Koller 2019) such as foodstuffs waste (Christopher et al. 2019), cereals and wood by-products (Cinelli et al. 2019), lipid and oil by-products (Cinelli et al. 2019), camelina oil (Bustamante et al. 2019), apple waste (Rebocho et al. 2019), feather (Pernicova et al. 2019), sugar molasses (Bozorg), carbon sources (Bustamante et al. 2019), methane (Ghoddosi et al. 2019), methanol (Mokhtari-Hosseini et al. 2009c), and glycerol (Koller 2019). Some reducing cost strategies are modeling (Shah-Hosseini et al. 2003b), suitable bioreactor and experimental designs (Khosravi-Darani et al. 2003), and recovery process (Khosravi-Darani and Vasheghani-Farahani 2005b).

Some PHA biosynthesis is (Chen et al. 2020):

1. Bacteria culturing and isolating with suitable growth and high efficiency in carbon sources.
2. Applying a high cell density culture process for product cost reduction.
3. Applying cheap and effective polymer extraction methods.
4. Transforming bacterial's genes to plants.

4.6 PHA Applications: Biomedical and Biopackaging

PHAs pose many applications in biopackaging and biomedical (Sabbagh Mojaveryazdi et al. 2012). PHB would be used in films for packaging, blow molded bottles, and paper's coating and used in reconstructive surgery regarding its biocompatibility. Amphiphilic PHAs are used in tissue engineering, drug delivery, artery augments, heart valves, cardiologic stents, implants, and dressing tablets (Hazer et al. 2012). PHB would change to HB in human blood, and therefore, it is not toxic for human applications. PHAs would be used as composite material due to having similar properties to petrochemical polymers (Sabbagh Mojaveryazdi et al. 2012).

PHA films have attracted interest in food packaging as they are renewable and biodegradable with water vapor barrier properties. PHB shows a better light barrier in the visible and UV areas than PHA (Park et al. 2002). PHB's problems are expensive, low melt process, low thermal stability brittleness (Thellen et al. 2008; Gregorova et al. 2009; Ohashi et al. 2009). The low thermal stability leads to reducing molar mass and viscosity. The carbon source costs nearly 40% of the total cost (Choi and Lee 1999). There is an interest in PHAs copolymer application instead of the homopolymer due to having better mechanical properties (Silvestre et al. 2011).

4.7 Main Approaches to Improve PHB Properties for Food Packaging

PHA properties would be developed by combining PHAs with other polymers and inorganic substances. PHA nanoparticles develop thermal stability, mechanical properties, process time, and temperature by thermal modification (Ohashi et al. 2009). The nanocomposites produced from PHB modify the polymer characteristics, and various nanoparticles make different properties in structure. Adding nucleating agents to PHB reduced the brittleness (Khanna and Srivastava 2005).

4.8 Production of Copolymers

Monomers may combine in various combinations to produce copolymers with vast properties in the PHA family (Park et al. 2002). The copolymers' properties relate to the monomer's composition and change the crystalline thermoplastic to elastomeric (Yun et al. 2008). This would increase the melting point, water permeability, and tensile strength but decrease the resistance (Pilla 2011). Various carbon sources affect the physicochemical characters of PHAs 34. PHBs are more complex, so they should be modified before applying to the packaging (Martínez-Sanz et al. 2013). By adding hydroxyvalerate (HV), the copolymer becomes more robust and flexible (El-Hadi et al. 2002a; Yun et al. 2008; Sudesh and Iwata 2008). Among PHAs, poly 3-hydroxybutyrate-co-3-hydroxyhexanoate is one of the most common polymers due to the proper properties for flexible films (Escapa et al. 2011). Escape et al. revealed polyhydroxy-6-acetylthiohexanoateco-4-acetylthio butanoate production by P. putida (Chen 2009). PHA polymers pose good thermal stability (till 200 °C), with acceptable processability (Hazer et al. 2012). PHA's properties are affected by monomer composition and chemical structure (Hofer et al. 2011; Reis et al. 2008).

4.9 Blending

Mixing with other biodegradable substances will decrease brittleness. In this process, some nucleating factors are added, and spherulites with better physical properties are made. The blending process depends on crystallinity, morphology, and glass temperature transition (El-Hadi et al. 2002b). Also, blending is known as tailoring PHAs properties as sustaining biodegradability (Ohashi et al. 2009). PHB blending with other biopolymers involving starches (Zhang and Thomas 2010), polyvinyl alcohol (Rychter et al. 2006), thermoplastic starches (Sanchez-Garcia et al. 2008), PCLs (Lovera et al. 2007; Olkhov et al. 2003), ethylene vinyl alcohol (Lee et al. 2005), and ethylene polymers (Oyama 2009).

There is a limitation of blending with polymers like PLA, and other polymers in some cases as they are immiscible. To develop the physical properties of PHB and to enhance the degradation of polymers, some additives can be used (Briassoulis 2007)

like nucleating factors, for example, glycerol as plasticizers, or lubricants like monoglycerol (El-Hadi et al. 2002b). By applying plasticizers, PHB properties are improved (Kotnis et al. 1995). The blended polymers should protect foods from water, oxidation, and light (Castro Lopez et al. 2013). The crystalline phase affects permeation, so enhancing polymers crystallinity is essential. The insertion of PLA with high crystalline PHB in the melt blending process increases the PLA crystallinity with better properties (Zhang and Thomas 2011). Having the same melting temperature, PLA and PHB can easily blend and enhance stability against water and oxygen transfer but decrease the PLA transparency (Arrieta et al. 2014a). Transparency is essential in materials improving food packaging (Arrieta et al. 2013). Packaging must protect food from UV (Razali et al. 2020b). The transparent films improving with increasing UV protection relates to the food packaging industry (Lagaron and Núnez 2012). PHB is a better light barrier in visible and UV light than PLA (Park et al. 2002). PHAs include cross-linking side-chain that decreased the crystallinity. Inserting monomers in polymers chains results in better thermal stability and decreased melting temperature (Hofer et al. 2011). Hazer et al. (2012) reported better the physical, thermal, and hydrophilic PHA traits by grafting reactions (Hazer et al. 2012).

Based on his study, Razali et al. (2020a, b) reported that 3 wt% EPO as a plasticizer increases the chain mobility of PHA and decreases the molecular interaction. Therefore, it can enhance the extensibility and flexibility of the PHA/EPO blends. It was also possible to conclude that higher EPO loading leads to higher elongation at break with lower tensile strength. Adding EPO as a plasticizer into the PHA matrix transfers stress to EPO and enhances PHA mobility and higher flexibility (Razali et al. 2020b).

4.10 PHA Nanocomposite Film

PHA nanocomposites and nanofillers would develop the food packaging (Lagaron and Núnez 2012). Applying nanofillers in polymers would modify crystallization, biodegradation rate, stability, morphology, and physical and thermal properties. A nanofiller should have a minimum of one dimension in the nanometric level, and isodimensional nanoparticles include three nanoscale dimensions. Whiskers and nanotubes have two dimensions on the nanometer scale, and layered crystal nanocomposites only have one dimension in the nanometer (Arora and Padua 2010). Some studies of montmorillonite clay incorporated as nanocomponents in various polymers like PE, nylon, PVC, and starch (Brody et al. 2008). PHA nanocomposites would be filled with silicates like montmorillonite, double hydroxides, multi-walled carbon nanotubes, and cellulose nanowhiskers (Azeredo 2009). Silica nanoparticles were used to raise the initial temperature of PLA degradation, polybutylene succinate, and poly(3-hydroxybutyrate-co-3-hydroxyvalerate). The physical properties were developed in low silica concentration and got worse in higher silica levels due to the accumulation of silica in the polymers (Brody et al. 2008).

Cellulose nanocrystal is a biobased and biodegradable nanoparticle (Xu and Qiu 2009) that presents higher stiffness and biodegradability with lower density and cost (Fortunati et al. 2013). PLA-PHB blend cellulose nanocrystal presents a novel perspective in food packaging technology (Arrieta et al. 2014a).

4.11 Other Roles of Nanotechnology in Food Packaging

Nanotechnology is potentially used in the food industry (Rashidi and Khosravi-Darani 2011) and causes some packaging properties like flexibility and stability and extending shelf life due to acting as oxygen scavenging and antimicrobial and biodegradability (Mozafari et al. 2008). Nowadays, producing ionic metal oxide nanoparticles with various shapes and sizes developed antibacterial agents (Miguel et al. 1997). The active packaging with antimicrobial ability creates high-performance metal nanoparticles in polymer films. A high surface area increases the metal and metal oxide nanomaterials antimicrobial activity such as Ag, Au, ZnO, SiO_2, Al_2O_3, TiO_2, Fe_3O_4, Fe_2O_3, and MgO (Cyras et al. 2007). The nanoparticles of TiO_2 and ZnO compared to Ag are safer in food packagings. Nanopackaging and nanoencapsulation are the two main nano-applications in the food industry via liposome (Mozafari et al. 2008).

4.12 Nanotechnology in PHB Application in Food Packaging

As previously reported, nanomaterials in packaging mixed with polymers matrix to ameliorate the properties like humidity and temperature and gas barrier in packagings.

4.12.1 Physical Properties

Inadequate flexibility is the main issue in using PHAs in food packagings. The blending process would diminish brittleness, and using nanofillers in PHAs would lead to a higher Young's modulus. These nano packaging substances compete with petrochemical polymers in food packaging with better PHA flexibility (Rashidi and Khosravi-Darani 2011).

4.12.2 Permeability

PHB films have better water vapor permeability, the same with PVC or PET (Miguel et al. 1997; Cyras et al. 2009), non-swelling, and less hydrophilicity than starch, cellulose, gluten, and chitosan (Miguel et al. 1997). Water solubility in PHAs is the main factor in enzymatic or nonenzymatic degradation (Yoon et al. 2000; Corrêa et al. 2008).

PHB films blend with other biodegradable polymers in various processing conditions (Thellen et al. 2008; Olkhov et al. 2003; Miguel et al. 1997; Iordanskii et al. 1999; Corrêa et al. 2008). PHAs reduce the water sensitivity and oxygen and CO_2 permeability with better barrier properties in organic solvents (Martínez-Sanz et al. 2013; Sanchez-Garcia et al. 2007; Kuusipalo 2000). The crystallinity effect on PHA permeability properties is reported (Sanchez-Garcia et al. 2008; Miguel et al. 1997; Yoon et al. 2000; Poley et al. 2005; deAzeredo 2009). Also, the PP, PLA, PET, and PCL oxygen permeability decreased by incorporating nanoclays. More investigation on PHA barrier properties in nanofillers is required (Sanchez-Garcia et al. 2008).

4.12.3 Thermal Instability

Thermal instability is one of the PHAs' limitations in processing (Arcos-Hernández et al. 2013; Plackett 2011). Some methods are used to improve thermal, such as thermal differential scanning calorimetry, GC/MS133 pyrolysis, and gravimetric analysis. PHA thermal degradation is due to non-radical random chain-scission reactions (Galego and Rozsa 1999).

Thermal instability is essential in more than 200 °C. Blending is a method for increasing PHA's thermal stability (Galego and Rozsa 1999). Also, adding nanofillers with MMT and LDH would develop PHAs thermal stability (Arrieta et al. 2014a; Ohashi et al. 2009; Plackett 2011; Galego and Rozsa 1999; Bruzaud and Bourmaud 2007; Wu et al. 2008; Botana et al. 2010) because of dispersion of silicate layers as barriers to O_2 and volatiles (Cho and Paul 2001). Nanocomposite thermal degradation is affected by dispersion degree, and the accumulation would make local heat (Bruzaud and Bourmaud 2007).

4.12.4 Migration

Migration is an essential issue in selecting monomers or polymers in PHA for food packaging. Up to now, no investigation of migration from PHA packaging has been reported. The migration from PHB films into food models was ethanol, acetic acid, and n-heptane (Park et al. 2002). The migration is less than the 50 mg kg^{-1} (recommended limit) totally, which shows PHAs for food packagings. There are still some considerations in bio materials food applications (Chowdhury 2008).

Migration, biodegradability, and shelf-life are so significant in food packaging. Degradation must be controlled and stopped during storage (Petersen et al. 1999b). Pure PHB is nontoxic. More investigations are needed to migrate degradation materials during processing (Thellen et al. 2008). The migration of PHA film nanoparticles into food should be regarded as more active than macroscale particles. Higher nanoparticles surface area enhances the migration and absorption (Li and Huang 2008). The toxicological effects of nanoparticles migrated from packaging into food require more research (deAzeredo 2009). Šimon et al. stated the particle

migration from nanocomposites and reported that nanoparticles with a 1-nm diameter would migrate (Šimon et al. 2008). Fe, Mg, and Si migration from biodegradable nanocomposite films to food models are introduced (Avella et al. 2005).

4.12.5 Biodegradation

A reduced rate of biodegradation of PHB or PHBV has been reported by increasing nanoparticle content (Escapa et al. 2011). Such observation can be attributed to the difficulty of penetration of microorganisms into the bulk of the material due to the formation of a tortuous path caused by nanoparticles (Schmidt et al. 2009). Also, decreased water permeability and antimicrobial effect of nanoparticles, such as MMTs, influence the reduction in the biodegradation rate (Martínez-Sanz et al. 2013). However, increased biodegradation of toughened PHB containing modified MMT is reported due to the terminal hydroxylated edge groups of the silicate clay layers that can absorb moisture from compost and act as initiation sites for polyester hydrolysis (Ray et al. 2003). As a rule, any factor which increases the hydrolytic tendency of PHAs may facilitate degradation (Pavlidou and Papaspyrides 2008).

The clay particles cause more polymer fragmentation and enhance degradation (Parulekar et al. 2007). Low temperatures enhanced the rate of PHB biodegradation and microorganisms' growth inhibition happened in high temperatures (more than 60 °C). Also, polymers' crystallinity is significant as amorphous areas are subjected to hydrolysis after microorganisms' attacks. It was reported that tomatoes remained fresh in PHB-coated paperboards compared to wrapping in low-density PE bags (Kantola and Helén 2001). Haugaard et al. evaluated orange juice packaging in PHB cups, and the results reported good performance in high-density and during storage under light (Haugaard et al. 2003). Hermida et al. reported no significant decrease in PHB properties in the presence of gamma radiation in food sterilization and packaging (Hermida et al. 2008).

4.13 Conclusion

Food packaging based on conventional plastics is not biodegradable and leads to environmental problems. The plastic recycling policy is not very practical and economical because of the contamination of food packaging. Biodegradable food packaging is a desirable option. Along with biodegradable materials advantages, there are some potential issues to be overcome like food safety and quality, cost-effectiveness, better water vapor permeability, and more accessible applications.

Many academic studies and research are being done to find new polymers sources with better properties and production techniques to obtain biopolymers, especially microbials that would replace the common nonbiodegradable and synthetic food packaging substances.

In this research, the microbial polymers used in food packagings were revised. Polysaccharides and PHAs from microorganisms have been studied.

Cost is the limiting affecting factor in PHA application in the food industry. Microbial polysaccharides and PHAs are more expensive than petroleum-derived plastics. Using mixed cultures with waste streams would be effective in decreasing the costs. PHA is limited in food packaging due to not having suitable flexibility. The blending methods may decrease brittleness and incorporating nanofillers in PHAs leads to higher Young's modulus and enhancing PHB toughness. More study on PHA improvement using nanofillers is required. Reduction of antimicrobial effect and water permeability in nanoparticles eliminates biodegradation rate.

A high number of biobased materials composed of microbial polysaccharides (e.g., BC) have been developed in the last few decades to make mechanical performances better, increase the O_2 barrier and the hydrophobicity, and enhance matrix-fiber interface compatibility, among other features. The methods contain additives like lipids, mixing with other polymers, multilayered membranes, nanoparticle usage, and modification of polysaccharides. Producing improved products regarding properties and price is among the future food trends. The waste disposal threat costs should be evaluated in economic values in direct and indirect manners. Applying microbial polysaccharide membranes compared to natural polysaccharides should be considered in all aspects of production costs.

Solutions for this limitation pointed out of microbial polymer would not be acceptable without research and study over the years. More investigations are needed in the potential migration of degradation issues during biodegradation and processing. There is still no available data about the migration of microbial polymer packagings like degradation products and nanoparticles in food. Some research has been done on cost-effective scaled-up productions. The incorporating of dispersed nanocomposite in packagings revealed novel techniques for extending foodstuffs' shelf life during refrigeration.

The active agents adding antioxidant, antimicrobial, and oxygen scavenging with antimicrobial nanocomposite packaging improve a cost-effective technique to control microbiological growth and high quality. Nanocomposite packaging will have a high portion in food packagings with better physical properties and performance in the near future. Studying the significant factors on microbial polisacharide nanocomposite and PHA degradation is the main point of view in future trends. Also, more enzymatic and genetic researches are required to clarify the relevance of biosynthesis and metabolism. This promising challenge is necessary for a novel sustainable strategy in food packaging.

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Polyhydroxyalkanoates (PHAs) in Food Packaging

5

Kianoush Khosravi-Darani and Fatemeh Yazdian

Abstract

Renewable sources such as agro-waste, vegetable oil, and starch can made biodegradable polymers. PHAs are organic plastics with biodegradable property which made by microbial synthesis. They have peculiar/unique physicochemical properties that gain consideration. Under surrounded nutritional situations, such as nitrogen, oxygen, and low amount of phosphorous with carbon sources increment, microbial synthesis produces sustainable polymers. PHAs as eco-friendly polymer may be produced by pure isolated or genetically modified bacteria. Due to the ban of conventional plastics, it is necessary to commercialize PHA for its benefits of biocompatible as well as biodegradability. Expensive carbon source is one of the major sustainable PHA production limitations. Two ways to overcome high total price of PHA is using agro-industrial chip wastes and metabolic strains.

Keywords

Biodegradability · Biopolyesters · Food packaging · Polyhdroxyalkanoates · Properties

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5.1 Introduction

5.1.1 Biopolymer

In 2018, the amount of producing plastics (359 million tonnes (MT)) was lower than consuming it (385 MT). Excessive use of plastics and their accumulation in nature as a persistent pollutant has endangered the life on earth (Geyer et al. 2017). With the production and recycling of plastic from previous years, using plastics will be higher than the production. Almost 56% of all plastics are used for manufacturing purposes, while the remaining is used for packaging market commodities. Only 173 MT are collected from recycling and landfilling from the total waste generated based on the statistics. Due to poor management of garbage disposal and segregation systems, another waste enters the ecosystems. According to Fig. 5.1, in 2018, the global flow of plastic material covered 80% of global GDP, and data are obtained from 44 countries and regions.

5.1.2 Polyhydroxyalkanoates (PHAs)

According to Fig. 5.2, the biopolymers can degrade in the environment and are also made from biological sources such as microorganisms, animals, plants, etc. (Kumar et al. 2020; Rajesh Banu et al. 2019).

The recent biopolymers show some of the synthetic polymers' properties, such as high tensile strength, resistance in front of moisture, and long shelf life with the help of advanced biotechnology processes (Sadasivuni et al. 2020). Polyhydroxyalkanoates (PHAs) are biopolymers with considerable and desirable properties like biodegradability, compostable properties, and easy conversion to different forms, making them used in industrial-scale production (Sirohi et al. 2020). One of the limiting factors for industrial applications of PHAs is the cost of

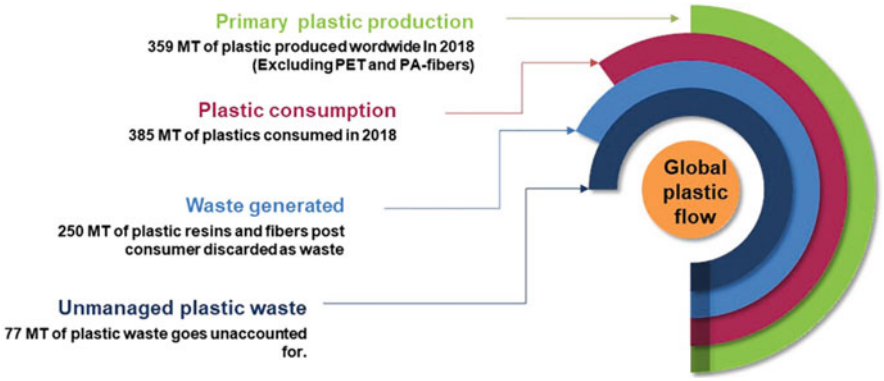

Fig. 5.1 Global plastic flow in 2018, containing cumulative data sourced from 44 countries and regions covering 80% of global GDP (Rai et al. 2021)

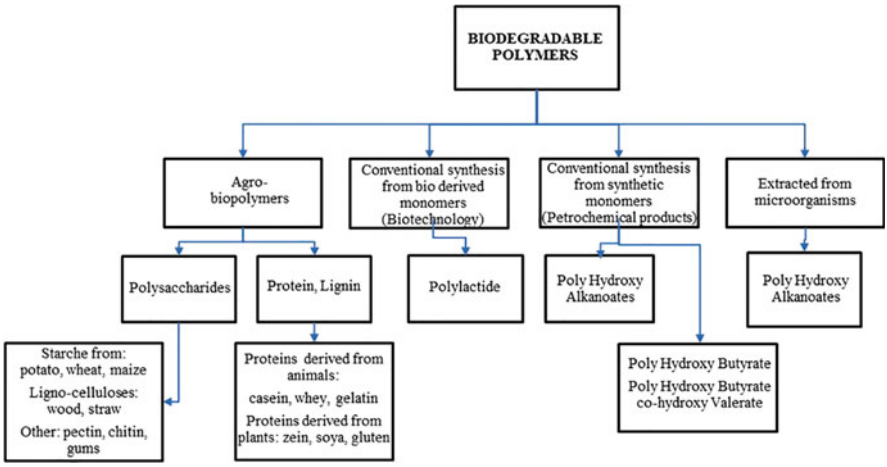

Fig. 5.2 Biodegradable polymers classification based on their origin

the raw materials, so applying available waste organic material is a good choice from the industries (Kumar et al. 2020; Mannina et al. 2019). Different carbon sources for the production of PHA are shown in Table 5.1.

5.2 Polyhydroxybutyrate (PHB)

Nowadays, bioplastics are used as eco-friendly biopolymers in industries like the food and pharmaceutical industries. They are appropriate in both mechanical and physicochemical properties, and they make no dangerous pollution upon disposal. PHAs, as microbial-produced biopolymers, can be used in food industries as packaging material (Dutt Tripathi et al. 2021). Sugar and lipid bacterial fermentation is the source of polymer production in nature. They are melted between 40 and 180 °C and are based on the used monomer in their synthesis and are thermoplastic or elastomeric materials. In addition, they can make excellent packaging films as single or in combination with other polymers (Tharanathan 2003). As the most usual type, PHB is made from a monomer of 3-hydroxybutyrate and possesses similar properties to PP. Its copolymer with polyhydroxybutyrate-valerate (PHBV) shows less stiffness and is more rigid (especially for packaging applications). This polymer leads to different behavior in aerobic conditions and anaerobic environments so that it degrades in 5-6 weeks and release CO_2 and H_2O in an aerobic environment. While in lack of oxygen, it degrades faster and produces methane. Different food waste types can be considered carbon sources to fabricate multiple PHA polymers with various physical and mechanical properties (Yu et al. 1998).

Table 5.1 Utilization route of different carbon source in microbes and PHA production

Carbon source			PHA-producing microorganism	Pathway	Culture condition	DCW (g/L)	PHA_{max} (% DCW)	References
	Carbon N	Compounds						
Sugar	C5	Xylose Arabinose	*Burkholderia sacchari* DSM 17165	Pentose phosphate pathway	Fed-batch with ternary mixture of glucose, xylose, and arabinose	146	72	
	C6	Glucose	*Pseudomonas putida* KT2440	Glycolysis pathway	Fed-batch	98	32	
		Cellulose	*Saccharophagus degradans* 2–40		Batch	1.2	12	
		Fructose	*Halomonas sp.* YLGW01		Batch	9	95	
		Mannose	*Halomonas organivorans*		Batch	4.6	83	
		Galactose	*Halomonas organivorans*		Batch	5.6	91	
C1 compound	C1	Formate	*Methylobacterium* sp.	Serine cycle	Batch	1.72	32.4	
		Methanol	*Methylobacterium* sp. MT074352.1		Batch	2	62	
		Methane	*Methylosinus trichosporium* OB3b		Batch culture with CH_4 supply	0.9	55.1	
		Carbon dioxide	*Tolypothrix distorta* TISTR8985	Calvin cycle	Phototropic culture with CO2 supply	0.09	4.4	
Polyol	C3	Glycerol	*Cupriavidus eutrophus* B- 10646	GlpK, DhaK pathway	Fed-batch	110	78	
	C2	Acetate	*Acinetobacter junii*	Acetyl-CoA pathway	Batch	2.46	72	

Short chain carbon fatty acid	C4	Butyrate	*Ralstonia eutropha* Re2133/pCB81	Crotonyl-CoA pathway	Batch	1.6	90	
Medium and long chain fatty acid	C16	Palmitic acid	*Cupriavidus necator* Re2058/ pCB113	β-oxidation pathway	Batch	9.7	74	
	C18	Stearic acid	*Pseudomonas putida* KT2440		Fed-batch	159.4	36.4	
Petroleum based	C6-C22	Alkane mixture	*Pseudomonas aeruginosa*		Batch	1.5	40.7	

5.3 Food Packaging

Food preservation in the distribution chain depends on food packaging. This polymer helps protect commodities against mechanical damages and pollution during marketing. Additionally, it helps maintain the shelf life of perishable foods. The development in active food packaging and new modified atmospheres are caused an increase in shelf life, safety, and quality of the food. In packaging technology, besides the benefits of food protection and other issues, e.g., financial, social, and environmental, it should be noticed that it is also essential (Marsh and Bugusu 2007).

The increasing drives the food packaging market in consuming of convenience foods. Packaged foods are almost half of the global sales of processed foods which is more than 1 trillion US dollars (Mahalik 2014). According to the technical requirements in the supply chain, marketing needs, and other standards, including convenience, visual appeal, features like opening easily, being portable, and single-use packaging, different types of packaging exist. In 2014, the rigid and pliable plastic packaging market was related to packaged commodities. The largest of them was food packaging. The other packaging like metal, paper, and board packaging came (Food Packaging Market 2014). In 2014, almost 60.5% of packaging was related to nonplastic productions. Based on the statistics, in 28 European Union countries, nearly 69% of the energy recovery and plastics recycling was regarding the recycling (25.8 million tons), while almost 31% still went to landfills (2015).

The purity level of polymers in food packaging applications is so important. Some impurities like proteins (c.2.0%) and lipids (c.0.5%) are made in microbial production of PHA (Juzwa and Jedliński 2006). These impurities can make a significant odor problem as packaging. So, to apply PHA in the food-packaging sector, the required treatment methods and standards should be investigated and developed (Koller et al. 2013). Using PHA in combination with other materials as a copolymer is one of the solutions to reach a material containing the favorite characteristics (Avérous and Pollet 2012) (Table 5.2).

PHA can be used in combination with other biodegradable polymers as an additive. PHA and bacterial biomass were blended with this material as a matrix in a study. Based on the results, adding PHA to Mater-Bi improves breaking point; additionally, a considerable increment was gained (Scaffaro et al. 2012).

Table 5.2 Properties of selected polyhydroxyalkanoates

Properties	PHB	PHBV (4–29% HV)	P3HB4HB	PHBHx (10% 3HHx)
Average molar mass, M_a ($\times 10$)	1–8	6	4	–
Melting temperature, T_m (°C)	175	157–102	150	127
Glass transition temperature, T_g (°C)	5–15	2–8	−7	−1
Crystallinity (%)	80	69–39	45	34
UV resistance	Good	Good	–	Good
Oxygen permeability, (mL mm m^{-2} atm^{-1})	2–10	5–14	–	–

Almost 24 companies produce PHA and its application worldwide; Metabolix is the most famous company with several prizes for having endeavor in protecting the environment. Biomer is an industrial producer of PHB in Germany which uses *Alcaligenes latus*. In cooperation with Korea and the USA, China produces PHBHx by using *Aeromonas hydrophila*. Copolymers HB and mcl HA, called Nodax, are applicable thermoformed and films. To produce P3HB4HB, recombinant *E. coli* and *Ralstonia eutropha* were used. *R. eutropha* can accumulate 80% PHBV in the cells and model the PHBV production process with high efficiency (Chen 2010).

5.4 Materials Guidelines for PHA Usage

Fortunately, PHAs as biopolymers are compostable in the industrial compost sections. To evaluate the ability of biodegradation and use as compost, standard methods have been published by International Standards Organization (ISO) and standard organizations such as (ASTM) in different conditions (Jayasekara et al. 2005). Methods, descriptions, limitations, guidelines for testing, explanation of results, and time frames are illustrated in these standard testing methods. For example, in the ASTM D 6400, the requirements are explained. Following the definitions, a compostable polymer has biodegradability.

In contrast, a biodegradable polymer degrades over a period of time and environment. It is distinct from the compostable polymer's biodegradability properties instead of compostability (Krzan et al. 2006). Based on the ASTM D 6400 standard, if the material's carbon has 90% biodegradation, it can be determined by producing CO2 in the laboratory for 180 days. It is called compostable polymer (Jyoti Sen et al. 2011).

5.5 Conclusion

Some biodegradable polymers are used in food packaging. The microbial system can convert biowaste into bioplastic. While, due to some problems in transportation, waste handling, pretreatment, and the need for unexpansive technologies for conversion compared with synthetic plastic-based on petroleum, scale-up synthesis of bioplastic is assumed a premature way to use carbon source in an extended form and accumulation of copolymers without using precursors that are costly, working on screening new strains and genetically engineered microorganisms is needed. Moreover, improving the downstream process is vital due to belonging almost 50% of the cost to it.

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Green Polymer-Based Biodegradable Packaging

6

Ruchi Sharma, Aparna Agarwal, and Rizwana

Abstract

With the decline in natural resources and increasing environmental waste concerns due to nonbiodegradable packaging materials, there is a need for novel approach of biopolymer-based packaging in order to enhance the quality as well as shelf life of food products. The biopolymer-based packaging involves active and intelligent packaging technology which helps in preventing the migration of moisture, controlling the respiration rate, retarding the oxidative damage, and enhancing the shelf life of the food products. Biopolymer-based packaging materials are considered at a wider pace as they are cheaper, biodegradable, environment-friendly and renewable. These are obtained from various sources including plant or animal protein, chitosan, cellulose, and starch. This review highlights the concept of biopolymers, its sources, characteristics, benefits, and limitations. It focuses on the types of biopolymers such as active and intelligent packaging. Also, it enlightens on bio-nanocomposites, green packaging, and application of biopolymers in other relevant areas.

Keywords

Green packaging · Biodegradable · Intelligent packaging · Food applications

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6.1 Introduction

Foods are an essential component of life and its protection play a vital role in maintaining the health of the consumers. For the protection of food products, various types of packaging materials are utilized such as glass, plastic, metal, paper, and paperboard. Along with the protection, packaging also helps the consumers in providing them beneficial information regarding the nutritional content and the way the product should be handled or stored. The use of plastics over other packaging materials increased from the long back time due to its low cost (Tang et al. 2012). Packaging is a vital component of the food sector which helps in enhancing the quality and safety of the food products. Its aim is also to provide safe, leakage proof, sound, clean, and contaminated free food products. Also worldwide, food packaging comprises of around 50% of the total other packaging sales which makes the packaging sector the heart of the food industries and led to the concentration over the importance of polymers in the food applications. Polymers play a vital role in the development of the country as from the past 50 years plastics are widely utilized in the manufacturing of packaging materials. During 2014–2015, India produced approximately 8.3 million tons of plastics and in 2018 about 99% of the plastics produced are mainly from petrochemical industries. Although these petroleum-derived plastics has been utilized in the manufacturing of packaging materials from a long back period, the production of these plastics leads to the release of various harmful gases, especially greenhouse gases which adversely affect the ecosystem and cause global warming (Yadav et al. 2018). This has led to the shift towards biopolymer-based packaging materials as it helps in providing protection, preservation, and enhancing shelf life by utilizing natural compounds. The nature-derived biopolymer also has the advantage of being biocompatible, biodegradable, flexible, barrier to gases, stable, chemical-resistant, and safe which provide the consumers an environment-friendly packaged food product (Gabor and Tita 2012).

In view of the discussed beneficial properties of biopolymer-based packaging materials over petroleum based nonbiodegradable plastics, this chapter highlights the novel approach of biopolymer based packaging materials by focusing on active and intelligent packaging for food products.

6.2 Biopolymers, Its Sources, and Characteristics

Biopolymers are derived from living matter and are present in the chain-like structure in the form of linear or branched cross-linked molecules. These usually constitute amino acid proteins, saccharides from sugars, or nucleic acid of nucleotides. These are made up of different monomers and can be considered as heteropolymers. The monomers are arranged in such a fashion to develop secondary structures and even a three-dimensional network to form tertiary structure (George et al. 2020). Biopolymers are effective substitute of harmful and nonbiodegradable conventional packaging materials. Biopolymers are considered as biodegradable, and thus it can be disposed in several ways including composting, decomposition in

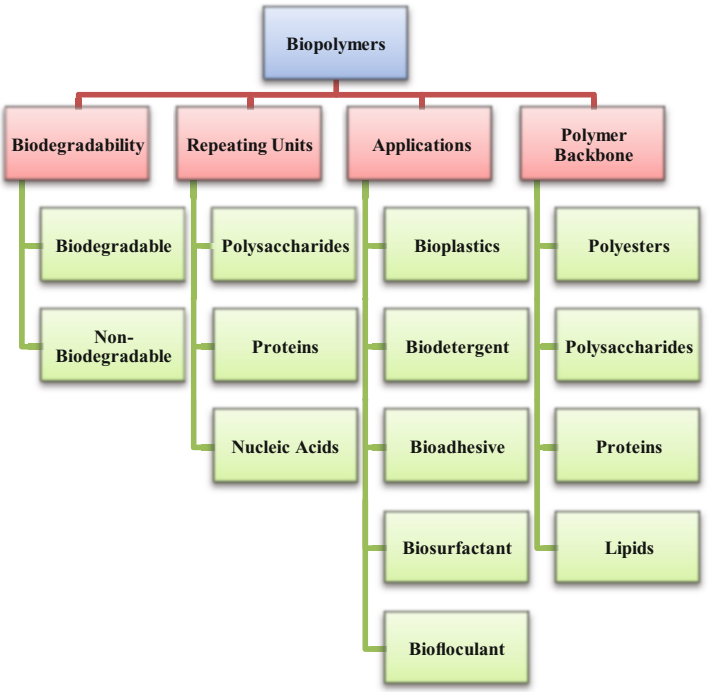

Fig. 6.1 Classification of biopolymers (Mohan et al. 2016)

soil or landfills, anaerobic digestion to produce useful byproducts, thermomechanical recycling, littering, dissolving in water, and carbon dioxide neutral incineration (Ilyas and Sapuan 2020). The main difference between the biopolymers and fossil fuels is that biopolymers are more sustainable and while degrading from bacteria they resulting in less amount of greenhouse gas emissions leading to the prevention from global warming. Biopolymers are majorly classified into four broad categories as shown in Fig. 6.1.

Firstly, they are divided on the basis of their biodegradability, i.e., biodegradable and nonbiodegradable. Also, as an alternative to biodegradability, they are classified as bio-based and non-bio-based. Secondly, they are divided on the basis of repeating units, namely, polysaccharides, proteins, and nucleic acids. Third, they are classified on the basis of application in different areas including bioplastics, biodetergent, bioadhesive, biosurfactant, and biofloculant. And last, biopolymers are categorized on the basis of polymer backbone involving polyesters, polysaccharides, polyamides, polycarbonates, and vinyl polymers (Mohan et al. 2016). Majorly three types of biopolymers for packaging materials are utilized in food applications, namely, polysaccharides, proteins, and lipids. These biopolymers provide a thin coating which is applied over the surface of the food product in order to enhance its quality as well as shelf life. Some biopolymers can also act as a carrier of colorings,

flavors, antioxidants, nutrients, and antimicrobial agents which can enhance the organoleptic characteristics as well as nutritional characteristics of the food product (Kraśniewska et al. 2020). Polysaccharide biopolymers are alginate, cellulose, carrageenan, chitin, gellan, curdlan, starch, xanthan, pectin, and pullulan, whereas protein biopolymers include gelatin, collagen, soy protein, whey protein, and zein. Furthermore, polylactic acid (PLA) and polyhydroxyalkanoates (PHAs) fall under the category of aliphatic polyesters (Gabor and Tita 2012).

Starch is considered as a hydrocolloid biopolymer which is extracted from the plants such as corn, potatoes, and rice, in small sizes. It constitutes of 70% amylopectin and 30% amylose with less than 1% lipids and proteins. It is used in the food industry as a thickening agent, gelling agent, and textural agent (Gabor and Tita 2012). It possesses benefits of having cost-effective and abundantly available biopolymer used in the manufacturing of sustainable packaging material (Mangaraj et al. 2019). Starch, when converted into foam through water steam, can also be used to replace the polystyrene foam in the packaging material (Siracusa et al. 2008).

Cellulose is an abundant amphiphilic biopolymer present in the nature. Nowadays, it is widely obtained from the green algae as well as from brown algae (Gabor and Tita 2012). It is a linear polymer containing macromolecular chains of cellobiose. Furthermore, it is crystalline and insoluble which makes it feasible to be converted into processable form (Vroman and Tighzert 2009).

Chitin is a biodegradable, nontoxic, biocompatible, and most abundant biopolymer present in nature after cellulose. It is available in the crystalline form and make up the structure of the cell walls of yeast and fungi (Malathi et al. 2014). Upon the deacetylation of chitin, a copolymer chitosan is produced which has antimicrobial and antibacterial properties and utilized in the form of coatings on various fruits and vegetables including peppers, strawberries and cucumbers (Wróblewska-Krepsztul et al. 2018).

Polyhydroxyalkanoates (PHAs) is a nontoxic polyester of hydroxyalkanoates which is obtained through microbial fermentation. It possesses low melting point, biocompatibility with UV light, better physical property, and better chemical property but lower mechanical property (Zhong et al. 2020). These biopolymers give excellent packaging films alone or in combination with synthetic packaging materials. On such type of PHAs is polyhydroxybutyrate (PHB), which provides similar functional properties to that of polypropylene, but it is more stiff and brittle in nature (Siracusa et al. 2008).

Polylactic acid (PLA) is a hydrophobic polymer which is usually produced from polycondensation of D- or L-lactic acid or through the ring opening polymerization of lactide (Vroman and Tighzert 2009). With the increased utilization, it has limitations of being less thermally stable and brittle in nature. This limitation can be overcome by plasticizing of polylactic acid which thus improves the crystallization (Pawar and Purwar 2013).

Plants extracts can also be utilized in enhancing the functionality of biopolymer-based packaging materials. Plant extracts consists of various functional and bioactive properties which help in improving the physicochemical properties of the packaging materials. One study revealed that the addition of star anise, cinnamon,

Table 6.1 Properties of biopolymers with their roles/applications (Mangaraj et al. 2019)

S. no.	Properties of biopolymers	Roles/applications
1.	Density	If density is high, it results in high transportation cost and thereby alters the mechanical properties
2.	Gas barrier property	Packaging materials should have the excellent barrier properties against gases in order to prevent the fruits and vegetables which are oxidative in nature from degradation
3.	Glass transition temperature	The biopolymers should have high glass transition temperature for the foods stored at lower temperatures and should have high melting point for the foods stored at high temperature
4.	Mechanical properties	For the ease of handing and transportation with no damage to the products, the biopolymers should have excellent mechanical properties such as strength, toughness, and viscoelasticity
5.	Biodegradability	The biopolymers should be biodegradable in order to provide eco-friendly and sustainable environment

and clove extracts increased the tensile strength and reduced the water vapor permeability of the partially hydrolyzed gelatin film (Wang et al. 2012; Hoque et al. 2011). There are various other properties of biopolymers which have specific roles and applications as described in Table 6.1 (Mangaraj et al. 2019).

6.3 Bio-nanocomposites

Although biopolymer-based packaging materials possess various functional and environmental benefits, but they also constitute many limitations. The biopolymer-based packaging materials have poor thermal, barrier, and mechanical characteristics when compared with the petroleum-derived plastic packaging materials. In order to combat these drawbacks, nanocomposites can be utilized which can improve the mechanical and barrier properties of the biopolymer-based packaging materials (Othman 2014). Bio-nanocomposites are a rising approach towards the development of packaging materials as they are well equipped with improved thermal, rheological, barrier, as well as mechanical properties. These properties are because of their high aspect ratio and greater surface area of the nanoparticulates (Rhim et al. 2013).

Nanotechnology is an important element in enhancing the functionality of packaging material. This technology involves the characterization and preparation of structures having 1–100 nm length. The nanomaterials are broadly classified into three categories, namely, platelets, particulates, and fibers. The nanocomposites due to their nano-size exhibit large surface-to-volume ratio and possess good mechanical, electrical, and thermal properties (Youssef and El-Sayed 2018). For the production of bio-nanocomposites, four different types of nanofillers are utilized, namely, carbon nanotubes, cellulose nanofillers, functional nanofillers, and nanoclays. Carbon nanotubes is a segment of carbon nanostructures which also involve other structures including carbon nanofibers, fullerene, grapheme nanosheets, and carbon nanoparticles, whereas cellulose is the cheaper, renewable, and nonbiodegradable

material which is utilized as a nanofillers in the production of bio-nanocomposites. Furthermore, for the preparation of clay-based nanocomposites, nanoclays, also referred as layered silicates are utilized, especially phyllosillicates. Also, functional nanofillers including hydroxyapatite, cellulose nanofibers, and silica nanoparticles are used in biomedical as well as biotechnological applications (Reddy et al. 2013). The major bio-nanocomposites utilized for packaging materials include polyhydroxybutyrate, polylactic acid, starch, aliphatic polyester, and poly(butylene succinate) (Sorrentino et al. 2007). Among the various natural polymers utilized, chitosan is one of the widely utilized biopolymer which has applications in food packaging material, artificial skin, and water engineering. Chitosan is widely used due to its functional properties including biodegradability, solubility, mechanical properties, functional groups, and biocompatibility. In order to enhance the functionality of chitosan, it is combined with the nanoparticles such as titanium dioxide. The bio-nanocomposites involving chitosan, titanium dioxide, and polyvinyl alcohol can be used as a packaging material for soft white cheese in order to enhance its antimicrobial activity and sustainability (Youssef et al. 2015).

Bio-nanocomposites have good mechanical, barrier, gas, and antimicrobial properties towards the moisture, oxygen, and flavors in order to protect the food materials and maintain its storage life. To highly preserve the food materials, maintaining its quality, safety, and freshness along with preventing the food from the attack of microorganisms, antimicrobial bio-nanocomposite packaging is the major approach. Also, antimicrobial packaging is a form of active packaging which helps in extending the shelf life of the stored and packaged food products. Various types of antimicrobial bio-nanocomposites are utilized in the food packaging depending on the type of filler incorporated (Sharma et al. 2020).

6.4 Active Packaging

Active packaging is a type of packaging in which there is a linkage between the product, environment, and the packaging material. This type of packing helps in enhancing the shelf life of the food product by maintaining its nutritional and functional properties. Active packaging also involves another class of packaging, i.e., antimicrobial packaging which further ensures the protection of the food products from invading microorganisms (Miteluț et al. 2015). The use of synthetic petroleum-based packaging materials which are nonbiodegradable leads to the environmental degradation. Thus, in order to mitigate this problem, active packaging based on the biopolymers derived from renewable sources including agro-industrial waste is an emerging trend. This can be achieved by extraction and isolation of nanoparticles from the renewable sources and further incorporating in the active packaging. Cellulose nanoparticles are widely used due to its nontoxic nature, lower thermal expansion, and greater binding properties with other binding agents such as chitosan.

In biopolymer-based active packaging, antimicrobial and antioxidant agents are widely incorporated to enhance the functionality of food products along with

refining the film properties with antimicrobial and antioxidant characteristics. One such antimicrobial and antioxidant agents are zinc oxide and curcumin, respectively. The combined addition of zinc oxide and curcumin increases the film properties against UV light, water, and gases. Also they help in providing the antibacterial activities against pathogenic microorganisms and thus ensuring the safety and improving the storage stability of packaged food products (Roy and Rhim 2020). Another antimicrobial and antioxidant agent is anthocyanin which can be incorporated inside the biopolymer-based active packaging films in the form of anthocyanin extract and thus act as a reducing agent and extend the shelf life of the packaged food product (Yong and Liu 2020). Furthermore, antioxidant active packaging can be employed in the meat products to prevent lipid oxidation. Lipid oxidation can cause off-odor, off-color, and undesirable textural changes as myoglobin oxidize and changes the color of the meat products and ultimately affect the purchase decision of consumers. Thus, it is essential to incorporate the antioxidant agents, especially natural antioxidants inside the packaging material help to interact with the headspace and meat product resulting in the prevention of lipid oxidation. Also, the antioxidant active packaging functions in two ways, first to use the emitters which can release the antioxidants inside the food and packaging material, and second is to absorb the undesirable components such as oxygen from the food or packaging material (Domínguez et al. 2018).

6.5 Intelligent Packaging

Intelligent packaging is also another type of essential packaging which helps in monitoring the packaging food in terms of its storage conditions along with informing the quality and safety of the packaged food product to the consumers. This packaging involves the utilization of labels inserted inside the packaging material or displayed over the packaging material in the form of label (Yong and Liu 2020). Furthermore, intelligent packaging systems are categorized into three broad groups including sensors, radio frequency identification system, and indicators. Among these, sensors are more widely used that can also help in determining the quality and history of the food product in terms of the variation in the color of the food product. The sensors developed from biopolymers are sodium alginate, sodium caseinate, and carrageenan ultraviolet light-activated intelligent packaging system. Among these, carrageenan sensor is the most effective as an oxygen leak indicator in food packaging applications with decrease migration into food products and higher tensile strength (Deshwal et al. 2018).

Various chemical sensors are utilized in the food packaging which are categorized under active and passive sensors depending upon the external power required or not for the detection. Biosensors are one such sensors that fall under chemical sensors, but their biological components are different from chemical sensors. Biosensors basically utilized the isolated and purified cells, antibodies, fungi, plant cells, animal cells, enzymes, and bacteria in the form of detectors (Nemes et al. 2020). Nowadays, there is an emerging need for the utilization of

natural pigments such as betalains, anthocyanin, and curcumin as a natural antioxidants that can be combined with the starch-based films to enhance the antimicrobial as well as antioxidant properties of the meat, milk, and seafood. It thus acts as an intelligent packaging system which detects and retains the freshness of the food products (Qin et al. 2020). Furthermore, intelligent packaging films are also produced by combining the biopolymers with various extracts of fruits and vegetables including berries, dark purple and black vegetables, sweet potato, and red cabbage (Wu et al. 2021).

However with the utilization of biopolymer-based intelligent packaging systems, it possesses various benefits and limitations in the food products. The major advantage is that the pigments containing intelligent films are temperature, pH, light, and ammonia-sensitive which helps in monitoring the deterioration of the food products. Also, the pigment-based intelligent system is cost-effective with improved sensing abilities and are safe as well as nontoxic for the food packaging systems. In addition to this, it has some limitations such as the pigment-based intelligent system is not feasible for a longer duration and also are more prone to thermal degradation (Bhargava et al. 2020).

6.6 Green Packaging and Its Characteristics

Nowadays there is an emerging concern regarding the environmental disruption by using plastic materials. Green packaging materials serves as an alternative towards the non-biodegradable materials so as to reduce the environmental pollution to a wider extent. Green materials help in replacing the petroleum derived plastics and also reduce the dependency on fossil fuels. These materials are produced from non-toxic components and are widely distributed in the nature such as chitin and cellulose (Darder et al. 2007). The green packaging is 100% biodegradable as compared to petroleum-based plastic packaging materials. It can be degraded from microorganisms or marine water through aerobic or anaerobic fermentation as illustrated in Fig. 6.2 (Moustafa et al. 2019). There are three major tests which can be employed for detection of biodegradability of the polymer, namely, laboratory tests, field tests, and simulation tests. Laboratory tests include clear zone test, enzyme test, and Sturm test. Field tests carried out in nature, water, soil, and landfill, whereas simulation tests involve laboratory reactor, landfill, water and soil. Laboratory and simulation tests are conducted in synthetic and complex environment, respectively, with defined conditions. On the other hand, field tests are conducted in complex environment with variable conditions (Mangaraj et al. 2019).

Green packaging is also referred to as an ecological packaging which is reusable, recyclable, and harmless to the humans, environment, as well as livestock. It is purely obtained from natural plants and provides a sustainable development to the packaged product throughout its life cycle. The main aim of green packaging is divided into four R and one D, namely, reduce, reuse, recyclable, reclaim, and degradation (Zhang and Zhao 2012).

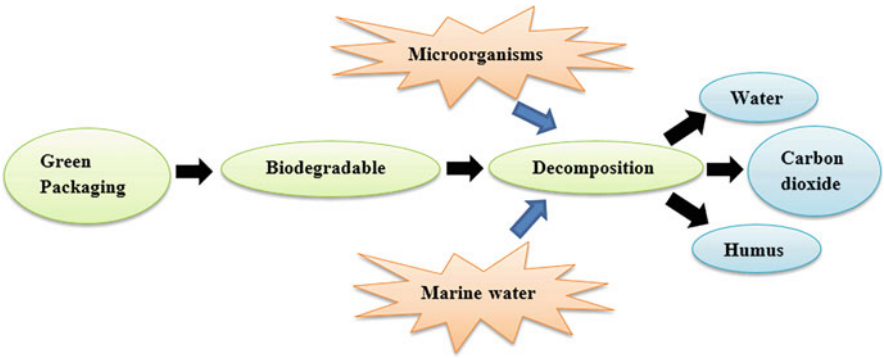

Fig. 6.2 Decomposition of green packaging (Moustafa et al. 2019)

For a packaging to be considered under green packaging category, it should possess certain characteristics including strength, barrier properties against light, heat, moisture, printing capabilities, and other chemical resistance which can accomplish the goal of food safety among the finished products. One such packaging material consists of poly (lactide), i.e., PLA which has the capability of barrier properties, recyclable properties, easily composting benefits, and natural resemblance (Ahmed and Varshney 2011). However, the higher cost utilized during the production of PLA creates a limitation towards its usage. However, cost-effective raw materials including agricultural waste helps in mitigating the higher cost barrier in the usage of PLA as a packaging material. Furthermore, polyhydroxyalkanoates (PHAs) have improved oxygen barrier and mechanical properties as compared to poly (lactide), but possess one limitation of being costly. Thus, reduction in the cost of producing PHAs generates a sustainable and effective green packaging with improved characteristics as compared from non-sustainable polypropylene packaging (Rabnawaz et al. 2017).

6.7 Application of Biopolymers in Other Areas

There are various applications of biopolymers in several fields including 3D printing technology, textiles, and other relevant areas. 3D printing is an emerging technology which is also referred as additive manufacturing to create three-dimensional materials through layer by layer placing of materials over each other such as plastics, metal, cells, and ceramics. This technology is widely utilized in various sectors such as food industry, textiles, healthcare, aeronautics, and architecture. However, there are many limitations while adopting this technology including sustainability, environment friendly, cost-effective, bio-based materials, and printer-friendly (Liu et al. 2019). Biopolymers derived from wood including cellulose, lignin, and hemicellulose are also utilized in 3D printing technology. These biopolymers derived from wood are bio-inert as well as possess biocompatibility with the environment. Thus,

wood derived biopolymers can be utilized in formation of bio-inks through tissue engineering technology (Xu et al. 2018).

Textiles is another area which is gaining a lot of attention in various industries including medicine, textile, and pharmaceutical. Due to the increased demand of textiles, various chemicals are added during production to provide antimicrobial characteristics to the textile materials. However, the chemicals utilized such as antibiotics, phenols, synthetic dyes, and inorganic salts possess harmful and toxic effects on the human health. Also, chemically manufactured textile materials are not environment friendly and non-sustainable. Thus, this creates the opportunity for the development of eco-friendly and bio-based textile materials (Shahid and Mohammad 2013).

There are different types of biopolymers which possess applications in different areas. Polyhydroxyalkanoates (PHAs) are widely utilized in the manufacturing of biomedical instruments, disposable films, and gloves. Poly-(ether ester) is employed in the medical areas for slow tissue healing procedure. Poly-(hydroxy acid) find their application in the development of food packaging materials, containers, floor mats, medical surgery devices, pharmaceutical products, and cutlery items. Poly-(alkylene dicarboxylate) is used in the manufacturing of food packaging materials, containers, bottles, pharmaceuticals, disposable sheets, and plastic bags. Polyamides such as nylon is used in the manufacturing of plastic materials and textile materials. Furthermore, vinyl polymers are used in paper manufacturing, textile industries, and manufacturing of packaging bags. Polyurethanes finds the application in the biomedical areas, foaming materials, and shock absorbing materials (George et al. 2020).

6.8 Conclusion

Biopolymers have unique opportunity to provide a greener and sustainable environment which does not only possess harm to environment, humans, and livestock but also creates a novel opportunity for a safer future. The biopolymers can be utilized in food packaging materials in the form of active as well as intelligent packaging. However, with the increased benefits of biopolymers in the packaging industry, there is one limitation, i.e., cost which needs to be considered while moving further towards the improvement and inclusion of biopolymers in the packaging as well as other areas. Furthermore, with the cost-effectiveness, future studies should also focus upon utilizing the evolving technology to create and add value to the food packaging materials by using smart sensors and nanomaterials and utilizing the bio-waste in the development of packaging materials.

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Role of Agro-Wastes in Economical Food Packaging Material Synthesis

7

Prabal Pratap Singh, Sukh Veer Singh, and Sadhan Jyoti Dutta

Abstract

Synthetic thermoplastic is one of the major concerns, which triggers plastic garbage as municipal waste globally. Government has mandated for ban of plastics meets the rising demand of biodegradable packaging materials synthesis from agricultural and processing wastage. The aim of chapter is to highlight the agro and processing waste (several parts of plants, by-product of cereals, fruit and vegetables, meat, and poultry)-derived biopolymers which are the most economical and eco-friendly biomaterial over petrochemical synthesis. These by-products are major source of lignocellulose, pectin, gelatine, etc. Moreover, gelatine is produced from meat or by-products of fish and poultry. Various biomaterials have been broadly incorporated into film and food grade packaging applications. Thus, agro-waste-based biomaterials may be sustainable approach to replace nonbiodegradable packaging. This review mainly concentrates on global scenario of agro-waste, classification of agro-waste, agro-waste utilization, synthesis of polymers, and its brief packaging application.

Keywords

Agro-waste · Biodegradable · Eco-friendly · Food packaging

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7.1 Basics on Agricultural Waste

India's economy depends on the agriculture sector. The second largest agro-based economy of our country is generated by crop cultivation throughout the year (Bhuvaneshwari et al. 2019). Agricultural crop residues get wasted in large amount. They are nonconsumable commodities which produce from postharvest processing. The conversion of agricultural wastage into commercial value which can be benefited to farmers. Its easy availability meets less cost of collection and transportation (Obi et al. 2016). "Waste created from diverse agricultural activities" is what agro-waste is defined as. Manures, seed bedding, leaves, plant stalks, hulls, and vegetable matter are all frequent agro-wastes in agricultural cultivation. The decomposition of plants part triggers organic matter in soil (Galí et al. 2009). Nowadays, biofuels and biogas are rising demand due to environmental and health issues. Hence, they can be alternative sources of energy for mitigating the concerns. Despite this, agro-waste includes animal waste (manure, animal carcasses), food processing waste, crops waste, and hazardous and toxic agricultural waste. In the case of food processing waste, only 20% of maize is canned, while the other 80% is thrown away. Crop waste includes corn stalks, fruit and vegetable drops and culls, sugarcane bagasse, and pruning's, among other things. In contrast, pesticides, herbicides, and insecticides refer to hazardous and toxic agricultural waste (Obi et al. 2016).

7.2 Global Scenario of Agro-Waste

Agamuthu (2009) reported that approximate 998 million tonnes (MT) of agricultural waste are found annually. The issue of agro-waste losses has the potential to be a significant source of social benefit. It may be used to fight hunger, increase income, and improve food security in impoverished areas all over the world. Food losses, understandably, have an impact on impoverished people's food security, as well as food quality, safety, the environment, and economic growth. The food losses are affected by several factors which vary throughout the world. "Assessment of Quantitative Harvest and Post-Harvest Losses of Major Crops and Commodities in India" carried out by the Central Institute of Post-Harvest Engineering and Technology (CIPHET) is shown in Table 7.1. Consequently, crop production decisions and patterns, internal infrastructure and capacity, consumer purchase and food usage habits, and marketing chains and distribution network all impact food losses. All of these factors are very reliant on the country's particular characteristics and location. Thus, "agro waste and food waste" refers to losses in agricultural techniques and the food chain (from farm to kitchen), as well as retailer and customer behavior (Parfitt et al. 2010).

Table 7.1 Food commodity production and their postharvest loss

S. N.	Food commodities	Production (million tonne)	Losses (%)	References
1	Cereals	135	4.65–5.99	Jha et al. (2015)
2	Pulses	23.22	6.36–8.41	
3	Oil seeds	59.56	3.08–9.96	
4	Fruits	90.2	4.58–15.88	
5	Vegetables	169.1	4.58–15.88	
6	Milk	187.7	0.92	Basic Animal Husbandry Statistics, DAHD & F, GoI (2018–2019)
7	Meat	8.11	2.71	Jha et al. (2015)
8	Poultry egg	103.32 billion	6.74	

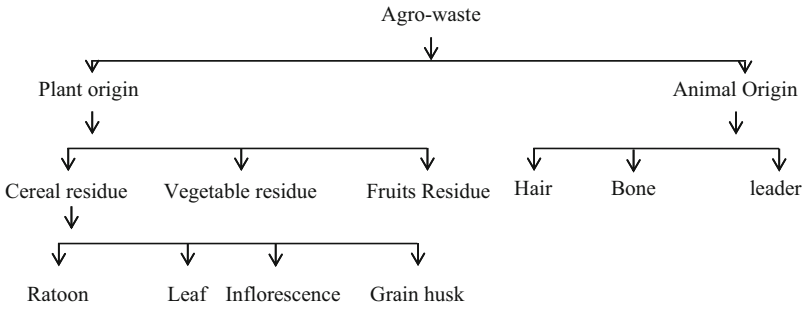

Fig. 7.1 Classification of agro-waste on the basis of origin

7.3 Classification of Agro-Waste for Packaging Material

Agro-waste can be exploited for the synthesis of packaging material. Agro-waste attracts the attention of researchers due to its biocompatibility. Biocompatibility refers to biodegradability, ecofriendly, and hazard free substrates. Agro-waste material is classified into different categories such as crop and animal (Fig. 7.1) waste residues, sugar, starch, and confectionary industry by-products, oil industry by-products, fruits and vegetables by-products, grain and legumes by-products, milk and milk by products, and meat and meat by-products, as well as distilleries and breweries also contribute in by products. Industrial wastes and its by-products are geographically observed. They contain low nutritive quality over large volume (Ajila et al. 2012).

7.4 Utilization of Cereal and Sugarcane Bagasse for Biodegradable Packaging Material

Biodegradable food packaging is easily decomposed under specific environmental condition (Avella et al. 2005). The various parts, namely, stem, leaf, seed, fruit, stalk, and grass/reed, of several plants are major source of lignocellulosic agro-waste. The rice straw, wheat straw, rice husk, corn cobs, corn husk, and buckwheat hulls are good source of lignocellulose, obtained from cereal crops. Some other plants and their parts such as palm, canola oilseed cake, groundnut shells, sugarcane bagasse, cassava bagasse, coconut coir, bamboo, hemp, pineapple crown, tobacco waste, and cork are also source of this cellulosic compound (Saba et al. 2016). The following are the utilization of cereal processing-based waste for the synthesis of packaging material.

7.4.1 Rice Straw and Rice Husk

Rice straw is composed of biomolecules such as cellulose (25.4–35.5%), hemicellulose (32.3–37.1%), and lignin (6.4–10.4%) which provide the characteristics like wood (Adwitiya and Venkatahalapathy 2015). Several researchers have exploited rice straw cellulose and reported that it produces packaging films, materials, and bioplastics because of its thermoplastic properties (Su et al. 2018). Rice straw-based cellulosic bioplastic with chitosan ratio variation (4:10) was found to be high water absorption capacity facilitates easy degradability (Pratiwi et al. 2017). Nanofibrillated cellulose and cellulose nanocrystals (CNCs) derived from agro-waste have recently been regarded as globally sustainable packaging materials. Rice straw CNCs have also been effectively blended with biopolymers (poly lactic acid (PLA) and poly vinyl alcohol (PVOH) as reinforcing fillers. It has been discovered that developing bio-nanocomposite with higher tensile strength, thermal, and morphological qualities is a green option (Chin et al. 2017; Perumal et al. 2018; Zhu et al. 2019). Rice husk is used for the synthesis for nanofibrillated cellulose (NFC) which used as coating on paper. It is also used for synthesis of PLA and its nanocomposite, NFC nanocomposite, and starch CNC bioplastic. PLA nanocomposite and starch CNC bioplastic films and the resistance properties against water and moister, respectively, are presented in Fig. 7.2.

Furthermore, rice husk (RH) is a rice by-product. It's made by covering rice grains with a thin, light-colored coating during processing. To preserve the seed, it is composed up of silica and lignin. Rice straw has similar bulk recovery characteristics, such as low bulk density (90–150 kg m^3), abrasiveness, toughness, and weathering resistance. Its one-of-a-kind composition has made it suitable for a wide range of packaging applications (Arjmandi et al. 2015). Rice husk cellulose nanocrystals are used to strengthen starch films. When cellulose nanocrystals were plasticized in starch-based bio-composites, these films displayed better reinforcing efficiency (6% filler loading) than any other filler (Johar and Ahmad 2012).

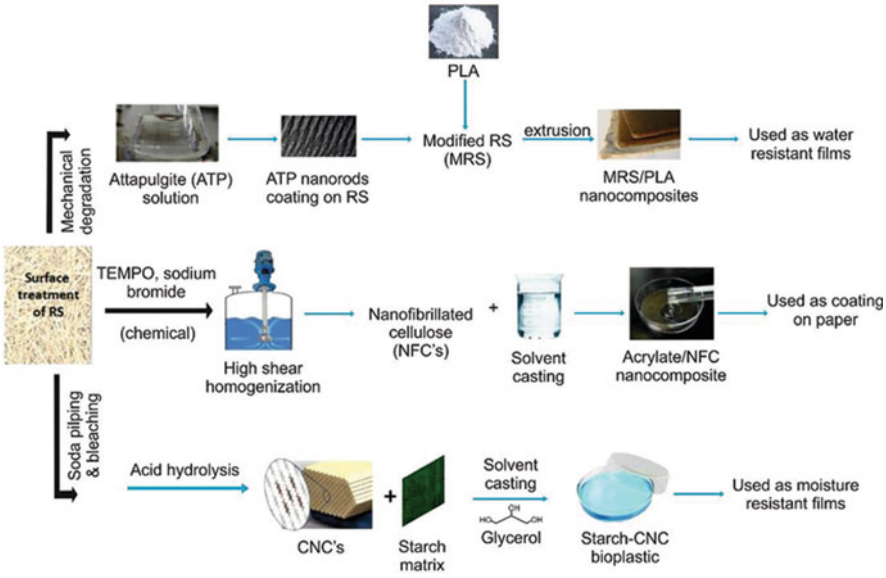

Fig. 7.2 Schematic of bioplastics and its composite synthesis from rice straw. (Adopted from Bhardwaj et al. (2020))

7.4.2 Wheat Straw

Wheat straw (WS) is a common by-product of agriculture. It's made from several components of the wheat plant. It is collected and discovered on a vast basis all over the planet. Over 1.3 kg of wheat grain recovery, approximately 1 kg of straw is generated (Khan and Mubeen 2012). This by-product (cellulose and hemicellulose) might be used in the packaging sector as a low-cost substrate. Wheat straw hemicellulose has shown to be an outstanding bio-based packaging material. This sort of packaging can be used as an edible inner package for low-moisture foods. It's also employed as the inner layer of a multilayer film, which is shielded from moisture by hydrophobic outer layers (Didone et al. 2017; Gençer and Eroğlu 2017). Wheat straw fibers have also been utilized to tune the water vapour transfer rate (WVTR) of the composite from 11 to 110 g m^{-2} day^{-1} when mixed with poly (3-hydroxybutyrate co-3-hydroxyvalerate) (PHBV) as the matrix (Berthet et al. 2015). This will likely broaden the use of PHBV-wheat straw fibre composites as food packaging materials for respiring horticulture items (Fig. 7.3).

7.4.3 Barley Straw and Barley Husk

The fourth most important grain crop is barley. It has 50 million hectares of cultivated land and produces 150 million tons of grain worldwide. The husk of barley is a by-product of the milling and brewing industries. It's a type of animal

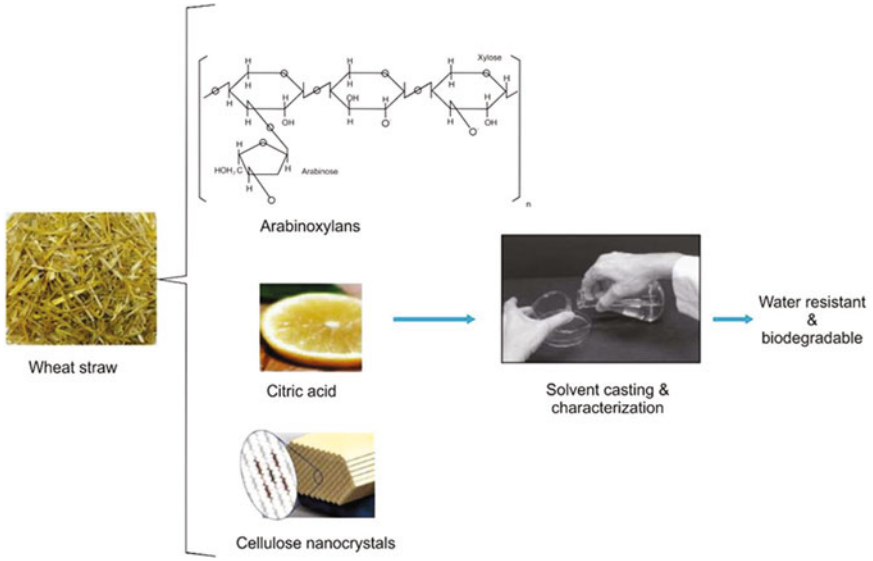

Fig. 7.3 Schematic of the process of making water-resistant and biodegradable films. (Adopted from Bhardwaj et al. (2020))

feed. Furthermore, cellulose from barley straw and husk is utilized to make packaging films in large quantities (Deshwal et al. 2021). Barley husk makes up 20% of the entire quantity of barley. It's a by-product of brewing and milling as well. This by product is composed of cellulose (30–35%), hemicelluloses (30–33%), and lignin (17–25%). The packaging materials with the high tensile strength and bending properties consist of these biomolecules and attribute suitability for packaging application. Moreover, it has a natural crystalline wax coating. This wax may be isolated and studied, and it has a variety of uses in the packaging industry as barrier and protective coatings. Börjesson et al. (2018) have reported that alkaline and acidic methods were used to extract cellulose (nanocellulose) and hemicellulose (arabinoxylan) fractions from dried barley husk in sufficient amounts to turn them into novel bio-based products. The CNCs of barley husk and straw have been effectively employed as fillers in polyvinyl alcohol (PVA) chitosan (CH)-based nanocomposite films with improved functions, according to Buono and Torre (2016). Strong electrostatic interactions and extensive hydrogen bonding between hydroxyl groups and anionic sulfate/amine groups of CNC of the PVA/CH polymeric mix have been ascribed to the excellent compatibility between CNC and nanocomposite films. The approach for production of PVA-CH nanocomposite films is summarized in Fig. 7.4.

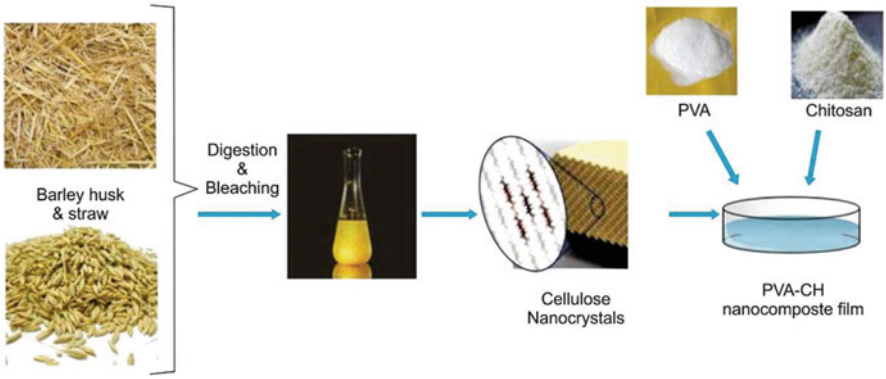

Fig. 7.4 Synthesis of PVA/CH nanocomposite film from barley by-product films. (Adopted from Bhardwaj et al. (2020))

7.4.4 Maize (Corn Cob and Corn Husk)

Maize (*Zea mays*), sometimes known as corn, has a global production of over 800 million tons per year in recent years (Nafziger 2010). It is a tropical grass with a large potential for maize production over the world. The grains are eaten or used to make various corn products, and they aid in the creation of corncobs (CC) and also corn husk (CH). CC amounts to about nine million metric tons annually in terms of agricultural wastes, which is 20% of the corn residue and 7% of the plant weight. The constituents of maize include 45% cellulose, 35% hemicellulose, and 15% lignin. Another major waste in the corn industry is the corn husk which is of economic significance. Maize cob is yet another major waste which is utilized as natural filler to produce bio-composites. There has also been rise in interest for chitosan (CS)-based materials to produce CC-based bio-composite films (Bhardwaj et al. 2020). There has also been the incorporation of glycerol to CC CNC-based chitosan films. These shows excellent results in developing biodegradable composites whose tensile strength value is 11.43 MPa as against 4.08 MPa in case of the control sample (de Andrade et al. 2019) shown in Fig. 7.4. Despite these advantages, there have been limitations in the applications of these films. The main reason was found to be their hydrophilic nature. Studies have been done to lower their hygroscopicity by adding nonpolar groups to the surface of cellulose nanofibers (CNFs) by silation, esterification, grafting, and other methods. In one study, esterification by ball milling was used to prepare esterified CNF. This resulted in the development of nanopaper with hydrophobicity (Kang et al. 2017) (Fig. 7.5).

Corn husk fiber is another waste leftover with a high cellulose concentration (31–39%), low lignin level (2–14%), and 4–5% ash content. They are thrown away and never used. As a result, they're used to wrap maize paste and unrefined sugar blocks. Nevertheless, they do not protect against moisture, oxygen, odor, or microorganisms and hence not acceptable for long term storage.

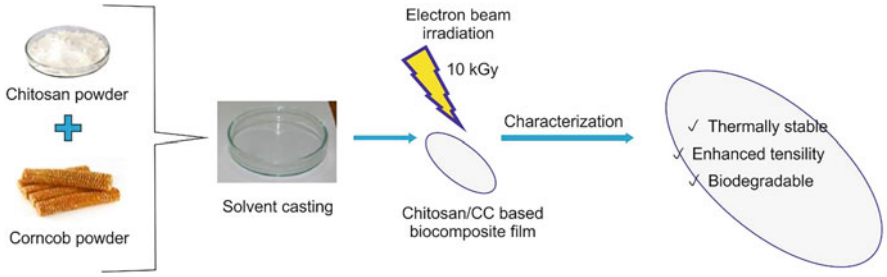

Fig. 7.5 Schematic of CS/CC bio-composite film for its characterization

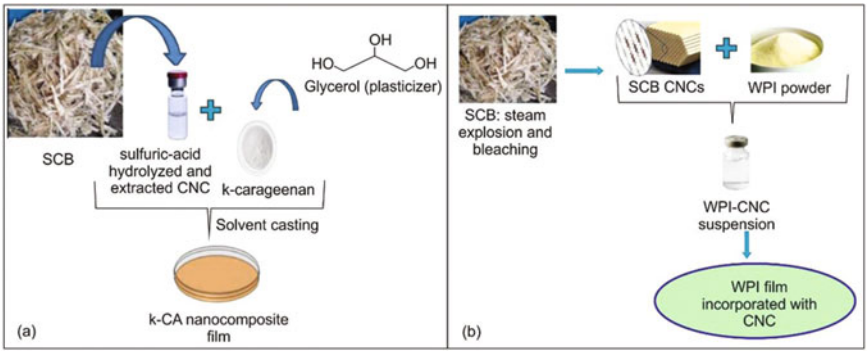

Fig. 7.6 (**a** and **b**) Schematic of process of making SCB-k-CA nanocomposite and WPI-CNC nanocomposite (Kassab et al. 2019, Sukyai et al. 2018)

7.4.5 Sugarcane Bagasse

Sugarcane bagasse (SCB) is a waste that is both renewable and biodegradable. It's a prominent sugarcane industry fibrous by-product. It's made after the sugar and jaggery juices are extracted. Sugarcane bagasse is generated in 300 million tons worldwide, with roughly ten million tons produced as agro-waste in India alone. Two tons of bagasse generate one ton of refined sugar, according to estimates. It accounts for a significant component of the waste residues (bagasse). As a result, additional care is required when it comes to their disposal or valuation. On a dry weight basis, bagasse comprises 45.3% α-cellulose, 52.42% cellulose, 21.69% lignin, 73.92% holocellulose, and 2.73% ash extractable (Pandey et al. 2000). Ghaderi et al. (2014); Samarasekara et al. (2015); and Vanitjinda et al. (2019) have reported and also been investigated extensively over the last decade that SCB cellulose and hemicellulose has the film-forming ability and potential as packaging synthesis (K-CA nanocomposite film and whey protein isolate (WPI)-CNC-based film), presented in Fig. 7.6a, b.

7.5 Utilization of Fruit and Vegetable Processing Waste for Biodegradable Food Packaging

Fruit and vegetable by-products as roots and tubers are produced around 40–50% of the total wastage. Among the by-products, fruits and vegetables peels, seed, shells pulp, skin, or pomace residue are amounted to 10–35% of raw mass (de Andrade et al. 2019). The huge amount of byproducts of fruit and vegetable are obtained from processing industry (Pfaltzgraff et al. 2013; Schieber 2017). They have large amount of bioactive compounds such as polyphenols, pigments, essential oils, enzymes, dietary fibers, and flavor compounds (Trigo et al. 2019). Pectin is a dimethyl ester of d-galacturonic acid that is abundantly found in plant cell walls. Pectin is divided into two categories based on the degree of methylation (DM): low methoxylpectins (DM $<$ 50%) and high methoxylpectins (DM $>$ 50%) (Frone et al. 2013). Pectin is extracted by innovative method from waste biomass. It is mainly found in peels of orange, banana, mango, pomegranate, lime, and seed. The effective extraction of this bio-based substance from waste biomass might be used to use it in food packaging applications. Efficient extraction might provide a solution to the major environmental issues associated with the food industry's disposal of wastes and by-products (Mellinas et al. 2020). In order to get the best gelling qualities, commercial finished pectin products frequently require a high GalA concentration (65%) and a certain degree of methylation (DM) (>55% for high methylation pectins and <55% for low methylation pectins). Food processing by-products such as citrus peels, apple pomace, and sugar beet pulp have historically been used to make commercial pectin (Putnik et al. 2017). Vartiainen et al. (2010) reported the process of making pectin-based films using a nanocellulose dispersion that is gently added to the pectin solution. Ultrasound equipment is used to sonicate nanocellulose dispersion.

Furthermore, pectin qualities are primarily determined by structure, especially degree of esterification (DE), film formation, gelling, and emulsifying capabilities (Mellinas et al. 2020). Pectin's uses include packaging, coatings on fresh and cut fruits and vegetables, and microencapsulating agents, in addition to food processing (Table 7.2). Pectin is water soluble but insoluble in organic solvents. Additionally, when dried pectin is combined with water, it hydrates quickly and forms clumps (Raj 2012).

7.6 Utilization of Dairy Processing Waste for Biodegradable Food Packaging

Cheese, casein, coprecipitate, and other traditional Indian dairy products such as paneer, chhana, and chakka are all made from whey. It's a translucent green liquid by-product of the dairy industry. In 2008, the production of whey amounted to approximately 186 million tons. Out of this, the European Union and the United States alone provided 70% of the total. They are extremely dangerous due to their extremely high biochemical oxygen demand (BOD) of 40,000 mg/kg. Because they include a substantial quantity of organic materials such as lactose, protein, minerals,

Table 7.2 Pectin-based materials used in food packaging applications

Type	Polymer matrix	Additive	Application	References
Film	LMP-bitter vetch protein	Transglutaminase	Drug delivery system	Porta et al. (2016)
Film	LMP	Ascorbic acid	AO system	Chiarappa et al. (2018)
Film	HMP	Clove EO	AM system	Nisar et al. (2018)
Film	HMP	Marjoram EO	AO system	Almasi et al. (2020)
Film	HMP-gluconaman	Tea extract	AO/AM system	Lei et al. (2019)
Film	Pectin-pullulan	AgNPs	AM system	Lee et al. (2019)
Film	HM-apple pectin	Chia seed hydrocolloid	AO system	da Silva et al. (2018)
Film	Chitosan-starch-pectin	Mint and rosemary oils Nisin	AO/AM system	Akhter et al. (2019)
Film	Fish gelatine-HMP	Hydroxytyrosol, dihydroxyphenylglycol	Preservation of beef meat	Bermúdez-Oria et al. (2019)
Film	HMP	Red cabbage extract	pH indicator	Dudnyk et al. (2018)
Film	Chitosan-HMP	Anthocyanin	pH indicator	Maciel et al. (2015)
Nanocomposite	Pectin	AgNPs, laponite	Coating polypropylene to improve barrier/AM properties	Vishnuvarthanan and Rajeswari (2019)
Nanocomposite	Pectin	Ag/AgCl-ZnONPs	AM system	Yu et al. (2019)
Nanofiber	HMP	AgNPs	Reinforcement, AM	Li et al. (2018)
Hydrogel	LMP-chitosan	Garlic and holy basil EOs	Bag to improve AM properties	Torpol et al. (2019)
Oleogel	HMP	Camelia oil Tp-palmitate	Drug delivery system	Luo et al. (2019)
Nanoemulsion	HMP	Lemongrass EO	Addition in Cassava starch film to improve biodegradation properties	Mendes et al. (2020)
Multilayer emulsion polymer	HMP-chitosan	Astaxanthin	Release of hydrophobic carotenoids	Liu et al. (2019)

EO essential oil, *AM* antimicrobial, *AO* antioxidant, *HMP* high methoxyl pectin, *LMP* low methoxyl pectin

and water-soluble vitamins, their disposal degrades the environment (Smithers 2008). The excessive cross-linking during the development of whey films under high temperature makes the whey films more brittle and highly tensile. Due to the weaker interactions of -lg gels, whey films formed by hydrostatic pressure have slower mechanical characteristics (Tedford and Schaschke 2000). These whey films have the advantages of being transparent and flexible with strong barrier qualities, but they also have the disadvantage of having weak mechanical strengths, as shown in Table 7.3. Irradiation treatments such as gamma and ultraviolet (UV) radiation are required to produce cross-links in the whey protein film. Cross connections are caused by dityrosine bridges created by gamma radiations and free radical formations induced by UV rays. Chemical modifications due to pH changes (alkylation, acetylation, succinylation) and biochemical modifications involving peptidases, hydrolysates, and transglutaminases enzymes have also been used to modify whey protein film properties in addition to physical agents such as heat treatment, extrusion, hydrostatic pressure, and ultrasonic treatment. The peptide bonds are cleaved by peptidases and whey protein which improves the flexibility of the films and also reduces the plasticizers necessary for preparing films (Schmid et al. 2009). While transglutaminase increases the water vapor barrier and mechanical characteristics of the films by forming a -(-glutamyl) lysine link (Schmid et al. 2014). Also, the potential of low-pressure glow plasma has been tested. They modify the protein films using surface ablation or etching, cross-linking, and modification of functional properties (Moosavi et al. 2020). The dielectric barrier discharge plasma is another innovative polymer surface modification approach. This is used for whey protein concentrate (WPC)/wheat cross-linked starch (WCS) composite films with enhanced mechanical and barrier properties (Song et al. 2019). Table 7.2 summarizes a latest prior art on the development of functional whey-based films with their respective applications.

7.7 Utilization of Meat and By-Products Processing Waste for Biodegradable Food Packaging

India is blessed with an abundance of cattle, which is rising at a pace of 6% every year. The livestock industry, which includes poultry and fish, is contributing significantly to the country's GDP, accounting for more than 40% of the entire agricultural sector and more than 12% of GDP. If animal by-products were used more effectively, this contribution would have been substantially higher. Efficient by-product usage has a direct influence on the economy and pollution levels. Non- or underutilization of by-products results in a loss of potential profits as well as an increase in the cost of removing these items (Article 2012). The by-products of meat are blood, liver, lung, kidney, brains, spleen, and tripe. Gelatin is found in all meat by products that is mainly used in making packaging material. Gelatin is composed of peptides and protein, produced by hydrolysis of collagen (part of protein) obtained from the bones, skin, and connective tissue protein of cow, buffalo, pigs, fish, and chicken (Djagny et al. 2001). There are different types of films are made by gelatin as it is

Table 7.3 Whey-based packaging films

Ingredients/formulations	Method	Functional properties/key findings	Proposed application	References
Poly (3-hydroxybutyrate-co-3-hydroxyvalerate) by *Bacillus megaterium* utilizing cheese whey permeate	Nano precipitation	High mechanical strength than other polymers	Plastic replacement	Nawab et al. (2017)
Whey-based films incorporated with natamycin and nano emulsion of α-tocopherol	Micro fluidization	Antioxidant activity and antibacterial activity against *C. albicans*, *P. chrysogenum*, and *S. cerevisiae*	Active food packaging	Agudelo-Cuartas et al. (2020)
Whey protein films and coatings added with prebiotic ingredients	Film forming	Diversification of functional foods in the market	Edible films for fruits and vegetables, dairy, meat, and bakery products	Fernandes et al. (2020)
Duplex and triplex laminated edible films using whey protein isolate, gelatin and sodium alginate	Solution casting	Composition with sodium alginate showed best water vapor and oxygen barrier; also highest tensile strength and elasticity	Miscellaneous food and packaging industries	Tyuftin et al. (2020)
Whey protein-based plastic	Copolymerization	It is economically feasible to produce plastics from whey wastes	Plastic replacement	Chalermthai et al. (2020)
Whey protein-gelatin-nano clay films with orange peel extract and tripolyphosphate	Solution casting	Biodegradable and antibacterial property	Food packaging	Shams et al. (2019)
Whey protein isolate/polyaniline	Solution casting	Semiconducting properties	Smart packaging to monitor electrical properties of foods	de Oliveira et al. (2019)
Whey protein film incorporated with green tea extract	Solution casting	Higher antioxidant capacity	Active packaging; delaying lipid oxidation of fresh salmon	Castro et al. (2019)
Whey protein film incorporated with green tea extract	Solution casting	Higher antioxidant capacity	Active packaging; delaying lipid oxidation of fresh salmon	

edible and biodegradable polymer (Wang et al. 2007). Edible packaging material made from gelatin has specific properties, which is most widely used in industrially. This packaging material has high melting point but easily melt-in-mouth and thermoreversible (Article 2012). Gelatin-based films are highly resistant to solvent as compare to other biodegradable film such as polysaccharide, sodium alginate (SA), carboxymethyl cellulose (CMC), and polystyrene (PS). Besides this, gelatin film demonstrates more flexibility and antioxidant and antimicrobial activity (Gómez-Guillén et al. 2011).

7.7.1 Production of Gelatin

Gelatin is manufacture from porcine skin, bovine hide, and bones. In addition, gelatin is produced from meat or by-products of fish and poultry. Firstly, collagen is obtained by separating the fat and albuminoids from the pork skin where as pure collagen is obtained by separating the minerals from the cattle bone. The separation of minerals, fat, and albuminoids is done by physical and chemical treatments. The treatments depend on the by-products of meat. There are three major processes of gelatin extraction are called acid process (type A gelatin), alkali process (type B gelatin), and enzyme process.

7.7.1.1 Acid Process (Type A Gelatin)

This process is used only to make gelatin from the skin of mammals such as cattle, pigs, goat, and sheep. Gelatin is suitable for making from dehaired skin. Typically, hairs are removed from skin by using hot dilute caustic soda or sulphate solution. This type of gelatin is called type A gelatin. The following process of gelatin extraction is given in Fig. 7.7. (Gelatin Manufacturers Institute of America 2012).

7.7.1.2 Alkali Process (Type B Gelatin)

The bone has high mineral content due to which takes more processing time. Reasonably, gelatin is produced from mammalian bone through alkali treatment (Stainsby 1987). Thus, the formed gelatin is called type B gelatin. The gelatin extraction from mammalian bone is done by the following process is given in Fig. 7.8.

7.7.2 Enzyme Process

Enzymatic process had higher gelatin production efficiency including lap processing time then chemical treatment (acid and alkali) (Hinterwaldner et al. 1977). The production of gelatin is obtained from mammalian skin and bone by using naturally occurring enzymes. The process in which proteolytic enzymes likes pepsin, pronase, esperase, alcalase, and neutrase are used (Vernon et al. 1939).

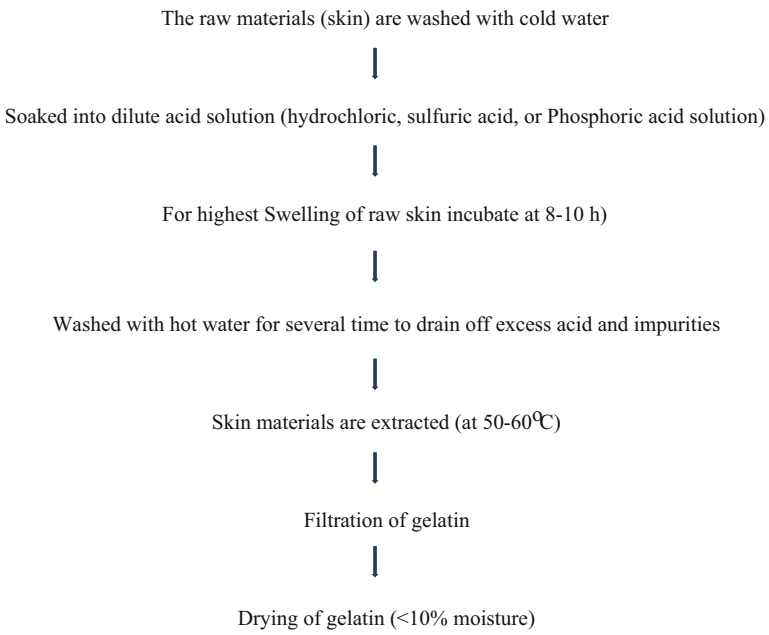

Fig. 7.7 The flowchart of gelatin extraction through acid process from meat and their by-products (Nur Hanani et al. 2014)

7.8 Conclusion and Future Prospects

The nonprofitable part of low-value products which are obtained during agricultural production is called agro-waste. It is obtained from various sector of agriculture such as cultivation, livestock, and aquaculture. Agro-waste might be processed commercially for synthesis of biopolymers. These biomaterials will strengthen the industrial manufacturing of MRS/PLA nanocomposite, acrylate/NFC nanocomposite, starch-CN bioplastic, PVA-CH nanocomposite film, K-CA nanocomposite, WPI-CNC incorporated film, and gelatin-based packaging. The exploitation of these types of biopolymers in packaging materials can reduce the toxic effect of nonbiodegradable packaging on food products and prevent negative impact on wellness and environment. The by-products obtained from crop and animal have a best potential to be transformed into useful products using ecofriendly technology. This technique will help in utilization of renewal resources and promote sustainable production. It will assist in increasing the income and fulfilling the need of food products packaging over increasing human population in future. Despite these, from the economic point of view, a new market will be created all over the world due to the processing of agricultural waste, which will provide employment opportunity.

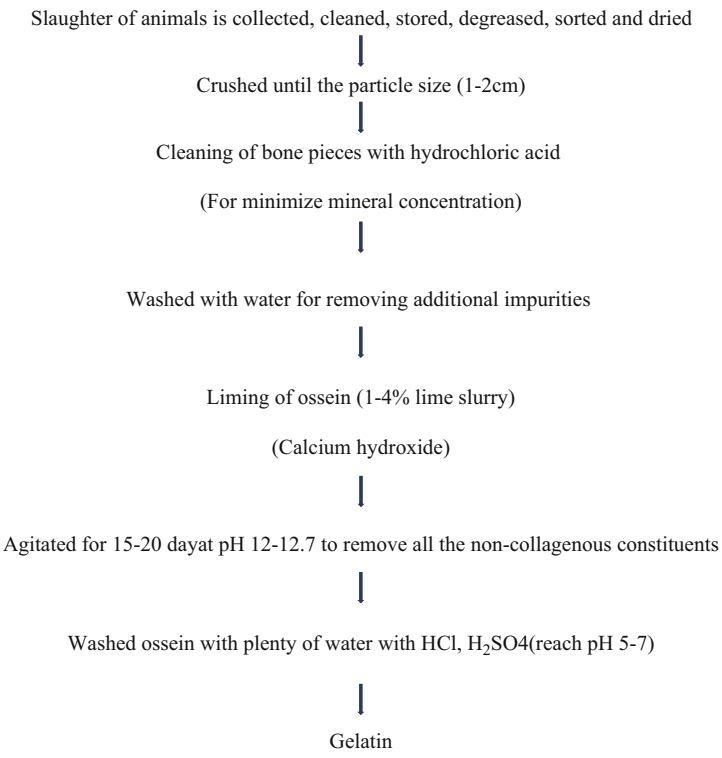

Fig. 7.8 The flowchart of gelatin extraction through alkali process from meat and their byproducts (Nur Hanani et al. 2014)

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Microbial Biopolymers and Enzymes Involved in the Biosynthesis of PHAs

8

Chhaya Goyal, Saloni Rai, Abhishek Dutt Tripathi, and Dinesh Chandra Rai

Abstract

Biopolymers are natural alternatives for synthetic polymers which can be obtained from natural sources and represent themselves as sustainable solution for nondegradable plastic. Biopolymers are plastic-like substances obtained from organic sources that have applications in the development of reliable, nontoxic, but degradable packaging materials. Organic sources of hydrocolloids, polysaccharides, lipids, and protein have been used to extract biopolymers. However, recently microbial production of biopolymers has received much attention. Polyhydroxyalkanoates (PHAs) are intracellular granules produced by certain microorganisms under nutrient stress. Several bacterial species (*Cupriavidus necator*, *Pseudomonas stutzeri*, *P. oleovorans*, *P. aeruginosa*, and *Bacillus megaterium*) and many fungal and algal species are known for PHA production. Structural and regulatory genes for PHA synthesis are present in an operon in producing microorganisms with slight differences. PHAs have many applications in various industrial sectors such as food, agriculture, and pharmaceuticals. PHA can be exploited in several ways like biofuel generation as well as can be used in packaging material.

This chapter provides a comprehensive information of biopolymers and their composites, microbial biopolymers, and main biosynthetic pathways used for PHA production. Important aspects of PHAs, its biosynthesizing genes, and their relevant proteins have also been summarized.

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Keywords

Bioplastic · Biopolymers · Food packaging · Polyhydroxyalkanoate · PHA synthase

8.1 Introduction

In present era, food packaging sector has gained a lot of attention among researchers, food scientists, and customers. Food packaging aids food industry in preserving the quality of product during storage, maintains food safety, and may extend the shelf life of packaged food products. Packaging materials serve as safety measure to protect the product from physical damages, natural contamination, and other external factors during its shelf life (Cazón and Vázquez 2020). Packaging materials especially plastic bags play a crucial role in our regular lifestyle as it is used in wrapping and conveniently carrying any product. Though, modern packaging material, obtained from petrochemicals, is reliable, but at the same time, these packages are intended for one time use, nonbiodegradable and cannot be recycled. The market value for food packaging materials is expected to reach $380 billion by 2022, as the demand for convenient foods is continuously rising. Among them, plastic utilization is the largest, contributing to more than 30% (Zhao et al. 2020). Petrochemically derived plastics that are used in day-to-day life are nonbiodegradable and adversely affect the environment (Tripathi et al. 2020). Recent reports indicated that the conventional petrochemical plastic accumulates naturally at a rate of 28 million tons annually, and its too slow degradation cause harmful effect on the environment. According to a recent survey report 2019, the worldwide production of plastic materials reached up to 370 million tons, which reflects the excessive use of plastics for packaging (source: Plastics Europe (PEMRG)/Consultic). Disposal of synthetic plastics causes emission of greenhouse gases (mainly carbon dioxide and methane) in the environment (Qamar et al. 2020).

Researchers working in this area are trying to solve these problems by substituting plastic-based materials with biodegradable or green packaging technology to attain sustainability, ecological security, and balance (Prasanna 2020). Biodegradable packaging materials have recently received much attention in the food and packaging industry due to concerns over environmental safety and security (Göksen et al. 2021). The major challenges arise due to petroleum-based plastic accumulation in the environment and rapid depletion of petrochemical resources, being used in their production. Large-scale reliance on petroleum-derived plastics has brought about rapid decrease of unrefined or crude petroleum and serious pollution problems. These factors are driving force for research into developing alternative sources and technologies to petroleum-based polymers (Muhammadi et al. 2015). Scientific research in this direction has led researchers to look for potential candidates of biopolymers such as polylactide, aliphatic polyesters, polysaccharides, and polyhydroxyalkanoates (PHA) having almost similar physicochemical and mechanical properties as conventional plastics and to develop

technologies to exploit them in best possible manner. Thus, biopolymers may serve as key alternatives to petroleum-derived polymers due to their biodegradability, biocompatibility, simple manufacturing processes, and wide ranges of applications in various sectors like medical field, agriculture field, and food industry (Anjum et al. 2016). Biodegradable polymers are natural or organic plastics source and may be obtained using renewable sources like vegetable oil, agro-waste, and starch. Among the biodegradable polymers, PHAs produced via microbial synthesis have gained much attention due to their specific physicochemical properties. Agro-industrial waste such as dairy processing waste (DPW) can also be used for PHA synthesis (Tripathi et al. 2021). Under nutrient limitations, these PHA granules are accumulated intracellularly as energy and carbon reserve by various microorganisms like bacteria, fungi, and algae. Synthesis of different types of PHA (viz., copolymers or homopolymers) depends upon microorganism, carbon sources, and culture medium (Urtuvia et al. 2014). Simple sugars like glucose and fatty acids are the main substrates for formation of PHA. β-Oxidation of fatty acid results in an increase in the acetyl-CoA concentration which is considered as the primary precursor for the formation of PHA. This increased amount of acetyl-CoA triggers the tri-carboxylic acid cycle in the microbial cell for PHA synthesis. Therefore, fatty acids act as nutritional supplement for PHA production. Many researchers have used lauric acid and oleic acid as nutritional supplements for PHA production in *Aeromonas hydrophila*, *Cupriavidus necator*, *Alcaligenes* sp., and recombinant *Escherichia coli* XY1-Blue pSYL105 (Srivastava and Tripathi 2013). Based on the carbon chain length, PHAs are classified into short-, medium-, and long-length polymers, and the main enzyme is PHA synthase (PhaC) for PHA synthesis that recognizes and polymerizes substrate into polymers of different chain length. PHA synthase enzyme is substrate specific, and this property is highly critical in determining the physical properties of PHAs. Based on amino acid sequence similarities, quaternary structures, and substrate specificity, PHA synthase has been classified into classes I, II, III, and IV (Liu et al. 2021). In this chapter, we have focused on different types of biopolymers, agro-industrial waste used to obtain biopolymers, and approaches used to extract and purify biopolymers. More specifically, microbial enzymes, genetic makeup of the operon responsible for PHA synthesis, and the pathways for biosynthesis of PHA have also been summarized.

8.2 Classification of Biopolymers

Biopolymers can be obtained mainly via three methods as shown in Fig. 8.1. Biopolymer can be extracted from biomass (polysaccharide and protein) and can be converted into films. The applications of biomass-based films in food products could help develop new avenues to develop novel food packaging systems. These films can be derived from several polysaccharide-based materials that may have cellulose, starch, hemicellulose, chitosan, pectin, alginate, carrageenan, pullulan, and kefiran as their constituents.

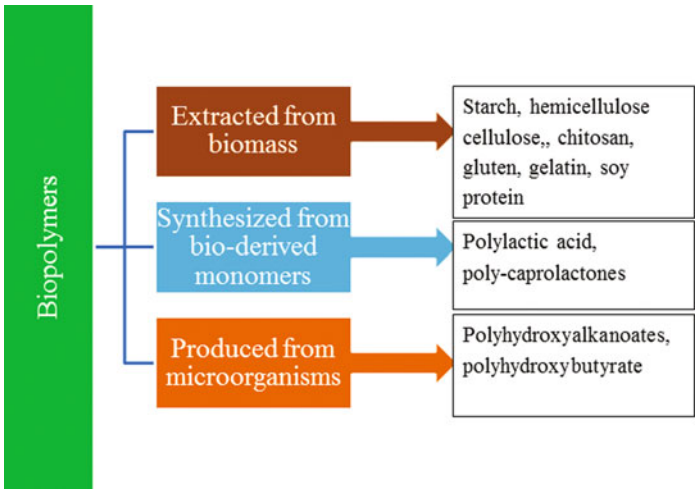

Fig. 8.1 Biodegradable packaging materials obtained from different sources

On the other hand, lipid-based materials that can be used as biomass for biopolymer extraction include waxes, acylglycerols, and fatty acids (Pérez-Gago and Rhim 2014). Among the protein-based substrates, collagen, corn zein, casein, wheat gluten, fish gelatin, and derivatives from quinoa, whey, egg white, myofibril, soy, and keratin can be the major ingredients of protein-based materials (Cazón et al. 2017). Regardless of the copious availability of the biopolymers, their use in food packaging is limited due to their poor barrier and mechanical attributes when compared to the conventional petrochemical-based packaging materials. To reduce the limitations exerted by biopolymer-based packaging, various physical and chemical treatment like thermal treatment, gamma irradiation, chemical modification, and incorporation of various additives such as nanoclay and plasticizer have been suggested in the past (Khalil et al. 2018). Along with the biodegradable packaging, it is also required to select the functionalized biopolymers in order to prevent the microbial contaminations (Roy and Rhim 2021). Chemically functionalized packaging films helps in averting microbial attack by delivering active components to the food and increasing the shelf life. Active packaging improves the antifungal, antimicrobial, as well as antioxidant functionality. The goal of active packaging is to improve its usefulness, including antimicrobial, antifungal, and antioxidant functionality. Antimicrobial films are made to enhance the shelf life of food through active agent interaction either inside the food or food package headspace, intending to hinder, diminish, or impede microorganisms' growth and development on food surface (Souza et al. 2021). Therefore, several composite biopolymers are developed by blending with other suitable materials as shown in Table 8.1.

Starch-based biopolymer composite is prepared by using different iron oxide concentrations as a binder. It was observed that this increase in binder concentration resulted in diminished absorption of water (Kumar et al. 2020). These days

Table 8.1 Lists of different blends of biodegradable polymers and their characteristics

Types of different blends	Film formation method	Film characterization	Remarks	References
Chitosan and polyvinyl alcohol	Solution casting method	FT-IR, SEM, XRD, DSC, TGA	Shelf life extension of minimally processed tomato	Tripathi et al. (2009)
Mango peel extract (MPE) was incorporated into fish gelatin films	Solution casting method	SEM	Thick, dense, and continuous structured film with excellent free radical scavenging activity and improvement in film strength	Adilah et al. (2018)
Hybrid nanocomposite film consisting of chitosan, gelatin, polyethylene glycol, and silver nanoparticles	Solution casting method	XRD, SEM	Enhanced mechanical properties and decrease in light transmittance in visible light region, transparent and homogenous nature of hybrid film, and packaging of red grapes in the hybrid film indicated shelf life extension of additional 2 weeks in	Kumar et al. (2018a)
TiO_2 nanoparticles + cellulose acetate (CA) or polycaprolactone (PCL) or polylactic acid (PLA)	Solution casting method	Measuring the thickness, color, UV-vis absorption spectra and UV-A transmission	CA film incorporated with 5% TiO_2 nanoparticles had highest bactericidal activity and achieved 1.69 log CFU/ml reduction. Whereas TiO_2-embedded PCL and PLA composite films did not show significant bactericidal property, UV-A-activated TiO_2 biodegradable polymer film inhibits *E. coli* O157:H7	Xie and Hung (2018)
Starch and poly (vinyl alcohol) (PVOH) + laponite RD (LRD)	Solution and melt-mix methods	TEM	Improved water vapor barrier and mechanical properties as well as controlled water resistance (solubility) properties	Sharma et al. (2017)
Polylactic acid polymer (PLA) and lignin nanoparticles (LNPs)		TGA, DSC	Elongation at break in the case of extruded bio-nanocomposites was	Yang et al. (2015)

(continued)

Table 8.1 (continued)

Types of different blends	Film formation method	Film characterization	Remarks	References
	Melt extrusion technique and solvent casting		positively affected by the presence of LNPs and favors the crystallization behavior of PLA matrix	
Encapsulate gallic acid in hydroxypropyl methylcellulose (HPMC)/polyethylene oxide (PEO) blend nanofiber	Electrospinning	DSC, TGA, and FTIR	Decreased oxidation of walnut during storage, showed strong antioxidant activity	Aydogdu et al. (2019)

biopolymer hydrogels are used in wide array of applications and are explored by researchers worldwide in scientific communities. Due to the existing ecological concerns and an imminent demand, researchers around the world are focusing especially on hydrogels derived from natural sources, because of their biodegradability, biocompatibility, and abundance. Hydrogels based on cellulose contains various natural biopolymers such as chitin, chitosan, and cellulose, like hydrophilic material that can hold an immense amount of water in the interstitial sites of their structures. These polymers also showed some notable properties like interaction with other chemical species, pH, time, temperature, and biological conditions other than an exceptionally high-water absorption capacity. Cellulose-based hydrogels have found tremendous application in medical devices for the treatment of tissues and organs and helping in proper functioning of body. In addition to this, these hydrogels are used to make smart materials in agricultural activities and have found applications for mechanical purposes in agriculture sector (Kabir et al. 2018).

Nowadays, various modification and formulation techniques are adopted to develop composite polymers. Modification of starch and oleic acid-based composites by UV rays and film development by solution casting method has been employed. At that point, physicochemical and packaging properties of the composites were explored. It was found that water contact angle was expanded, and water vapor permeability of the specimens was diminished by oleic acid composition. But no change was found due to exposer of the starch-oleic acid solution to UV rays. However, the oleic acid emulsions of biopolymer play a role in reduction of elasticity, tensile strength, and tensile energy to break. But, the elasticity of the film was increased, simultaneously. So, it can be concluded that the virgin starch-oleic acid composition was one of the best modification methods for decreasing the sensibility of starch to moisture as a packaging material (Jahangir-Esfahani et al. 2020). Various scientists reported that use of essential oils into starch-based packaging can enhance their stability and retain their flavor and functional properties. Essential oil components (EOCs) derived from aromatic plants possesses lots of antimicrobials (bacteria, fungi, and yeast), and this also have potential to be used as antimicrobial additives in food packaging materials. One of the shortcomings of using essential oils in food packaging is their strong odor that can alter the fresh food's organoleptic properties (Syafiq et al. 2020). Similarly, various metallic compounds like zinc oxide (ZnO), silver (Ag), and copper oxide (CuO) metallic nanoparticles were used in preparation of carboxymethyl cellulose (CMC) nano-biocomposite films. Nano-biocomposite films have shown antibacterial properties against several pathogens such as *Escherichia coli* and *Staphylococcus aureus* making them even more dynamic and increase its utility in food packaging sector (Ebrahimi et al. 2019).

8.3 Biodegradable Packaging Materials Produced by Microbes

8.3.1 Polyhydroxyalkanoate (PHA)

Polyhydroxyalkanoate (PHA) is an eco-friendly, naturally derived and biodegradable polymers, synthesized by numerous bacteria as an intracellular storage material for carbon and energy (Chuah et al. 2013). PHAs can be categorized into homopolymers and copolymers based on their structure. Homopolymers have single monomer as their building block, and PHA copolymers have two or more different building block monomers. Examples of copolymers include poly(hydroxybutyrate-co-hydroxyvalerate (PHBV), poly(hydroxybutyrate-co-hydroxyoctanoate) (PHBO), poly(3-hydroxybutyrate-co-3-hydroxyvalerate-co-3-hydroxyhexanoate) (P3HB3HV3HHx), poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) (PHBHx), and poly(3-hydroxybutyrate-co-4-hydroxybutyrate-co-3-hydroxyhexanoate) (P3HB4HB3HHx) poly(3hydroxybutyrate-co-3-hydroxyvalerate-co-4-hydroxybutyrate) (P3HB3HV4HB) (Ibrahim et al. 2021). Polyhydroxyalkanoate (PHA) are most important family of biopolymers that are synthesized by different microbial strains of bacteria, fungi, algae, etc. as shown in Table 8.2, and these microorganisms use different energy and carbon resources for the production process, and this represents a suitable model for reducing the burden of plastic induced pollution. Based on number of carbon atoms involved in their monomer structures, PHAs can be categorized into three main categories:

(a) Short-chain PHAs consist of 3–5 carbon atoms.
(b) Medium-chain PHAs consist of 6–14 carbon atoms.
(c) Long-chain PHAs consist of more than 15 carbon atoms.

8.3.1.1 Microbial Production of Polyhydroxyalkanoates (PHAs)

Accumulation of PHAs was first reported in the bacterium *Bacillus megaterium* in the year 1926. Since then, various microbial strains have been shown to accumulate PHAs as intracellular granules or secrete the polymer extracellularly. Efficient production of PHAs has been reported from certain plants that have been genetically engineered (Gumel et al. 2013). The genes required for PHA production relevant proteins, and their roles have been discussed in Sect. 8.4.1. The characteristics of microbially produced PHA and PHB, their advantages, and limitations are described in Table 8.3.

PHAs possess molecular weight ranging from 20 to 30 MDa and can be brittle as well as elastic. PHAs showed properties like biodegradability, biocompatibility, piezoelectrical, optically active, sources of chiral monomers, hydrophobic and impermeable to gases (Chen 2010). PHAs have been beefed up as an alternative to the conventional plastics because they showed similarities with them in certain parameters such as high melting temperature (175 °C) and relatively high tensile strength (30–35 MPa). After disposal, they are degraded by microorganisms and converted to water and carbon dioxide under aerobic condition and methane under anaerobic conditions (Reddy and Mohan 2012). But, the major drawbacks for PHAs

Table 8.2 List of microbial strains and their sources of carbon for production of polymer

Microbial strain	Carbon source	Type of biopolymer	References
Ralstonia eutropha H16	Glucosa, fructose, acetic acid, valeric acid	PHB, PHV	Urtuvia et al. (2014)
Alcaligenes sp. NCIM No. 5085 + *Bacillus megaterium* MTCC No. 8075 + *Pseudomonas aeruginosa MTCC 2474*	Cane molasses, sucrose, maltose, rice bran, wheat bran, orange peel powder, fructose, glucose	PHA, PHB	Tripathi et al. (2019)
Burkholderia sp. DSMZ 9243	Sucrose or gluconate	PHB, P (3HPEa)	Urtuvia et al. (2014)
Burkholderia cepacia ATCC 17759	Xylose:levulinic acid	P(3HB-co-3HV)	Urtuvia et al. (2014)
Burkholderia sacchari IPT189	Sucrose:propionic acid	P(3HB-co-3HV)	Urtuvia et al. (2014)
Burkholderia xenovorans LB400	Glucose	PHB	Urtuvia et al. (2014)
E. coli K24K (pJP24K)	Milk whey, corn steep liquor	P(3HB)	Leong et al. (2014)
E. coli CT1061	Glycerol	P(3HB)	Leong et al. (2014)
Synechococcus subsalsus	Standard medium	PHA	Costa et al. (2018)
Spirulina sp. LEB-18	Standard medium	PHA	Costa et al. (2018)
Paracoccus sp. LL1	Corn stover	PHB	Sawant et al. (2015)
Cupriavidus necator	Peanut oil	PHA	Pérez-Arauz et al. (2019)
Pseudomonas putida KT2440	Raw glycerol	mcl-(3-PHA)	Poblete-Castro et al. (2014)
Pseudomonas pseudoflava	Synthetic wastewater	PHA	Reddy et al. (2017)
Cupriavidus sp. CY-1	Toxic compounds	PHB	Reddy et al. (2015)
Acinetobacter juni BP25 and *Aeromonas hydrophila* ATCC 7966	Acetate and butyrate	PHB	Anburajan et al. (2019)

(continued)

Table 8.2 (continued)

Microbial strain	Carbon source	Type of biopolymer	References
Bacillus sp. CYR1	Fatty acid-acetic:propionic: butyric:caproic acid	PHA	Reddy et al. (2020)
Cupriavidus necator PTCC 1615	Brown seaweed *Sargassum* sp.	PHB	Azizi et al. (2017)
Rhodococcus sp. EF028124.1 and *Bacillus cereus* FM-4 EU794727	Hydrolyzed polyacrylamide (HPAM)-containing wastewater	PHA	Zhao et al. (2019)
Pseudomonas entomophila	Fatty acids	PHA	Wang et al. (2017)
Aspergillus niger and *Saccharomyces cerevisiae* L2612	Starch	PHA	Yang et al. (2020)
Aspergillus fumigatus	Glucose, fructose, sucrose, and lactose	PHB	Lodhi et al. (2011)
Streptomyces lydicus MM10	Glucose, fructose, sucrose, mannitol	PHB	Aly et al. (2015)
Synechococcus subsalsus	Standard medium and limited nitrogen medium	PHA	Costa et al. (2018)
Spirulina sp. LEB-18	Standard medium and limited nitrogen medium	PHA	Costa et al. (2018)
Chlorella fusca LEB 111	Xylose and arabinose	PHB	Cassuriaga et al. (2018)

production remains its production cost, and lack of comparable robust attributes of conventional packaging material to an extent that the technology can be commercialized. For the development of economical bioplastics, investigations should be made to lower down the relevant production factors such as nutrition requirement and growth characteristics of microorganisms involved in the PHA biosynthesis and also the raw materials like carbon, nitrogen, and source. Several studies have emphasized on the use of agro-industrial wastes as a cost-competitive carbon source. Nowadays, blending with approved biodegradable materials such as cellulose acetate butyrate (CAB) has also attracted much attention as a superior approach to manufacture commercially compatible bioplastics (Jain and Tiwari 2015).

8.3.2 Polyhydroxybutyrate (PHB)

PHB is another important biodegradable polymer and is natural β-hydroxy acid linear polyester. The biochemical structure of the repeating units of these polyesters is depend on the microbial strain and the feed provided to it. It is a homopolymer of 3 hydroxybutyrates. In general, PHB accumulation is enhanced by sufficient

Table 8.3 Characteristics of microbially produced biodegradable polymers

Types of biodegradable polymers	Properties	Sources	Advantages	Disadvantages	References
PHA	Good tensile strength, printability, flavor and odor barrier properties, heat sealability, grease and oil resistance, temperature stability and are easy to dye, low volume of the biopolymer	Obtained with pure microbial cultures grown on renewable feedstocks (i.e., glucose) under sterile conditions	High barrier properties towards oxygen permeation, or low gas permeability properties, prevents the oxidative spoiling of products	High production costs, brittleness, and low thermal stability in the molten state	Mangaraj et al. (2019), Keskin et al. (2017), Tripathi et al. (2020)
PHB	Relatively high glass transition and melting temperatures	Naturally occurring β-hydroxy acid produced by enzymatic synthesis of a large variety of bacteria	Biodegradability, biocompatibility, availability	High production cost, thermal instability, and poor mechanical properties, due to secondary crystallization and slow nucleation rate, brittleness	Yeo et al. (2018), Tripathi et al. (2020)

availability of an appropriate carbon source and a limiting supply of nitrogen, phosphate, or dissolved oxygen or certain micro-components like sulfur, potassium, tin, iron, or magnesium. PHB are present in the cytoplasm of the producing cell in granule form have a diameter of 0.2–0.7 μm and are enclosed within a lipo-proteinaceous membrane (2 nm thickness). These granules can be isolated in their native form or by solvent and enzymatic extraction method (Mangaraj et al. 2019). The production of PHB depends on several factors like rate of accumulation of polymer in the cell, cost of substrate, and PHB yield/substrate unit are some of the important factors (Tripathi et al. 2021). PHB have several characteristics that makes it suitable for polyester like material. It is promising candidate that has shown low toxicity, biocompatibility with various kinds of cells, piezo-effect, thermo-plasticity, biodegradability, high absorption capacity, high degree of crystallinity, and selective gas barrier properties. Apart from these, PHB also showed high viscosity in a liquid state, chemical inactivity, solubility in chlorinated solvents and resistance against ultraviolet radiation, and relatively low melting temperature. However, it is a rigid and comparatively brittle polymer, and it has low impact resistance, poor thermal stability, and significant hydrophobicity (Ibrahim et al. 2021). Various extraction and purification methods of these biopolymers are described in Table 8.4.

8.4 Biosynthetic Pathways Involved in the Production of Biopolymers

Synthesis of polyhydroxyalkanoate (PHA) and polyhydroxybutyrate (PHB) have been studied in many bacterial strains such as *Pseudomonas putida* and *Cupriavidus necator*. There are three main metabolic pathways for PHA biosynthesis starting from glucose and fatty acids. A map of metabolic pathways resulting in PHA formation has been summarized in Fig. 8.2.

Through metabolic engineering, the pathways for PHA/PHB synthesis have been optimized for increased production either by elimination of competitive reactions or redirecting flux towards a product to increase precursor availability. **Acetyl-CoA** is the main precursor in most of the biosynthetic pathways for PHAs production. As shown in Fig. 8.2 in **Pathway I**, glucose can be utilized as carbon source to produce acetyl-CoA, followed by metabolism to acetoacetyl-CoA and 3-hydroxybutyryl-CoA, and their conversion to short-chain length (scl)-PHA.

Pathway II involves the β-oxidation of fatty acids in bacteria producing PHA. When fatty acids enter the β-oxidation cycle as substrate, it leads to the generation of R-3-hydroxyacyl-CoA monomers ultimately resulting into the formation of medium chain length PHA. **Pathway III** involves the de novo synthesis of PHAs from fatty acids wherein acetyl-CoA is directed to malonyl-CoA to 3-ketoacyl-ACP for forming R-3-hydroxyacyl-CoA monomers (Khatami et al. 2021).

Table 8.4 Recent approach for extraction and purification of PHAs

Methods	Claims	Benefits	Drawback	References
Thermo-separating-based aqueous two-phase extraction (ATPE)	Recovery yield and purification factor up to 72.2% and 1.61-fold, respectively; twice recyclable	Safe and relatively eco-friendly phase-forming components, rapid separation with low energy input, large capacity handling, and ease of scalability	Inefficient recycling of most phase-forming components, making it less economical as well as bringing negative impacts to the environment	Leong et al. (2017)
Biological recovery process by using mealworm, which is the larva of mealworm beetle (*Tenebrio molitor*) to recover PHA granules from *Cupriavidus necator*.	Mealworm can be grown in high densities, require less water and space, breed prolifically and can consume up to 10% feed of their body weight per day	In comparison to chloroform extraction, it showed no signs of reduction in the molecular weight and dispersion of the PHA molecules, requires less chemicals and solvents compared to most of other recovery processes, non-PHA residual cellular materials are not wasted but used as feed by the mealworm	–	Murugan et al. (2016)
Extraction of short-chain-length poly-[(R)-hydroxyalkanoates] (scl-PHA) by the "anti-solvent" acetone under elevated temperature and pressure	Product purity (98.4%) and extraction yield (96.8%), and is by far faster than established chloroform extraction method (20 min vs. 12 h)	Less time is required for extraction of high-quality polymer without negatively impacting the structural features of the bio-polyester	Security precautions have to be taken into account considering the removal of oxygen from the overall system; in addition, high-quality	Koller et al. (2013)

(continued)

Table 8.4 (continued)

Methods	Claims	Benefits	Drawback	References
			materials for vessels and sealing are required	
Solvent extraction methods	Involves three steps-pretreatment, solvent extraction, and polymer purification. Biomass containing higher amounts of PHA required less methanol during the pretreatment step but more acetone in the solvent extraction step than biomass containing less PHA	Solvent extraction is utilized when high purity is required, removes the endotoxins of the cells	Low temperature (below 40 °C) may affect the recovery rates	Jiang et al. (2006), Raza et al. (2018), Muneer et al. (2020)
Supercritical fluid extraction technology	SCG oil was efficiently extracted (>90% yield) by $scCO_2$ in a pilot plant, act as source for PHA production by *C. necator*, resulting in a product yield of 0.77 kg of PHA per kg of SCG oil (97 kg per ton of SCG processed)	Highest product quality and recovery is achieved, P (3HB) exhibited very good physical and chemical properties	The polymer exhibited brittle behavior, with very low elongation at break (1.3%), tensile strength at break of 16 MPa and Young's modulus of 1.0 GPa, complex method and dependent on process parameters	Cruz et al. (2014)
Digestion method for enhanced recovery and purification of P (3HB-co-3HHx) from recombinant *Cupriavidus necator*	High PHA purity and recovery yield both in the range of 80–90% were obtained when 10–30 mg/ml of cells were incubated in	Simple, efficient, and economical method, high PHA purity, recovery and thermal stability can be	PHA recovery by sodium hypochlorite digestion leads to low molecular mass P(3HB) as a result of	Anis et al. (2012)

(continued)

Table 8.4 (continued)

Methods	Claims	Benefits	Drawback	References
	NaOH at the concentration of 0.1 M for 60–180 min at 30 °C and polished using 20% (v/v) of ethanol	obtained with dilute ammonia digestion	degradation by these chemicals	
Flotation method	Simple extraction with various organic solvents followed by self-flotation of cell debris was tested. The cells were mixed with chloroform at 30 °C for 72 h and later subjected to self-flotation of cell debris overnight at room temperature. This method allowed efficient recovery of 85% (w/w) of P(3HB) with purity of 98%	Cost-effective as additional steps such as centrifugation and wastage of polymer during recovery could be avoided	Requires several consecutive flotation steps, consumption of large volume of toxic and volatile solvents	Kunasundari and Sudesh (2011)

8.4.1 Enzymes Involved in the Biosynthesis of PHA

Combining all the three anabolic pathways involved in the PHA synthesis by microorganisms, there are more than 39 enzymes that catalyzes the biochemical reactions to run the three pathways. However, the key enzymes actually responsible for biosynthesis of PHA are β-ketothiolase (PhaA), aceto-acetyl coenzyme A (CoA) reductase (PhaB), and PHA synthase (PhaC1 and C2, PhaE, PhaR) (Muneer et al. 2020). Along with these PHA-synthesizing enzymes, a family of granule associated proteins called "Phasins" encoded by *PhaP*, *PhaF*, *PhaI*, *GA14*, and *Mms16* are also involved in regulating the PHA granule's structure, morphology, and their accumulation (de Almeida et al. 2011; Galán et al. 2011; Dinjaski and Prieto 2013). The organization of Pha Operon differs slightly in the genome of representative microbial species as shown in Fig. 8.2. Other enzymes, namely, 3-ketoacyl acyl carrier protein (ACP) reductase (FabG), Acyl-ACP-CoA transacylase (PhaG), and Enoyl-C (PhaJ) also play role in pathways for PHA synthesis. As shown in the Fig. 8.2 in

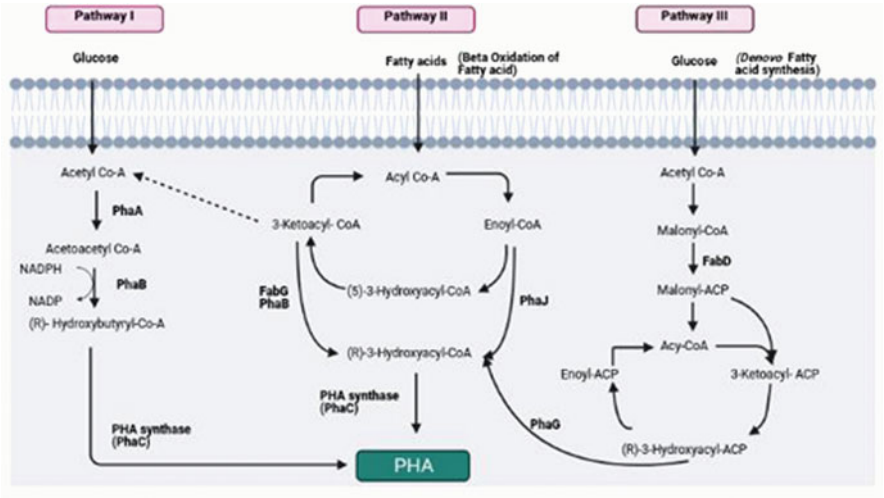

Fig. 8.2 Biochemical pathways involved in the synthesis of PHA. Enzymes involved in the synthesis of PHA are β-ketothiolase (PhaA), Acetoacetyl coenzyme A (CoA) reductase (PhaB), PHA synthase (PhaC), 3-ketoacyl acyl carrier protein (ACP) reductase (FabG), Acyl-ACP-CoA transacylase (PhaG), and Enoyl-C (PhaJ) (Created using BioRender and reproduced from Khatami et al. 2021))

pathway I, the biosynthesis of short-chain length PHAs from its precursor takes place in three steps and the first biochemical reaction in this series is a Claisen-type condensation of two molecules of acetyl-CoA resulting in the formation of acetoacetyl-CoA. This step is catalyzed by a **β-ketothiolase** (acetoacetyl-CoA thiolase; EC 2.3.1.9) encoded by *phaA* gene. Further, acetoacetyl-CoA is reduced by an **acetoacetyl-CoA reductase** (EC 1.1.1.36) encoded by *phaB* gene. The resultant product of second reaction (R)-3-hydroxybutyryl-CoA undergoes polymerization reaction catalyzed by a PHA synthase encoded by *phaC* gene.

8.4.2 PHA Synthase (PhaC)

PHA synthase is an important enzyme responsible for polymerizing monomers, and the specificity of this enzyme is even more critical in determining PHA monomer composition. PHA synthases encoded by *phaC* gene can be categorized into four classes based on the reaction mechanisms it catalyzes and the kinetics of the enzyme. This categorization of PHA synthase enzyme into four groups corresponds to the basic structure of the enzyme; the composition of its subunits and specificities to various kind of monomers. Nucleotide sequences of PHA synthase from different microbial species also have differences. On the basis of sequence similarity, they have been grouped into four classes as shown in Fig. 8.3. Class I, Class III, and Class IV PHA synthase use propionate, valerate, butyrate, and hexanoate as precursors and forms short-chain length (scl)-PHAs.

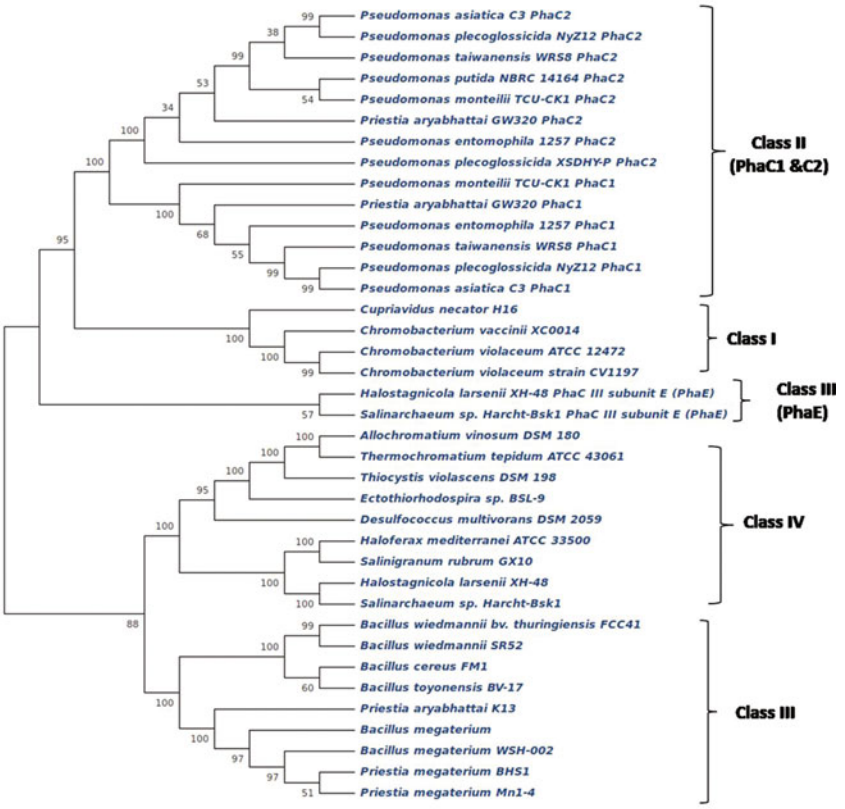

Fig. 8.3 Phylogenetic tree of naturally occurring PHA synthases in representative microbial species from class I to IV. Nucleotide sequence alignments and phylogeny were conducted using MEGAX (Kumar et al. 2018b)

Contrary to this, Class II PHA synthase synthesize mcl-PHAs by using alkane (C6 to C14) precursors (Mezzolla et al. 2018). A lot of interest has been shown to elucidate the properties of scl-co-mcl PHA using a PHA synthase with low specificity, as copolymer of scl-PHA and mcl-PHA have better industrial prospects. Chek et al. (2019) have deduced the crystal structures of catalytic domain of PhaC from *Cupriavidus necator* and *Chromobacterium* sp. USM2. In general, short-chain length PHA are brittle and stiff and display a high degree of crystallinity, whereas medium-chain length (MCL) PHA displays low tensile strength, low crystallinity, and low melting point and is flexible (Philip et al. 2007).

Class I PHA synthase enzymes generally utilize the scl-HAs (C3–C5), and the molecular weight of its single subunit ranges between 60 and 70 kDa (Tsuge 2016). The most studied, Class I PHA, are those obtained from the strains of *Cupriavidus necator*. In a recent study, the comparison of the relative positions of amino acid

residues of class I PHA synthase from *Cupriavidus necator* has revealed that the alanine at position 510 of $PhaC_{Cn}$ is near catalytic histidine at position 508 and that may have possible implications in the open-close regulation. This phenomenon has indicated a crucial role in substrate specificity and activity of PhaC (Chek et al. 2019). **Class II** PHA synthases also has one subunit either PhaC1 or PhaC2. It has been observed that PhaC1 exhibits a higher rate of catalysis and forms lower molecular weight PHAs as compared to those formed by PhaC2. However, both subunits PhaC1 and PhaC2 have almost similar specificities to substrates (Guo et al. 2013). Natural $PhaC_{Pa}$ from *Pseudomonas aeruginosa* is an example of class II PHA synthase and polymerizes CoA thioesters of medium chain length monomers (6–12 carbon). During de novo synthesis of fatty acids and β-oxidation of fatty acids, these CoA thioesters are available in bacteria (Tsuge 2016). **Class III** PHA synthase is a heterodimeric in nature, and two subunits are required for its catalytic activity. The two subunits, i.e., PhaC subunit (MW ~ 40 kDa) and PhaE subunit (MW ~ 40 kDa) have been categorized into two clades based on similarities in nucleotides sequence. PhaC subunit of the class III PHA synthase has more similarity with the PhaC subunit of class I, II, and IV PHA synthase, while the PhaE subunit of the class III PHA synthase has been reported to have less similarity to the other subunits of the PHA synthases. The PHA synthase from *Allochromatium vinosum* is representative of the class III PHA synthase that consists of two subunits $PhaE_{Av}$ (40.53 kDa) and $PhaC_{Av}$ (39.73 kDa). PHA from *Haloarchaea* also belongs to Class III and can be easily isolated without maintaining strict sterile conditions (Han et al. 2010). **Class IV** PHA synthase is also heterodimeric enzyme consisting of two subunits: PhaC and PhaR (Mw of PhaR is approximately 20 kDa) and have been obtained from *Bacillus megaterium* and *Bacillus cereus.* PhaR subunit of class IV PHA synthase is observed to have the capability of cleaving alcohol, and thus it can regulate the molecular weight or modify the structure of PHAs (Tsuge et al. 2015).

The protein products of several genes (as enzymes or structural proteins) are responsible for the rate of production, structure, and accumulation of PHA granules. The genes responsible for biosynthesis of PHA granules are present in the form of clusters. Different microorganisms have a set of genes or operon that acts in harmony with the external environment for the production of PHA granules as shown in Fig. 8.4. Cupriavidus necator, the most studied microorganism for PHA synthesis, possess an operon *pha CAB* that governs the synthesis of three enzymes PHA synthase (*pha*C), β-ketothiolase (*phaA*), and acetoacetyl-CoA reductase (*phaB*). Several species of *Pseudomonas* such as *P. aeruginosa*, *P. putida*, and *P. oleovorans* are known for sustainable production of PHA. The operon for PHA synthesis in *Pesudomonas* species is present in a slightly different manner. Phasin proteins encoded by *phaF1* gene are present downstream to *pha*C1 gene. Phasins (PhaF and Pha1) are granule associated proteins that stabilize the granular structure of PHAs. Genetic engineering approach has been applied to improve the efficiency of PHA synthase and to modify the substrate specificity for the development of more diverse copolymers or new polymers with desired attributes (Tsuge 2016). *Pseudomonas* species have been observed to produce several PHA with different chain lengths via β-oxidation of fatty acids or in situ synthesis of fatty acids as substrate. During β-oxidation of fatty acids, the chain length decreases by two carbons. Efforts

Fig. 8.4 Organization of PHA synthesizing genes in genomes of different microorganism

have been made through genetic engineering in *Pseudomonas putida* for weakening of the β-oxidation cycle by selectively deleting the chromosomal genes related to β-oxidation. Consequently, the fatty acid structure is maintained when it is used as substrate by this mutant *Pseudomonas putida* KTQQ20 and the composition of the PHA can be controlled (Meng and Chen 2017). *fadA*, *fadAx*, *fadB*, and *fadB2x* are some of the key genes that regulate degradation of fatty acids which were detected for the production of desired copolymers. 3-Hydroxyacyl-CoA dehydrogenase and acyl-CoA dehydrogenase along with *phaG* encoding 3-hydroxyacyl-CoA-acyl carrier protein transferase were also deleted to make the fatty acid β-oxidation activity defective and hence the production of desired copolymers was achieved (Meng and Chen 2017).

8.5 Conclusion

Depleting nonrenewable petrochemical-based packaging material is responsible for the adoption of biopolymer-based packaging materials. Bioplastics derived from PHA and PHBs have become a putative alternative for petroleum-derived polymers. Although, expensive production and recovery cost of biopolymers are principal constraints in the industrial production of biopolymers. However, this problem can be overcome by selecting cheaper and inexpensive raw materials like agro-industrial waste possessing precursors for the production of biopolymers. In addition to that, an efficient recovery process can further minimize biopolymer production costs. Several bacteria such as *Pseudomonas putida*, *Pseudomonas aeruginosa*, *Bacillus megaterium*, and *Cupriavidus necator* have been known for greater efficiency and high production rates of PHAs. Besides bacteria, several algae, and fungi have also

been studied for PHA synthesis. Among the several enzymes (PhaA, PhaB, PhaC, PhaE) participating in microbial production of PHA, PhaC is the key enzyme for PHAs synthesis. It recognizes appropriate monomers and incorporates them in the PHA polymer chain. Recent developments in the metabolic engineering of PHA synthase enzyme and associated pathways along with improved downstream processing for efficient recovery have the potential for hyper production of PHAs.

8.6 Future Aspects

Biopolymer-based packaging has emerged out as one of the prime sustainable solutions for plastic waste and associated pollution. Microbial polyesters can also be used in pharmaceuticals and food sector. There is a need to explore the better use of these microbial polyesters as PHAs can play an important role in improving the material science, health sectors, and other industries. Newer interventions can be made in the fields such as tissue engineering and drug delivery using PHAs and copolymers. Biopolymer-based interventions in the field of health care and medicine may pave newer paths to solve the existing ways of treating diseases, nerve regeneration, and drug delivery. Plastic-based chemicals can be replaced with biopolymer-based plastics, and microbial polyesters can be used for the production of biofuels. In spite of having diverse applications of microbially produced polymers, there are limitations such as selection of potential microbial candidate for hyper and controlled production of PHAs, source of nutrition, expensive purification, and recovery protocols. In-depth studies are required in order to make it cost effective and increase the productivity so that it can be more competitive. Further, for large-scale production at industrial level, all the laboratory experiments should be validated at pilot scale. Continuous innovation and global support is the utmost requirement for bioplastics to fully demonstrate its socioeconomic benefits and existing challenges posed by the use of conventional petroleum-based plastics. Nowadays, researchers across the globe are involved in making it cost effective, improving fermentation techniques, delivering recombinant organisms, and making the recovery process efficient.

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9 Metabolic Engineering for Synthesis of Biodegradable Polymers with Potential Application in Food Packaging

Ali Basirattalab, Maryam Afarin, Ali Sattari, and Iran Alemzadeh

Abstract

Nowadays, metabolic engineering is a well-known approach to deal with bioproduction problems in bio-based material manufacturing. Various types of cells, such as plant cells, bacteria, algae, and fungi, take substrates and, through metabolic networks, including a complex amalgamation of metabolic pathways, convert them into valuable products. Metabolic engineering is implementing biological tools such as genetic engineering, evolutionary engineering, and modifying cultivation methods to manipulate metabolites' biosynthesis to increase, decrease, block, and create pathway(s) involving in the biosynthesis of one or more special product(s). Metabolic engineering plays a pivotal role by designing or modifying metabolic pathways in microorganisms or cell-free systems for biodegradable biopolymers' bioproduction with potential in food packaging applications. This chapter presents recent advances in pathway engineering for the synthesis of biodegradable biopolymers with potential application in food packaging, such as polyhydroxyalkanoates (PHAs), including poly (b-hydroxybutyrate) (PHB), poly(3-hydroxybutyrate-co23-hydroxyvalerate) (PHBV), bacterial cellulose, xanthan, and pullulan.

Keywords

Biodegradable biopolymers · Metabolic engineering · PHA · PHB · PHBV · Xanthan · Pullulan · Food packaging

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9.1 Introduction

With increasing concern about environmental protection, sustainability, and decreasing waste, demand for degradable biopolymers with potential packaging usage rises year by year. According to Smithers' report—The Future of Bioplastics for Packaging to 2022—although bioplastics are not significant in the current packaging market, they will grow very strongly, more than doubling in value to 2023. One of the constraints against the widespread usage of biopolymers for packaging is such polymers' mass production. Demand for cheap and easy biopolymers' production has driven research toward developing new methods to produce biodegradable polymers for food packaging. Metabolic engineering is an approach that can be used to enhance the production of biopolymers that have microorganism origins. Some of the most famous biopolymers acquired from microorganisms or genetically modified bacteria are polyhydroxyalkanoates (PHAs), including poly (b-hydroxybutyrate) (PHB), poly(3-hydroxybutyrate-co23-hydroxyvalerate) (PHBV), bacterial cellulose, xanthan, and pullulan. Mainly there are four main strategies in cells' metabolic engineering with the purpose of increasing the production of specific metabolites:

1. Amending DNA sequence
2. Manipulating competing carbon fluxes
3. Optimizing culture medium or substrate utilization
4. Recombinant expression in other cells or cell-free systems

This chapter will delve into recent advances in metabolic engineering of cells, which are practical for PHAs, xanthan, and pullulan production.

9.1.1 Food Packaging Biopolymers

In the recent years, food packaging industry has ameliorated for the application of bio-based material and replacing synthetic material by conventional due to low emission of hazardous material, antioxidant characteristics, antimicrobial properties, and biocompatibility and biodegradability configurations. Microbial-based biomaterial could utilize in food packaging industry. Nearly all microbial biopolymer-based biomaterials have carbohydrate base such as polyhydroxyalkanoates (PHAs), including poly(b-hydroxybutyrate) (PHB), poly(3-hydroxybutyrate-co23-hydroxyvalerate) (PHBV), bacterial cellulose, xanthan, and pullulans. In this book chapter, latest advances in bio-based food packaging materials are undertaken, and further approaches for metabolic pathway production and commercial application of these eco-friendly materials are discussed.

9.2 Polyhydroxyalkanoates (PHAs)

For the first time, Beijerinck discovered polyhydroxyalkanoates in 1888, but until 1925, their structure and composition were unknown (Park et al. 2005). The oil crisis of the 1970s ushered companies to move toward new plastics driven from alternative sources. One of them was PHA that many companies worldwide reached to industrial-scale production of this biopolymer. PHA characteristics such as renewability, biodegradability, and low vapor permeability made it an attractive food packaging option. Not only does it provide efficient protection for foods, but also it can be improved by copolymerization with other monomers. In Table 9.1, we compared a type of PHAs named PHB with an artificial plastic polypropylene (PP).

Various microorganisms under special conditions produce PHA in the form of granules. PHA has a protective role for cells and enzymes under environmental stress conditions (Valdés et al. 2018). For example, *Thermus thermophilus*, a gram-negative bacteria, produce scl-co-mcl-PHA-mcl-coscl-PHA from octanoate under extreme temperature (75 ° C) (Pantazaki et al. 2003) or a gram-negative Halophil bacteria, Halomonas TD01 biosynthesize PHB from glucose under high saline culture (60 g/L NaCl) (Tan et al. 2011).

Many other Archaea, gram-positive bacteria, gram-negative bacteria, and photosynthetic bacteria have been discovered, which can amass PHA aerobically and anaerobically. PHB production by *Ralstonia eutropha* in low-cost culture media such as molasses as sole carbon sources was investigated (Bozorg et al. 2015). At present, more than 150 microorganisms producing PHAs is recognized (Mitra et al. 2020).

9.2.1 PHA Biosynthetic Mechanisms

The type of carbon sources we provide microorganisms determines the structure of produced PHAs. There are three main pathways to synthesize PHAs, and it can be extended to 14 minor pathways. The combination of active and inactive states of these pathways and various proportional fluxes in different active pathways

Table 9.1 Comparison properties of polyhydroxybutyrate (PHB) and polypropylene (PP) (Alemzadeh 2013)

PHB	PP	Property
175	176	Melting point
80	70	Crystallinity
5E10	2E5	MW
−4	−10	Tg
1.25	0.905	Density
4 40	1.7 38	Tension stress for 1 GPa and 2 MPa
6	40	Tensile strength (%)
Weak	Good	UV protection
Weak	Good	Solubility resistance

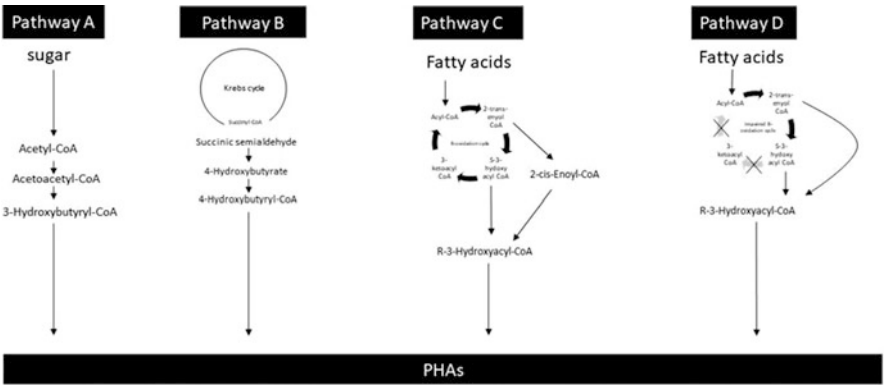

Fig. 9.1 Four pathways that synthesize PHAs and have been mentioned in the text

determines the structure of final PHAs. The metabolic engineering approach can be used here to produce various PHAs by co-expression of related genes to some specific pathways (Chen et al. 2015).

For instance, in 2010, Zheng-Jun Li and colleagues co-expressed pathways A (Fig. 9.1; Meng et al. 2014) (from *Ralstonia eutropha*) and B (Fig. 9.1) (from *Clostridium kluyveri*) together in *E. coli* and produced poly(3-hydroxybutyrate-co-4-hydroxybutyrate) [P(3HB-co-4HB)] from unrelated carbon sources (Li et al. 2010). In pathway A, the sugar after converting to acetyl-CoA take this path, acetyl-CoA → acetoacetyl-CoA → 3-hydroxybutyryl-CoA, and in pathway B, the acetyl-CoA will be processed in TCA (tricarboxylic acid) cycle, and from the cycle, succinyl-CoA will continue through succinic semialdehyde → 4-hydroxybutyrate → 4-hydroxybutyryl-CoA. Then the cell synthesizes a double block PHA from both 4-hydroxybutyryl-CoA and 3-hydroxybutyryl-CoA, named P(3HB-co-4HB). The metabolically engineered *E. coli* produced 9.4 g/L cell dry weight containing 65.5% P(3HB-co-11.1 mol%4 HB) using glucose as the carbon source in a 48 h shake flask growth. Combining two pathways to produce novel PHAs has become a common method nowadays. Many similar papers describe this approach to build new PHAs. For example, in Table 9.2, we have depicted several articles that used this method.

9.2.2 Role of β-Oxidation Cycle

An important cycle that directly plays a role in pathways C and D (Fig. 9.1) is the β-oxidation cycle that synthesizes medium-chain-length (mcl) PHAs from most fatty acids (Fig. 9.2; Chung et al. 2011; Liu et al. 2011). The fatty acid, through the cycle, will be converted to enoyl-CoA. Subsequently, enoyl-CoA will be processed by R-3-hydroxyacyl-CoA hydratase to form R-3-hydroxyacyl-CoA (PhaG) (Sudesh et al. 2000), and then PHA synthase produces mcl PHAs from these monomers. A β-oxidation impaired *P. entomophila* LAC23 can be used to synthesize

Table 9.2 Some examples of novel PHA synthesis by co-expression of related genes

PHA	Host	Carbon source	Key genes	Method	Reference
PHAs with 3HB, 3 HV, 3HHx, 3HO, and 3HD monomers	*Cupriavidus necator*	Canola and avocado oil	fadE and phaJ	Plasmid (pMPJAS03)	Flores-Sánchez et al. (2020)
[P(3HB-co-3HHx)]	*Cupriavidus necator* transformants	Palm oil	phaJ1, PhaC, and PhaBCn		Tan et al. (2020)
3-HHx	*Cupriavidus necator*	Canola oil	phaC2	Plasmid (pMRC03)	Valdés et al. (2018)
PHBHHx	*Aeromonas hydrophila* 4AK4	Dodecanoate	phaPC, phaCJ, phaPCJ, phbAB, vgb, or fadD	Plasmid (pBBR1MCS-2)	Qiu et al. (2006)

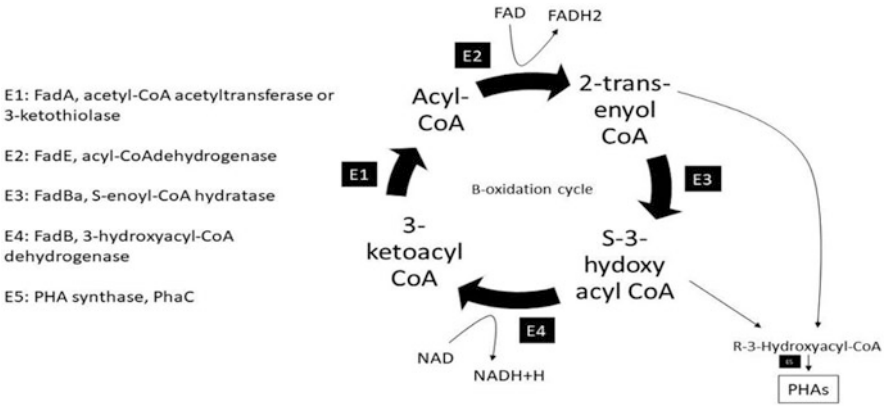

Fig. 9.2 β-Oxidation cycle and its enzymes

medium-chain-length PHAs (Park et al. 2005; Wang et al. 2017a, b). In the β-oxidation cycle, there are S-3-hydroxyacyl-CoA dehydrogenase encoded by two genes, fadB and fadB2x; 3-ketothiolase encoded by fadA; acetyl-CoA acetyltransferase encoded by six genes in *P. entomophila*, including fadAx, PSEEN 0664, PSEEN 2543, PSEEN 2795, PSEEN 3197, and PSEEN 4635; enoyl-CoA hydratase encoded by PhaJ; and PHA synthase encoded by PhaC. A combination of knockout genes of these genes can produce various PHAs and microorganisms with different growth rates. For example, *P. entomophila* LAC26 that had lost fadB, fadA, PSEEN 0664, and PSEEN 2543 genes amassed over 90 wt % PHA consisting of 99 mol % 3HDD, and *P. entomophila* LAC25 that had lost

fadB, fadA, PSEEN 0664, PSEEN 4635, and PSEEN 4636 genes produced improved mcl PHAs along with increasing 3HDD contents. *P. entomophila* LAC25 synthesized P(2.1 mol%3HD-co-97.9 mol%3HDD) with the broadest temperature range between T_g and Tm among all reported mcl PHAs (Chung et al. 2011). In 2010, Qian Liu and colleagues deleted PhaG-related gene (PP1408) that led to synthesize novel PHAs. PhaG, encoded by gene PP1408, exhibits a 3-hydroxyacyl-CoA-acyl carrier protein transferase activity. Thus, deletion of phaG could decrease the influence of PHA de novo synthesis (Liu et al. 2011). An approach that can be used to synthesize novel PHAs based on metabolic pathways uses various carbon sources with a particular ratio that leads to the carbon source process through different metabolic pathways and gives biopolymers consisted of two or more monomers. In 2017, Ying Wang and colleagues used *P. entomophila* LAC23, a mutant with impaired β-oxidation, to synthesize novel mcl PHAs via providing sodium octanoate and dodecanoic acid for the culture media. By changing the ratio of the two carbon sources of cell culture duration, they could control constitution of the two monomers in P(3HO-co-3HDD) (Wang et al. 2017a, b).

9.2.3 Manipulation Ribosome Binding Site and Promoters

Accumulation of PHAs (such as PHB, PHBV, etc.) is based on the expression of phbCAB operon and other homologous genes (Chen and Jiang 2017). Transcription and translation kinetic impact on protein formation and consequently structures, by manipulating kinetics of translation and transcription processes of phbCAB operon and other homologous genes responsible for the synthesis of PHAs. The two most important factors that control the kinetics of translation and transcription are promoter and ribosome binding sites. In prokaryotes, a region upstream of the start codon on the mRNA is called the ribosome binding site (RBS). In prokaryotes, a cell conducts transcription and translation simultaneously. This phenomenon makes translation initiation the most important regulator step of protein synthesis in prokaryotes. Therefore, engineering RBS and promoters is a method to regulate enzyme activity and PHA synthesis (Chen et al. 2019a, b). Methods like chromosomal regulation, making libraries, sequence manipulation, and binding strength have been used to study the effect of RBS on PHA synthesis (Li et al. 2016a, b; Oesterle et al. 2017). Even there are softwares to predict the best sequences in order to develop different binding strengths for RBS sequences (Salis et al. 2009; Li et al. 2016a, b). Oligo-linker meditated assembly (OLMA) is a novel semirational method to design and optimize the PHB pathway in *Cupriavidus necator* (Zhang et al. 2015). Implemented PLMA method had led to synthesize high content engineered *E. coli* with up to 92% PHB content (Li et al. 2016a, b).

The promoter is another option to manipulate PHA synthesis. Change or amend promoters can regulate the PHA synthesis process, and also it is a standard method in designing cell factories and optimizing metabolic pathways. There are common inducible promoters for *E. coli*, such as Plac, Ptrp, and PT7. An emerging host for creating a cell factory to produce PHAs is *Halomonas bluephagenesis*, but those

common promoters are not efficient in this strain (Chen et al. 2018). Therefore, novel promoters have been developed to use in *Halomonas bluephagenesis*. For example, by mining the phage genome, a T7-like RNA polymerase-promoter has been developed that elongated the length of *H. bluephagenesis*, and ultrahigh PHB accumulation (92% of CDW) was realized in *Halomonas* TD01 (Zhao et al. 2017). In 2019, Fengjie Zhao and colleagues identified five strong promoters as P4, P6, P9, P16, and P25 with transcriptional level, GFP fluorescence intensity measurements, RNA-seq, and promoter prediction. The three promoters P4, P6, and P16 were separately integrated into upstream of the phaC operon in the genome of *P. mendocina* NK-01, which created the recombinant strains NKU-4C1, NKU-6C1, and NKU-16C1. After deleting the phaZ gene encoding PHA depolymerase, the NKU-phaZ-16C1 strain produced 17–23% wt more medium-chain-length PHAs (Zhao et al. 2019).

9.2.4 CRISPR Technology

CRISPR/Cas9 is a new technology that has been used to increase PHA synthesis in *E. coli* and other microorganisms. In 2019, Jung and colleagues deleted four genes (pflb, ldhA, adhE, and fnr) that blocked some metabolic pathways and unwanted product synthesis. The amalgamation of deleting these four genes and overexpressing pntAB to catalyze NADH and NADAPH's interconversion increased PHA production and cell growth in *E. coli* (Jung et al. 2019). The CRISPRi is a system derived from CRISPR/Cas9 that regulates the gene expression in the genome scale by inhibiting the transcription process. CRISPRi is a powerful tool to study and regulate multigene expression in genome scale. Lv and colleagues used CRISPRi to synthesize PHAs in novel pathways. *E. coli* has sad, sucC, sucD, sdhA, and sdhB genes. Sad encodes semialdehyde dehydrogenase, and four others encode succinyl-CoA synthase and succinate dehydrogenase. By implementing CRISPRi, they expressed a sad gene under regulation by single-guide RNAs (sgRNAs) from the CRISPRi system that led to the synthesis of 4-hydroxybutyrate (4HB). This experiment made P3HB4HB composed of 1–9 mol% 4HB considering sgRNA. Regulated expression of four genes (sucC, sucD, sdhA, and sdhB genes) by CRISPRi system managed to synthesize P3HB4HB composed of 1.4–18.4 mol% considering sgRNA (Lv et al. 2015). Additionally, the CRISPRi system is used to synthesize PHBs. By the regulated expression of phaCAB operon by CRISPRi system, a diversity of phaC enzyme was made that led to PHB content ranged from 1.47 to 75.21% cell dry weight, and molecular weights ranged from 2 to six million Da, with a polydispersity of 1.2–1.43 in 48 h during shake flask culture (Li et al. 2017). In another effort, CRISPR/Cas9 used to delete prpC, encoding 2-methylcitrate synthase, in *H. bluephagenesis* TD01 that increased PHBV synthesis. Also, the prpC gene is involved in PHBS production in *H. bluephagenesis* TD01; by deleting the prpC gene, they managed to synthesize a novel PHBV with more 3 HV percentages that made the former biopolymer better in thermodynamic properties (Qin et al. 2018).

9.3 Bacterial Cellulose (BC)

Present advancement on the production, qualification, and demand for bacterial cellulose enhanced biomass utilization and development of bio-based products which has become a regular model in progression metabolic engineering. Cellulose produced by bacteria is a generator for this feasible evolution. BC properties highly depend on culture conditions and the bacteria that is used to produce BC. Also, the drying method may change the material crystallinity and therefore changes its properties. Extracting impurities with alkaline solution may increase BC mechanical strength. However, extreme alkaline conditions could damage the BC matrix. Air-drying, freeze-drying, and vacuum drying are methods for BC drying. Drying of BC in hot air results in a denser film that follows better mechanical strength and less water and air permeability (Chen et al. 2011; Alange et al. 2017). Cellulose needs to be modified to be a water barrier in high humidity. However, BC is a sound oxygen barrier that can be used in an unmodified form for food packaging (Cazón and Vázquez 2020).

9.4 Pullulan

Pullulan, as an important exopolysaccharide, is a linear glucan which has maltotriose repeating units linked by glycosidic bonds (Chen et al. 2019a, b). Pullulan's distinctive physical features, as well as its elastic properties and ability to form fabrics, compression moldings, and oxygen impermeable films, are attributable to this special linkage pattern (Ma et al. 2015). Owing to the biocompatibility and biosafety of this polysaccharide and its high solubility in water, pullulan is a suitable candidate for food packaging (Sheng et al. 2015). Pullulan is produced extracellularly by *Aureobasidium* spp. This microorganism can produce extracellular polymers such as pullulan, poly malic acid, and water-soluble β-glucan in large amounts (Li et al. 2016a, b; Alemzadeh 2009).

For improving pullulan production via a genetic approach, it is necessary to understand the mechanism of pullulan synthesis. Pullulan biosynthesis is a complex metabolic process. Li et al. proposed a metabolic pathway for pullulan biosynthesis. The enzyme phosphoglucose mutase converted 6-phosphate glucose to 1-phosphate glucose at the start. Next, 1-phosphate glucose and uridine diphosphate (UDP) catalyzed by uridine diphosphate glucose (UDPG) pyrophosphatase and the products of this reaction are UDPG and pyrophosphoric acid (PPi). Cofactors in mentioned reaction include ATP and NADPH (Li et al. 2015). UDPG is a prevalent precursor metabolite for synthesis of polysaccharide in many microorganisms. So, UDPG as starting and elongation unit creates the pullulan polysaccharide chain; the catalyzer of this reaction is glycosyltransferase (Chen et al. 2017). Furthermore, a pullulan synthase participates in pullulan biosynthesis (Li et al. 2016a, b).

There is additional information available about this metabolic process and affecting factors that can enhance or decrease the pullulan production. For instance, Sheng

et al. indicate that uridine phosphorylase and uracil availability are essential in synthesis of this polysaccharide (Sheng et al. 2014).

Knowing signaling pathways and transcriptional regulators in pullulan biosynthesis could be used for its production improvement. In a recent study, the authors found out the expression of genes that were involved in pullulan biosynthesis such as in the nuclei; the transcriptional activator Msn2 regulated UDPG pyrophosphorylase (Ugp1). The Ugp1 enzyme limits the rate of pullulan biosynthesis. Besides, they found out that Msn2 activity and subcellular localization were regulated by a signaling pathway named cAMP-PKA. When the activity of this signaling pathway was low, the expression of UGP1 gene was high, and the pullulan synthesis increased. In contrary, when its activity was high, the transcriptional activator Msn2 was in the cytoplasm, and pullulan synthesis was stopped because the UGP1 gene could not be expressed (Yang et al. 2020).

Genetic manipulation methods have been used for metabolic engineering of various species of *Aureobasidium* spp. aiming to increase the pullulan production. In metabolic engineering, homologous overexpression of metabolic pathway enzymes is a popular technique and can be done by increasing the content or activity of the enzyme. It will alter the metabolite fluxes and, as a result, an increase in final product yield. Li et al. used homologous overexpression of UGPase to increase the pullulan production yield in *A. pullulans* (Li et al. 2016a, b). Since UGPase is a rate-limiting enzyme in synthesis of carbohydrate, it may be a suitable target for metabolic engineering. They have done homologous expression of UGPase from *A. pullulans* NRRL Y-12974 in wild-type organism via integrative plasmid pAPE16 powered by constitutive strong ADH promoter. The selector marker was hygromycin resistance gene. The results showed that in the transformant strain, UGPase function and intracellular UDPG content improved by 3.6 and 4.7 times, respectively, compared to the parent strain. Also, compared to the parent strain, the engineering strain's pullulan yield increased by 1.7 times (Li et al. 2016a, b). In another study, it confirmed again that in the pathway of pullulan synthesis, UPG gene was the most important gene for pullulan production by *A. pullulans* CBS 110374 (Guo et al. 2018a). Furthermore, they overexpressed the genes involved in the putative pullulan biosynthesis pathway including UDP glucose pyrophosphorylase gene, glucosyltransferase gene, and α-phosphoglucose mutase gene, separately in *A. pullulans* CBS 110374. Also, to investigate the effect of the glucosyltransferase gene on pullulan synthesis, it was deleted. To determine the function of the apolipoprotein gene in pullulan production, it was overexpressed or deleted. Overexpression of UDPG pyrophosphorylase and apolipoprotein genes increased the pullulan production by 16.93 and 8.52%, respectively. So, UDP glucose pyrophosphorylase and apolipoprotein genes are pivotal in pullulan biosynthesis. Also, they found out that two glucosyltransferase genes, namely, UGT1 and UGT2, are not the essential genes in pullulan biosynthesis, cause overexpression of them, and cannot increase the production of pullulan (Guo et al. 2018a). Furthermore, according to Wang et al., disrupting the CREA gene, which encodes a glucose repressor, will boost pullulan output (Wang et al. 2017a, b).

Substrates of pullulan production are limited to glucose, sucrose, agricultural wastes, and hydrolysate of inulin, since its producing microorganism, *Aureobasidium* spp., cannot produce an enough amount of amylase, inulinase, and cellulase (Prajapati et al. 2013). As a result, the substrate range for pullulan production should be widened by manipulating the producer microorganism by metabolic engineering. Fructose and glucose are known as proper substrates for *Aureobasidium* spp. to produce pullulan (Li et al. 2015). A variety of microorganisms produce exo-inulinase which turns inulin into major fructose and minor glucose by cutting the nonreducing end of this molecule's terminal fructose residues (Duan et al. 2008). Inulinase activity produced by *Aureobasidium* spp. is very low. So to use inulin as pullulan production substrate, the INU1 gene of *Kluyveromyces maximum* was inserted and expressed in *Aureobasidium melanogenum* P16. The inulinase enzyme activity which is produced by genetically manipulated *A. melanogenum* was 40.92 U/mL, while the wild-type strain yield was 7.57 U/mL. Subsequently, in a 10 liter fermenter, 70.57 g/L of pullulan was obtained from inulin (138.0 g/L) after 108 h. Also, cell growth of the transgenic strain carrying the heterologous gene was promoted (Ma et al. 2015).

The ability to ferment xylose is needed for using lignocellulosic materials for the production of high value-added products. Nevertheless, *Aureobasidium pullulan* xylose consumption capacity is low (Zou et al. 2016). The yeast *Spathaspora passalidarum* can efficiently utilize xylose, and this microorganism encodes two XR and two XDH (Yu et al. 2017). In a study, by heterologous expression, two pathways were built and compared in *A. pullulans*, namely, *S. passalidarum* XR-XDH and *Piromyces* sp. XI. The results demonstrated that the creation of *Piromyces* sp. XI pathway cannot increase the xylose fermentation. But, opposed to the wild strain, recombinant *A. pullulans* with overexpressed XYL1.2 and XYL2.2 processed a considerable amount of xylose and produced 97.72% more pullulan (Guo et al. 2018b).

Researches indicated that polysaccharides with higher average *M*w and narrow molecular weight distribution have better biocompatibility. Thus, pullulan with a high *Mw* has a better performance and a larger range of applications (Liu et al. 2017). *Mw* of pullulan produced by *A. melanogenum* is affected by enzymes such as α-amylase, glucoamylase, and isopullulanase (Liu et al. 2018). Metabolic engineering is being used in some researches to enhance the *Mw* of pullulan. For instance, *A. melanogenum* TN3–1 is a strain of *A. melanogenum* that was isolated from honey producing pullulan with 1.6×10^5 g/mol *Mw*. It was edited using the Cre/loxp site-specific recombination system, which included the continuous deletion of multiple genes in the genome to enhance the *Mw* of the derived pullulan, allowing it to be used in food packaging. The AMY-PKS-11 mutant was produced by deleting both duplicated AMY1 genes encoding α-amylase and duplicated PKS1 genes at the same time. It could turn 140.0 g/L of glucose to 103.50 g/L of pullulan with *Mw* of 3.2×10^5 g/mol (Chen et al. 2019a, b).

Another study demonstrated that the molecular weight of pullulan is affected by GTF genes. So, increasing transcription and expression of GTF genes may lead to the production of high molecular weight pullulan (An et al. 2019) (Table 9.3).

Table 9.3 Summary of researches aiming to improve pullulan production via genetic manipulation

Microorganism	Manipulation	Improvement	Reference
Aureobasidium pullulans	Homologous expression of UGPase	1.7-fold times increase in pullulan yield on glucose	Li et al. (2016a, b)
	Overexpression of genes encoding apolipoprotein and UDPG pyrophosphorylase	8.52 and 16.93% pullulan production increasement, respectively	Guo et al. (2018a)
	Overexpression of *XYL1.2* and *XYL2.2* (with the aim of xylose-consuming capacity)	97.72% increasement in pullulan production	Guo et al. (2018b)
Aureobasidium melanogenum	Expression of INU1 gene from *Kluyveromyces maximum* in wild strain (with the aim of using inulin as substrate)	70 g/L pullulan produced with inulin (138.0 g/L) as substrate in 108 h in 10-L fermenter	Ma et al. (2015)
	Both duplicated AMY1 genes encoding α-amylase and duplicated PKS1 genes were removed at the same time (with the aim of production of colorless high mw pullulan)	103 g/L pigment-free pullulan from 140.0 g/L glucose with a mw of 3.2×10^5 g/Mol	Chen et al. (2019a, b)

9.5 Xanthan

Xanthan is a neutral, water-soluble exopolysaccharide that contains pentameric repeating units with the β-1,4-linked D-glucose backbone and trisaccharide side chains made up of mannose-(β-1,4)-glucuronic acid-(β-1,2)-mannose attached to alternate glucose residues in the backbone by α-1,3 linkages (Jansson et al. 1975). Xanthan was the second microbial polysaccharide after dextran that was used commercially (Elella et al. 2020).

Due to its serious pseudoplastic behavior and rheological features, xanthan gum is suitable for film-forming and subsequently a good microbial polysaccharide for food packaging (Raschip et al. 2020). For instance, a xanthan-based packaging was produced for the preservation of fish and meat. This packaging showed a good reduction in oxygen access to these foods, and it could inhibit the growth of aerobic microorganisms which led to extending the shelf life. Also, under this coating, myoglobin maintained its native state, so the meat had a richer color (Giro et al. 2020).

Xanthan is produced through aerobic fermentation by various *Xanthomonas* strains such as *Xanthomonas pelargonii*, *Xanthomonas campestris*, etc. (Elella et al. 2020). The metabolic reconstruction of xanthan pathway in *Xanthomonas phaseoli* pv. *manihotis* showed that *gum* cluster genes of this microorganism, composed of 12 genes (gumB–gumM), are essential for the last steps of xanthan biosynthesis (Botero et al. 2020; Galván et al. 2013). In a study, the effects of overexpression of gumB and gumC gene in *Xanthomonas campestris* on the

production, composition, and viscosity of produced xanthan were investigated. The results showed that overexpression of GumB, GumC, or both genes simultaneously did not alter the amount or the chemical composition of produced xanthan. Although by increasing the GumC protein levels fivefold, the xanthan viscosity slightly increased, GumB overexpression did not change xanthan viscosity. Co-overexpression of GumB and GumC resulted in higher xanthan viscosity than individual gene overexpression. Furthermore, the atomic force microscopy results demonstrated that in the co-overexpression case, longer polymer chain was achieved compared to xanthan produced by parent strain. The authors suggest that GumB–GumC protein levels regulate xanthan chain length, which alters polymer viscosity (Galván et al. 2013).

Some researches illustrated that there is a strong connection between the xanthan production pathways and the carbohydrate utilization pathways, through the branched reactions catalyzed by phosphoglucomutase, mannose-6-phosphate isomerase, and 1-deoxy-D-xylulose 5-phosphate synthase (Botero et al. 2020). In a research, the role of the central carbon catabolism in xanthan biosynthesis was investigated by inactivation of the gene in pentose phosphate pathway named glucose 6-phosphate dehydrogenase gene and the expression of the *pfkA* gene in glycolytic pathway of *Xanthomonas oryzae*. The results showed that glucose 6-phosphate was increased in the mutant strain with gene disruption along with production of xanthan compared to the wild type. Results of this work illustrate that enhancing xanthan biosynthesis requires focusing on the core carbon metabolism (Jang et al. 2012).

Xanthomonadins, a water-insoluble yellow pigments, are by-products of xanthan production via *Xanthomonas*. So, produced xanthan include xanthomonadins as pigment impurities, which require a purification process and increase the overall production cost of this polysaccharide. The xanthomonadins dissolve in organic reagents, and to precipitate the xanthan gum, ethanol is commonly used (Zhang and Chen 2010). To reduce the amount of ethanol for the purification process and subsequently the total cost of xanthan processing, *Xanthomonas* sp. has been genetically modified. The Vitreoscilla globin (vgb) gene was inserted into the pigA gene, which is responsible for xanthomonadin synthesis, under the control of the LacZ promoter. The engineered strain required less ethanol for purification processing, according to the findings (Dai et al. 2019) (Table 9.4).

9.6 Conclusion and Future Perspectives

Biopolymers (microbial) as food packaging materials have been wildly used in developed countries. Although biopolymers have many advantages, some drawbacks prevent using biopolymer further for food packaging. Producing synthetic polymers is more feasible than biopolymers, and also most of the biopolymers show more limited performance. Cellulose-based biopolymers have the broadest commercial applications. However, other biopolymers are not ordinarily used for packaging foods. Researchers have been investigated new methods for producing

Table 9.4 Recent developed xanthan-based films for food packaging

Biopolymers	Test for food packaging	Description	Reference
Xanthan Gellan	–	Good thermal and water barrier properties Environment friendly packaging	Rukmanikrishnan et al. (2020)
Xanthan coatingon poly lactic acid film	Precooked sliced Turkey breast	Over 30 days in anaerobic packaging at 4 or 10 °C, *salmonella* sp. and *L. monocytogenes* growth is reduced.	Radford et al. (2017)
k-carrageenan xanthan gellan	–	The transparent films with soft texture, good elasticity, and excellent break strength	Balasubramanian et al. (2019)
Chitosan xanthan	–	Highest tensile strength in high content of xanthan	Balasubramanian et al. (2019)
Xanthan curdlan	–	– Highest tensile strength in the same rational of polymers – Excellent mechanical and moisture barrier properties	Mohsin et al. (2020)
Xanthan	Fresh meat and fish	– Lower mass loss – Extend shelf life due to lower microbial contamination – Low cost and environment friendly	Giro et al. (2020)

and modifying other biopolymers, and it is anticipated that biopolymers' production increases rapidly in the near future. Considering that biopolymers are produced from renewable resources and can be recycled easily, some governments are supporting the use of biopolymers more. Biopolymer production will become more economical, and with more suitable properties, biopolymers will be used in food packaging more widely.

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Downstream Processing Strategies for Synthesis of Biodegradable Polymers

10

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Abstract

Biodegradable materials are used as an alternative for conventional plastics in consumer goods and medical applications. Since these materials have high production costs, their overall market share is still marginal. Due to having high energy request and significant demands in oil-derived solvents and chemicals, downstream processing is one of the bottlenecks in the biopolymer value chain. So careful study thorough of the environmental function of biopolymer recovery processes to improve their applicability is so important. In this study, deserving insights on biopolymer downstream processing environmental hotspots and to the way of their optimization accordingly will be prepared. Moreover, downstream alternative processes for high-grade and low-grade purifications from a techno-economic and an environmental perspective, possibilities of scale-up and challenges were evaluated.

Since large amounts of energy for solvent recovery are needed in methods relying on solvent extraction, to reach higher efficiency in impurity removal compared to the mechanical disruption or chemical digestion needs more costs and impacts in all classifications. For having higher quality, solvent extraction is used. Moreover, solvents can be reasonably obtained from an integrated biorefinery. Optimization of chemical digestion is able to be reached by adding

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a chemical recovery unit. It seems that the most promising technology is mechanical disruption in terms of environmental performance.

Keywords

Biodegradable polymer · Downstream processing · Biopolymer recovery · Separation · Purification

10.1 Introduction

10.1.1 Biodegradable Polymer

In the field of packaging, different types of biodegradable polymers, natural and synthetic, are used (Ghanbarzadeh 2013). Polymers are categorized as synthetic, natural, and modified natural polymers depending on their origin (Khosravi-Darani and Bucci 2015). The classification of polymers from the environmental perspective, based on the origin of raw materials, is from two types of sources, renewable (i.e., of biological origin) and nonrenewable/fossil (i.e., coal, natural gas, and oil) (Rydz et al. 2015) (Fig. 10.1). In this study, the properties and potential applications of

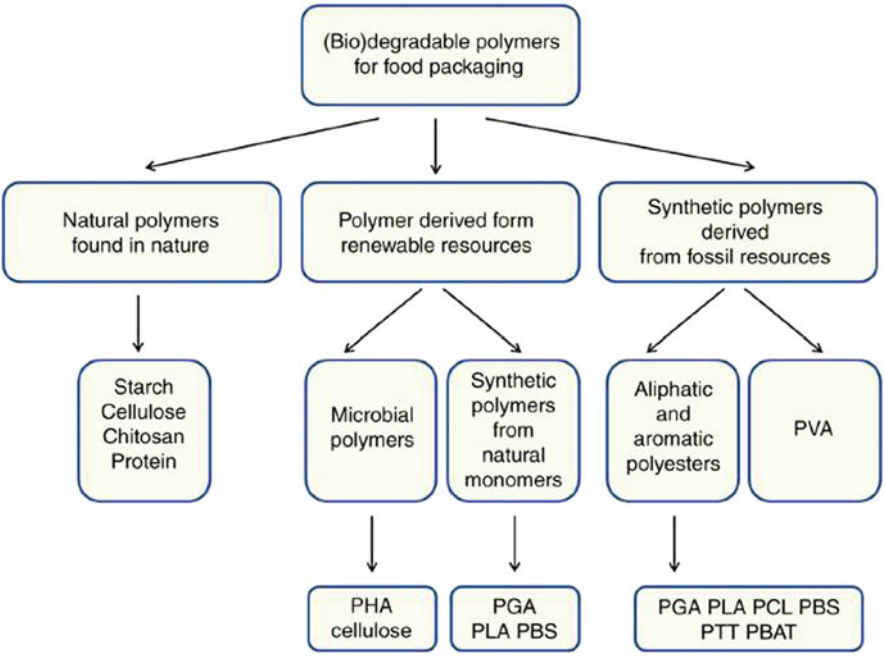

Fig. 10.1 Classification of biodegradable polymers for food packaging application (Rydz et al. 2015)

main biodegradable natural, microbial, and synthetic polymers in the field of food packaging have been focused.

Biodegradable materials have promising characteristics in some fields such as packaging and the medical sector. One of the important characteristics of thermoplastic biodegradable polymers, like polyhydroxyalkanoates (PHAs), polycaprolactones (PCL), and poly(lactic acid) (PLA), which are arisen from renewable resources, is having the ability to be processed with conventional plastic machinery (Khosravi-Darani and Bucci 2015).

10.1.2 Biodegradable Polymer Application

PHAs have different applications in disposal usage, packaging, and medical application. Among the uses of PHBV (poly(3-hydroxybutyrate-co23-hydroxyvalerate)), it can be mentioned in blow molded bottles, packaging of films, paper coating, and also medical applications (reconstructive surgery potential) which is resulted from its slow hydrolytic degradation and biocompatibility. Mcl-PHAs are used in, for example, making scaffolds for the regeneration of nerve axons and arteries which are coatings and medical temporary implants. Additionally, amphiphilic PHA copolymers are applicable in tissue engineering, drug delivery, and cardiovascular area, like implants, artery augments, pericardial patches, cardiologic stents, microparticulate carriers, vascular grafts, heart valves, and dressing tablets. Since PHB is degradable to HB that exists in human blood in high concentration, it is nontoxic and useable for implanting in mammalian organs. PHBV is the only structural polymer or part of degradable composites which has effective application for disposable personal hygiene. Because of comparable properties of PHAs to petrochemical polymers, they can be used in composite material instead of them. Regarding to the previous information, some properties of PHA-based films such as water vapor barrier properties, renewability, and biodegradability have led to their use for food packaging application due to its. PHB are better light barrier in the visible and ultraviolet light regions than PLA. In spite of having comparable characteristics of PHB with synthetic thermoplastics, there is a limitation in widespread usage because of cost drawbacks and narrow melt processing window due to brittleness and low thermal stability in the molten state. This polymer has low thermal stability during processing, which leads to a reduction of the molar mass and viscosity. Almost 40% of the total operating cost is related to the cost of the carbon source. PHB can be made by using different unexpensive carbon sources. Since PHAs have poor mechanical properties, their application is that they are used as copolymer instead of the homopolymer in the world (Tripathi et al. 2021). Degradation conditions and biodegradability rates of biopolymers are shown in Table 10.1 (Rai et al. 2021).

Table 10.1 Degradation conditions and biodegradability rates of biopolymers

Bioplastic		Degradation conditions	Biodegradability	
			(%)	Days
PLA based	PLA/PHB (75–25%)	Synthetic material containing compost, 58 °C	100	35
PHA and PHB based	PHB	Soil	64.3	180
	PHB	Soil	98	300
	PHA	Soil 35 °C	35	60
	PHA	Soil/compost (90/10%), 25 °C, 65% humidity	40–50	15
	PHA	Soil, 60% moisture, 20 °C	48.5	280
	PHA/Rice husk (60/40%)	Soil, 35 °C	>90	60
	PHB	Microbial culture from soil	~18	18
	PHBV	Microbial culture from soil	~41	18
	PHB	Compost, 58 °C	79.9	110
	PHB	Compost, 70% moisture, 55 °C	~80	28
	PHB	Sea water, 25 °C	80	14
	PHB	Sea water, Static incubation, 21 °C	99	49
	PHB	Sea water Dynamic incubation 12–22 °C, pH 7.9–8.1	30	90
	PHBV	Sea water Static incubation, 21 °C	99	49
	PHB	River water Real conditions ~20 °C	43.5	42
	PHB	Brackish water sediment, 32 °C, pH 7.06	100	56
	PHB	Marine water, 28.75 °C (average temperature, pH 7–7. 5)	58	160
	PHB/CAB (50/50%)	Soil	31.5	180
PA based	Nylon 4 (polyamides, bio-based)	Sea water, 25 °C	80/30	25/21
	Nylon 4 (polyamides, bio-based)	Composted soil, 25 °C, 80% humidity, pH 7.5–7.6	100	120
PBS based	PBS	Compost, aerobic, pH 7–8, 58–65 °C	90	160

10.1.3 Future of Biopolymer

Nowadays, most of plastics are made of fossil fuels, like natural gas and coal and also crude oil. As it is obvious, their persistence in the environment is so high, and hence, their end-life is unpredictable. Based on the statistics, plastic production capacity in the world of plastic in 2013 was increased compared to 2012 and 2010; it was 3.9% and 9.7%, respectively. Although, to elevate the effectiveness and efficiency of bio-based plastics, several decades of research and development have been done, they are still produced in small amount compared to the conventional ones. Despite tripling production capacity between 2013 and 2020, bio-based polymers have dedicated to themselves only 2% and 4% of the total polymer production in 2013 and 2020, respectively. According to the observations, biodegradable polyesters, like PHA and PLA, had the fastest rates of market growth among bio-based polymers.

10.1.4 Life Cycle Assessment of Biopolymer

The effect of product's environmental or process on the design and operational phase is determined by a systematic and standard method that is known as life cycle assessment (LCA). LCA has four steps, as the following:

(i) Description of the goal and scope of the considered application and the system, its function and the related functional unit, system boundaries, selection assortment effect, and the impact of evaluation method.
(ii) In this phase, the inventory analysis includes determination of relevant inputs and outputs of a product system by data collection and calculation procedures.
(iii) The evaluation of inventory results leads to potential environmental impacts.
(iv) Critical review, data sensitivity determination, and result presentation are done in the interpretation phase.

Life cycle costing (LCC) is one base of the full life cycle sustainability evaluation. Moreover, it is an economic assessment aligned with LCA in terms of system boundaries, functional unit, and methodological steps. Capital and operational costs are two parts of general costs. By using correlations based on individual equipment's characteristic size, the delivered equipment costs were estimated, so that the total capital investment was estimated with the help of a Lang factor of 5.03, a characteristic from a solid-fluid processing plant, and a 2019 CEPCI (Chemical Engineering Plant Cost Index) of 607.5 (Pérez-Rivero et al. 2019). With the detection of the LCAs which is lacking, which evaluate only the biopolymer downstream processing, in selected LCA studies on biopolymer production, the useful information is able to be collected.

In present decade, studies have focused more on different processes of configuration assessment like production of PHA using mixed cultures, PHA production comparison from various feedstocks, and assessment of more effective categories or

downstream processing as a specific bioplastic value chain phase. Most research in the period 2000–2010 had focused on assessments, the comparison of the feasibility of biopolymer production and oil-based plastics, etc. (Saavedra del Oso et al. 2020).

10.1.5 Downstream Technologies for Biopolymer Extraction

Biopolymers like PHAs have the ability to accumulate microbial cells inside, and in order for them to recover, non-PHA cell biomass separation is needed. PHA downstream process has an essential role in material quality and production cost. At first, PHA production and biomass separation from the broth were done. Then, cell biomass was further exposed to PHA extraction by some techniques, such as sedimentation, centrifugation, and flocculation. They are various factors that should be considered before a PHA extraction and way of selection like microbial strain, type of PHA, loading PHA in biomass, effect on PHA properties, and PHA application (Koller et al. 2013).

Biomass drying is the prerequisite pretreatment step; major ways of extraction process are thermal treatment, lyophilization, and microwave-assisted drying. In Akdogan et al.'s study, different drying methods for PHA extraction from *B. megaterium* were compared. According to their results, due to energy efficiency and processing time, microwave-assisted drying method was more desirable (Akdoğan and Çelik 2018).

There are different mechanical methods such as homogenization in high-pressure, ultrasonic digestion, bead mills, and chemical methods for cell disintegration. In order to extract PHA (polyhydroxyalkanoate), various techniques exist like digestion by sodium hypochlorite, halogenated solvents, SDS (sodium dodecyl sulfate), and enzymatic digestion. Solvent extraction is a method to increase product recovery, limit polymer degradation, and remove endotoxin (Akdoğan and Çelik 2018).

Chloroform, dichloromethane, and polychlorinated ethane are halogenated solvents for PHASCL and PHAMCL solubility and extraction which surpass non-PHA cell biomass. After PHA extraction, some solvents like ether, hexane, acetone, methanol, and ethanol were used for PHA recovery or precipitation. After PHA extraction, the solvent mixture that is hard to manage remains. Using distillation as a reutilization process is costly, if it is disposed of in the open; also, they have high environmental and health risks. Additionally, nonhalogenated solvents like n-methylpyrrolidone, ethanol, acetic acid, acetone, and tetrahydrofuran can be used to extract PHA. PHA is solvable at low temperature up to 2% w/v in ethanol and acetone. In a study, various solvents (acetone, ethanol, acetyl acetate, and butyl acetate) at a higher temperature for PHA recovery from *C. necator* were investigated. It was demonstrated that using butyl acetate leads to 96% recovery and 99% purity which is applicable in extraction at 103 °C in 30 min incubation time (Aramvash et al. 2015).

According to the studies, using dimethyl carbonate to extract PHA is associated with more than 85% PHA recovery with more than 95% purity (Samorì et al. 2015). Additionally, to extract PHA from biomass of *C. necator* in dry and wet states, a

mixture including acetone/ethanol/propylene carbonate (A/E/P, 1:1:1 v/v/v) was used. The recovery and purity were reported 85% and 92% from dry biomass and 83% and 90% from wet biomass, respectively (Fei et al. 2016).

Since supercritical fluids are easily evaporated without any additional drying steps and have certain hydrophobicity, they are supposed to be suitable solvents to extract compounds. CO_2 as a widely explored supercritical fluid has several advantages such as low toxicity, low cost, moderate critical temperature and pressure, and nonflammability. In another study, optimized condition using supercritical CO_2 (sCO_2) for PHA extraction from *R. eutropha* with 89% recovery was obtained as follows: exposure time 100 min, pressure 200 atm, and temperature 40 °C (Hejazi et al. 2003). Digestion and solubilization of non-PHA are one of the PHA extraction methods, that is, leaving PHA as insoluble solid. When several chemicals, such as polyhydroxyalkanoates (PHAs), sodium hydroxide, sulfuric acid, and potassium hydroxide, are used, they accumulate inside the microbial cells; so non-PHA cell biomass separation is needed for recovery. Process related to PHA downstream has an important role in material quality and cost of production. In order to have more PHA extraction of recovered cell biomass, some techniques like sedimentation, centrifugation, and flocculation were used after PHA production and separation of biomass.

There are various parameters that should be considered before choosing a method for PHA extraction, including type of PHA, microbial strain, application of PHA, impact on PHA properties, and PHA load in biomass (Koller et al. 2013). Before extraction process, drying of biomass with some methods such as thermal treatment, lyophilization, and microwave-assisted drying is a vital step. With comparison of various drying methods for PHA extraction from *B. megaterium*, microwave-assisted drying method is more desirable in energy efficiency and processing time terms which is reported by Akdogan et al. (Akdoğan and Çelik 2018).

Different chemical and mechanical methods like ultrasonic digestion, high-pressure homogenization, and bead mills have been mentioned for cell disintegration. Based on the studies, there are various techniques to extract PHA, such as SDS, halogenated solvents, enzymatic digestion, and digestion by sodium hypochlorite, so that using solvent extraction has limited degradation of the polymer, high product recovery, and removal of endotoxin (Akdoğan and Çelik 2018). For extraction and solubility of PHASCL and PHAMCL, some halogenated solvents like dichloromethane, chloroform, and polychlorinated ethane have been demonstrated for leaving behind non-PHA cell biomass. Ethanol, hexane, methanol, ether, and acetone are solvents that are used in the precipitation or PHA recovery after PHA extraction. If remained solvents after PHA extraction are disposed in the open, it is hard to manage high environmental and health risks, and its reutilization by distillation is a costly process. Acetic acid, ethanol, tetrahydrofuran, n-methylpyrrolidone, and acetone are nonhalogenated solvents which are used for PHA extraction. Acetone and ethanol can dissolve PHA up to 2% w/v at low temperature. Different solvents, including acetone, ethanol, acetyl acetate, and butyl acetate, are used at a higher temperature for PHA recovery from *C. necator* and have 96% for recovery and 99% for purity with butyl acetate-assisted extraction at 103 °C in 30 min incubation time (Aramvash et al. 2015).

In order to have cell biomass disintegration, some chemicals such as sodium hypochlorite, sulfuric acid, potassium hydroxide, sodium dodecyl sulfate, and sodium hydroxide can be used (Burniol-Figols et al. 2020). Sodium hypochlorite as an oxidizing agent has the ability to oxidize cell components and makes them water soluble and PHA release. At first, hypochlorite lyses cell, and then disintegrated cell was pelleted by centrifugation and washed with a solvent of various polarities (acetone, water, or ethanol). After that, polymer pellet was dissolved in chloroform and used for PHA film preparation (Saratale and Oh 2015).

In another study, enzymatic methods were used for PHA extraction under mild conditions that was energy efficient. Neves et al. used various commercial enzymes to extract PHA from *C. necator* and explained that enzyme Celumax R FC has better membrane hydrolysis at temperature 60 °C and pH 4 with 93.2% PHA recovery and 95% purity (Neves and Müller 2012). According to Kosseva et al.'s study, with investigation of the downstream processing process of PHA from different feedstocks, the cost of treatment with NaOH was obtained as 1.72 $ for P(3HB) from wastewater-VFA enriched, 4.1–6.8 $ for P(3HB) from methane, 1.65 $ for PHA from switchgrass, and 1.56 $ for PHA from crude glycerol (Kosseva and Rusbandi 2018). Despite many reports on the PHA extraction process at the lab scale, working on the development of a process is required that is more efficient and cost-effective at the industrial scale. There are conventional steps in the biopolymer downstream processing that are shown in Fig. 10.2 with most usual methods for each step (Saavedra del Oso et al. 2020).

Based on Fig. 10.3, methods relying on solvent extraction (blue and black ones) need large amounts of energy to recover solvent. Using a solvent instead of mechanical disruption or chemical digestion has many benefits, including as follows: it is outweighed in both all impact categories and costs. Therefore, solvent extraction is only recommended where a higher quality is required (Valentino et al. 2017). Employing more easily recoverable solvents leads to optimization of both economic and environmental performances of these processes. It seems that mechanical disruption (green one) is a priori the preferable method for downstream processing from an environmental and economic perspective 0.26 €·kg^{-1} PHA versus 0.77 €·kg^{-1} PHA, mainly because lower amounts of chemicals and surfactants were needed than in processes which employ only chemical digestion (red one).

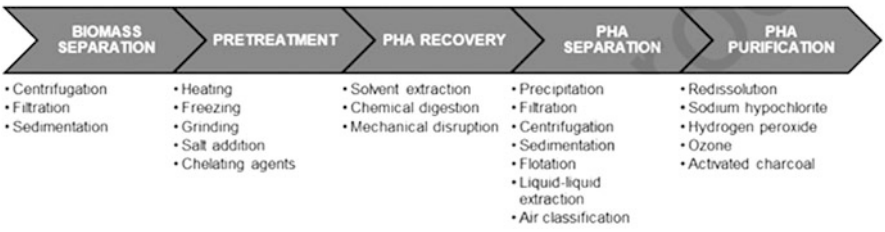

Fig. 10.2 Conventional steps in the PHA downstream processing and most common methods for each step

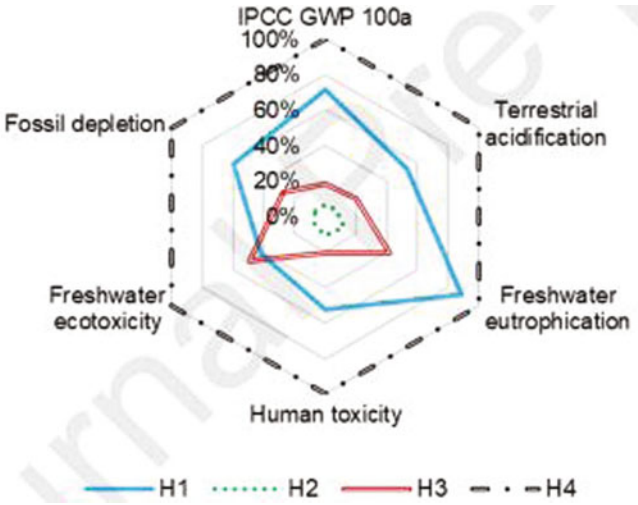

Fig. 10.3 Comparative of characterization of high-grade PHA processes (Saavedra del Oso et al. 2020)

10.1.6 Conclusion

The downstream process has complexity and adding cost, so different strategies can be used for making the downstream process easy. Cells with small size cause more complexity in the downstream process; thus in order to change cell size and shape, cell engineering makes simplicity in the downstream process. The effect of using large-sized cells is accumulating and incretion in biopolymer amount (40–80%) and also promoting gravity separation of cells from broth. Aggregation and formation of compact cell flocs are the ability of cells that is called bio-flocculation and can help biomass in culture recovery. In order to downstream cost reduction, for self-flocculation, engineered *Halomonas campaniensis* strain LS21 was used by deleting etf operon encoding two subunits of electron transferring flavoprotein, and cells were able to sediment at the fermenter bottom within 1 min after stopping agitation. To decrease the downstream cost and remove the requirement of cell disruption, biopolymer extracellular secretion is practical. Some researchers fused PhaP which is a PHA granule binding protein, with HylA signal peptide. Then, its expression in PHA producing *E. coli* resulted in secretion of 36% of total PHA in culture medium was studied. For having the biopolymer production more economic and replacing a reality in synthetic plastic at a commercial scale, mentioned strategies should be further explored. A microbial system is able to convert biowaste into bioplastic. However, there are some problems such as pretreatment requirements, the difficulty in handling of waste, transportation, and unavailability of effective and affordable conversion technologies in comparison with petro-based synthetic plastic to produce bioplastic from waste at an industrial scale. Based on the studies, work on the new microbes' exploration should be paid attention, as well as

existing biopolymer accumulating microbe engineering for a wide range of using carbon sources and copolymer accumulation without the costly precursors' addition. Additionally, since almost 50% of the cost belongs to the downstream process, the downstream process improvement is required.

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Functionality Test Methods for Biodegradable Polymers

11

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Abstract

Petroleum-based materials are being used for packaging of the food products for a long time. However, their resistance to biodegradation has a harmful impact on the environment, and therefore, the trend is shifting towards the use of biodegradable polymers. Besides their ability to degrade naturally, it is also important that they possess similar quality like conventional plastic-based packaging in terms of its stability towards light, oxygen, water and strength which are recognized by ISO (International Organization for Standardization), OECD and ASTM (American Society for Testing Materials) so as to promote usage at commercial level. It is essential to understand the properties of the film not only to check for the biodegradability but also for their application in long-term packaging, protection of the contained product from environmental obstacles and transportation and properties of food itself. Besides, the use of active packaging involves incorporation of certain bioactive agent which add to the functionality of the packaging material. There are various methods that are used to test the properties of the polymer. In this chapter, an overview of different methods to test for the functionality of the polymers will be discussed, in consideration to their degradation, strength and barrier properties against various environmental factor. In addition to this, international standards for biodegradation test for the material and for sample preparation are also described.

Keywords

Biodegradability · Test methods · Biopolymers · International standards

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11.1 Introduction

As the methods are being developed to enhance the shelf life and preserving the nutrients of the food, its packaging is also an essential part to be considered. Packaging of the food helps in creating a barrier that can add to the stability of the product and reduce the rate of deterioration of the product. However, most of the packaging materials are plastic which constitutes about 47% among all. In addition to this, more than 70% of the plastic packaging is in the food and drinks market (ALL4PACK, 2016). This also indicates an increase in waste and harm to the environment. The deteriorative impact of synthetic polymers on the environment is one of the reasons to switch to bio-based polymers. However, it is also essential that the alternative to plastic is also efficient like it. The use of nanofillers such as clay and metal oxides in biopolymers are found to be beneficial in improving the quality and functional properties of the packaging material (Othman, 2014; Jamróz et al., 2019). They are also being used in a diverse range of food products including fruits, vegetables and dairy and meat products (Youssef et al., 2015; Mathew et al., 2019; Xu et al., 2018; Donglu et al., 2016). Edible packaging is also in trend which also forms a part of active packaging (AP). Active packaging is the technique in which packaging material is incorporated with certain agents that can exhibit properties like anti-oxidative and antimicrobial and thus ensures the safety of the food (Zanetti et al., 2018; Li et al., 2018; Yousuf et al., 2018).

While designing a polymer, certain properties are required to be considered for both their long-term and commercial uses. Some of those properties include light weight but high strength of the polymer, lack of conductivity, resistance to corrosion, environmental stress and low manufacturing cost (Brinson & Brinson, 2015). In addition to this, the use of biopolymers has also proved to be beneficial in improving the engineering properties of the soil. It was in 1971, when a research by Aspiras et al. (1971) was conducted where aggregation of soil particles was observed by the biopolymers. After that, a lot of research has been done to know the consequence of biological activity on the properties of the soil. Moreover, the soil permeability has been shown to reduce with the use of environmentally safe biopolymers, and therefore, their application in cementing material is also under focus (Ivanov and Chu, 2008; Blauw et al. 2009).

The need is the same performance of biopolymers in every aspect to plastic packaging materials. Therefore, their properties are tested for different parameters like water permeability, gas transmission rate, strength and biodegradability. There are various methods that have been developed to check for each of these parameters depending upon the environment conditions, raw material for packaging, intended use of the product and more. But there are certain standard methods which have been developed by organizations like the American Society for Testing Materials (ASTM) and International Organization for Standardization (ISO) which are discussed further in the chapter.

In this book chapter, various methods for testing the properties of the biopolymer have been discussed. Since the prime objective of development of biopolymers is

their biodegradability, therefore, it is more focused. The standard methods provided by international organizations have also been presented.

11.2 Mechanical Properties of Biopolymers

The mechanical properties of a polymer are determined by both its composition and certain factors such as pressure, temperature and strain rate (Siviour & Jordan, 2016). The mechanical properties of the film involve testing for the tensile strength, elongation at break and elastic modulus. The testing is done using a Testometric machine, following the procedure and standards in agreement with the standard method ASTM D882 (2009). Before testing, the film is formed into strips of size 110 × 20 mm and then conditioned for 48 h in a chamber (desiccator) maintained at 23 °C and 53% relative humidity (RH). The desiccator contains a saturated solution of $Mg(NO_3)_2$. After 48 h, the film is mounted between tensile grips and grip separation to be performed at 50 mm. The speed of the mechanical crosshead should be set at 5 mm/min. The films should be analysed in at least five replicates. The force should be applied till the film gets fractured (Hosseini et al., 2016; Mohajer et al., 2017; Sheikhi et al., 2020). Following formulae are used to estimate the value of mechanical strength of the film (Alizadeh-Sani et al., 2018).

$$\text{Tensile strength} = \frac{\text{Load at Break}}{\text{Original width} \times \text{Original thickness}} \tag{11.1}$$

$$\text{Elongation at break}\% = \frac{\text{Elongation at rupture}}{\text{Initial gauge length}} \times 100 \tag{11.2}$$

11.2.1 Stress-Strain Properties

The stress-strain properties are also used to measure and analyse the strength of the material. There are various methods to determine the strain such as using the electrical strain gages. In this method, the gages are attached to the sample with the help of an adhesive and then with the application of load; the deformation and thereby the change in the resistance of the film are monitored. However, these electrical resistance gages are poor conductors of heat and therefore can cause error in measuring the strain due to the softening of the material due to the heat. This problem can be counteracted with the use of thick films (Brinson and Brinson, 2015).

Besides, as it is challenging to predict the long-term behaviour of the polymer due to the time restrictions, a master curve can be plotted using the time-temperature superposition principle (TTSP). With this, one can determine the data for about 50 years by studying the properties of the polymer for a few hours under different temperature conditions (Tao et al., 2018; Pohl et al., 2016). Also, the mechanical

behaviour of the polymer changes according to the time and strain rate, that is, from elastic rubbery response to brittleness (Brown et al., 2006; Rae and Brown 2005; Rae and Dattelbaum, 2004).

11.3 Water Resistance

The water resistance of a film is determined by measuring various properties of the film such as its solubility in water, moisture absorption and permeability to water vapour. Exposure to water can increase the chance of spoilage of the product; therefore, the barrier against water is an important property of the packaging material. Some of the methods to evaluate the water resistance are discussed below.

11.3.1 Water Solubility

It measures the amount of dry soluble content of the film after getting immersed in water. The process includes drying of the sample (approx. 0.0001 *g*) in the oven at 110 °C for 24 h. This is followed by its weighing to determine the initial dry weight and then immersion in distilled water for 24 h at 25 °C. Afterwards, that film is filtered and dried for 24 h at 110 °C (Gontard et al., 1994; Mohajer et al., 2017; Alizadeh-Sani et al., 2018; Sheikhi et al., 2020). The water solubility percentage can be calculated using

$$\text{Water solubility } (\%) = \frac{\text{Initial dry weight} - \text{Final dry weight}}{\text{Initial dry weight}} \times 100 \qquad (11.3)$$

11.3.2 Water Vapour Permeability

In order to determine the water vapour permeability, the following method suggested by ASTM E96 is used. For the process, it is necessary to create a relative humidity of 100% inside the film. To achieve this, the film is sealed in a permeation cup (diameter 20 mm and depth 45 mm) filled with distilled water which is then placed inside a desiccator which contains silica gel at 20 °C. The cups are then needed to be weighed for 48 h at a period of 3 h. Calculation can be done using the following formula:

$$\text{Water Vapour Permeability} = \frac{c \times x}{A \times \Delta P} \qquad (11.4)$$

where C = transmission rate of water vapour (gram/second); X = thickness of the sample film in millimetres; A = area of the film (mm^2); ΔP = difference in the water vapour pressure across the film (Pascal).

11.3.3 Moisture Absorption

Another method to study for the water resistance property is to determine the moisture absorption by the film. For this, a film with dimension 20 × 20 mm was taken and dried. It was then kept under conditions with relative humidity of 0%. The film was weighed after 24 h. It was then transferred to a desiccator which contains saturated calcium nitrate to increase the relative humidity level to 55%. Weighing of the sample was done at frequent intervals till constant reading is obtained (final weight) (Alizadeh-Sani et al., 2018):

$$\text{Moisture absorption } (\%) = \frac{W_i - W_f}{W_i} \times 100 \tag{11.5}$$

where: W_i = sample's initial weight; W_f = sample's final weight (at 55% RH).

11.4 Thermal Stability

To ensure food safety and longer shelf life, various methods are being developed for food processing and usually involve thermal processing methods. Packaging of food acts as a barrier layer and helps in preservation. Although many antimicrobial compounds are nowadays being added to the packaging material, their low thermal stability limits their use. Thus, the importance of thermal stability of the packaging material can be understood (Sung et al., 2013; Kanmani & Rhim, 2014).

The thermal stability of the biofilm is measured by carrying out thermogravimetric analysis (TGA). In this method, the sample is taken (4–5 mg) and heated up to 700 °C at a rate of 10 °C/min. Heating is carried out under a nitrogen atmosphere (flow rate 50 mL/min). The thermal degradation behaviour of the sample is observed through the TGA curve plotted between weight of the sample and temperature. TGA curve is used to determine the thermal degradation temperature, rate of degradation, weight of residual sample and also the temperature at which maximum degradation occurs (Maqsood and Seide, 2019; Shankar and Rhim, 2017; Shi et al., 2014).

Another method to measure thermal stability is by using differential scanning calorimeter (DSC). A nitrogen atmosphere is a requirement here also. The films are dehydrated in a vacuum oven for about 24 h. After that approximately 10 mg of the dried sample is taken in an aluminium pan and sealed. It was then scanned over a range of 30–150 °C with a heating rate of 10 °C/min. For reference, blank aluminium pan is used (Cazón et al., 2018; Arfat et al., 2017; Abdollahi et al., 2013).

11.5 Light Barrier Property

There are certain food materials which get degraded by exposure to UV light. Food containing a high amount of lipid, for example, are prone to light-induced oxidation. Therefore, besides having good mechanical, water and gas permeability properties, the material should also be resistant to UV light (Li et al., 2011; Ramos et al., 2013).

The light transmittance (opacity) through the packaging is measured by using UV/Vis spectrophotometer. The wavelength of light used ranges from 200 to 800 nm. The light barrier property considers two aspects—barrier against UV light and transparency to visible light. Both of these aspects are measured using spectrophotometer at 280 nm and 660 nm, respectively (Shankar and Rhim, 2017). The opacity of the film is generally measured at 600 nm. To measure this, the film is cut in rectangle shape and is placed directly in a spectrophotometer cell. For reference sample, an empty cell is used. The opacity is then calculated using the following formula. The test should be conducted in triplicates for accuracy (Cazón et al., 2018; Vejdan et al., 2016; Abdollahi et al., 2013).

$$\text{Opacity/Transparency} = \frac{\log \%T_{600}}{\text{Thickness of the film}} \tag{11.6}$$

where $\%T_{600} = \%$ transmittance at 600 nm.

11.6 Gas Transfer Property

The gas transfer property of biopolymer plays a decisive role in maintaining the shelf life of the food product. Most of the foods are susceptible to oxygen, undergo oxidative degradation and get spoiled. Besides, different foods have different atmospheric requirements for longer shelf life. For example, foods like carbonated beverages need packaging material having a low CO_2 transfer rate. Therefore, it is important to choose a packaging material that can support this requirement.

There are different methods to measure the gas permeability, but the general method involves two compartments with the packaging film in between. One compartment is filled with gas whose transmission needs to be measured, and the other is vacuum with a detector to measure the quantity of gas transferred. The following section describes some of the methods to determine the gas transfer (Martinez and Artés, 2005):

(a) Coulometric Sensor-Based Test
Coulometry is an electrochemical method. The sensor here measures the electric current that is generated every time oxygen flows through the sensor and thus gives exact measurement. There are two methods that are standardized by ASTM using the coulometric sensor—ASTM D3985 and ASTM F1927-14. The instrumentation of the method is simple, with two chambers—one is filled with oxygen and the other with nitrogen with a semi-barrier of the film in

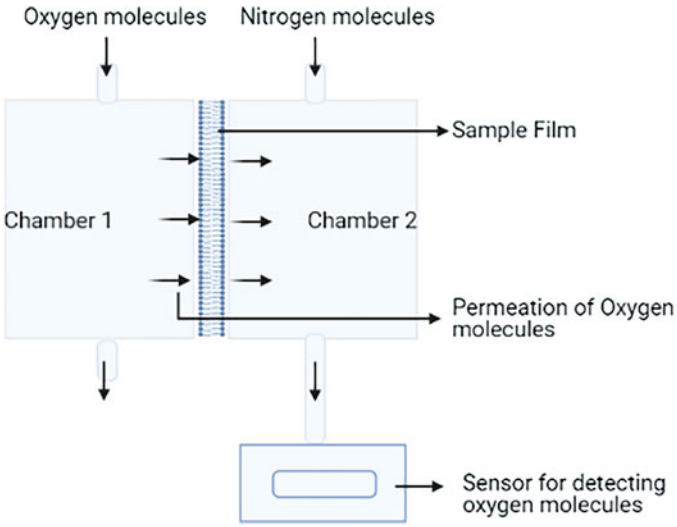

Fig. 11.1 Instrument design for the coulometric method of gas permeability

between. As the oxygen permeates to the nitrogen chamber, the sensor detects it and generates electric current as illustrated in Fig. 11.1. In ASTM D3985, this method needs to be performed in dry condition only, that is, where relative humidity is <1%. This limits its use. In another method, ASTM F1927-14, the method can be performed at different relative humidities (American Society for Testing Materials, 2014).

(b) Continuous Flow Method.
In this method, 2–3 chambers kept at atmospheric pressure are separated by a film, and the permeability of the gas (O_2 or CO_2) is measured by calculating the difference in partial pressure on both sides. Nitrogen is used as a carrier gas in this method. As soon as the gas under study permeates through the film, it is carried to the flux metre by the nitrogen, and its flux is measured. The next step is reaching the detector (gas sensor or gas chromatograph) which then quantifies the concentration of gas transferred (Cissé et al., 2012; Vargas et al., 2007; Martinez and Artés, 2005). The permeability can be calculated by the following formula (Valentas et al., 1997):

$$P = \frac{QX}{At\Delta p} \tag{11.7}$$

where P = permeability of the gas (g/s-m^2 Pa); Q = quantity of the gas diffused through the film (g or mL); X = film thickness (m); A = area exposed of the film (m^2); t = time taken for the process; Δp = difference in partial pressure on both sides of the film (Pa).

To measure the amount of gas permeated through the film, pressure sensors of high precision are placed in the chamber with low pressure (where the test gas will reach after permeating through the film). The amount of gas can then be calculated using the ideal gas equation:

$$N = \frac{PV}{RT} \tag{11.8}$$

where N = amount of gas (mol); V = volume of gas permeated (m^3); P = pressure of the gas permeated (Pa); R = gas constant (m^3-Pa/(mol-K)); T = temperature of the gas (K).

11.7 Biodegradation Test

There are various testing methods and standards available for determining biodegradability, but for getting trusted results, an appropriate selection of testing methods is necessary. The selection criterion of the testing method must be based on the chemical characterization of the testing material and its intended use. The degree of biodegradation is related to the change in weight, chemical, mechanical and physical properties, evolution of CO_2, etc. And all these changes can be measured through various testing procedures (Niaounakis, 2014; Ahmed, 2018). Table 11.1 represents information on different biodegradability tests used on different polymers in various studies.

These tests can be performed outside in the natural environment, or a simulation of the natural environment can also be created. In field tests, for the composting process, natural environmental conditions are used such as burial of specimen material into soil, pond, etc. Strict regulation cannot be applied to the testing conditions like RH (relative humidity) and temperature. This limits the practical applications of field tests due to less reliable results. The simulation/screening test method has no such type of limitation as field testing. In this, the test is conducted in a regulated enclosed chamber where conditions similar to the natural environment are created. It is generally used for the determination of CO_2 evolution residues during the composting process. Enzymatic test and aquatic test belong to screening test methods. These tests perform under aerobic and anaerobic conditions. Tests that measure the CO_2 evolution are also known as Sturm tests (Gu 2003; Bastioli, 2020).

Three biodegradability test methods are generally used for the practical testing of biopolymeric material that involves compost environment test, CO_2 compost test and the standard compost test. But there are also other methods of testing used in different studies.

1. Compost Environment Test
   In this method, weight loss of sample is directly linked with the degree of compostability of testing material. Compost environment method involves visual examination of sample by turning the bio-waste within a gap of 6 days. After

Table 11.1 Biodegradability studies of biopolymers derived from various sources

S. No.	Biopolymer	Sample used	Testing method	Testing conditions and results	Additional information	References
1.	Renewable resources					
a)	Polylactic acid (PLA)	PLA bottle	ISO 14855 ASTM D6400	Mineralization 64.2%, at 55% RH, 58 °C, time duration 63 days	For reference, corn starch was used	Kijchavengkul et al. (2006)
b)	Poly (3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV)	Biopol	Controlled composting test	Average biodegradation 88%, whereas for cellulose powder 84%	Cellulose powder as reference material	Doi and Fukuda (2013)
c)	Nano cellulose reinforced thermoplastic starch	Film and powder form	ASTM D 5338-92 and ISO 14855:1997	Showed complete starch mineralization, average cellulose biodegradation 96.8%, duration 47 days	Max starch concentration 100 g, minimum 30 g	Volova et al. (2006)
d)	Protein	Wheat gluten biopolymer	Modified Sturm test	Complete degradation of whole gluten material in aerobic fermentation within 36 days		Domenek et al. (2004)
2.	Petrochemical sources					
a)	Polybutylene succinate (PBS)	Powder and film	ISO 14855	Biodegradation 71.9%, for powder 60.7% for film after 90 days at 580 °C	*Aspergillus versicolor* identified as the best PSB degrading microorganism	Sirichalarmkul and Kaewpirom (2021)
b)	Polycaprolactone (PCL)	Powder	Enzymatic degradation test using Amano lipase PS	More rapid degradation of smaller-sized PCL powder (0–125um)	125–250 μm used as reference material	Funabashi et al. (2007)
3.	Blends of material					
a)	Poly(hydroxybutyrate) (PHB) and polyvinyl alcohol (PVA)	Film	Biological oxygen demand (BOD) test	High degradation and final degradation ratio of PHB blend film than pure PHB film		Ikejima et al. (1998)

(continued)

Table 11.1 (continued)

S. No.	Biopolymer	Sample used	Testing method	Testing conditions and results	Additional information	References
b)	Poly(butylene succinate-coadipate) (PBSA) with 5–30% (by wt.) starch	Extruded blown film	Respirometer	Higher biodegradability in soil when starch content raised to 20%		Rudnik (2019)
c)	PHBV with corn starch (30–50%)	Film	Composting method	Degradation of starch higher than PHBV. Weight loss of 30% starch blended with PHBV was 7% (0.056% weight loss/day), while the PHBV component of a 50% starch blend of PHBV lost 41% weight (0.328% weight loss/day)	Testing time period 125 days	Ebnesajjad (2012)

complete degradation of the control sample, measurement of weight is taken for calculating weight loss in the sample as it is directly related to biodegradability (Ahmed, 2018).

2. Standard Compost Test (ASTM D5338)
   This test measures the CO_2 evolution from the sample. In this method, a 5 L flask is filled with mature compost and the sample film in a dry weight ratio of 6:1. The flask is then externally heated. The composting environment is controlled (temperature, humidity and aeration) which is similar to composting conditions in the natural environment. This method determines the rate and degree of biodegradation performed aerobically. The amount of carbon that has been converted to carbon dioxide is being calculated here (ASTM, 2021).
3. CO_2 Compost Test
   Carbon present in the testing material is converted into CO_2 by keeping the polymer in a mixture of mature compost. After the testing period, the amount of CO_2 evolution is measured by gas chromatography, by titration or by various other methods (Singh et al. 2017).

   In a study performed by Das et al. (2018), the biodegradation of low-density polyethylene (LDPE) was performed by using fungal species. In their study, they used the following method to check for CO_2 evolution. Flask containing LDPE film and a mineral salt medium (100 mL) was taken, and CO_2 free air was passed through it at the rate of 2–3 bubbles/min. After this, inoculum (fungus strain) was added, and then the flask was incubated for two months at 37 °C. The CO_2 evolved when the degradation process was trapped in KOH solution (forming K_2CO_3). The quantity of CO_2 was then estimated by titrating it against 0.1 M Ba $(OH)_2$. The mineralization level of CO_2 was calculated using following equation (Sturm 1973; Das and Kumar 2015):

$$\text{Mineralization level} = \frac{\text{Test } CO_2 - \text{Control } CO_2}{\text{Theoretical } CO_2} \tag{11.9}$$

   where Test CO_2 = atmospheric and metabolic CO_2; Control CO_2 = only atmospheric CO_2.

   Theoretical CO_2 is calculated using the following formula:

$$\text{Th.}CO_2 = \text{Quantity of polymer taken } (g) \times \frac{\text{Molecular weight of } CO_2}{\text{Molecular weight of Carbon}} \tag{11.10}$$

4. Soil Burial Method
   For laboratory-based testing, it is the most widely and commonly used method. Weight loss by specimen sample is determined in this method. Firstly, testing material is cut into specified dimension and then buried at a certain depth into the soil having RH 20–40% maintained by a regular water sprinkler system. For weight measurement, the sample should be taken out at a regular interval of 2 weeks, washed with distilled water and vacuum dried till the achievement of

constant weight (Thakore et al. 2001). In this, biodegradation occurs due to the presence of a group of microorganisms present in the soil (Rudnik, 2019; Pandey et al., 2016).

To test the biodegradation, a method has been mentioned by Mustapha et al. (2019) that simulates conditions of a home composting system. The procedure involves cutting the film samples in rectangular pieces 8 × 2 cm and they are weighed. The samples were then buried 15 cm deep in the soil. The samples were exposed to sun and rain for two months. After that, they were recovered from the soil, cleaned of dirt and compost attached and dried at 120 °C for 15 min. The samples were then weighed again and the weight reduced is calculated using the following formula:

$$\text{Weight loss}\% = \frac{M_0 - M_1}{M_0} \times 100 \tag{11.11}$$

where M_0 = mass of the sample after two months; M_1 = mass of the before two months/initial mass

5. Respirometry Method (Closed Bottle Test)
The method is based on the guidelines of the Organisation for Economic Co-operation and Development for testing biodegradation in aqueous medium. In this method, Karlsruher flasks were filled with the test solution (no air bubbles) and closed tightly and kept in dark. Test solution contains the test substance mixed in mineral medium (2–5 mg/L) and the inoculum of microbes containing mixed populations, generally derived from sewage treatment plant otherwise from river or lake. The degradation is performed by the microorganisms. The duration of the test is 28 days. Here, the oxygen concentration is measured as the microbes consume oxygen during the biodegradation process. The oxygen level is measured electrochemically using an oxygen-sensitive electrode at regular intervals under continuous stirring. This method works best with substances that are water soluble. The test should be carried out in duplicate. For reference, blank inoculum is used (OECD-301D).

The calculation of percent degradability, first the biological oxygen demand (mg O_2/mg test sample), is calculated by the following formula. To calculate the theoretical oxygen demand, the elemental composition of the compound should be known ($C_cH_hCl_{cl}N_nNa_{na}O_oP_pS_s$), and for ThOD without nitrification, formula given in Eq. (11.14) is used:

$$\text{BOD} = \frac{\text{O}_2 \text{ uptake by test solution} - \text{O}_2 \text{ uptake by blank solution (mg per L)}}{\text{Amount of test sample (mg per L)}} \tag{11.12}$$

$$\%\text{Biodegradation} = \frac{\text{BOD}}{\text{ThOD}} \times 100 \tag{11.13}$$

$$\text{ThOD} = \frac{16\left[2c + ½(h - cl - 3n) + 3s + \frac{5}{2p} + \frac{1}{2na} - o\right] \text{mg/mg}}{\text{Molecular weight of the compound}} \quad (11.14)$$

6. Microbial Degradation Test
   Unlike the soil burial method, in this process, degradation occurs due to the action of the specified microorganism. Test material is placed into the sterile culture medium for 24 h. After completion of incubation, medium is inoculated with specific microbial culture. Incubation of inoculated film is done for optimal time period. Washing of film with ethanol followed by subsequent drying at minimum temperature is done after completion of incubation period. Weight measurement of incubated film is taken and compared with the control sample. Surface characterization by microscope is analysed for film before and after the microbial culture treatment (Ashish and Priyanka, 2012).

11.8 Antioxidant Activity

Another parameter that can be tested is the antioxidant activity of the film. In most of the edible films, oxidative rancidity can be a problem, and therefore incorporation of antioxidants can be proven useful. Adding of essential oils to the coating shows an improved antimicrobial and antioxidative property (Li et al., 2018). The antioxidant activity is determined by using 2,2-diphenyl-l-picrylhydrazyl (DPPH) as a free radical. For preparing the standard, butylated hydroxytoluene (BHT) is used. After that, stock solution of the sample is prepared in ethanol. Different dilutions are prepared from the stock solution (say 0, 25, 50, 75 and 100 mg/mL), and to each of the dilution (0.2 mL), add 3.8 mL of DPPH solution. Incubate the sample for 30 min in dark and then measure the absorption at 517 nm. The percentage antioxidant activity (%AA) can be calculated using the following formula (Alizadeh-Sani et al., 2018):

$$\%\text{AA} = 100 - \frac{\text{absorption of control} - \text{absorption of sample}}{\text{absorption of control}} \times 100 \quad (11.15)$$

In a study by Valentino et al. (2020), an active coating was prepared by addition of essential oil of gallic acid and rosemary to 4% sodium caseinate solution. Different dilutions of the samples were then prepared to test their antioxidant activity. The result showed an increase in the antioxidant activity of the film prepared by essential oil compared to only sodium caseinate solution.

Besides, the addition of antioxidants to the biopolymer film is shown to affect its other functional properties. Benbettaïeb et al. (2018) studied the release kinetics and antioxidant activity of chitosan-fish gelatin edible films. It was found that with the addition of antioxidants to the film, about 30% fall in water vapour permeability and a rise of about 50% in the tensile strength of the film occurred.

11.9 Antimicrobial Activity

Conventional packaging is now replaced by edible film packaging because of the biodegradable properties it possesses. However, they are more susceptible to microbial degradation which would then affect the food packed inside. Addition of essential oils to the films is found to improve the stability and other characteristics of the biopolymer and thus prevent contamination of the product (Campos-Requena et al., 2017; Syafiq et al., 2020). The most common method to test the antimicrobial activity of the film is disc diffusion method. This method is specified in ISO 22196: 2007. In this method, the culture medium (such as nutrient agar and potato dextrose agar) is prepared, and the inoculum of the microbe to be tested is spread over the medium in a Petri dish. The next step is to place the film on the medium surface. The sample is then incubated at 35 ± 1 °C, relative humidity <90% for about 24 h (depending upon the microbe to be tested). To test the efficacy of the film, the clear zone of inhibition formed around the film is measured as shown in Fig. 11.2. To find out the minimum inhibitory concentration (MIC), that is, the minimum concentration of the extract that can result in a visible zone of inhibition, dilutions of the sample are prepared (Iturriaga et al., 2012).

11.10 International Standards for Biopolymers

Strength and durability are one of the major aspects of any biopolymer to be used and manufactured at an industrial level. Most of these standards are set by the American Society of Testing Materials (ASTM). It was organized in 1988 and has published over 12,000 standards in about 90 industrial sectors worldwide. ASTM not only provides standard methods against particular parameter but also for specific materials or products like chitosan- and alginate-based materials. Table 11.2 represents the list of some standards and testing procedures set by ASTM and ISO regarding the properties especially related to biodegradation.

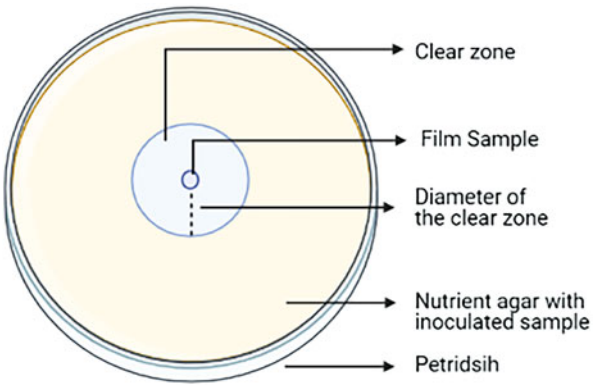

Fig. 11.2 Illustration of the zone of inhibition formed by the disc diffusion method

Table 11.2 Various standard methods by international organizations for functionality test of biopolymers

Parameter to be tested	Standard followed	Test method
Biodegradability	ASTM D5338-15 (2021)	The test method is used for evaluating the aerobic biodegradation of plastic materials. The method is performed under controlled composting conditions at thermophilic temperature.
	ASTM D6954-18	This standard method tests for the degradation of plastics in the environment by employing both biodegradation by microbes and oxidation.
	ISO 14852: 2018	This method is used to determine the aerobic biodegradability of plastic materials in an aqueous medium. This method analyses the evolved CO_2.
	ISO 14853: 2016	This method is used to determine the anaerobic biodegradability of plastic materials in an aqueous medium. This method analyses the evolved biogas.
	ISO 14855-1: 2012	This method is used to determine the aerobic biodegradability of plastic materials under controlled composting conditions. This method analyses the evolved CO_2.
	ASTM D 5929-18	The standard test method measures the biodegradability of materials by exposing it to source-separated organic municipal solid waste composting conditions. The test is performed by using respirometry.
	ISO 20200: 2015	The test is performed in a laboratory by creating a simulation of composting conditions. It then determines the degree of disintegration of plastic materials.
	EN ISO 17556: 2019	The method is used to determine the ultimate aerobic biodegradability in the soil. It uses a respirometer and measures either the oxygen demand or the carbon dioxide evolved.
	EN 14806: 2013	This defines method for the preliminary evaluation of the disintegration of packaging materials. The test is performed in a simulated composting condition at a laboratory level.
Gas permeability	ASTM D3985	The standard test method uses a coulometric sensor and determines the transmission rate of oxygen when passed through a plastic film.
	ASTM F1307-20	This standard test method also uses a coulometric sensor and measures the oxygen transmission rate when the gas is passed through dry packages.
	ASTM F 1927-20	Using a coulometric sensor, this standard test method is used for determining the oxygen gas transmission rate, its permeability through the film and permeance at controlled relative humidity through the film.
	ASTM D1434-82(2015) e1	The standard test method measures the gas permeability characteristics of plastic film and sheeting.

(continued)

Table 11.2 (continued)

Parameter to be tested	Standard followed	Test method
Water vapour permeability	ASTM D1653-13	The method is employed for evaluation in the organic coating films for determining their water vapour transmission property.
	ASTM F1249-20	This test method uses a modulated infrared sensor and measures the water vapour transmission rate in plastic films and sheets.
	ASTM E96/E96M-16	This method by ASTM also measures the water vapour transmission property of different materials.

11.11 Summary

The demand of consumers is towards safer natural materials, and the risk of environmental pollution also makes the industry shift towards biopolymers. In order to be classified as biodegradable, the biopolymer must follow the standards set by the international organization like ASTM and ISO. The various methods for testing the functionality of the biopolymer depend on numerous factors which need to be considered before applying any method. Since the trend is the application of edible films, research is showing an improvement in water vapour and gas permeability. Moreover, addition of certain bioactive agents like essential oils improves the stability of the product and reduces deterioration rate. Additionally, combination of different raw materials can provide a product with better proper properties; therefore, more research needs to be done in order to completely replace non-biodegradable materials.

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Nanocomposite Biodegradable Polymers for Food Packaging

12

Amir Heydari and Naeimeh Eghbalifam

Abstract

Because of rising environmental concerns, the need for biodegradable packaging materials has recently surged. Due to their biodegradability, biopolymers and nanocomposites have become critical issues. Various nanoparticles can be regarded as an effective method for enhancing the functional qualities of the nanocomposites. Most nanoparticles considerably increase biopolymer resistance to humidity and water, improve mechanical characteristics, and decrease water vapor and gas permeability. As a result, wastes from packaging materials generate major environmental problems. Global regulations have boosted the need for bio-based, bio-renewable, and biodegradable materials. Because of their biodegradability and biocompatibility, novel packaging materials are becoming increasingly popular. As a result, using these materials can assist in alleviating the waste dilemma. Unfortunately, because natural polymers have a low barrier and mechanical qualities, the application of bio-based films for food packaging is severely limited. As a result, natural polymers were seldom chemically changed and were frequently blended with synthetic polymers to broaden their applications in food packaging industries. Although intriguing findings have been obtained, developing a viable bio-nanocomposite still presents several hurdles. Nanotechnologies open new avenues for increasing health, prosperity, and quality of life while minimizing environmental impact.

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Keywords

Nanocomposites · Biodegradable polymers · Biocompatibility · Food packaging · Nanotechnology · Mechanical properties

12.1 Introduction

Recently, the demands for biodegradable packaging materials have increased due to growing environmental concerns. Biopolymers and their nanocomposite have emerged as an important subject because of their biodegradability. Some properties of the biopolymers are not suitable for industrial applications. Using different nanoparticles can be considered as an effective strategy to reinforce the functional properties of the achieved nanocomposites. Most nanoparticles significantly increase the resistance of biopolymers against humidity and water, improve mechanical properties, and diminish the water vapor and gas permeability. For this, wastes of the packaging materials especially the applied polymers cause very serious environmental problems (Kirwan and Strawbridge 2003; Avella et al. 2005). Due to global regulations, the demand for using bio-based, bio-renewable, and biodegradable materials is increased sharply (e.g., alginate, cellulose, chitosan, collagen carrageenan, corn zein, soy, starch, etc.) (Trache et al. 2017; Singha and Thakur 2008; Tharanathan 2003; Tongdeesoontorn et al. 2020).

The use of new packaging materials is becoming more common due to their biodegradability and biocompatibility (Attaran et al. 2017; Kumar et al. 2017). So the use of these materials can help to tackle the waste crisis. However, bio-based packaging, like common packaging, must support several essential functions, including food containment and protection and the transmission of information about the product to users as well as sensory quality and protection (Robertson 2016).

Unfortunately, since natural polymers have low barrier properties and weak mechanical properties, the use of bio-based films for food packaging has been severely restricted. As a result, natural polymers were rarely chemically modified and were often mixed with synthetic polymers to expand their uses in more unusual situations (Guilbert et al. 1997; Petersen et al. 1999). Although interesting results have been achieved, there are still many challenges to obtaining a successful bio-nanocomposite. Nanotechnologies present new possibilities for improving health, prosperity, and quality of life while lowering environmental effects (Sorrentino et al. 2007).

12.2 Nanocomposite Properties and Classification

Composites typically are hybrid materials including two phases: a continuous (polymer matrix) and a discontinuous phases (fillers) (Matthews and Rawlings 1999). Nanocomposites are multicomponent materials in which the length of at

least one dimension of filler is in the range of 1–100 nm. Different properties of nanocomposites such as mechanical, thermal, etc. are often distinct from those of their constituent materials (Sen 2020).

Nanocomposites are a novel approach to enhance polymer properties. In contrast to neat polymers and traditional composites, nanocomposites have enhanced barrier properties, mechanical strength, and heat resistance (Arora and Padua 2010). In recent research, nanocomposites made of polymers are considered more interesting than other varieties of nanocomposites. Polymer-based nanocomposites benefit from properties such as the ability of film forming and dimensional variability (Al-Johani and Salam 2011).

Nanocomposite materials can be classified into two categories based on the use of polymeric material in the composite. Non-polymer-based nanocomposites are a type of nanocomposites without any polymers or polymer-derived materials. In other words, they are inorganic nanocomposites and classified into three categories of metal-based nanocomposites, ceramic-based nanocomposites, and ceramic-ceramic-based nanocomposites (Khandoker et al. 2011).

12.3 Biopolymer-Based Nanocomposite

Biopolymers are polymers that can be degraded or broken down by natural phenomena and will convert to environmentally friendly components such as carbon dioxide and water. Biopolymers are known to be preferable products to petroleum-based plastics due to biodegradability, stability, and abundance (Liu et al. 2005; Muratore et al. 2005). These materials are the most widely utilized bio-based polymers for applications of food packaging. Recently, biopolymers derived from synthetic polymers including microbial products such as polyhydroxybutyrate and chemically prepared polymers from natural monomers such as polylactic acid, polycaprolactone, and polyvinyl alcohol have been developed as a result of technological advances (Rhim et al. 2013; Fahmy et al. 2020).

Synthetic biopolymers have several benefits, including the ability to improve the different various appearances and mechanical properties. The different groups of biopolymers used for food packaging are shown in Fig. 12.1. Biopolymers can be classified into two main groups of natural and synthetic based on the biopolymer's sources.

Unfortunately, as opposed to nonbiodegradable petroleum-based products, the usage of biopolymers as food packaging materials has disadvantages such as low mechanical, thermal, and barrier properties. As a result, several scientific attempts have been made to enhance the properties of biopolymers (Fahmy et al. 2020; Arfat et al. 2014; Di Maio et al. 2014; Nafchi et al. 2013).

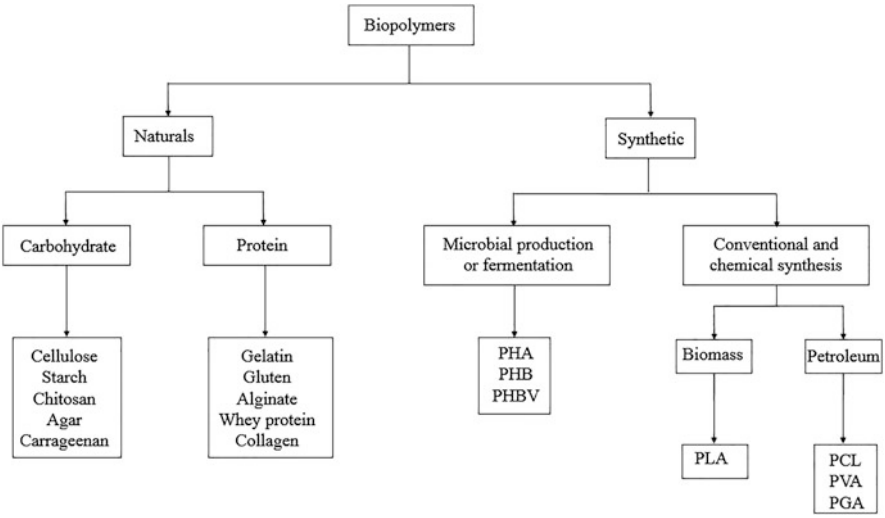

Fig. 12.1 Categories of the biopolymers (Adopted from Rhim et al. (2013 (Rhim et al. 2013)))

12.3.1 Carbohydrate

12.3.1.1 Cellulose

Cellulose is another important biopolymer. Cellulose consists of repeating units of D-glucose linked through ß-1,4 glycosidic bonds (Thakur et al. 2012). It has a crystalline structure and includes close chain packing of cellulosic polymer that does not dissolve in an aqueous solution (Singha and Thakur 2010; Liang and Wang 2020). To enhance the water solubility of cellulose, it is alkalized and then reacted with methyl chloride, chloroacetic acid, and propylene oxide to produce carboxymethylcellulose, methylcellulose, hydroxypropyl methylcellulose, and hydroxypropyl propyl cellulose (Sadeghi-Varkani et al. 2018; Dehghani et al. 2018). All of the named materials can form strong films that are usually tasteless and odorless while being moderately flexible, translucent, and oil and fat resistant (Shah et al. 2016; Kerch 2015).

12.3.1.2 Starch and Derivatives

Among the biopolymers, starch and derivatives have been widely used as a selective case to produce bio-nanocomposite materials for use as food packaging because of their excellent properties (Charles et al. 2003; Pan et al. 2014; Tang et al. 2008). Studies have shown that starch when mixed with a nonbiodegradable material degrades totally in soil and water and can facilitate the biodegradability of that material. However, starch has low strength without physical or chemical modification (Tang et al. 2008).

Glycerol and some other materials with low molecular weight are popular plasticizers for starch and hydrophilic polymers. Effective mechanical, oxygen,

and moisture protections are required in these applications. Both these demands will also not be fulfilled by thermoplastic starch (TPS) alone. The hydrophilic property of the starch causes output differences before and after processing as the water content changes. Various methods have been identified to solve this shortcoming.

Clay as a filler can enhance the properties of TPS for these applications (Motelica et al. 2020; Naidu and John 2020; Jiang et al. 2020).

More recently, starch/clay nanocomposite films are the most common research about biodegradable material for food packaging and other applications (Yoon and Deng 2007; Chen and Evans 2005). Mechanical characterization results showed that mechanical properties of TPS were improved by the addition of a low percentage of sodium montmorillonite (Park et al. 2002).

12.3.2 Proteins

To build the complex structures needed for film preparation, the protein must be denatured (Thakur and Voicu 2016). Fibrous proteins and protein clusters are the most common forms of protein. Hydrogen bonds bind protein fibers together tightly (Thakur et al. 2014). The protein complex is a spherical structure bound by an ionic and hydrophobic covalent bond (disulfide) and hydrogen. Protein films are formed by protein solutions by using a suitable solvent or a combination of water and ethanol. To form complex structures used for film making, the protein must be denatured (Thakur and Voicu 2016).

Because of their ability to shape films, different proteins have been used in industrial applications for a long time (Milani and Tirgarian 2020). Casein, whey protein, gelatin, egg white, and fish myofibrillar protein are the most common animal-derived proteins for different applications (Zhao et al. 2008). Soybean protein, zein (corn protein), and wheat gluten are considered plant-based proteins (Hernández-Muñoz et al. 2003; Lee et al. 2005). Using nanocomposite technology, especially nanoclays, significant attempts have been made to enhance the properties of different proteins. Whey protein has attracted considerable attention for the film forming and coating process (Arora and Padua 2010).

12.3.3 Microbial Production or Fermentation: PHA

PHA (polyhydroxyalkanoate), a polyester of various hydroxyl alkanoates derived from microbial fermentation, is another promising commodity used in packaging. PHAs are nontoxic crystalline thermoplastic elastomers with a lower melting point. They have unique properties and are biocompatible. The compositions of PHA monomers affect these properties. Due to their weak strength, and noncompliance with common heat treatment methods, and sensitivity to thermal degradation, PHAs are limited in their use (Li et al. 2016).

12.3.4 Conventional and Chemical Synthesis

12.3.4.1 PLA Nanocomposites

Biopolyesters can be produced by usual chemical methods. To date, polylactic acid has been investigated a lot as the most common synthetic biopolymer for renewable packaging (Tang et al. 2020). Polylactic acid (PLA) as a long-lasting, biocompatible, biodegradable material with excellent properties has attracted considerable attention. Bacterial fermentation and petrochemical synthesis are the most popular ways to make lactic acid. PLA's hardness, transparency, processability, and biocompatibility have made it a common biodegradable polymer for packaging materials (Zhong et al. 2020).

The widespread use of PLA for packaging is limited due to its high cost and poor efficiency as compared to other polymers. The low gas barrier properties of PLA are the most significant drawback for its use in food packaging. PLA nanocomposites can improve polymer properties and expand their application (Tang et al. 2020). Nanocomposites of PLA and clay reveal very good barrier properties (Thellen et al. 2005).

12.4 Packaging Technology

According to statistics from the United Nations' Food and Agriculture Organization, FAO, approximately every year, one-third of all food processed is wasted due to microbial activity causing shelf life expiration or spoilage (Motelica et al. 2020). Food spoilage is the process of contaminating foods, causing them to lose their flavor, appearance, and nutritional value, as well as allowing pathogenic bacteria to flourish, lowering the product's quality and rendering it inedible. Contamination of food may occur when it is exposed to the air during slaughtering, manufacturing, or packaging. Bio-based antimicrobial packaging agents designed to enhance food safety can be used to combat food contamination that poses a risk to customers' health (Sung et al. 2013).

Petrochemical polymers have low cost and suitable barrier properties, so they are currently used in the majority of food packaging materials. But due to their nonbiodegradability, these polymers have caused a great deal of environmental concern around the world (Makaremi et al. 2019; Guo et al. 2019; Clark et al. 2020). Therefore, the demand in the food industry for the production of new packaging products is increasing, which is mainly focused on natural or environmentally friendly biopolymers. Although changing the commonly used packaging materials is the easiest way to achieve antimicrobial action, environmental pollution is gradually limiting the use of nondegradable polymers.

12.4.1 Active Packaging

The key processes that induce unfavorable alteration in the quality of food items thus affecting their protection are oxidative reactions and microbiological changes. The current issue is to develop packaging materials that will enable foods to last longer inside the package (Benbettaïeb et al. 2018). Definition of active materials in European Commission (EC) Regulation No. 450/2009 is as follows: "active materials and articles mean materials and articles that are intended to extend the shelf-life or to maintain or improve the condition of packaged food; they are designed to deliberately incorporate components that would release or absorb substances into or from the packaged food or the environment surrounding the food."

Active packaging is used to continuously change the internal environment by interacting with the food continuously for the duration of the shelf life. Consumers demand for high quality, and natural goods is driving the popularity of active packaging. Active packaging systems are used to increase or decrease components such as oxygen, carbon dioxide, ethylene, and moisture and also release antimicrobial agents (Ozdemir and Floros 2004). Scavenging systems can absorb unfavorable compounds from the food (Guleria 2020). Nanocomposites with antioxidant and antimicrobial properties can extend food storage time by inhibiting their spoilage (Sarfraz et al. 2021).

12.4.1.1 Antioxidant Agents

One of the most common causes of food spoilage is lipid oxidation. This is particularly true in the case of high-lipid products like nuts, fish, and vegetable oils. The breakdown of polyunsaturated fatty acids induces lipid oxidation, which leads to the formation of toxic aldehydes and nutrient deficiencies (Jamróz and Kopel 2020).

Antioxidants can prevent the oxidation of fats and proteins. Antioxidants delay the production of off-flavors and enhance the color stability of the food. In addition to active packaging, food oxidation can be avoided by removing or reducing oxygen, such as by covering items in high barrier materials in an anaerobic environment. Furthermore, packaging with synthetic antioxidant-releasing mechanisms has been commonly used in food packaging to resist lipid oxidation. Natural antioxidant compounds, on the other hand, have sparked renewed interest in recent years. Various studies have reported improved oxidative stability in various foods using tocopherols, polyphenols, and plant extracts, including essential oils (Yildirim et al. 2018).

12.4.1.2 Antimicrobial Agents

The addition of antimicrobial compounds to the biopolymer matrix can help to increase the storage time of different processed foods. The active ingredient's antimicrobial activity could be mediated by one of four mechanisms: (1) membrane breakup with ATPase inhibition, (2) leakage of important biomolecules from the cell, (3) disruption of the proton motive force, and (4) enzyme inactivation (Pisoschi et al. 2018).

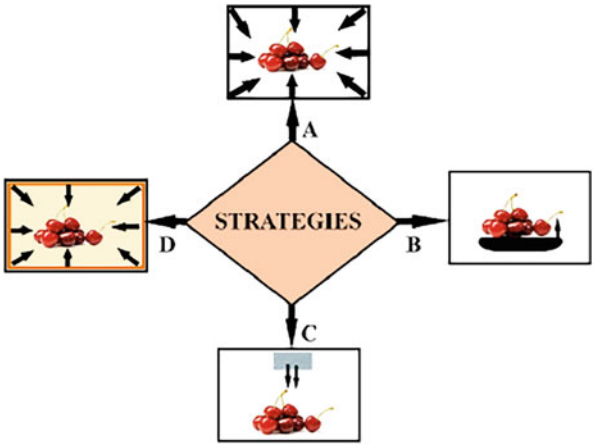

Fig. 12.2 Main strategies employed to obtain antimicrobial packaging. The antimicrobial agents can be incorporated into the polymeric film (**A**), indirect contact from pads (**B**), released from sachets (**C**), or coated onto polymeric film (**D**). Adopted from Motelica et al. (2020 (Motelica et al. 2020))

When developing antimicrobial active packaging, it is critical to strike a balance between the kinetics of microbial growth and the regulated release rate of antibacterial agents. Antimicrobial packaging systems are classified into the following four categories (Fig. 12.2):

1. Addition of volatile antimicrobial substance to the packaging pad.
2. The insertion of antimicrobial compound into a packaging material.
3. Coating of the package by polymers such as polysaccharides which are used to cover the container and play a carrier role for the antimicrobial agents. Therefore, the active compounds can be released onto the food environment by two different mechanisms of volatile materials' evaporation into the environment or migration to the surface of product.
4. The use of polymers with intrinsic antimicrobial, for example, chitosan (Motelica et al. 2020; Mousavi Khaneghah et al. 2018).

Antimicrobial packaging techniques are divided into two categories. The first category includes packaging materials that allow active agents to move into the food due to direct interaction between the antimicrobial surface and the preserved food. Food that is covered with plastic or vacuum-packed is packaged in this way. A second approach is to get the antimicrobial substance into the container but not directly on the food; here, modified atmosphere packaging (MAP) may be described (Mousavi Khaneghah et al. 2018; Zhang et al. 2021). Various antimicrobial compounds incorporated in different packaging systems are presented in Table 12.1.

12.4.2 Controlled Release Packaging

Controlled release packaging is an active packaging that focuses on the releasing processes. This method uses packaging as a transport system to efficiently distribute

Table 12.1 Antimicrobial packages and their applicability (Adopted from Motelica et al. (2020 (Motelica et al. 2020))

Product preserved	Packaging material	Antimicrobial agent
Iceberg lettuce	Cellulose	Clove and oregano oils
Cucumber	Chitosan	Limonene
Tomato	Chitosan	TiO2 nanoparticles
Strawberries	Chitosan/CMC	Chitosan/citric acid
Strawberries	PLA	AgNPs
Strawberries	Chitosan/CMC	Mentha spicata oil
Strawberries	Gelatin	Butylated hydroxyanisole
Fish	PLA	Thymol
Crap fillets	Alginate/CMC	*Ziziphora clinopodioides* oil/ZnO
Rainbow trout fillet	Chitosan	Grape seed extract
Salmon	PLA	Glycerol monolaurate
Shrimps	Chitosan	Carvacrol
Shrimps	Gelatin	ZnO/clove oil
Chicken	Chitosan	Acerola residue extract
Poultry	Chitosan	Ginger oil
Chicken	Gelatin	Thyme oil
Chicken	Pullulan	Nisin
Chicken	Chitosan/PET	Plantaricin
Ostrich meat	Kefiran/ polyurethane	*Zataria multiflora* oil
Lamb meat	Chitosan	*Satureja* plant oil
Ground beef	PLA/NC	*Mentha piperita* and *Bunium persicum*
Ham	Chitosan/starch	Gallic acid
Salami	Whey protein	*Cinnamomum cassia* and *Rosmarinus officinalis* oils
Cheese	Chitosan/PVA	TiO_2
Cheese	Cellulose /chitosan	Monolaurin
Cheese	Starch	Clove leaf oil
Cheese	Agar	Enterocin
Cheese	Zein	Pomegranate peel extract
Peanuts (roasted)	Banana flour (starch)	Garlic essential oil

actives to the food at a controlled rate over a long period. Control release packaging keeps the content of antimicrobial substances of the food at a specific target level, thereby slowing microbial growth kinetics and keeping the food healthy for consumption (LaCoste et al. 2005). Controlled release packaging, or time release packaging of active compounds, has been used for a long time as a viable way of incorporating medications like antibiotics and antimicrobials into food packaging. For food packaging, the idea of controlled release packaging is still a challenge. To investigate the release kinetics of a packaging system, it needs to measure the release

rate of the active substance into a food simulant or its performance in controlling microbial growth and increasing the product's shelf life (Mastromatteo et al. 2010).

12.5 Mechanical Properties

Mechanical properties guarantee that processed foods are safe from outside forces and that packing materials are strong enough to store packaged goods. Bioplastics have a variety of strength properties, and depending on the application, they can be considered to be adequate or insufficient (Ncube et al. 2020). Mixing with other materials is one of the methods to enhance the mechanical properties of the composite. Bioplastics may be combined with other biodegradable materials, such as natural fibers, to create a cost-effective biodegradable composite. Natural fibers come from natural materials, and they have a wide range of properties because of differences in different crop planting and harvesting conditions. As a result, mechanical properties can be difficult to estimate correctly (Dicker et al. 2014).

12.5.1 Factors Affecting the Mechanical Properties of Polymers

The most common parameters indicating mechanical properties are stiffness, strength, and elongation-at-break. A variety of factors affect these mechanical properties that molecular weight can be the most important. The polymer chains are becoming increasingly intertwined, as they get longer. To cause a polymer sample to split into two pieces, the polymer chains must physically sever. As a result, the more twisted a polymer is, the more chains must be separated to separate the final polymer sample. As polymer chains may unfold to a greater extent without splitting, elongation-at-break increases; however, further entanglements result in a decrease in elongation at break. Although there are no generally accepted hypotheses that link Young's modulus to molecular weight due to the complexities of molecular interactions and a lack of detailed knowledge, stiffness increases with molecular weight. Since chains arranged next to each other in the crystalline region are closely bound to each other, crystallinity influences mechanical properties. As a result, they become resistant to deformation, and their stiffness is likely to improve dramatically when compared to the amorphous polymer process. Since crystallites behave as extra entanglements or can be called high-strength particles, strength usually increases (Gleadall 2015; Heydari et al. 2013).

During processes such as fiber drawing or extrusion, amorphous polymer chains may become oriented in a similar way to crystallinity. Oriented amorphous polymer chains are less balanced than crystalline zones, but they are more densely packed than unoriented amorphous polymer chains. As a result of the tighter interaction between the chains, both strength and stiffness improve when compared to a completely unoriented amorphous polymer. Polymer type/composition, as well as manufacturing techniques/conditions, affects mechanical properties before deterioration.

12.6 Water Sensitivity

Most of the biopolymers are very sensitive to water and water vapor based on their high amounts of hydroxyl groups (Quesada et al. 2016). This sensitivity limits their industrial applications, especially for packaging. Water sensitivity can be considered by the contact angle, water solubility, swelling ratio, water absorption capacity, and water vapor uptake. For all of these tests, hydrophilicity or hydrophobicity of the polymer surface can be discussed (Heydari et al. 2013). Most of the nanoparticles in the polymer cause the surface to be hydrophobic. When a water droplet is contacted on a polymer, an attraction between the water and polymer occurs which strength of the attraction is dependent on the properties of the polymer and nanoparticles (Bera et al. 2020). At a lower contact angle, polymer and water adhere better to each other. This strong attraction accelerates water penetration to the matrix of polymer and affects all of the water-dependent properties. Therefore, at higher contact angles, water and polymer have a weak attraction. The behavior of the polymer surface is a most parameter for all the water-related parameters which can accelerate or lessen the sensitivity to the water.

The outside of the packaging materials can be affected by environmental moisture and usually can be prevented by proper packaging design. One of the commonly used methods is using the multilayer packaging technique (Anukiruthika et al. 2020), although using this method increases the final price of the product. For dry foods, usually, the humidity in the headspace is negligible. Using hydrophobic packaging materials such as petroleum-based polymers is seemingly a good solution. But due to environmental regulations related to minimizing solid wastes, it is necessary to find biodegradable alternatives with suitable water resistance (Din et al. 2020). Sometimes, gradient force between the headspace and environment causes an increase in the moisture inside the packaging. For this, water vapor permeability (WVP) must be considered to prevent any moisture to penetrate the packaging (Yadav et al. 2020).

For the packaging of fresh fruits and vegetables, water is a very important component. During the packaging of these products, oxygen will convert to carbon dioxide and water due to respiration rate and transpiration. It makes the water vapor and water droplets inside the packaging (Kontominas 2020). On the other hand, moisture inside the packaging will prepare good conditions for microorganisms (Quesada et al. 2016). Therefore, using antimicrobial agents must be considered.

12.7 Water Vapor and Gas Permeability

Oxygen transmission rate (OTR) and water vapor permeability (VWP) are very important factors to have a proper material for food packaging applications. Most of the biopolymers are hydrophilic, so they can absorb some water or water vapor into their matrix. This available water can be absorbed by the biopolymer which causes undesirable changes (Stroescu et al. 2018). An increase in the permeability of the gases is one of the most important drawbacks. The absorbed water can act as a

plasticizer for biopolymers. Plasticizer agents reduce the intramolecular attraction between the polymer chains. They form hydrogen bonds between plasticizer and polymer molecules (Kontominas 2020). Catalano et al. were studied the effect of relative humidity on the gas permeability and swelling in some membranes (Catalano et al. 2012). They found that the permeability of all of the studied gases was increased markedly by an increase in the humidity. The barrier properties or the permeability of the different gases are very important for the packaging industries. The permeability of the packaging can be constrained by an increase in thicknesses. This method will increase the weight and cost of the packaging. It is a better solution to use nanoparticles to set the desired permeability. Change in barrier properties of nanocomposites can be described by the torturous path effect (Liu et al. 2018). The length of the diffusion path will increase due to an increase in tortuosity, and tortuosity is a function of some parameters such as the amount and size of the nanoparticles (Tan and Thomas 2017). Different nanoparticles have different properties such as shape, size, and geometry. The unidirectional orientation of nanoparticles causes a significant increase in the barrier properties (Weon and Sue 2005). For this reason, plate-like nanoparticles such as sodium montmorillonite (virgin and chemically modified) due to their high aspect ratios are used widely. The plate-like nanoparticles have more surface area for physical and/or chemical interaction by polymer molecules (Chong et al. 2016).

The permeability of a polymeric membrane is dependent on the properties of the continuous phase (polymer) and dispersed phase (nanoparticles). Also, permeability can be affected by good adherence between the polymer matrix and nanoparticles (Wu et al. 2020). The lower permeability against gases and water vapor is due to the tortuous pathway obtained by nanoparticles. Wolf et al. were studying the effects of the shape of the fillers on the barrier properties of nanocomposite (Wolf et al. 2018). Nanoparticles with higher aspect ratios make a more tortuous path for gases and water vapor diffusion through the polymers; therefore, using these nanoparticles decreases the permeability compared to spherical- or rod-shaped nanoparticles. Morimune-Moriya et al. were studying the effect of the aspect ratio of graphene oxide for polyvinyl alcohol nanocomposites (Morimune-Moriya et al. 2019). The barrier properties were increased with increasing graphene oxide aspect ratio. They discussed that water is forced to pass through a more tortuous pathway for the presence of graphene oxide with a high aspect ratio. Their results have good agreement with theoretical values obtained by mathematical equations.

Fathi Achachlouei and Zahedi were reported that the water vapor permeability of CMC-based nanocomposites was decreased with sodium montmorillonite and TiO2 nanoparticles (Fathi Achachlouei and Zahedi 2018). Also, Yousefi et al. reported the same behavior for wheat starch-based nanocomposites containing montmorillonite/TiO2 nanoparticles (Yousefi et al. 2019). Sometimes, a very high barrier polymer is needed. For components that are very sensitive to oxygen or moisture, it is necessary to try to minimize the permeability. Busolo et al. made a very high barrier polymer based on polylactic acid (Busolo et al. 2009).

Dispersion and distribution of nanoparticles in the matrix polymer must be considered. A nanocomposite with the specified amount of a nanoparticle may reveal

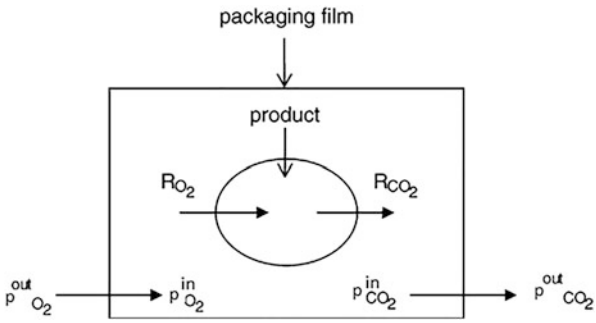

Fig. 12.3 Schematic of modified atmosphere packaging

different permeabilities due to the dispersion or distribution. In the case of agglomeration of the nanoparticles, the barrier properties will be lower than expected. Therefore, there is a maximum level for nanoparticles to incorporate in the polymer. Using surface modification can decrease the agglomeration (Favela-Camacho et al. 2019).

Another point for using the nanoparticles is relative permeability. As reported in most of the researches, the permeability of gases decreases using nanoparticles. But it is very important to know that this decrease in permeability is not the same for the different gases. For example, a decrease in oxygen permeability is not equal to carbon dioxide or nitrogen. Catalano et al. were reported that the relative permeability shows a complex dependence on the relative humidity (Catalano et al. 2012). Koh et al. were studying the effects of different layered silicate nanocomposites on the permeability of the gases (Koh et al. 2008). They found that different types of nanoparticles (Cloisite 15A, Cloisite 20A, and Cloisite 30B) and different amounts of nanoparticles (0–0.8 wt. %) show different permeabilities and relative permeabilities. It is one of the less-known applications for food packaging while well known for industrial applications such as natural gas sweetening. For some applications such as gas separation or gas purification, relative permeability must be considered as an affecting factor. For the food industries, relative permeability has a very important role in modified atmosphere packaging. The optimum and equilibrium gas composition is directly dependent on the relative permeability. It must be noted that the transient pattern and change in gas composition over time are strongly dependent on the permeability of oxygen, carbon dioxide, and nitrogen (Heydari et al. 2012). To have a better description, the schematic of modified atmosphere packaging is presented in Fig. 12.3.

The mass balance of the gases is presented in Eqs. (12.1) and (12.2) as below:

$$\frac{dn_{O_2}}{dt} = -R_{O_2}M + Pe_{O_2}\frac{A}{l}\left(p_{O_2,out} - p_{O_2,in}\right) \tag{12.1}$$

$$\frac{dn_{CO_2}}{dt} = R_{CO_2}M - Pe_{CO_2}\frac{A}{l}\left(p_{CO_2,in} - p_{CO_2,out}\right) \tag{12.2}$$

where R is the respiration rate expressed in volume of gas generated/consumed per unit of time (t) and weight of the product (M), Pe is the permeability, l is the thickness, A is the mass transfer area, n is the number of molecules, and p is the partial pressure. At equilibrium, Eqs. (12.1) and (12.2) are equal to zero and Eq. (12.3) is as below:

$$\frac{p^{\mathrm{Eq}}{}_{\mathrm{O_2,in}} - p_{\mathrm{O_2,out}}}{p^{\mathrm{Eq}}{}_{\mathrm{CO_2,in}} - p_{\mathrm{CO_2,out}}} = -\frac{\beta}{RQ} \tag{12.3}$$

where $RQ = R_{\mathrm{CO_2}}/R_{\mathrm{O_2}}$ and $\beta = Pe_{\mathrm{CO_2}}/Pe_{\mathrm{O_2}}$.

Sometimes relative permeability is called permselectivity. Permselectivity can be customized according to the selection of the polymer, type and amount of nanoparticles, plasticizer, and film preparation method.

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Biopolymer-Based Active and Intelligent Packaging for Food Applications

13

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Abstract

Food packaging has a considerable vital effect in preserving the food quality from any physico-chemical and environmental damage. The requirement of consumers and industry for improved quality food has resulted in the production of active and intelligent food packaging technology in recent years. Traditionally, plastic material is applied in the food industry owing to its extensive accessibility and excellent mechanical properties at a low cost. The rising environmental and health concern of plastic packaging waste has conducted to the introduction of eco-friendly materials. Bio-based polymer materials can be treated for the formation of biodegradable plastics. To succeed in this aim, biopolymers should be inexpensive, biodegradable, and richly accessible. Bioplastic packaging

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substances derived from sustainable biomass could be applied as a continuous replacement to petrochemically derived plastic substances. This chapter highlights the progress in biopolymer-developed packaging with considering active and intelligent packaging.

Keywords

Biopolymers · Blends · Extrusion · Solvent casting · Electrospinning · 3D Printing · Layer by layer

13.1 Introduction

The requirement of consumers and industry for improved quality food has resulted in the fabrication of active and intelligent food packaging technology (Aider 2010; Brizio and Prentice 2014). Monitoring and controlling the quality of food products in actual time are essential for an active or smart packaging. In this connection, bio-derived food packages' emergence is considered an ongoing activity (Wen et al. 2016). Bio-derived packaging for food is commonly formulated from obviously existing biopolymers alone or in combination with synthetic biodegradable polymers with effective film- and coating-producing characteristics. In this chapter, the described active films are commonly carbohydrate-based polymers comprising chitosan, starch, cellulose, and pectin (Abugoch et al. 2016).

Moreover, the application of proteins (Abugoch et al. 2016) and the blend of other natural carbohydrates with artificial polymers and proteins as well as other biodegradable polymers such as poly-lactic acid (PLA) (Samsudin et al. 2014), which are applied for active and intelligent bio-packaging in food, have been described. The expansion of these polymers' application in food packaging due to their biodegradability provides a certain environmental advantage, leading to decreasing ecological pollution. Furthermore, active ingredients can be added to the polymeric background, which is valuable to convert the biodegradable polymeric film into an inexpensive active or smart polymer. According to this technique, different kinds of active and intelligent packaging systems such as antimicrobial (Wen et al. 2016) and antioxidant (Li et al. 2014), pH indicator (Silva-Pereira et al. 2015), the time-temperature indicator (TTI) (Brizio and Prentice 2014), and oxygen barrier monitoring (Marek et al. 2013) films have been developed. Therefore, bio-packaging for food can be a multipurpose and inexpensive technique to monitor and protect the foods against environmental conditions. In conclusion, biopolymer films have various promising functions in the food sector. This chapter considers several of these functions and evaluates the difficulties connected with the fabrication of active and smart biodegradable packaging in the food systems.

13.2 Food Packaging Revolution

13.2.1 Conventional Food Packaging

Traditional food packaging is recognized according to the four main functions (protective barrier, communication, convenience, and containment). The protective barrier can be described as maintaining food and foodstuffs in a reduced volume and avoiding its leak or damage and preserving it versus promising contamination and changes. Communication can be described as food packaging communication through valuable facts about the included foodstuffs and their nutritional properties, along with guides about preparation. Convenience can also be described as the condition provided by packaging for consumers to enjoy food the way they choose. Food packages might be fabricated concerning specific lifestyles, such as portability and multiple single portions. Containment can be described as the most important function of the package, and its role in easy transportation or marketing cannot be denied (Vanderroost et al. 2014).

13.2.2 Progresses in Food Packaging

The critical function of packaging due to connecting with the product's safety and quality cannot be denied. The principal aim of food packaging is to enclose and preserve the food so that it convinces the industrial economic necessities and consumer favorites, preserves the quality, and decreases damaging effects on the environment. The primary role of packaging, including protection, convenience, containment, and communication, is implemented with traditional packaging systems. Several new styles in the packaging systems have been developed to answer the consumer requirement relating high quality and safe food with improved shelf life (Appendini and Hotchkiss 2002). Protection and communication roles are now being converted into active and intelligent packaging. The problem of foodborne microbial prevalence has been led to rapid advances in the food packaging area. One of the significant parameters in the packaging industry's rapid innovations is the problem of foodborne microbial outbreaks, which need the utilization of antimicrobial agents in the packaging system (Appendini and Hotchkiss 2002). In the past few years, active packaging, intelligent packaging, and biopolymer-based packaging have been expanded and effectively utilized in food packaging to enhance communication, improve food properties, prolong its shelf life, and present indications about healthiness and control its freshness. These innovative technologies, by implementing different methods including monitoring temperature and moisture, incorporating chemicals, and applying an effective packaging system through the elimination of several microbial, biochemical, and enzymatic reactions, extend food's shelf life. The promising features of innovative packaging systems comprising sustainability and biocompatibility of eco-friendly polymers, monitoring and supervising capability of intelligent packaging, and

interchangeable and dynamic function of active packaging have been caused the revolution from conventional packaging models toward innovative approaches.

13.2.2.1 Intelligent Packaging

Intelligent packaging (Fig. 13.1) can be described mainly as packaging that comprises an indicator inside or outside the packaging to report facts related to the feature of the packaged food's history (Dobrucka and Cierpiszewski 2014). Based on the other description, intelligent packaging can also be termed as smart packaging, in such a way that some properties of contained food or the surroundings which bordered the food within packaging are detected by packaging to inform the producer, retailer, and consumer about the condition of the product (Hutton 2003). Intelligent packaging appliances are efficient in detecting and preparing information about packaged food's properties and function and can guarantee the product's safety and quality and container integrity and are being developed for purposes such as product accuracy and product monitoring (Day and Potter 2011). Intelligent packaging devices are classified as sensors, time-temperature indicators, microbial growth indicators, and gas-sensing dyes. Intelligent packaging also clarifies facts about food quality. The product's history in the food supply chain can be followed via intelligent packaging (Puligundla et al. 2012). Intelligent packaging should not be mistaken with active packaging.

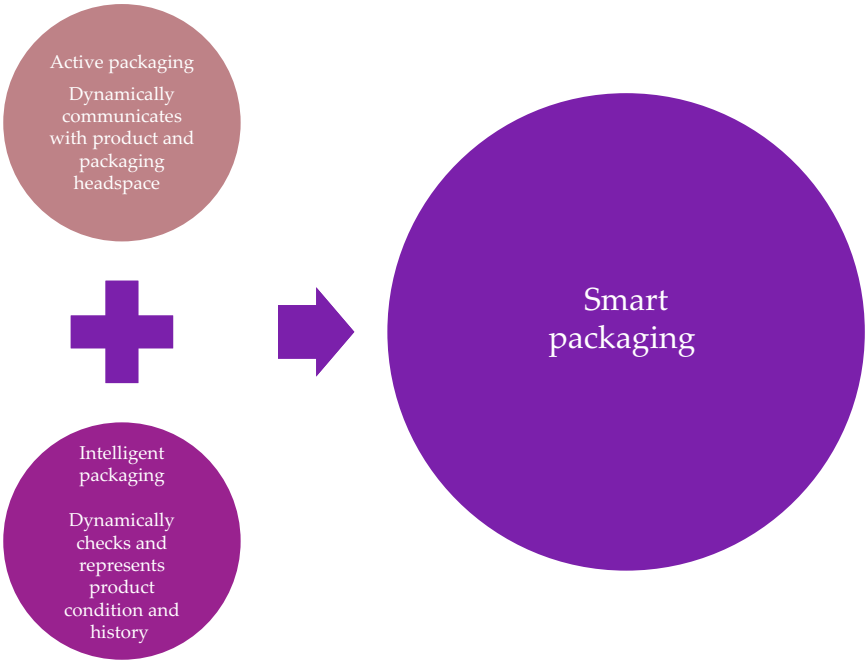

Fig. 13.1 Classification of smart packaging

13.2.2.2 Active Packaging

Active packaging is related to improving the protection role of traditional food packaging. This purpose could be achieved by incorporating a component within the packaging to allow the absorption or release of materials into/from the packed food product or the atmosphere around the food product (Day and Potter 2011). Therefore, active packaging can be explained as a structure in which the product's shelf life is extended, and the condition of packed food is improved through the cooperation of product, package, and the surroundings (Miltz et al. 1995). Cooperation of intelligent and active packaging led to the development of smart packaging. Smart packaging supports a complete packaging explanation that examines alterations in the surroundings (intelligent) and/or in the product and performs versus these alterations (active). Although the theory of smart and intelligent packaging is habitually described as equivalent in literature, they are not similar. Three major technologies are recognized for intelligent packaging, including sensors, indicators, and radio frequency identification (RFID) systems (Kerry et al. 2006). These technologies are different in physical structure, and the quantity and sort of data involved and distributed (Vanderroost et al. 2014) interact.

13.3 Development of Films for Biodegradable Food Packaging

Typically, active and intelligent films are developed applying the casting method (Arzate-Vázquez et al. 2012), which can fabricate films cost-effectively. In this technique, biopolymer dispersions are prepared by adding the determined content of biopolymer in water, and then the suspension is transferred over a glass cover and dried to reach constant weight. The fabrication of active and smart films using this method needs polymers with great strength and the capability to make networks of organized and heat-resistant copolymers.

As complicated mechanisms are not involved in the casting method, it can be applied as a versatile, low-cost, quick, and easy film preparation method. This method has been broadly applied in the film formation processes (Barbosa-Pereira et al. 2014) and indicates the selected method for the fabrication of innovative and developed active and smart polymer films. Other methods also fabricated the films for active food packaging. For instance, curcumin, as a bioactive agent, has been effectively incorporated in a chitosan-PVA silver nanocomposite film (Vimala et al. 2011), and layer-by-layer (L-b-L) thin films with utilization in active food packaging, for instance, oxygen barrier (Laufer et al. 2013), antioxidant (Shutava and Lvov 2012), and antimicrobial packaging, have been reported (Hosseini et al. 2016).

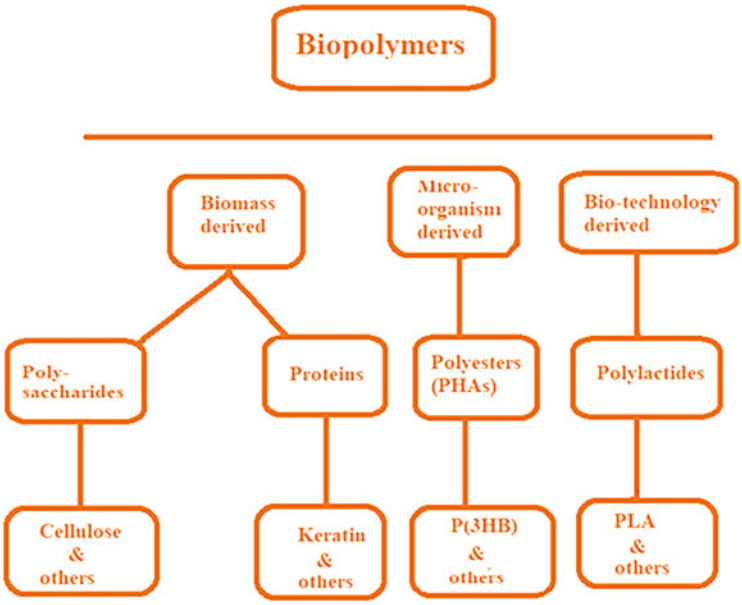

Fig. 13.2 Category of biopolymers (PHAs, PHB, PHBV, and PLA refer to polyhydroxyalkanoates, polyhydroxybutyrate, 3-hydroxybutyrate-co-3-hydroxyvalerate, and polylactic acid, respectively) (Iqbal et al. 2015)

13.4 Polymers from Renewable Resources

Biopolymers/natural polymers are identified as polymers produced through metabolic processes via living creatures, including plants and microorganisms. Fig. 13.2 indicates the category of biopolymers based on their source (Iqbal et al. 2015). Carbohydrate-based biopolymers included starch, chitosan, cellulose, or lignin- and protein-based biopolymers such as keratin, collagen, and gelatin, and polyhydroxyalkanoates, for example, polyhydroxy butyrate (PHB) with its copolymer 3-hydroxybutyrate-co-3-hydroxyvalerate (PHBV), have been described. Lignocellulose wood fibers comprise a considerable content of celluloses and hemicelluloses. Development of films from these biopolymers indicates appropriate toughness, tensile strength, great apparent shine, and suitable clearness (Darni et al. 2017). Commonly, cellulose is modified throughout the chemical process of dissolution to accelerate the fracture of polymer molecules. Cellulose by-products that are achieved after chain breakage can be redeveloped as coatings.

13.4.1 Polymers Derived from Microbes

Polylactic acid (PLA), polyhydroxyalkanoates (PHAs), and exopolysaccharides (EPS) are considered as three main biopolymers which are generated through fermentation (Qamar et al. 2020). The monomers for the production of PHA, PLA, and BioPE (biopolyethylene) can be achieved from biodegradable sources. Among different renewable biomaterials, sugarcane and corn waste materials are valuable sources since their monomers indicate a lower polymerization quantity. Therefore, their separation from plant suppliers is comfortable.

13.4.1.1 Polylactic Acid (PLA)

Fermentation of sugars, generally cornstarch, led to develop bio-derived lactide and lactic acid. A remarkable route for lactide and lactic acid generation is the biomass of lignocellulosic after hydrolysis. In comparison to traditional thermoplastics, PLA has a lower processing temperature (de Kort et al. 2019). PLA can be purified through electrodialysis, solvent separation, adsorption, distillation, and reverse osmosis (Huang et al. 2020). Enhancing raw substances reduces the expenses of transition processes, but the cost of hydrolysis and the fermentation of enzymes will increase (Nampoothiri et al. 2010). Following fermentation, existent proteins are separated via filtration methods. Bio-transition of lactate to sodium hydroxide and lactic acid can be achieved through bipolar electrodialysis. Generated lactide is purified via vacuum distillation, and finally, lactic acid is condensed and polymerized to generate PLA (Pal and Katiyar 2017). Lately, several PLA-based films have exhibited desired physical-mechanical and biological properties in comparison to synthetic polymers. In the last few years, considerable attention toward physically or chemically modifying PLA to attain its desired properties for consumption has been increased (Nazrin et al. 2020). The expansion of eco-friendly matters by combination with other polymers is a topic of interest. Furthermore, the fabrication of PLA-based composites incorporated by various nanoparticles is a promising method for induction of desired functionality and reducing production cost (Bilal et al. 2020).

13.4.1.2 Polyhydroxyalkanoates (PHAs)

PHAs include a wide collection of biopolymers. PHAs can convert to PLA through thermal treatment and are produced via renewable raw compounds (e.g., fatty acids, maltose, glucose) through biotechnological alteration due to various microorganism effects (Nobuta et al. 2016). Polymers with diverse structure blocks and distinct properties can be fabricated by selecting different microorganisms, carbon sources, additives, and experiment settings. Several forms of PHAs can be applied in packaging and textile industries, as well as medicinal implants. Limited utilization of PHAs as bioplastics has been reported. The reason for that can be explained by the high fabrication and recovery cost of PHAs. To solve this issue, high-cost feedstocks should be replaced with cost-effective raw materials, including the application of wood-derived raw compounds comprising hemicelluloses that can be applied for the fabrication of microbial PHAs (Qamar et al. 2020).

13.4.1.3 Exopolysaccharides (EPS)

EPS are complicated biopolymers, mostly including carbohydrates produced via several microbial species (Asgher et al. 2020). Various types of polysaccharides have been identified which include alginate, dextrin, glucans, levan, etc. Among other EPS classes, kefiran is considered a valuable source because of being water-soluble and having biodegradable properties (Judith Araceli Piermaria et al. 2009). Kefiran production is achieved through milk fermentation in kefir production (Hu et al. 2007). Numerous valuable characteristics of kefiran have been caused to be considered for population health promotion, for example, desirable antioxidant and antimicrobial capacities (Romero et al. 2013), anti-inflammatory capability, etc. Furthermore, kefiran has been applied widely in food systems as emulsifying, stabilizing, and thickening agent (Judith A Piermaria et al. 2008). Novel features of films synthesized from kefiran such as biocompatibility, biodegradability, being safe, having excellent emulsifying and stabilizing properties, and superior WPI and mechanical features have attracted scientific attention (Júnior et al. 2020). Moreover, kefiran-synthesized film bioplastics have indicated outstanding appearance features and could be successfully fabricated via edible plasticizers such as glycerol (Idumah et al. 2019). Consequently, the expansion of kefiran-based films can cause the suitable generation of coatings and packaging substances with enhanced physico-chemical characteristics and environmentally friendly property.

13.4.2 Wood-Based Polymers

13.4.2.1 Celluloses and Hemicelluloses

About 40–50% and 25–30% of lignocellulosic weight is related to cellulose and hemicelluloses, respectively. Cellulose films exhibit mechanical properties, great surface gloss, and outstanding transparency (Guzman-Puyol et al. 2019). Generally, the cellulose is modified throughout the dissolution procedure to simplify the fracture of the polymer molecules. Cellulose products achieved after polymer molecules' breaking can be redeveloped as biodegradable film fabrication and additional barrier functions. Hemicelluloses, as wood-derived hydrophilic and complex heterogeneous polysaccharides, are amorphous in that their structure is less ordered and possesses very low thermal resistance (Qamar et al. 2020). Films synthesized from hemicelluloses are weak; nevertheless, hemicellulosic-based film properties such as flexibility, toughness, and minimal oxygen permeability can be improved by adding plasticizer (Yuan et al. 2020). These films indicate a significant function in product packaging owing to their minimal oxygen permeability. Application of softwood hemicelluloses and the glucuronoxylan (hardwood hemicelluloses) in the fabrication of biodegradable films with improved oxygen barrier features and flexibility in the forms of composites/blends with bioplasticizer has been reported (Martins et al. 2015). However, the prepared films were susceptible to aqueous uptake. In this condition, increasing the polymer content enhanced WPI (whey protein isolate) and mechanical performance of packaging.

13.4.2.2 Starch

Starch, due to its important film-developing characteristics, being accessible and cost-effective is considered as the main familiar plant-derived polysaccharide for the fabrication of eco-friendly films (Hassan et al. 2018). Abundant biodegradable coatings or packaging films have been developed from different starches alone or combined with the other polymers to increase the product's shelf life (Ojogbo et al. 2021). In Red's study storage, Crimson grapes were increased using composite coating prepared from cornstarch/gelatin plasticized with sorbitol. The final bio composite characteristics such as solubility and mechanical characteristics were improved after blending gelatin within the starch matrix. Furthermore, the WPI of the composite film decreased considerably compared to waxy cornstarch and modified mixtures of films (Farayde Matta Fakhouri et al. 2015). Mango kernel starch has been applied successfully as a packaging matrix to extend the shelf life of tomatoes. The ripening procedure of tomatoes was lowered efficiently after using this packaging material which was examined by evaluating several physical and chemical factors (Nawab et al. 2017). The application of this important biopolymer is not limited to the packaging and bioplastic sector, such a way that the application of starch in native or modified form has been expanded in pharmaceutical systems (A. Sharma et al. 2019).

13.4.2.3 Lignins

Every year, about 50–60 million tons of lignin are synthesized in paper and pulp industries based on approximation. From this amount, only 2% is used for commercial applications, and 98% is consumed in boilers as an inexpensive fuel (Bajwa et al. 2019). The possible employment of lignin-derived biomass as a low-cost reinforcement was investigated in polyurethane formulations to substitute synthetic polymers and subsequently bettered the polyurethane's mechanical and thermal characteristics. The capability of lignin in replacing phenolic substances in phenol-formaldehyde (PF) resin production has been proven. Recently, lignin has been used as a biodegradable blend for the phenols in PF resin fabrication (Bajwa et al. 2019). Phenolated lignin-PF resins indicated improved physicomechanical features than pristine lignins. In recent years, the fabrication and application of aldehydes originated from lignin biomass were described as a promising formaldehyde substitute (Foyer et al. 2016).

13.4.3 Protein-Based Polymers

13.4.3.1 Collagen and Gelatin

Collagen and gelatin are two types of animal-based biopolymers. Collagen is recognized as a rich source of protein in nature (Arora and Padua 2010). In animals, nearly 20–25% of body weight is related to collagen. The collagen structure has been formed of three cross-linked α-chains, whereas collagen in denatured form is entitled gelatin and consisted of several polypeptides and proteins. Collagen includes plenty of several amino acids, including methionine, hydroxyproline/proline, and glycine

(Matmaroh et al. 2011). The extrusion process is applied for collagen-based bioplastic fabrication with different utilizations (Oechsle et al. 2017), whereas film fabrication gelatin needs a wet process through the development of film-producing dispersion. Biodegradable films that are prepared from collagen indicate suitable mechanical characteristics. For example, hydrolyzed collagen films revealed excellent mechanical performance (Fadini et al. 2013). Nevertheless, gelatin films provided inadequate mechanical and barrier characteristics, which indicate their hydrophilic character (Ciannamea et al. 2018).

13.4.3.2 Wheat Gluten Films

Wheat gluten films containing plasticizer can be fabricated through the severe extrusion process and subsequently compression and molding as final treatments (Zubeldía et al. 2015). Various interactions such as hydrophobic and hydrogen as well as disulfide bonds participate in the film formation process. Disulfide bonds are generated by sulfhydryl groups (Sharma et al. 2017). Polymers are denaturized through heat treatment that in this condition, native hydrophobic and disulfide groups hidden within protein structure were exposed. Additional disulfide bonds are generated as a result of the oxidation of gluten during the drying process. Film transparency is influenced by the gluten purity and casting solution, which can be alkaline or acidic (Gutiérrez-Jara et al. 2020). Wheat gluten-developed films showed uniformity, good gas barrier, and suitable mechanical properties (Mojumdar et al. 2011).

13.4.3.3 Soy Protein Film

The development of bioplastic films can also be performed using soy proteins for packaging applications. Soy protein-based films are transparent, elastic, and economical than other protein-derived biofilms (Otoni et al. 2016). Furthermore, in low moisture content, they reveal suitable oxygen barrier characteristics (Denavi et al. 2009). The most significant drawbacks of soy protein-developed films are their low heat stability, low mechanical strength, and being allergenic versus low-density polyethylene (LDPE). Film fabrication from the aqueous solution of soy protein isolate on stainless steel covers has been reported at high temperatures. Film development from other protein-derived raw materials such as pea protein, pistachio globulin protein, canola protein, etc. has been described (Zhang et al. 2018).

13.4.3.4 Whey Protein Films

Whey protein has remarkable efficient properties and film-developing capabilities (McHugh et al. 1994). High clearness, low oil, and gas permeability at approximately low moisture content have been attributed to whey protein-based films (Qamar et al. 2020). Nevertheless, films developed from whey protein indicate weak moisture permeability of whey protein-based film (Fang et al. 2002). The incorporation of lipids into the film matrix is one of the most promising methods to reducing the moisture barrier and several functional features of whey-developed films (Bahram et al. 2014). However, considering the cooperation formed among different biopolymers throughout coating development, it is essential for the

fabrication of packaging material with desirable physico-chemical characteristics and functionality. Çakmak et al. (2020) fabricated edible whey protein isolate films containing glycerol as a plasticizer. Bergamot oils and lemon were incorporated as bioactive compounds into developed bioplastic films. Results revealed strong antimicrobial activity of essential oil-incorporated films. Furthermore, considerable oxygen and WVP (water vapor permeability) were described.

13.5 Processing of Biodegradable Packaging Substances

Commonly, for achieving the favorite desirable physicomechanical and biological properties in the packaging, a combination of biopolymers and additives is used. Plasticizers are commonly added to develop thermal properties, workability, and brittleness, but the subsequent material is not considered a composite. The plasticizers applied in biodegradable packaging were broadly evaluated (Mekonnen et al. 2013). Two methods were applied to fabricate packaging materials which are termed as "wet process" (WP) and "dry process" (DP). The "WP" includes dissolving or dispersing the polymer in a solvent that will be separated via evaporation later; therefore, a film on a support will be formed. This procedure is very general in laboratory methods and in the case of most biopolymers is applied. The "DP" is dependent on the thermoplastic characteristic of the substances, comprises the mixture and melting of the biopolymer that is capable of forming a film through laminating or blowing (e.g., bags or sheets), or is inserted in a mold (e.g., bottles). A single material or a composite can be fabricated by these two methods (Agarwal et al. 2014). The final properties of packaging materials are greatly influenced by the methodology which is applied.

13.5.1 WP

The WP depends on the casting and solvent evaporation where the biopolymer is dissolvable. This approach is identified as the "solution casting" technique and is broadly applied in the fabrication of biodegradable films and different synthetic materials where dry processing is generally applied. The WP is commonly employed to develop the bio-nanocomposites applied as coatings, as the film-forming dispersion is poured on an area (mostly on foods), producing a coating layer that will dry and fabricate a film. In solvent, generally, water is used, but ethanol and other organic solvents can be utilized. At first, the biopolymer is dissolved in the presence or absence of heating (for several biopolymers, the employment of temperature is essential) until the dissolution of the biopolymer is completed. Next, several corrections to the film-forming dispersion can be implemented, including adjusting the pH or plastering agents and/or surfactants' employment. For the development of nanocomposites, the nanoparticles are added to the film-producing dispersion and subsequently blended. The nanoparticles' dispersity in the film matrix is intensely affected by the previous treatments employed throughout the mixing step and

sometimes the application of ultrasounds or high-pressure homogenization. However, applying these approaches in biodegradable films' fabrication should be examined precisely because they can alter the biopolymer's structure.

13.5.2 DP

Packaging materials can be generated through dry processing as a low-cost method in comparison to wet processes. In addition to lower cost, the DP method is environmentally friendly because of the absence of organic solvents. Processing methods, including film blowing, extrusion, or injection molding, are applied to fabricate synthetic films and are being adjusted to biodegradable film. Proteins and polysaccharides are influenced by thermal processing, displaying a limited processing strength range and therefore decreasing their application in traditional extrusion or molding technologies. However, based on the report of several authors, dry processes have been applied successfully to produce packaging materials from polysaccharides and proteins, for example, starch and gelatin composites, chitosan and starch composites (Fakhouri et al. 2013), and soy protein and agar (Garrido et al. 2018) composites, demonstrating the potential of this inexpensive procedure to fabricate these materials. Nevertheless, there is limited information on biodegradable nanocomposites' dry processing, and more examinations are required to discover exact processing factors, distinct additives, or preparations.

13.5.3 In Situ Polymerization

In the condition of applying in situ polymerization, the nanoparticles are blended with a dispersion of monomers, and following polymerization activation, the nanoparticles are preserved in the biopolymer composition. However, this method application is limited, and to the best of our knowledge, this technique can only be used to PLA.

13.5.4 Bilayer Systems

A substitute method for the fabrication of biodegradable composites is applying a bilayer or a multilayer system. In this bio-nanocomposite fabrication method, a layer is deposited on the film used as a carrier base for the combination of nanoparticles. This procedure gives some advantages; for example, thermosensitive nanoparticles (which cannot be combined through dry processes) can be deposited through this technique. Furthermore, nanostructures that should perform on the outside area of the packaging substance and contact inside the food can be developed through this technique. Three deposition procedures can be applied, layer-by-layer, coating, and electrospinning; deposition of nanostructures can be performed effectively through

each of these three methods. Furthermore, the transport characteristics of packaging films can be enhanced by applying these techniques (Flores-López et al. 2016).

13.6 Application of Biopolymers in Active Packaging

Polymers produced chemically have a higher request for packaging applications due to being low permeable, having excellent mechanical characteristics, and low cost. However, the most crucial disadvantage of these materials is that they cannot be disposed of safely by the environment. Environmental concerns are explained via the application of non-sustainable raw substances to fabricate the packaging structure, and no biodegradable packaging materials are accumulated in the environment. For overcoming this challenge, traditional chemically synthesized packaging materials have been substituted with biodegradable materials. These biodegradable packaging substances are achieved from renewable sources, and with the application of natural polymers, environmental pollution was decreased. In the following sections, the application of biodegradable materials to fabricate active and intelligent packaging has been reviewed.

13.6.1 Moisture Absorbers

The shelf life of food can be increased by controlling their moisture. The quality of the food products is decreased in leaching solutions such as blood or additional fluids in fish and meat products. Also, the growth of microbes and the oxidation of fat are accelerated when additional water is present within the packaged foods. The moisture absorber procedure is based on water absorption, the application of the excess water is removed, and the relative humidity in the headspace of packaging is controlled. For achieving this goal, extremely hygroscopic and dehydrating compounds, including cellulose fibers, polypropylene glycol, carbohydrates, minerals, polyacrylate salts, molecular sieves, silica gel, and calcium oxide, etc., should be applied in the packaging system. The kind of moisture absorber is selected according to the product's weight and size; besides the original water activity of the absorber is important (Realini and Marcos 2014) (Table 13.1).

13.6.2 Antimicrobial Packaging

Throughout the production procedure, microbiological pollutions are possible to happen when the food manufacturing procedure is inadequate or insufficient, though several of these techniques are not applicable in the condition of food products, including fresh meat. The antimicrobial properties of several compounds, including essential oils, carbon dioxide, chlorine dioxide, ethanol, organic acids, antibiotics, and spices, etc., have been demonstrated in the food industry (Ribeiro-Santos et al. 2017). Application of various antimicrobial agents in packaging systems for

Table 13.1 Several kinds of biodegradable packaging with added compounds versus some microorganisms

Bio-based packaging	Antimicrobial compound	Purpose microorganisms	Reference
Hydroxypropyl methylcellulose	Kiam wood extract (*Cotylelobium lanceolatum*)	S. aureus, L. monocytogenes, and E. coli O175:H7	Khwaldia et al. (2014)
Gelatin obtained from the skin	Essential oils from bergamot and lemongrass	*L. monocytogenes*, *E. coli*, *S. aureus*, and *S. typhimurium*	Ahmad et al. (2012)
Whey protein	Lactic and propionic acids, chitooligosaccharides, and natamycin	*S. aureus*, *Y. lipolytica*, and *E. coli*	Ramos et al. (2012)
Wheat gluten	Potassium sorbate	*Fusarium incarnatum* and *Aspergillus niger*	Türe et al. (2012)
Soy protein	Nisin, EDTA, and grape seed extract	*L. monocytogenes*, *S. typhimurium*, and *E. coli* O175:H7	Sivarooban et al. (2008)
Carboxymethylcellulose	Potassium sorbate	*Aspergillus parasiticus* and *Aspergillus flavus*	Sayanjali et al. (2011)
Fish skin gelatin and egg white	Clove essential oil	*E. faecium*, *V. parahaemolyticus*, *C. perfringens*, and *P. aeruginosa*	Núñez-Flores et al. (2012)
Triticale protein	The essential oil of oregano	*S. aureus*, *P. aeruginosa*, and *E. coli*	Aguirre et al. (2013)
Sunflower protein	Essential oils of clove	*Clostridium perfringens*, *E. faecium*, *B. coagulans*, *B. cereus*, *V. parahaemolyticus*, *P. fluorescens*, and *A. niger*	Sánchez-González et al. (2013)
Pea protein isolate, hydroxyl propyl methylcellulose, methylcellulose, or sodium caseinate	Bacteriocins	*L. innocua*	Acquah et al. (2020) and Sánchez-González et al. (2013)

extending food products' shelf life through releasing essential oils, plant extracts, carbon dioxide, and allyl isothiocyanate was reported (Echegoyen and Nerín 2015). The efficient application of chlorine dioxide present in solid, liquid, and gaseous microorganisms against different microorganisms such as fungi, bacteria, and several viruses in fish, poultry, meat, confectionery, baked foods, and dairy products has been proved (Qin et al. 2017). The decomposition of grapes can be delayed using SO_2, and a combination of other treatments such as gamma-radiation and thermal

Table 13.2 Different biopolymers with natural antimicrobial agents applied in the fabrication of the packaging system

Biopolymers		Antimicrobial ingredients	Applied product	References
Cellulose and derivatives	Cellulose	Pediocin	Meat	Rodriguez-Lafuente et al. (2010)
	HPMC	Ethanol/citric acid/ sorbic acid	Tomato	Rodriguez-Lafuente et al. (2010)
	Cellulose-based paper	Nisin/Lacticin 3147	Cheese/ham	Johnson et al. (2018)
	Alginate	Nisin	Beef	Mishra et al. (2021)
		Nisin	MRS broth/ skim milk	Mishra et al. (2021)
		Nisin	Poultry	Natrajan and Sheldon (2000)
	Chitosan	Sodium benzoate/ potassium sorbate	Culture media	Sánchez-González et al. (2011)
		Acetic/propionic acid	Meat	Ouattara et al. (2000)
	Carrageenan	Chlortetracycline/ oxytetracycline	Poultry	Natrajan and Sheldon (2000)
Proteins	Wheat gluten	Sorbic acid	Ethanol water	Janjarasskul and Krochta (2010)
	Corn zein	Lysozyme/nisin	Culture media	Gómez-Estaca et al. (2010)
	Soy protein	Lysozyme/nisin	Culture media	Padgett et al. (2000)
	Whey protein	Potassium sorbate	Water-glycerol	Ozdemir and Floros (2001)
		p-Aminobenzoic/ sorbic acids	Culture medium	Ozdemir and Floros (2001)
Polysaccharide	Starch and derivatives	Potassium sorbate	Strawberry	Perdones et al. (2014)

treatment increases its effect. The major function of CO_2 in the packaging atmosphere for preventing the microorganism's activity and reducing respiration speed in fruits and vegetables has been proven. In antimicrobial packaging based on CO_2, it should continuously release to keep the required concentration in most packaging films. More amounts of CO_2 (10–80%) are needed to control the microbial growth upon the surface of meat products, extending their shelf life (Zorić et al. 2016) (Table 13.2).

13.6.3 Carbon Dioxide Emitters

Sachets and absorbent materials with the capability of emitting CO_2 are applied for protecting the meat-based products. The shelf life of salmon (Fabra et al. 2018) and cod fillets (Zhu et al. 2016) has been improved through the application of carbon dioxide emitters into vacuum packaging. In previous research, the shelf life of various food products was extended through applications of carbon dioxide emitters and MAP by preventing the collapse of packages (Holck et al. 2014). The incorporation of CO_2 emitters within packaging films was developed in recent years. Recently, a study has been performed on the CO_2 emitter applications in the active packaging for monitoring the quality of meat products consumed as ready-to-eat (Chen and Brody 2013).

13.6.4 Oxygen Scavengers

The shelf life of muscle-based products can be extended by eliminating residual O_2 molecules by applying different scavengers. O_2 scavengers are commonly developed based on iron powder oxidation. In recent years, the replacement of metal-based scavengers with organic ones such as catechol, ascorbic acid, and polyunsaturated fatty acids has been considered deeply which can be incorporated within packaging materials (Yoon et al. 2014). Oxygen scavengers incorporating microbes were considered a replacement for chemical scavengers due to consumer preference and sustainability. In recent years, the application of enzymes in active packaging has been widespread in the food industry (Olsson et al. 2013). The oxidation and rancidity of packed foods in chilled states can be avoided efficiently using developed active packaging. The oxygen barrier activity of polymer films can be enhanced through a combination of unsaturated functional groups with oxygen absorption capability (Zhang et al. 2017a). Successful application of a natural, free radical scavenger such as α-tocopherol and a transition metal for the fabrication of a system with oxygen-absorbing capacity has been reported (Kirschweng et al. 2017). In another study, the combination of α-tocopherol-loaded nanoparticles and iron chloride was incorporated into the gelatin-based films with efficient oxygen-scavenging capacity (Byun et al. 2012).

13.6.5 Antioxidant Packaging

One of the important factors in the emergence of food spoilage is fat oxidation caused by microbial growth. Moreover, the shelf life, functionality, and nutritional quality of foods are reduced, and their taste and aroma are varied via lipid oxidation in foods (Busolo and Lagaron 2012). Oxidation of foods can be slowed down through the application of oxygen scavengers and antioxidant packaging. Recently, the utilization of antioxidants with natural origin, including vitamin E and the phenolic compounds, has been considered deeply (Bonilla et al. 2018). Edible

coatings with antioxidant capability are applied to monitor oxygen concentration in foods to decrease lipid oxidation, microbial growth, and textural alterations (Ahmed et al. 2017). The main reason for the oxidation of food products is radicals (mainly hydroxyl and superoxide) formed during the oxidation procedure. Food oxidation can be prevented through the elimination of these radicals throughout their formation. The application of natural compounds with the capability of trapping radicals can prevent food ingredient oxidation. For example, the application of active packaging (high-density polyethylene, ethylene vinyl alcohol) film based on α-tocopherol can delay the oxidation procedure of milk powder efficiently (Fakhouri et al. 2018). In another study, cellulosic films containing cysteine and sulfite were covered on apple slices to achieve brighter apples with reduced browning (Yang et al. 2019).

13.7 Application of Biopolymers in Intelligent Packaging

Smart edible coatings as adhesive markers are fixed to packages that reveal the product's condition to the consumer through an "on/off" switching operation in reaction to variations in external or internal factors (Pavelková 2013). The product's status regarding its safety and quality is indicated by checking exterior or interior factors that are used for demonstrating if food is safe, fresh, ripped, firmed, or not (Toro-Márquez et al. 2018). HACCP's (Hazard Analysis and Critical Control Point) and QACCP's (Quality Analysis of Critical Control Point) systems can be improved with the application of smart edible coatings (Biji et al. 2015). The shelf life of various foods is affected by several factors, mainly temperature and pH (Biji et al. 2015); hence, most exterior or interior factors are examined through monitoring the variation in temperature, pH, or a derivative material connected with chemical or biological changes affected by temperature or pH (e.g., degradation of food ingredients and microbial growth). Smart edible coatings, according to the principle of checking exterior or interior factors, are categorized into three forms: indicators, data carriers, and sensors (Fig. 13.3) (Biji et al. 2015).

13.7.1 Indicators

The existence of a matter in a qualitative or semiquantitative condition can be detected using indicator systems (Ghaani et al. 2016a). Generally, an observable reaction was detected via the application of indicator systems, including color alterations due to the biological substances, redox oxidation, or a physical alteration (Pavelková 2013). These indicators include the following:

13.7.1.1 Temperature Indicators (TIs)

The cooling and heating of foods below or above a critical temperature can be detected using TIs related to denaturation of proteins or growth of microbes throughout freezing or defrosting procedures (Vanderroost et al. 2014). During

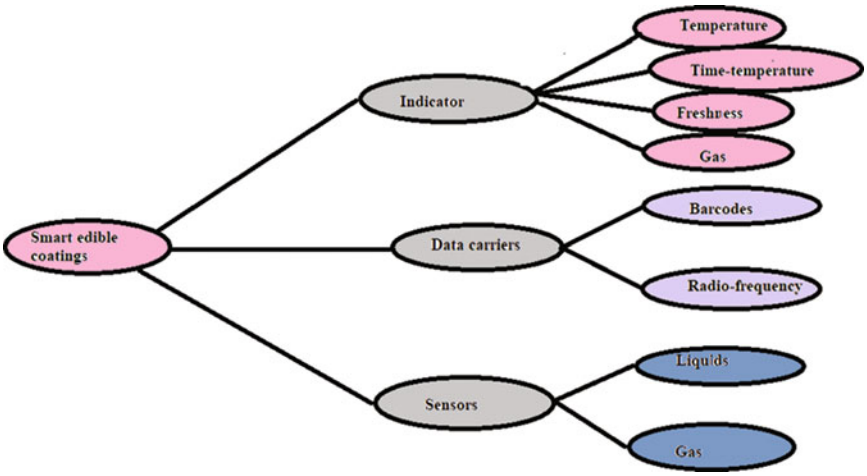

Fig. 13.3 Division of smart edible coatings regarding the basis of checking exterior or interior factors. Adapted from Ghaani et al. (2016a)

heat-sensitive polymerization in TIs, the applied monomers, including acetylene groups (R1C ≡ C–C ≡ CR2), are converted into polydiacetylene (R1[C = C – C = C]nR2), which led to changing the color from red to blue when subjected to high temperature or radiation (Wang et al. 2015). Reversible or irreversible color alteration in various temperature ranges can be observed in TIs through a combination of azobenzene groups with acetylene groups (Wang et al. 2015). Several combinations including acetylene group such as 5,7-dodecadiyn-1,12-diol-bis (octadecyl urethane), 5,7-dodecadiyn1,12-diol-bis (methoxycarbonyl urethane), and 2,4-hexagon-1,6-bis (alkylurea) are also utilized to fabricate smart edible coatings. Fresh-Check® and HEATmarker® from TempTime (New Jersey, USA) are several kinds of smart edible coatings comprising acetylene polymers. A small loop of a polymer enclosed through a printed reference circle made the structure of the FreshCheck® label. By exposing the package to high temperatures, changing the loop color from light to dark can be observed gradually. For the HEATmarker®, a similar operation and changing the color of a light rectangular region can be detected. But potential toxicity of the polydiacetylene compounds was limited to their application for food packaging (Wang et al. 2015). Recently, the development of TIs based on glass transition (Tg) and melting (Tm) temperatures of the polymer's applied label has been considered. Monitor Mark™ (St. Paul, Minnesota, USA) is a temperature indicator determined by Tg. By exposing to the temperatures upper than Tg in this label, a viscoelastic compound (blue stained fatty acid ester) transfers into a porous film. The colorimetric reaction is detected from diffusion distance and influenced by temperature, the concentration of diffusing polymer, and its Tg. Bump Mark can be introduced as a temperature indicators (TIs) which is designed based on Tm. This smart edible coating indicator is composed of a flat gelatin coating placed on a bumpy plastic layer. In the presence of high temperatures, gelatin coating

converts to a liquid system, and the bumpy layer is uncovered, representing that the food should not be consumed (Brunel University London 2014). Several times at laboratory scale with the application of anthocyanins and chlorophyll as sensitive compounds and Cs as matrix have been developed. A permanent color change for a temperature range between 40 and 70 °C is observed with the application of these TIs (Maciel et al. 2012).

13.7.1.2 Time-Temperature Indicators (TTIs)

Temperature changes over time can be monitored using TTIs. Polymers or ingredients with sensitivity to light (spiropyran and spirooxazine) or even oxygen controlled by redox reaction are applied in these labels (Mohebi and Marquez 2015). Spiropyran and spirooxazine as colorless compounds absorb light at the range of 200–400 nm. At 500–600 nm, by exposing to the light at a controlled temperature due to the isomerization of these compounds, they become colorful (Kreyenschmidt et al. 2010). The most accepted smart edible coating dependent on photosensitive ingredients and natural pigments, for example, benzylpyridines, is OnVu™ by Freshpoint (Switzerland) that changes color from blue to white with time (Pavelková 2013). Several TTIs based on oxygen-sensitive ingredients (redox reaction) such as anthraquinone and derivatives have been developed. The color of these ingredients modifies from colorless to beige, being affected by time and temperature. But due to being expensive and possessing toxic effects, their application is limited (Pavelková 2013). Recently, the development of TTIs with the application of nanoparticles has been considered. In a study, hydrogen tetrachloroaurate trihydrate was added in alginate-developed coatings, and in the presence of high temperature (40 °C), the change in coating's color from gray to red was observed (Zhang et al. 2017b). The development of gold nanoparticles (AuNPs) from hydrogen tetrachloroaurate trihydrate in the presence of temperature and time caused the changing of the color of developed coating. Several other TTIs with application of enzymes as sensitive ingredients have been developed in the laboratory stage (Table 13.3).

13.7.1.3 Freshness Indicators (FIs)

FIs as smart tools can monitor food quality during the supply chain. This purpose is performed by monitoring the microbial growth, chemical variations, or gases included in the ripening procedure (Mohebi and Marquez 2015). Toxin Guard® (Toxin Alert, Canada) is a kind of FIs that is applied to meat products. Detecting the presence of several microorganisms, including *Escherichia coli*, *Listeria monocytogenes*, *Salmonella* spp., and *Campylobacter* spp., can be performed through antibodies located on polyethylene edible coating (Biji et al. 2015). SensorQ™ by the Food Quality Sensor International (FQSI) can be introduced as another example of FIs, including a green dye bromocresol fixed on a polymeric edible coating. At the condition of microbial prevalence, produced amines in meat products interact with the label and its color change (Fuertes et al. 2016).

RipeSense developed via RipSense™, and ORT (Office of Research Trainees) research is applied for controlling the quality of fresh fruit via changing its color in response to aroma substances, ethylene, and carbon dioxide released throughout the

Table 13.3 Recently developed smart edible packaging

Division	Polymeric carrier	Indicator	Responsive	Reference
TTIs	Cornstarch/iodine	Amylase	Heat	Brizio and Prentice (2015)
	No medium	Urease/ carbamide		Peng et al. (2013)
	No medium	Lipase/glycerol/ tributyrate		Peng et al. (2013)
	Cellulose	Chlorophenol red		Zabala et al. (2015)
	Trilaurin/tripalmitin	Lipase		Tsironi and Taoukis (2018)
FIs	Agar/potato starch	Anthocyanin	pH	Choi et al. (2017)
	Cornstarch/nanoclays			Gutiérrez (2018)
	Plantain starch and flour			Gutiérrez et al. (2016)
	Chitosan			Halász and Csóka (2018)
	Starch/polyvinyl alcohol			Liu et al. (2017)
	Chitosan/cornstarch			Bento et al. (2015)
	Bacterial cellulose			Pourjavaher et al. (2017)
	Cornstarch			Prietto et al. (2018)
	Chitosan/agarose			Z. Wu et al. (2018)
	Cassava starch	Green tea/basil extracts		Piñeros-Hernandez et al. (2017)
	Chitosan/κ-carrageenan	Curcumin		Pereira and Andrade (2017)
GIs	Ethyl cellulose	Anthocyanin/ polylysine	Carbon dioxide	Saliu and Della Pergola (2018)
	Alginate	Thionine	Oxygen	Vu and Won (2013)
	Polyaniline	Polyaniline	Volatile basic nitrogen	Yu et al. (2018)

TTIs Time-temperature indicators, *FIs* Freshness indicators, *GIs* Gas indicators

ripening procedure (Ghaani et al. 2016a). Production of several other FIs with anthocyanin application, which is affected by light, oxygen, and heat, is performed in the laboratory stage (Table 13.3). In several types of research, the application of nanoparticles for the anthocyanin stabilization (Araque et al. 2018) or the development of physicochemical characteristics of biopolymer-fabricated packaging (Herrera et al. 2017) was investigated.

13.7.1.4 Gas Indicators (GIs)

GIs are utilized mainly to examine the existence of poisonous gases generated through the disintegrating foodstuff procedure into boxes, threatening the consumer's health. Another function of GIs is to control the existence of oxygen and carbon dioxide intensities. The primary purpose can be applied in vacuum packaging, representing that the package was sealed suitably or not. The other one is applied for atmosphere-modified packaging (Fuertes et al. 2016). Redox dyes including methylene blue, 2,6-dichloroindophenol, or N,N,N′,N′-tetramethyl-p-phenylenediamine at the presence of a reducing substance such as reducing carbohydrates and sodium hydroxide as an alkaline material is used to ensure the colorimetrical reaction of the tag when subjected to the gas. Several well-known samples of GIs exist as the Shelf Life Guard developed by UPM, Freshilizer developed by the Toppan Printing Co., Ageless Eye™ developed by the Mitsubishi Gas Chemical Co., Vitalon® developed by the Toagosei Chemical Inc., and Tufflex GS developed by the Sealed Air Ltd. (Ghaani et al. 2016a). The application of several sensitive compounds, including ethyl cellulose, alginate, and polyaniline, has led to the development of GIs on a laboratory scale (Table 13.3).

13.7.2 Data Carriers

Data carriers as edible coatings include programmed detection tools; these tools enhance the food production chain's data flow (Ghaani et al. 2016a). Traceability of the product, automatization, and fake product identification can be performed by using data carriers. The product's condition is not clarified for the consumer (McFarlane and Sheffi 2003). Data carriers are divided into barcode and radio frequency identification (Fuertes et al. 2016). A design of parallel areas and slabs has been developed as well as the structure of barcodes to express 13 digits of data. One-dimensional barcode is incorporated in marketable edible coatings to express several information about the product, including type number, producer, type of product, and others (Fuertes et al. 2016). The incorporation of the two-dimensional barcode can provide further information (Bugnicourt et al. 2013). Support data information can be provided using a data carrier device called radio frequency identification (RFID). Food product identification and location can be performed through a specific tag that emits radio waves as a radio frequency identification (RFID) device (Fuertes et al. 2016). Generally, RFID structure is combined by an identifier comprising a microchip attached to a small probe, a collector that releases and accepts data in the forms of radio waves, and a web server that joins the RFID tools and initiates targets (Bibi et al. 2017). RFID is categorized into two sets: passive and active. In passive RFID, the collector is responsible for supplying the power, whereas in active RFID, power is supplied via an internal battery. A combined RFID is called partial passive RFID; this data carrier employs a battery to preserve information on the identifier or power the electronic structure (Biji et al. 2015). A hybrid RFID (Ghaani et al. 2016a) entitled semi-passive RFID, in this device, preserving the memory on the tag or powering the electronic system is

performed using a battery (Biji et al. 2015). As against barcode, RFID could be examined robotically without person's involvement in any orientation. Biopolymer-fabricated coatings can be combined in RFID structure. In previous studies, a coating was developed from wheat gluten, and its electrical and dielectric properties were observed to be humidity sensitive. Because of that, it can be applied for controlling moisture in packaged foodstuffs.

13.7.3 Sensors

Sensors are applied in the liquid or gas state to detect a particular material termed analyte through cooperation among the analyte and the sensor (Biji et al. 2015; Ghaani et al. 2016b). Sensors as systematic tools act via a direct spatial connection among a receiver and a signal converter with an electrical amplifier's aid (Thevenot et al. 1999). Following the cooperation among the receiver and a particular analyte, surface chemistry can occur in the receptor as the sensor's sensing section (Ghaani et al. 2016a). Converting the chemical indicator from the receiver to a measurable electrical signal is performed using a transducer. Transducers are categorized as electrical, electrochemical, thermal, optical, piezoelectric, and acoustic. As a final step, the amplifier is applied to enhance the electrical indicator that will be displayed to the customer through the software system. Biosensors are identified as a kind of sensors with a natural structure as a receiver including enzymes, microorganisms, antibodies, cell receiver, DNA, phage, tissues, and biomimetic constituents. Foodborne pathogens, endotoxins, mycotoxins, and pesticides can be detected using enzyme-based biosensors (Kim et al. 2018; L. Wu et al. 2019). Commonly, biopolymers are employed for developing most of the enzyme-based biosensors because of originating from natural sources and their promising interaction with living cells (Sawant 2017). Enzyme stabilization or connection to the biosensor can be performed via physical entrapment using biopolymers. For example, immobilization of horseradish peroxidase in Cs and Cs-gelatin coatings was performed successfully to identify hydrogen peroxide in nutrients.

13.8 Conclusions

The application of biopolymers in the manufacturing of edible coatings is expanding continuously. It is essential to consider that fabricated edible coatings using biopolymers can indicate valuable food industry features. Multilayer edible coatings, including natural ingredients and nanoparticles with particular characteristics, can be developed using the L-b-L technique, indicating functions in smart and active packaging in the food systems.

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Application of Biopolymer Blends as Edible Films and Coatings in Food Packaging

14

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Abstract

Biopolymers' production and application have been increased during the last decade all around the world. This rapid switch from conventional polymers to new biopolymers makes it essential to consider their characteristics deeply due to the correlation of physicochemical properties with biopolymers' functional properties. Biopolymers are one of the few renewable materials appropriate for food packaging. However, nearly all of them have inferior properties that are not suggested for packaging without any modification. As a result, various techniques have been examined by scientists to achieve the required specific characteristics. Blending is one of the most widely used methods in this field. In this chapter, a short review of food packaging, different types of materials used for food

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packaging, and their properties are discussed. In the following, different kinds of biopolymers and their preparation techniques are summarized. The properties of each biopolymer blend are also emphasized. Finally, applications of biopolymer blends in food packaging are highlighted.

Keywords

Bio-based polymer materials · Bioplastic · Eco-friendly materials · Intelligent packaging · Food shelf life

14.1 Introduction

Food packaging is traditionally meant to function as a mechanical supporter for packaged food from the surrounding environment. Moreover, it serves as a barrier to the transfer of gases, aromatic compounds, and water, besides its marketing and communication roles (Robertson 2013). Petrochemical-based plastics have been used as packaging materials for food products wildly because of their excellent mechanical properties such as tear and tensile strength, flexibility, impermeability to water and gases, heat stability, and so on (Siracusa et al. 2008). However, recently, plastics are not eco-friendly and biodegradable; increasing environmental problems and depletion of fossil reserves, attention has been switched to biopolymer usage in the food packaging industry (Arikan and Ozsoy 2015).

The word "bio" refers to the biodegradability of biopolymers. These kinds of polymers can easily break down by enzymes produced by microorganisms and left nontoxic by-products like water, carbon dioxide, etc. (Siracusa et al. 2008). Biopolymers can reduce reliance on fossil resources, greenhouse gases, and carbon footprint. They have advantages compared to traditional petrochemical-based plastics. Biopolymers are produced from polysaccharides, proteins, lipids, and their derivatives (De Leo et al. 2018). However, each of these materials has some characteristics which are not suitable for food packaging. Although polysaccharides and proteins show appropriate mechanical and barrier properties, they are quite sensitive to moisture (Rhim and Ng 2007). In contrast, lipid-based films have poor mechanical characteristics and excellent water vapor impermeability properties (Vodnar et al. 2015). These properties mean more water loss, oxygen reaction rate, and respiration rate in food products, affecting packaged food's shelf life (Hassan et al. 2018).

All these drawback features of natural biopolymers trigger researchers to investigate the usability of biopolymer blends with better mechanical and barrier properties and carry antimicrobial and antioxidant components (Haghighi et al. 2020). Blending is one of the easiest ways to create new materials with desirable characteristics. Blending biopolymers can be done by inexpensive mechanical procedures, which makes this process suitable for industries. During the blending, biopolymer materials mixed. Therefore, a wide range of properties can be achieved economically (Imre and Pukánszky 2013).

14.2 Food Packaging

According to Lockhart (1997), packaging can be defined as a socio-scientific discipline that ensures products are delivered to their intended users in the best condition. Another definition of packaging is that it is a coordinated process of preparing goods for transport, storage, distribution, retailing, and end-use (Coles and Kirwan 2011). There is generally a distinction between different levels of packaging. The primary package acts as the initial barrier, usually the most important barrier, between the product and the environment. Primary packaging examples include metal cans, paperboard cartons, glass bottles, and plastic pouches. It is frequently only the primary package that the consumer purchases at retail outlets. A secondary package, for example, a corrugated case or box, contains a number of primary packages. Physical distribution carriers are increasingly used for displaying primary packages in retail outlets. A tertiary package comprises several secondary packages, with the most common example being a stretch-wrapped pallet of corrugated cases. A quaternary package is frequently used in interstate and international trade to facilitate the handling of tertiary packages. Particular containers can have their temperature, humidity, and gas atmosphere controlled; this is necessary when distributing frozen foods, chilled meats, and fresh fruits and vegetables (Robertson 2013). Packaging in the food industry is designed to contain and protect foods, provide mandatory information about foods, and facilitate food handling from distribution to the consumer's table. The primary purpose of packaging food products is to achieve preservation and safe delivery until they are consumed. The quality of the food product will deteriorate both physically and biologically during distribution. The use of packaging in food products extends the shelf life and keeps the food products safe. In addition to traceability and indications of tampering, packaging also serves as a marketing component of food products (Marsh and Bugusu 2007).

14.2.1 Different Types and Properties of Packaging Materials

Food packaging encompasses many aspects, including the food itself, selecting, labeling, designing packaging materials, storage, transportation, and distribution. Throughout the whole food product's life cycle, these elements are present. Food packaging engineers need to understand how these elements interact in order to deliver optimized packaging systems to both manufacturers and consumers in terms of cost, convenience, protection, and marketing. A wide variety of materials have been used to pack food over the years—paper, wood, vegetable fibers, metals, plastics, glass, etc. Some food products require a combination of packaging materials to provide the best packaging solution. Packaging material selection is mainly determined by the characteristics and type of food being packaged. Besides the market image, environmental issues and costs must also be considered. Therefore, it is essential to know the nutritional value of the food and the characteristics of the packaging materials used (Kim et al. 2014).

14.2.1.1 Application of Metals in Food Packaging

Metal can provide good protection against physical damage or impact during transportation, distribution, handling, and storage of food products. It also can provide a good barrier against water, oxygen, and gases because of its impermeability. On the other hand, metal is not suitable for modified atmosphere packaging (Oraikul and Stiles 1991). A typical packaging material used in metal packaging containers is tinplate. In 1810, Peter Durland invented the canning process, which preserved liquid foods and extended their shelf life. The metal aluminum is abundant in the Earth's crust, and it was first isolated in 1825 by Danish chemist Hans Christian Oersted (Kim et al. 2014). Metal cans have been used to store various food products all over the world since the 1900s. Cans are commonly used for storing carbonated and non-carbonated drinks. Moreover, metal cans can be filled with hot or cooked food products to extend storage life without adding preservatives. Beverages such as beer and carbonated drinks are packaged under pressure, while most food cans are made at ambient pressure and temperature (Katiyar 2017).

14.2.1.2 Application of Glasses in Food Packaging

The glass is one of the oldest used food packaging materials, which comes in containers, bottles, bowls, trays, cups, etc. Approximately, 3000 BC is the earliest evidence of glass being used as a packaging material. In 1892, glass container manufacture was mechanized on no small scale, and several significant developments took place in the decades that followed. The first fully automated machine for making bottles was created in 1903 (Robertson 2013). For food packaging, glass is usually combined with other materials such as metal, cork, plastic, rubbers, and so on in a single container. What type of enclosure is required depends on the nature of the food items to be stored. The packaging of food sensitive to the environment outside the package or those that need to be sterilized by heat will be sealed with a rubber gasket.

Foods like vinegar tend to react with metals or plastics. This is why glass bottles are the perfect packaging material since such food items do not hurt them. The chemical structure of glass, composed of Si-O bonds, is thought to be responsible for its chemical inertness. Additionally, since its pores are so small, it is ideal for storing aromatic foods since the gaseous molecules are unable to pass through them (Katiyar 2017). As a food packaging material, glass has both disadvantages and advantages. As a result of physical impact and high pressure, it may break. However, it has good barrier properties against gases and chemicals and is suitable for heat processing at high temperatures.

Furthermore, glass can serve as an insulator to keep foods fresh during storage. Most glass containers used in food and beverage can be recycled and reused (Kim et al. 2014). Regardless of how many times it is recycled, its purity and properties are not lost. Nevertheless, glass packaging's major disadvantage is its brittle nature, limiting its use in several areas. Glass pots are very brittle and become very heavy due to their structure and cannot be shaped into critical shapes or sizes for various forms of packaging (Katiyar 2017).

14.2.1.3 Application of Papers in Food Packaging

Besides general commodities like writing, tissues, and newsprint, the paper also serves as packaging material such as wrapping paper, grocery bags, and shipping sacks. Corrugated packaging and folding cartons are two main subcategories of paperboard (Twede et al. 2014). Paper, corrugated board, and paperboard are produced from the pulp, the fibrous raw material. This material is made from plant fiber and is a renewable resource. The pulping goal is to separate cellulose fibers from other components of wood such as hemicellulose and lignin as much as possible (Robertson 2013). There are numerous advantages to paper and paperboard packagings, such as low costs and machine processability during production and ease of collection, reuse, and recycling afterward. It is available as a lightweight and biodegradable material that fulfills the requirements for various commodities, including folding cartons, corrugated boxes, and bags. Besides, it is ideal for displaying product information and nutritional value for marketing purposes (Kim et al. 2014). However, paper and paperboard do not offer a suitable barrier against gases and water vapor. According to Kugge and Johnson (2008), a sized commercial kraft paper has a water vapor transmission rate (WVTR) of 426 g m^{-2} day^{-1} at low humidity levels. Therefore, in many packaging applications, a barrier against water vapor or gases such as O_2 is needed. Paper and paperboard can be improved by coating or laminating with other materials, such as oils, waxes, polymers (plastics), and metals, to form more effective gas or wet barrier properties and strength. Paraffin wax has a low cost, is entirely nontoxic, and resists water vapor. Paperboard coated with wax presents a significant challenge for recycling since the wax has to be separated from the fibers before they can be reused (Robertson 2013). Lahtinen et al. (2009) reported moisture barrier and heat-sealing properties of PLA extrusion-coated paperboard.

14.2.1.4 Application of Plastics in Food Packaging

Plastics are highly suitable for food packaging applications due to the fact that the plastic melt can be easily molded and can be processed in a variety of shapes and forms. Since plastics are cost-effective, lightweight, transparent, chemically resistant, and heat resistant and have many other useful characteristics, the use of plastic in food packaging is continuously increasing (Lopez-Rubio et al. 2004). Polyolefins (PO) and polyesters are the most widely used plastics in the food packaging industry. There are other common materials such as polystyrene (PS), polyvinyl chloride (PVC), ethylene vinyl alcohol (EVOH), and polyamide (PA). Some plastics are more suitable for the food packaging industry. For instance, polyethylene (PE) and polypropylene (PP) are widely used due to their barrier properties, chemical resistance, strength, and durability, as well as their ease of processing, reuse, and recycling (Lau and Wong 2000). The packaging's functional properties are enhanced using several plastics derived from petroleum and the combination of these materials. The disposal of these materials and their degradation rate present many environmental, health, and economic concerns.

Moreover, petroleum-based raw materials and the production cost, fluctuations in oil prices, degradable capacity, and accumulating waste pose a significant threat to

the environment. Petroleum-based plastics for food packaging are challenged by the need to reduce carbon emissions and plastic waste disposal, the requirement for materials with new characteristics including antimicrobial properties, and particle migration challenge. Moreover, there are serious health concerns regarding the monomer residues in plastics, along with other components such as stabilizers and plasticizers. There is a growing demand for food packaging, which is continuously being influenced by a wide range of factors to determine which packaging is better for the environment in the long term (Siracusa et al. 2008).

14.3 Biopolymer Materials

Biopolymer materials are considered to be natural polymers made by living organisms. These polymers are known to be biodegradable. Referencing materials as biodegradable indicates that they can be broken down by enzymatic living organisms, such as bacteria, fungi, or yeast. Hydrocarbons and methane are the final end products of biodegradation under anaerobic conditions (Othman 2014). Since biodegradability is not dependent on the raw materials' origin but only on the polymers' chemical composition, biodegradable polymers can be made from renewable raw materials or petroleum-based raw materials. For this reason, it is often helpful to classify biodegradable packaging according to its origin and production method (Robertson 2013).

Generally, biopolymers fall into one of the following three categories:

1. Natural biopolymers are polymers derived from biomass, including polysaccharides, proteins, and lipids.
2. Synthetic biopolymers are polymers chemically synthesized derived from renewable bio-derived monomers.
3. Polymers are developed by microorganisms (Adeyeye et al. 2019).

14.3.1 Natural Biopolymers

Due to their natural origin, all-natural polymers are biodegradable and leave no residue in the environment. There are some enzymes. The advantages of natural biopolymers over plastics for food packaging applications include the fact that they are biodegradable, renewable, abundant, nontoxic, antimicrobial, and antioxidant and being environmentally friendly (Sam et al. 2016). Production of these packaging materials uses polysaccharides such as starch, cellulose, and chitosan, proteins such as casein and gluten, and lipids such as waxes. Although polymer derived from biomass is biodegradable, polymer synthesized from bio-derived monomers must be tested for biodegradability. Furthermore, biopolymers have to be processed under the same conditions as conventional plastics (Debeaufort and Voilley 2009).

14.3.1.1 Polysaccharides

Polysaccharides can be homopolysaccharides made up of a single monosaccharide, or heteropolysaccharides, which contain two or more sugars. Homopolysaccharides consist of linear chains of polysaccharides, like curdlan and pullulan. In contrast, heteropolysaccharides are polysaccharides made up of different copies of the oligosaccharide like xanthan. Polysaccharides are the most abundant macromolecules in nature. Compound carbohydrates mainly consist of glycosidic bonds. They are components of plant structures like cellulose and animal exoskeletons, such as chitin, and act as sources of stored energy in plants (Thakur and Voicu 2016).

14.3.1.2 Proteins

A protein is a large and complex macromolecule having specific amino acids, sequences, and molecular structures. Proteins are commonly used for making films because they are edible, supply nutrients, are mechanically strong, and possess good barrier properties. A protein-based film acts as an oxygen barrier that protects food from spoilage (Schmid et al. 2012). Food wastage may be prevented by using such containers in packaging during food distribution chains. Edible films prepared from protein have higher barrier properties than those derived from polysaccharides and lipids. Protein-based films can be used for the packaging of a small amount of food. Edible protein films are often derived from protein solutions as the solvent evaporates. Protein films are derived from several animal and plant sources, including egg, milk, and oilseed (Adeyeye et al. 2019).

14.3.1.3 Lipids

The desire to decrease moisture loss by packaged or non-packaged foods makes lipids a right candidate for use as ingredients in edible films and coatings. To improve film performance, polysaccharides and proteins are usually combined with lipid materials to form composite films and coatings (Pérez-Gago and Rhim 2014). The combination of hydrocolloid and lipid materials imparts acceptable structural integrity to the hydrocolloid film and good barrier properties to water vapor, making it ideal for use on a wide variety of surfaces (Greener and Fennema 1989). Lipid compounds used to make lipid-based edible films and coatings commonly include fatty acids, neutral lipids, waxes, and resins (Hall 2011).

Hydrocolloid-lipid edible coatings have successfully been applied to meat, cereals, confectionery, fruits, nuts, fresh and freshly cut fruit and vegetables, and dried fruits (McHugh and Avena-Bustillos 2012). When it is not desirable to consume the final package, such as wrapping and bagging foods, edible packaging could be composted. The wraps, which contain various concentrations of fatty acids, fatty alcohols, bee wax, and vegetable oil, can significantly reduce moisture loss and browning in fresh-cut apples (McHugh and Senesi 2000). Pouches made from zein and oleic acid can preserve the quality of individually wrapped cheese slices (Ryu et al. 2005).

14.3.2 Synthetics Biopolymers

14.3.2.1 Poly(Lactic Acid) (PLA)

PLA is a biodegradable, thermoplastic classed in the aliphatic polyester category and can be produced by the polymerization of lactic acid (LA) derived from synthetic sources and agricultural feedstocks such as cornstarch, sugarcane, cassava roots, etc. PLA is made up of simple lactic acid, a common hydroxycarboxylic acid found in nature (Martinez et al. 2013). LA can be readily synthesized from carbohydrate-based feedstocks such as corn, tapioca starch, etc. The PLA has been extensively studied in the past few decades as the biodegradable property lends it to numerous uses, particularly in food packaging and medical applications (Mallegni et al. 2018). PLA can be easily processed by thermoforming and injection blow molding due to its greater thermal processability. When compared with other bioplastics, PLA is superior to other conventional thermoplastics (Katiyar 2017). PLA is a colorless, rigid, glossy thermoplastic polymer with the comparable tensile strength to commercial polymers. PLA is a pseudoplastic, non-Newtonian fluid that behaves like a classic, flexible-chain polymer above its melting point (Ahmed and Varshney 2011). Although PLA has the above advantages, it also has some disadvantages: low heat stability and low barrier capabilities. PLA applications in various fields, including biomedical and food packaging, have been limited due to these limitations.

14.3.2.2 Poly(Butylene Succinate) (PBS)

PBS is an aliphatic thermoplastic polyester synthesized through the transesterification process or direct esterification. The most traditional method to produce PBS is the direct esterification of succinic acid with 1,4-butanediol. In addition to being derived from petrochemicals, monomers can also be obtained via fermentation from renewable feedstocks such as glucose, starch, xylose, and so on (Xu and Guo 2010). Because of its ester bonds, PBS is biodegradable and has strong mechanical properties, making it suitable for several applications, including agricultural mulch films, bags, packaging films, and flushable products (Hongsriphan and Pinpueng 2019).

14.3.2.3 Poly(Glycolic Acid) (PGA)

Although PGA has a similar structure to PLA, it has a higher heat distortion temperature and excellent mechanical properties, especially exceptionally high gas barrier properties (Jem and Tan 2020). This aliphatic thermoplastic polyester is derived by polycondensation or ring-opening polymerization of glycolic acid. Glycolic acid can be derived from petroleum or renewable resources such as sugarcane, beets, and pineapple (Lapporte and Toland 1973).

14.3.2.4 Poly(Trimethylene Terephthalate) (PTT)

Poly(trimethylene terephthalate) (PTT) is a type of polyester that has good mechanical strength, processability, and thermal stability (Byun and Kim 2014). This linear thermoplastic polyester is synthesized via condensation polymerization of 1,3-propanediol and terephthalic acid or dimethyl terephthalate. Plant waste can be

converted into the monomer 1,3-propanediol, which makes PTT a biodegradable polymer. The PTT presents excellent mechanical properties, which may be further enhanced by using additives (Bikiaris et al. 2006). PTT is transparent and heat resistant like polyesters but is more flexible and elastic than PET. Those features make PTT an adequate substitute for non-biodegradable polymers like PET and PBT (da Cruz 2019).

14.3.2.5 Poly(ε-Caprolactone) (PCL)

PCL is a biodegradable, biocompatible, semicrystalline polymer with a low glass transition temperature. The slow degradation of PCL makes it ideally suited to long-term delivery for more than 1 year. This has led to the development of various delivery systems based on it, including microspheres, nanospheres, and implants (Sinha et al. 2004). This semicrystalline polymer has a low melting point (60 °C) and a glass transition temperature of about −60 °C (Jiang et al. 2018). PCL packaging materials demonstrate excellent flexibility and high resistance to water and organic solvents but are vulnerable to microbial attacks (Salević et al. 2019).

14.3.2.6 Poly(Butylene Adipate-Co-Terephthalate) (PBAT)

Poly(butylene adipate-co-terephthalate) is a widely used synthetic polymer that is biodegradable and derived from fossil resources (Li et al. 2018). This polyester is an aliphatic-aromatic polyester with carbonyl groups throughout the polymer chain. Because transesterification reactions prepare this synthetic polymer under controlled conditions, its properties are usually repeatable and predictable (Rodrigues et al. 2016). Since PBAT can be degraded under different conditions, it is used in biodegradable plastic films (Bilck et al. 2010). PBAT biodegradation is affected by its chemical structure and the conditions under which it degrades in the environment. It can be used in many applications, including packaging materials (trash bags, food containers, film wrapping), hygiene products, biomedical applications, and industrial composting (Arrieta et al. 2015; Maldonado et al. 2018).

14.3.2.7 Poly(Vinyl Alcohol) (PVA)

The monomer of polyvinyl alcohol (PVA) has not been isolated, and it only exists as a polymer. The PVA is made from vinyl acetate monomer in a multi-stage process when the monomer is polymerized into polyvinyl acetate and then hydrolyzed to PVA. Ethanol is the most suitable renewable base material. PVA has high tensile strength, is easy to form a film, and has good bonding and adhesive capabilities. With increasing hydrolysis, its water resistance increases, making it more effective at adhering to hydrophobic surfaces. In addition to its application in adhesives, PVA is used in the manufacture of biodegradable polymer films and ceramics, reprography, and photography (Rajeswari et al. 2021). The metabolic degradation of PVA by microorganisms was described by Kawai (1995). In microbially active environments, PVA usually degrades within a few weeks, and in a water environment, *Phanerochaete chrysosporium* degraded 73% of PVA within 5 days (Huang et al. 2002).

14.3.3 Microorganisms

14.3.3.1 Polyhydroxyalkanoates

The polyesters known as PHAs are produced in nature by various microorganisms as a carbon and energy storage source. Based on the monomers' composition, PHAs exhibit hard crystalline to elastic properties (Koller 2019). Since they have similar properties to synthetic polymers and are entirely degradable in aerobic conditions to water and carbon dioxide, PHAs can replace synthetic polymers (Lee 1996).

14.3.3.2 Pullulan

Aureobasidium pullulans, formerly known as *Pullularia pullulans*, is a fungus that produces an extracellular water-soluble polysaccharide known as pullulan. Sucrose and other carbohydrate sources are used in fermentation to produce it, along with additional growth nutrients. This polysaccharide is made up of only glucose monomers. Nieto (2017) reports that pullulan films exhibit excellent mechanical properties and are highly oxygen-impermeable. Since it is mostly tasteless and edible, Zhao et al. (2019a, b) propose its application in the food industry to produce edible films.

14.3.3.3 Curdlan

Curdlan is a linear β-glucan, a high molecular weight polymer of glucose discovered by Harada et al. (1979). Curdlan consists of β-(1 → 3)-linked glucose residues that form elastic gels upon heating in aqueous suspension. Curdlan gels come in two types: low-set curdlan, gels between 40 °C and 60 °C, and high-set curdlan gels at 80 °C or above. These gels are reversible, just as agar and gelatin gels are (Miwa et al. 1994). The polymer is produced by bacteria that are not pathogenic, like *Agrobacterium biovar* in a fermentation process in which bacterial cultures are grown in a medium containing maltose, sucrose, nitrogen, and phosphate. This gelling agent is odorless, helping it be used in food industries for gelling purposes (Brodnjak 2017).

14.3.4 Biopolymer Blends

Generally, a polymer blend involves blending two or more polymers or copolymers to achieve improved physical properties (Cazon and Vázquez 2020; Khan et al. 2018). The purpose of polymer blending is to produce composite materials cost-effectively and straightforwardly, which combines useful features from various components and may improve their attributes and minimize their shortcomings (Parameswaranpillai et al. 2014; Unger et al. 2014).

For the development of biodegradable films, protein-based films from animal sources like gelatin, collagen, casein, whey protein, and plant sources like soy protein isolate, corn zein, kidney bean protein isolate, quinoa protein, and wheat gluten have been studied due to their abundance, good mechanical properties, and excellent gas barrier properties (Arfat et al. 2017).

14.4 Biopolymer Blends Fabrication Processes

Traditionally, edible packaging preparation has been categorized into two processes: the wet process and the dry process. To form edible packaging, a sufficiently cohesive and continuous structural matrix must exist. The covalent bonds, hydrogen bonds, and ionic bonds are formed during the process. Compared to other bonds, covalent bonds provide a more stable framework for polymer networks.

14.4.1 Solvent Casting

In the solvent casting, the polymer is dissolved in an organic solvent to create a homogeneous solution. For edible packaging, water and ethanol are the most common solvents. The solvent solution is heated above the melting point, homogenized (for an emulsion system), and cast on a flat surface while cooling. The solution is then poured into a mold or substrate, and the solvent evaporates at room temperature or under heat, leaving polymer films. Air-drying, hot surface drying, microwave drying, and infrared drying are examples of drying methods. Air-drying usually occurs at room temperature, resulting in a more homogeneous polymer network than a high-temperature drying process. Under vacuum, any remaining solvent can be removed from the newly formed film (da Cruz 2019; Li and Ye 2017).

14.4.2 Extrusion

Extrusion is commonly done with dry polymer pellets or chips. During the fabrication process, the packaging materials are heated above the glass transition temperature and forced through the extruder using the extrusion screw. The parameters to be controlled during the process include temperature, feed rate, screw configuration rate, product inlet pressure, and outlet pressure, which will affect conformational changes, aggregation, and chemical cross-linking (da Cruz 2019; Janjarasskul and Krochta 2010). Extrudates are cooled and solidified with water or coolants as they are pushed out. Concerning the thermomechanical process, extrusion is more severe than casting technology. Determining the packaging behavior depends on the degree to which the active compounds or packaging materials will degrade during the process (Gómez-Estaca et al. 2014). One of the reasons for antioxidant activity loss is the high temperatures. Therefore, casting processes cause a small loss of antioxidants due to the milder manufacturing and processing conditions (Lopez-de-Dicastillo et al. 2010).

14.4.3 Electrospinning

The electrospinning process is a simple, relatively low-cost method by which continuous nanoscale fibers are produced from a diverse range of polymer materials using a high-voltage electric field. When sufficient electrical force is applied to overcome the droplet's surface tension, a charged jet emerges from the Taylor cone and eventually expands into an expanding helix. A fine fiber is received in the final step using stretching the polymer solution droplet onto the ground collector (Zhang et al. 2020). A novel approach to construct nanostructured packaging materials is electrospinning (Fernández et al. 2008). Electrospinning is a low-cost, easy, and versatile way to make fibers of all sizes, from nanometers to micrometers. The solution properties, environmental conditions, and processed conditions must all be considered to produce a good film (Fabra et al. 2015). It has been demonstrated that electrospinning is an effective method for the fabrication of three-dimensional and functional nanofiber mats by immobilizing or encapsulating suitable substances within the matrix (Niu et al. 2020).

14.4.4 Three-Dimensional Printing

A three-dimensional printing process is a controlled robotic process in which a product is built layer by layer from a computer-based design produced by a computer program or downloaded from certain online services (Dankar et al. 2018). The food industry has adapted printing technology commonly used in the construction industry to food applications. Extrusion printing, inkjet printing, and binder jetting are some of the major printing technologies applied to food products (Le-Bail et al. 2020). One of the easiest to develop three-dimensional printing processes is extrusion-based, and it is the one that has the most applications in foods (Tan et al. 2018). This method uses a robotic arm with a syringe to extrude material through a nozzle while moving across a surface. The deposition of successive layers is conducted by positioning the cylinder with a three-dimensional model at predetermined locations (Liu et al. 2017). Inkjet printing is a method of printing food ink using a series of pneumatic membrane nozzles that fling small drops onto moving objects. Since inkjet printers tend to work best with low viscosity materials, they are most often used for flat printing products rather than constructing complex food products (Le-Bail et al. 2020). In binder jetting, a powdered material is evenly distributed across a fabrication platform, and then the two successive powder layers are connected by spraying a liquid binder (Holland et al. 2018). A powder layer is applied to each layer, typically using a counter-rotating roller. Liquid binding agents are added to the powder bed with an inkjet print head later (Ziaee and Crane 2019).

14.4.5 Layer-by-Layer (LbL) Assembly

Layer-by-layer assembly consists mainly of alternately depositing oppositely charged layers followed by a washing step in between. Various deposition processes can be used, such as spray, immersion, electromagnetism, and fluidics (da Cruz 2019). This technique is widely used for creating functional surface coatings, usually under aqueous conditions that are used to develop multifunctional controlled drug release coatings. LbL film's functional behavior is related to its physicochemical properties (Alkekhia et al. 2020). LbL assembly consists of alternating depositions of compounds with complementary interactions, resulting in multilayered structures. In 1991, Decher and Hong applied LbL to polyelectrolytes, and this method gained increasing popularity for its numerous applications (Decher and Hong 1991). A significant benefit of LbL assembly, especially for biomedical applications, is that a substrate may be easily coated with a range of physicochemical properties and geometries without causing damage to the substrate (Saurer et al. 2013). With LbL assembly, large surface areas can be coated efficiently while still allowing for nanoscale resolution, making precise control of biological interactions possible. Additionally, the mild aqueous assembly condition allows it to incorporate small molecules and biologic agents without damaging the compounds with solvents, temperatures, pH, and ionic strengths (Krogman et al. 2013). Additionally, it has the potential to incorporate and preserve the biological activity of therapeutic agents, coat multiple substrates ranging from nanoparticles to implants, and exhibit tuned, targeted, and responsive drug release behaviors (Alkekhia et al. 2020).

14.5 Application of Biopolymer Blends in Food Packaging

In the modern food industry, there are many challenges that need specific approaches to overcome them. One of the most challenging issues is related to food product packaging that has a short shelf life. Despite preserving food effectively, conventional packaging, such as plastic, creates negative environmental problems. This means that everyone in this industry, mainly food engineering and packaging experts, needs to look for alternatives to overcome this severe problem caused by packaging materials (Rajeswari et al. 2021). Besides, the product's total cost can also be related to packaging materials since the contribution of packaging to the product's total cost is very significant. As a result, the food industry needs to find new and more economical packaging materials. In search of the optimal material, edible bio-based films were examined for their ability to prevent moisture loss, water absorption, oxygen penetration into the food matrix, aroma loss, and solute transport (Dutta et al. 2009). One of the most promising methods for maintaining food quality is the use of active bio-based films as packaging materials. Presently, bio-based materials are used to protect foods stored at cool temperatures. Fast-food packaging, egg cartons, fresh fruits and vegetables, dairy products, yogurt, and organic foods are examples of possible applications. Some bio-based packaging materials exhibit a

high gas permeability, suggesting that they may be useful in packaging respiring foods such as fruits and vegetables.

The biofilm based on chitosan and different materials such as plant proteins, polysaccharides, and antimicrobial peptides has shown promise as a potential active biofilm. Combining chitosan with polysaccharides, proteins, and their derivatives improves chitosan-based films' functional properties (Aider 2010; Cazon and Vázquez 2020). Polysaccharides such as pectin, starch, alginate, carrageenan, xanthan gum, xylan, and glucose and various derivatives of these polysaccharides can be blended with chitosan (H. Wang et al. 2018). Food packaging could be enhanced with chitosan-protein blend film. Its functional properties may be superior to single proteins and chitosan film, promoting their use in food packaging (Basta et al. 2015).

14.5.1 Antimicrobial Packaging

Extending the shelf life of fresh potatoes, agar/collagen/alginate ternary blend films containing grapefruit seed extract and silver nanoparticles were used. These films demonstrated strong antimicrobial activity. They also prevented condensed water formation on the surface of the packaging film. Furthermore, it helped prevent the greening of potatoes during storage. This film's application for highly respiring fresh agricultural products was recommended (Wang and Rhim 2015).

They packed fresh spinach with agar/konjac glucomannan/k-carrageenan blend films containing Cloisite 30B. The packaging material demonstrated antimicrobial activity against Gram-positive bacteria. Due to their high moisture absorption capacity, bio hydrogel films are an appropriate replacement for silica gel as a desiccant. It was suggested that these films be used as antifogging materials for packaging highly respirable agricultural products, such as spinach (Rhim and Wang 2013).

Antimicrobial properties of alginate/clay nanocomposite films enriched with essential oils of clove, coriander, caraway, marjoram, cinnamon, and cumin were studied. The results indicate that the films have antimicrobial effects against three important food pathogens, *Escherichia coli*, *Staphylococcus aureus*, and *Listeria monocytogenes*, for 12 days. These oils' highest antimicrobial effect was observed in films incorporating marjoram essential oils, followed by clove and cinnamon's essential oils (Alboofetileh et al. 2016).

Starch and gallic acid, chitosan, and carvacrol were used to prepare bioactive biopolymers using subcritical water technology. To evaluate the films' antimicrobial activity, their effects against *Listeria monocytogenes* strain on ham during a 28-day storage period at 4 °C were investigated. Starch films with gallic acid (0.3 g gallic acid/g starch) had the least antimicrobial activity effect on ready-to-eat ham and delayed growth of *Listeria monocytogenes* by 1 week. On the other hand, starch films with chitosan (0.025 g/g starch) and carvacrol (0.048 g/g starch) and starch films with chitosan (0.15 g/g starch) and gallic acid (0.1 g/g starch) completely inhibited the organism's growth throughout the whole storage period. After 4 weeks

of refrigerated storage, starch films with chitosan and gallic acid continued to inhibit the organism's growth (Zhao et al. 2019a, b).

14.5.2 Antioxidant Packaging

Vejdan et al. studied the oxidative stability of fish oil with gelatin/agar bilayer films that contained TiO_2 nanoparticles. By increasing TiO_2 concentration, fish oil photo-oxidation was hindered. In addition, the samples covered with the nanocomposites exhibited the lowest levels of peroxide value change, thiobarbituric acid change, conjugated diene, and color change (Vejdan et al. 2017).

A bio-based and biodegradable bilayer system was prepared, and catechin was incorporated to make the system antioxidant active. The outer layer was made of poly(3-hydroxybutyrate-co-3-hydroxy valerate), while the inner layer comprised antioxidant electrospun fibers derived from PLA and PHB blends and enhanced with 1% and 3% catechin. There was a more significant antioxidant effect in the systems with higher catechin levels (Arrieta et al. 2019).

By incorporating a natural antioxidant agent into soy protein-based films, bioplastic materials have been developed as active food packaging. The film formulations are composed of soy protein isolate combined with carboxymethyl cellulose (CMC) and/or catechin. Catechin-incorporated soy protein isolate or soy protein isolate film spiked with CMC films demonstrated a synergistic antioxidant effect (Han et al. 2015).

14.5.3 Active Packaging

De Lacey et al. produced an agar-based bioactive film containing probiotic strains (*Lactobacillus paracasei* L26 and *Bifidobacterium lactis* B94) and green tea extract that were applied to hake fillets. These films delayed both the production of H2S and the growth of total viable bacteria. As a result of the films' application, the count of beneficial lactic acid bacteria in fish increased, significantly extending the shelf life of the hake fillets for 1 week (De Lacey et al., 2014).

Kumar et al. studied green grapes packed in agar-based edible films that contain ZnO nanoparticles. Packaged grapes in nanocomposite films containing 2 w% and 4 w% of nano-ZnO looked fresh for up to 14 and 21 days, respectively. Results indicated that agar-ZnO composite films are an effective packaging agent for extending green grapes' shelf life (Kumar et al. 2019).

For the development of active packaging systems, PHA-, PHB-, and PLA-based films can be used as carriers of active compounds. These systems can extend the shelf life of food products (Marina Patricia Arrieta et al. 2014). Various essential oils are commonly added to PLA and PHA to impart antioxidant and antimicrobial activity (Armentano et al. 2015). Because essential oils tend to evaporate at ordinary temperatures, blending them directly into thermoplastic polymeric matrixes at high temperatures may result in a high loss rate (Muñoz-Bonilla et al. 2019).

14.6 Conclusion

In the marketing process, packaging plays an important role in protecting the product and providing food safety assurance. Conventional plastic packaging materials fulfill the expectations of the ideal food packaging materials. Although plastics are not biodegradable, their use as food packaging has resulted in the food industry being viewed as a pollution source in society. In response to these issues, bio-based and biodegradable materials have received much attention in recent years. Biodegradable polymers and their blends are environmentally friendly and sustainable plastics. Within a specified time, after their service life is over, they are completely disassembled and degraded. This phenomenon prevents the accumulation of these biopolymers like petroleum-derived plastics in the environment. By developing polymeric blends utilizing biopolymers or bio-based polymers, improved physico-chemical, structural, and barrier properties may be achieved while still retaining their inherent biodegradability. They can be used as individual packaging materials, food coating materials, active ingredient carriers, and a separator of the compartments of heterogeneous ingredients within foods. In order to optimize the properties of biopolymers for industrial use, it is crucial to identify the mechanisms by which biopolymers are formed as films. Conducting further research on biodegradable polymeric blends on an industrial scale will lead to the development of biopolymeric products with different potential applications.

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Standards and Guidelines for Testing Biodegradability of Bioplastic

15

Ladan Rashidi

Abstract

Bioplastics or bio-based plastics are made from biological sources, a small portion of the worldwide plastic market, and need more research and commercialization. Here, the overview of standards of specification and test methods, which are written by international or national standardization bodies of various countries for evaluating biodegradability of bio-plastic products and materials in different environments, including soil, marine, landfill, and so on, under both aerobic and anaerobic conditions, is presented. Some certification organizations apply these standards to test and evaluate bio-based plastic materials and products. In addition, similarity and differentiation between standard test methods are described.

Keywords

Plastics · Standard · Biodegradable plastics · Test methods

15.1 Introduction

Plastic consumed by people worldwide is a polymer derived from petroleum or natural gases which is waterproof, chemically stable, lightweight, resistant to corrosion, and inert.

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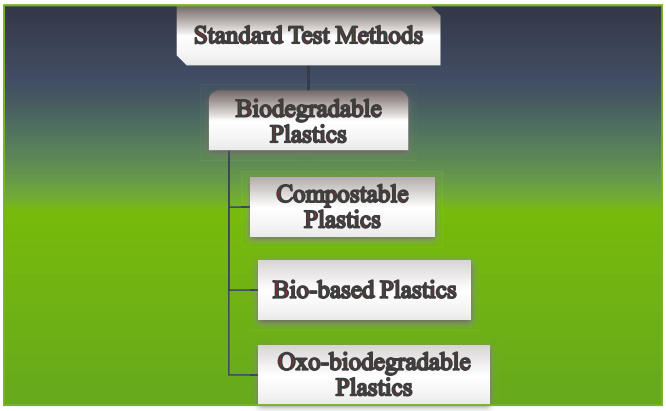

Fig. 15.1 Standard test methods and biodegradable plastics

Nowadays, there have been significant efforts to develop and industrialize biodegradable plastics called "bio-plastic," which have low resistance in the environment (Ojeda 2013).

Bioplastic is a biodegradable plastic, or contains bio-based content, or has both bio-based content and biodegradable properties. In addition, biodegradable plastic is a type of plastic that is biodegraded under activation of naturally—occurring microorganisms, including bacteria, algae, and fungi, within a definite degradation time as per confirmed standards, including ASTM (American Society for Testing and Materials) D6400 (ASTM D6400-19 2019), ISO (International Standards for Organization) 17088 (ISO 17088 2012), EN 13432 (BS EN 13432 2000), etc. (Kubowicz and Booth 2017).

Oxo-degradable plastics are the conventional plastics, including PET (polyethylene terephthalate), PE (polyethylene), and PP (polypropylene), which are generally promoted as biodegradable, and contain additives for accelerating the oxidation process called prodegradants (ISO 17088 (ISO 17088 2012), BS 8472 (BS 8472 2011)) (Ammala et al. 2011). They quickly segment into large amounts of microplastics when subjected to a combination of oxygen and sunlight, and these microplastics take a long time to biodegrade (Karlsson and Albertsson 1998) entirely. In addition, composting is a natural decomposition using microorganisms, including fungi, actinomycetes, and bacteria, inside a similar soil called humus, the soil conditioner (Biernbaum and Fogiel 2004). In this natural process, microorganisms consume organic matter as a food source, create carbon dioxide, and yield the hummus as a final production (Rynk 1992).

A dissimilarity between compostable plastic and biodegradable plastic is that a compostable plastic undergoes degradation using a biological process to yield inorganic compounds, water, CO_2 and biomass, and other recognized compostable materials. It remains no visible toxic or identifiable residues. The compostable plastics are biodegradable; nevertheless, the inverse is incorrect (Gopferich 1997).

However, plastic biodegradation depends on the chemical nature of the polymer and the environmental factors, including temperature, moisture, oxygen, and pH, which the plastics are located.

The biodegradation process is an enzymatic reaction that depends on polymer bonds and polymer biodegradation mechanisms. The factors that affect the biodegradability of plastics include crystallinity, hydrolyzable functional groups of the polymer, molecular weight, size, shape, and structural composition of copolymer (Gopferich 1997).

The attention for the increase of biodegradable plastics to be securely utilized in food and agriculture applications has led to the improvement of intense work at the standardization level. These standards play a critical role in biodegradable plastic production (ASTM D6400-19 2019; BS EN 13432 2000). Therefore, standard test methods cover three kinds of biodegradable plastics: bio-based plastics, compostable plastics, and oxo-degradable plastics (Fig. 15.1). To warranty market transparency, tools are necessary to connect statements applied advertising messages and the biodegradability of the real plastic.

The most significant standardization works in bio-based plastics; biodegradable and compostable packaging has been performed over the past 18 years (Barrena et al. 2011). There are standard specifications and test methods for bioplastics' characterization of biodegradability and compostability. These standards study the degradation of plastics using test methods that simulate laboratory-scale environmental conditions. In this chapter, the current situation regarding biodegradability standards and significant gaps is discussed, which would have a bearing on improving the plastic biodegradability characteristics for the open environment conditions.

The standard test methods and specifications are to be developed by various legislative organizations, including the International Organization Standardization (ISO), American Society for Testing and Materials (ASTM) International, Association Francaise de Normalisation (AFNOR), and British Standards Institution (BSI), in order to confirm and validate the biodegradability of bio-based plastics and so on. The following will discuss the role of these organizations and their developed standards for bio-based plastics.

15.2 Standards of Test Methods and Specifications

Generally, standards are most important in everyday life, but their purpose is not often misunderstood or unknown. Various test methods can be applied to assess biodegradable bio-plastic. Clarifying the targets of standards is so important, as standards specify the types of selections and feasible opportunities in our social life (Busch 2011). These standards are the written and enforced legislation or set the specified limitations, whose practice or product must meet to confirm a particular organization. Standardization is an essential tool that sets requirements for procedures, products, and services and is applied for specifying criteria and benchmarks to coordinate the conduct in society and industry.

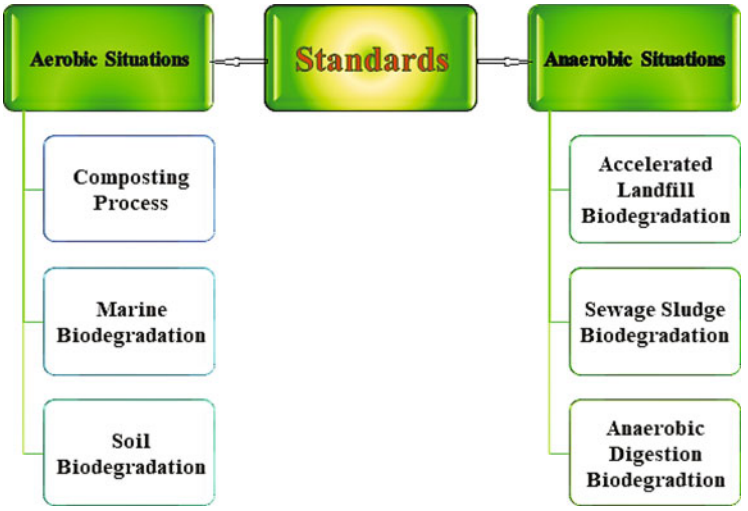

Fig. 15.2 Classifications of standards based on aerobic and anaerobic situations

Various standard test methods have been defined to evaluate the biodegradability of bioplastics. Most of these standard methods measure carbon dioxide (CO_2) emission or oxygen consumption under environmentally controlled situations (Dentzman and Hayes 2019).

In the ASTM and ISO standards, based on aerobic and anaerobic situations, three principal areas of aerobic biodegradation standards, including composting, marine biodegradation, and soil biodegradation, and three main areas for anaerobic biodegradation standards such as accelerated landfill biodegradation, biodegradation of sewage sludge, and anaerobic digestion biodegradation are defined (Fig. 15.2) (Zhonga et al. 2020).

In the following, the essential standard test methods used to approve biodegradability of bioplastics written by different organizations are described.

15.3 International Standards for Organization (ISO) Standards for Biodegradability of Bio-Based Plastics

The International Standards for Organization (ISO) is an organization of representatives from national standard organizations providing industrial and commercial standards with partnership of 162 member countries. ISO standards are published for measuring the ultimate anaerobic and aerobic biodegradability of plastic products in the aqueous environment, activated sludge, soil, compost, and digesting sludge (Busch 2011; Dentzman and Hayes 2019). In the following, a list of ISO standards for biodegradation of bio-based plastics is presented in Table 15.1.

In addition, each standard is briefly described as follows:

Table 15.1 List of ISO standards for biodegradation of bio-plastics

Standard no.	Title
ISO 846	Plastics—Evaluation of the action of microorganisms
ISO 14853	Plastics—Determination of the ultimate anaerobic biodegradation of plastic materials in an aqueous system—Method by measurement of biogas production
ISO 14851	Determination of the ultimate aerobic biodegradability of plastic materials in an aqueous medium—Method by measuring the oxygen demand in a closed respirometer
ISO 14852	Determination of the ultimate aerobic biodegradability of plastic materials in an aqueous medium—Method by analysis of evolved carbon dioxide
ISO 14855-2	Determination of the ultimate aerobic biodegradability of plastic materials under controlled composting conditions—Method by analysis of evolved carbon dioxide—Part 2: Gravimetric measurement of carbon dioxide evolved in a laboratory-scale test
ISO 14855-1	Determination of the ultimate aerobic biodegradability of plastic materials under controlled composting conditions—Method by analysis of evolved carbon dioxide—Part 1: General method
ISO 17088	Specifications for compostable plastics
ISO 16929	Plastics—Determination of the degree of disintegration of plastic materials under defined composting conditions in a pilot-scale test
ISO 10210	Plastics—Methods for the preparation of samples for biodegradation testing of plastic materials
ISO 13975	Plastics—Determination of the ultimate anaerobic biodegradation of plastic materials in controlled slurry digestion systems—Method by measurement of biogas production
ISO 15985	Plastics—Determination of the ultimate anaerobic biodegradation under high-solids anaerobic-digestion conditions—Method by analysis of released biogas
ISO 17556	Plastics—Determination of the ultimate aerobic biodegradability of plastic materials in soil by measuring the oxygen demand in a respirometer or the amount of carbon dioxide evolved
ISO 18830	Plastics—Determination of aerobic biodegradation of non-floating plastic materials in a seawater/sandy sediment interface—Method by measuring the oxygen demand in closed respirometer
ISO 19679	Plastics—Determination of aerobic biodegradation of non-floating plastic materials in a seawater/sediment interface—Method by analysis of evolved carbon dioxide
ISO 20200	Plastics—Determination of the degree of disintegration of plastic materials under simulated composting conditions in a laboratory-scale test
ISO 22403	Plastics—Assessment of the intrinsic biodegradability of materials exposed to marine inocula under mesophilic aerobic laboratory conditions—Test methods and requirements
ISO 22404	Plastics—Determination of the aerobic biodegradation of non-floating materials exposed to marine sediment—Method by analysis of evolved carbon dioxide
ISO 22526-1	Plastics—Carbon and environmental footprint of bio-based plastics—Part 1: General principles
ISO 22526-2	Plastics—Carbon and environmental footprint of bio-based plastics—Part 2: Material carbon footprint, amount (mass) of CO2 removed from the air and incorporated into polymer molecule

(continued)

Table 15.1 (continued)

Standard no.	Title
ISO 22526-3	Plastics–Carbon and environmental footprint of bio-based plastics—Part 3: Process carbon footprint, requirements and guidelines for quantification
ISO 22766	Plastics—Determination of the degree of disintegration of plastic materials in marine habitats under real field conditions
ISO 23977-1	Plastics—Determination of the aerobic biodegradation of plastic materials exposed to seawater—Part 1: Method by analysis of evolved carbon dioxide
ISO 23977-2	Plastics—Determination of the aerobic biodegradation of plastic materials exposed to seawater—Part 2: Method by measuring the oxygen demand in closed respirometer
ISO 16620-1	Plastics—Biobased content—Part 1: General principles
ISO 16620-2	Plastics—Biobased content—Part 2: Determination of biobased carbon content
ISO 15314	Plastics—Methods for marine exposure
ISO/DIS 23517-1	Plastics—Biodegradable mulch films for use in agriculture and horticulture—Requirements and test methods regarding biodegradation, ecotoxicity and control of constituents
ISO/DIS 23517-2	Plastics—Biodegradable mulch films for use in agriculture and horticulture—Part 2: Requirements and test methods regarding product characteristics of mulch films

- ISO 846 specifies test methods for measuring the deterioration of plastics because of fungi and bacteria or soil microorganisms' actions which the aim of this test methods does not determine the biodegradability of plastics but the type and extent of deterioration can be measured by ISO 846, including visual examination and/or alterations in mass and/or changes in other physical attributes (ISO 846 2019).
- ISO 17556 test method is used to determine the final aerobic biodegradability of plastic materials (including natural polymer, synthetic polymer, copolymers and mixtures of them, plastic materials containing additives as plasticizers or colorants, and water-soluble polymers) in soil using the determination of the oxygen demand in the closed respirometer or the quantity of carbon dioxide evolved. Biodegradation is determined at 20–28 °C via determining oxygen consumption or carbon dioxide evolution during incubation time (six months to two years) (ISO 17556 2003).
- ISO 14853 is a screening method of anaerobic biodegradation which the test materials are exposed to sludge for up to a 90-day period, longer than the retention time of normal sludge (25–30 days) under anaerobic digester (the digesters at industrial sites may need to have the longer retention time). This test method can be used for natural/synthetic polymers, copolymers, or mixtures of them, plastic matters containing additives, water-soluble polymers, and materials without inhibitory behavior on microorganisms existing in the inoculum (ISO 14853 2016).
- The ISO 14851 test method covers the determination of aerobic biodegradability degree of plastic matters, including plastics comprising formulation additives using measuring of oxygen demand in the closed respirometer and expose of

test materials in an aqueous medium in the laboratory situations with an inoculum obtained from activated sludge. The test method could be applied for natural polymer or synthetic polymer, copolymers, or mixtures of them, plastic matters containing additives, water-soluble polymers, and materials without inhibitory behavior on microorganisms present in the inoculum (ISO 14851 2019).

- ISO 14855-1 presents a test method for measuring the ultimate aerobic biodegradability of plastic matters (on the basis of organic compounds) in the controlled composting situations using determination of CO_2 quantity evolved and the rate of the plastic disintegration at the end of the test. This standard test method is applied for simulation of typical aerobic composting situations for the solid-blended municipal waste organic fraction. The inoculum is obtained from compost in which the composting happens in the environment with monitoring and controlling aeration, temperature, and humidity. In this test method, conversion of the carbon to evolved carbon dioxide and its rate of conversion are measured (ISO 14855-1 2012).
- ISO 14855-2 covers a test method for measuring of the ultimate aerobic biodegradability of plastic matters in the controlled composting situations using gravimetric measurement of CO_2 evolved determination. This method presents the optimum degree of biodegradability using controlling and adjusting and controlling aeration, humidity, and temperature of the composting vessel, which can be used for natural/synthetic polymers, copolymers, or mixtures of them, materials containing additives, water-soluble polymers, and the materials that have not inhibitory impact on microorganisms present in the inoculum (ISO 14855-2 2018).
- ISO 16929 is applied for determining the disintegration degree of plastic materials in the pilot-scale aerobic composting test in the defined conditions, which is a part of total scheme in order to evaluate plastic's compostability as predetermined in ISO 17088 (ISO 17088 2012). This test method is also used for determination of the test material, which is influenced on the composting process and the obtained compost quality (ISO 16929 2019).
- ISO 17088 presents test methods and requirements for labeling (as compostable) and identification of plastic matters or products which are made of plastic matters which are appropriate for recovery via aerobic composting. Therefore, four perspectives of this standard are included: decomposition during composting, negative efficacies on the composting process and the composting facility, negative efficacies on the quality of the resulted compost, and biodegradation (ISO 17088 2012).
- ISO 14852 specifies a test procedure in which the amount of CO_2 evolved is measured for evaluation of the aerobic biodegradability degree of plastic materials, including plastics having additives. For this purpose, sample is subjected to a synthetic environment under controlled laboratory conditions to the inoculum from mature compost or soil under aerobic condition, mesophilic condition, and activated sludge condition. This test method can evaluate the biodegradation to be enhanced using calculating the carbon balance (ISO 14852 2018).

- The ISO 19679 test procedure is a simulation of the habitat which exists in various sediment or seawater areas, including sublittoral in the sea that specifies a procedure for determining the degree and rate of aerobic biodegradation in the plastic matters when settled on marine sandy sediment at the interface between seawater and the seafloor, via determining evolved CO_2 under the controlled and monitored laboratory conditions (ISO 19679 2020).
- The test method of ISO 10210 explains methods for test sample preparation applied for determining ultimate anaerobic and aerobic biodegradability of plastic matters in the aqueous environment, controlled compost or anaerobic digesting sludge, and soil. This test method is applicable for copolymers, natural polymers or synthetic polymers, or mixtures of them, plastic matters containing additives, plastic composite materials containing inorganic or organic fillers, and also products constructed from the mentioned substances (ISO 10210 2012).
- The standard test method of ISO 13975 is applied for the evaluation of the ultimate anaerobic biodegradability of plastics in the controlled anaerobic slurry digestion system containing a solid concentration (about 15%) that is applied for garbage or livestock feces and the sewage sludge treatment. This test procedure is determined by the percentage and rate of the organic carbon conversion in the test materials to methane and CO_2 resulted as biogas (ISO 13975 2019).
- ISO 18830 and ISO 19679 are two test methods which are applied to measure the rate and degree of aerobic biodegradability of plastic matters, by the oxygen demand measurement in the closed respirometer and the evolved CO_2, respectively, when they are located on marine sandy fouling at the interface between seafloor and seawater. The test method is performed under laboratory situations of the habitat existed in various sediment/seawater areas (ISO 18830 2016).
- ISO 20200 covers a test procedure for measuring the degree of plastic materials' decomposition when subjected to the laboratory-scale composting surroundings which is not applicable under composting conditions (ISO 20200 2015).
- ISO 22526 has constituted in three parts in which part 1 covers the common mains and the system borders for the carbon and environmental footstep of bio-based materials. This part is a guidance and the introduction document for other parts of ISO 22526 series which is useable for plastic matters or polymer resins that they are fossil-based or bio-based constituents (ISO 22526-1 2020).
- Part 2 describes the material carbon footmark as the mass of CO_2 eliminated from the air and inserted into plastic and defines a designation procedure to quantify it; this test method is used for plastic materials or productions and polymer resins which are wholly or partly based on bio-based constituents (ISO 22526-2 2020).
- Also, part 3 covers guidelines and commitments for quantifying and reporting of the process of carbon footstep of bioplastic materials. This standard can be applied for processing carbon footmark studies (P-CFP) of plastic matters, being sectional carbon footprint of the production (ISO 22526-3 2020).
- The standard of ISO 22403 describes test procedures and criteria for indicating inherent biodegradability in marine surroundings of virgin plastic substances and polymers with no primary surroundings' exposure or pretreatment. All test methods are performed at temperatures in the mesophilic range under aerobic

conditions for showing ultimate biodegradability, that is, conversion into biomass, CO_2, and water. Rates of biodegradation and lifetime of products made from biodegradable plastic materials in the sea are generally influenced by the specific environment situations and by shape and thickness (ISO 22403 2020).

- The test method of ISO 22404 is applied for determining the rate and degree of aerobic biodegradation level of plastic substances by determining the CO_2 evolved by the plastics, when subjected to marine sediments sampled from the sandy tidal region and protected wet by saltwater under conditions of laboratory (ISO 22404 2019).
- In addition, ISO 22766 covers test methods for determining the degree decomposition of plastic matters subjected to marine habitats under actual area conditions including the sandy eulittoral and the sandy sublittoral. The marine areas included the sandy sublittoral and the sandy eulittoral region where plastic substances can either be placed deliberately (e.g., biodegradable fishing nets) or end up as litter because of undutiful human manners (ISO 22766 2020).
- ISO 23977 includes two parts which part 1 presents a test procedure for determining the rate and degree of the aerobic biodegradation level of plastic substances specified by the evaluation of the CO_2 evolved from plastic substances when subjected to seawater sampled from coastal areas under the controlled laboratory conditions (ISO 23977-1 2020).
- In part 2, the amount, degree, and rate of the aerobic biodegradation are measured by calculating the oxygen demand in the closed respirometer when subjected to the defined conditions similar to ISO 23977-1 (ISO 23977-2 2020).
- ISO 15985 describes a laboratory test method for determining the ultimate anaerobic biodegradability of plastic matters on the basis of organic compounds under high amount of solids (upper than 20% total solids) and static non-mixed of anaerobic digestion situations by measuring evolved CO_2 and methane (as biogas) at ending test. Plastic samples are subjected to methanogenic inoculum which is obtained from anaerobic digesters acting just on pretreated household waste (ISO 15985 2014).
- ISO 16620-1 defines the common basics and the calculation procedures for measuring the bio-based content of plastic matters. The calculation procedures are based on the carbon mass or mass of each ingredient in the plastic productions or materials, polymer resins and monomers, or additives derived from bio-based or fossil-based constituents (ISO 16620-1 2015).
- ISO 16620-2 standard presents the calculation test procedure for measuring the bio-based carbon content in polymers, monomers, and plastic matters and productions in the basis of the carbon-14 content measurement. These data of the bio-based content of plastics are useful for evaluation of environmental effect (ISO 16620-2 2019).
- ISO 15314 defines three test procedures for the plastics' exposure in the marine medium which method A is about exposures where specimens float on the surface, method B defines exposures where specimens are immersed, and method C describes exposures where specimens are perfectly immersed. This standard

defines the common requirements for the device and test methods for application of the test methods mentioned (ISO 15314 2018).
- ISO/DIS 23517 is a test method which is under development consisting of two parts: part 1 specifies test methods and requirements regarding biodegradation, component control, and ecotoxicity, and part 2 defines test methods and requirements regarding product characteristics of mulch films. In part 1, the plastic materials used to produce mulch films and the mulch films itself regarding characteristics, including control of constituents, adverse impacts on terrestrial organisms, and biodegradation, are defined (ISO/DIS 23517-1(en) 2021).
- In part 2, the characterization of mulch films with regard to relevant physical product characteristics such as optical, dimensional, and mechanical is specified. In fact, these two parts of Standard No. 23517 are applicable for biodegradable plastic materials to produce mulch films or biodegradable mulch films ready to be applied for usage in horticulture and agriculture (ISO/DIS 23517-2(en) n.d.).

15.4 American Society for Testing and Materials (ASTM) Standards for Biodegradability of Bio-Based Plastics

ASTM is an international organization with over 140 member countries providing standards for a wide variety of products and processes. The important working group for reduction of problems and safety increase of plastics is the ASTM International's subcommittee on environmentally degradable plastics or bio-based products (D 20.96), which it is a part of the plastic committee. Subcommittee D20.96 started its work of developing much-needed standards to establish biodegradability and degradability and also evaluate the effect of degraded plastics (ASTM D6400-19 2019). The following test method standards are used for the evaluation of biodegradable plastics provided by the ASTM organization. Table 15.2 indicates a list of ASTM standards for biodegradable plastics:

- ASTM D5338 presents a procedure for the degree and rate determination of aerobic biodegradability of plastic products until placed in the composting process under controlled laboratory situations at thermophilic temperatures, which obtained test results are reproducible and repeatable. The test samples are exposed to the inoculums, which are obtained from compost from municipal solid waste and aeration; humidity and temperature of the environment are in a careful and attentive way monitored and checked (ASTM D5338-15(2021) 2021). The test procedure is equivalent to ISO 14855 standards (ISO 14855-1 2012; ISO 14855-2 2018).
- ASTM D6400 is a standard specification applied for plastics and plastic products which are planned to be composted under aerobic situations in municipal and industrial aerobic composting possibilities, wherever thermophilic situations are attained (ASTM D6400-19 2019). This specification covers the necessities for matters and products labeling as "compostable in aerobic industrial and municipal composting facilities." This standard is equivalent ISO 17088 (ISO 17088 2012).

Table 15.2 List of ASTM standards for biodegradation of bio-plastics

Standard no.	Title
ASTM D 6400	Guide for Assessing the Compostability of Environmentally Degradable Plastics
ASTM D 5338	Standard Test Method for Determining Aerobic Biodegradation of Plastic Materials Under Controlled Composting Conditions, Incorporating Thermophilic Temperatures
ASTM D 6868	Standard Specification for Labeling of End Items that Incorporate Plastics and Polymers as Coatings or Additives with Paper and Other Substrates Designed to be Aerobically Composted in Municipal or Industrial Facilities
ASTMD 5929	Standard Test Method for Determining Biodegradability of Materials Exposed to Municipal Solid Waste Composting Conditions by Compost Respirometry
ASTM D 5975	Standard Test Method for Determining the Stability of Compost by Measuring Oxygen Consumption
ASTM D 5988	Standard Test Method for Determining Aerobic Biodegradation of Plastic Materials in Soil
ASTM D 5526	Standard Test Method for Determining Anaerobic Biodegradation of Plastic Materials Under Accelerated Landfill Conditions
ASTM D 7475	Standard Test Method for Determining the Aerobic Degradation and Anaerobic Biodegradation of Plastic Materials under Accelerated Bioreactor Landfill Conditions
ASTM D6954	Standard Guide for Exposing and Testing Plastics that Degrade in the Environment by a Combination of Oxidation and Biodegradation.
ASTM D 5511	Standard Test Method for Determining Anaerobic Biodegradation of Plastic Materials Under High-Solids Anaerobic-Digestion Conditions
ASTM D 7473	Standard Test Method for Weight Attrition of Plastic Materials in the Marine Environment by Open System Aquarium Incubations
ASTM D 7991	Standard Test Method for Determining Aerobic Biodegradation of Plastics Buried in Sandy Marine Sediment under Controlled Laboratory Conditions
ASTM D 6691	Standard Test Method for Determining Aerobic Biodegradation of Plastic Materials in the Marine Environment by a Defined Microbial Consortium or Natural Sea Water Inoculum

- ASTM D6868 specification presents end items that includes plastic films/sheets, or polymers are incorporated (either through lamination, extrusion or mixing) to substrates and the entire end item is planned to be composted under aerobic conditions in municipal and industrial composting possibilities, where thermophilic temperatures are achieved (ASTM D6868 2021).
- ASTM D5975 is a standard test procedure for the determination of the compost sample stability exposed to a well-stabilized compost using measuring oxygen consumption under controlled composting situations on a laboratory scale involving active aeration, which an aerobic composting occurs in an environment, where temperature, aeration, and humidity are monitored in a careful way and controlled (ASTM D5975 2017). This test method evaluates the compost stability; it is an important parameter regarding plant tolerance and phytotoxicity of the compost. In this method, the rate of oxygen consumption is determined. No

similar test method is recognized for this standard in ISO method (ASTM D5975 2017).

- The test method of ASTM D5929 describes the material biodegradation properties by reproducibly subjecting substances to conditions generic of municipal solid waste (MSW) composting. The conditions for composting a material are controlled by a synthetic compost matrix and measure of the acclimation time, cumulative carbon dioxide production, cumulative oxygen uptake, and percentage of theoretical biodegradation over the term of the test (ASTM D5929 2018). In this method, key factors of biodegradable process including theoretical carbon dioxide and theoretical oxygen uptake are measured (ASTM D5929 2018).
- The test method of ASTM D7475 determines the degree and rate of aerobic and anaerobic biodegradation of plastic matters in the accelerated aerobic-anaerobic bioreactor landfill experiment environment. This test procedure can simulate the conversion from aerobic to anaerobic environments over time as landfill depth gains and also the anaerobic biodegradation happens under dry (more than 30% total solids) and static non-mixed situations (ASTM D7475 2020). Duration of this test method is 30 days as the compromise time period. The test results are according to the extent to that the plastic is transformed to methane and gaseous carbon in the form of carbon dioxide (ASTM D7475 2020).
- ASTM D6954 standard is a guideline which describes the framework or road plan to contrast and categorize the controlled laboratory rates of degradation and grade of physical property damages of polymers via thermal and photooxidation processes and also the biodegradation and ecological effects in disposal environments (which includes exposure in compost, landfill, and soil in which thermal oxidation may happen and land cover and agricultural usage in which possibility photooxidation may happen too) and specified applications after degradation (ASTM D6954 2018). Accelerated oxidation data should be gained at temperatures of the selected environment, for example, in landfill 20 °C–35 °C, in soil 20 °C–30 °C, and in composting facilities 20 °C–65 °C. This test method needs no more than 24 months for oxidation and biodegradation in the targeted use and disposal options. ASTM international biometer test is used for carbon dioxide evolution proper to the selected environment. There is no ISO test method standard equal to described test method in the ASTM D6954 (ASTM D6954 2018).
- The standard test method of ASTM D5526 determines the rate and degree of anaerobic biodegradation of plastic matters in the accelerated-landfill test environment and is also planned to yield blends of household waste and plastic materials after various degrees of decomposition under resemble landfill situations. The test substances are exposed to a methanogenic inoculum operating only on pretreated household waste. The anaerobic decomposition happens under dry (more than 30% total solids) and static non-mixed situations (ASTM D5526 2018). In this method, the percentage of carbon conversion in the sample to carbon gaseous form under resemble landfill situations is evaluated. There is no equivalent to this test procedure in ISO standard (ASTM D5526 2018).

- The test method of ASTM D5511 determines the grade and rate of anaerobic biodegradation of plastic substances in high-solid anaerobic situations which plastic matters are subjected to the methanogenic inoculum obtained from the anaerobic digesters applying just on pretreated household waste. The anaerobic biodegradation performs under high solids, higher than 30% total solids, and static non-mixed situations (ASTM D5511 2018). The conversion percentage of carbon in the plastic sample to carbon gaseous form under high-solid digester conditions treating municipal solid waste is evaluated (ASTM D5511 2018). The test procedure is equivalent to ISO 15985 (ISO 15985 2014).
- By the ASTM D5988 test method, the degree and rate of aerobic biodegradation of all plastic materials are determined under laboratory conditions such as formulation additives exposed to soil, which these plastic matters are not preventative for the bacteria and fungi existing in soil and mineralized by soil microorganisms. By the result of this method, the time over those plastics which will remain in the aerobic soil surroundings can be estimated. Determining aerobic biodegradation degree is performed by determining evolved carbon dioxide as a function of time (ASTM D5988 2018). This test procedure is like ISO 17556 (ISO 17556 2003).
- ASTM D6691 standard is applied to determine the degree and rate of aerobic biodegradation of plastic matters, including formulation additives subjected to pre-grown population of minimum ten aerobic marine microorganisms of recognized type or native population existent in natural seawater. The test procedure is performed under controlled laboratory situations and measured the quantity of biogas (CO_2) created during such an exposure (ASTM D6691 2017). No ISO test method is equivalent to this test procedure.
- ASTM D7991 presents a test procedure for determining the biodegradation level of plastic materials subjected to the simulated laboratory conditions of environment existing in the sandy tidal zone (ASTM D7991-15 2015). In this method, seawater and sediment are sampled from the sandy beach in the tidal zone. The natural microorganism existing in the sediment can biodegrade the plastic, and the evolution of carbon dioxide as a consequence of the aerobic microbial respiration is measured by this test method. There is no equal ISO standard for this method (ASTM D7991-15 2015).
- ASTM D7473 presents a test method for determining the weight loss as a function of non-floating plastic matter time (such as formulation additives). In this method, materials are incubated under changeable, open, and marine aquarium situations as representative of aquatic surroundings close to the coasts and near the bottom of a body of water in the lack of sunlight and especially UV and visible parts of the spectrum (ASTM D7473 2012). The aim of ASTM D7473 test method is to gain data for prediction of real-world experiences based on the amount and speed of biodegradation data of the same matters gained from the laboratory test method ASTM D6691 (ASTM D6691 2017), but this method is not a replacement to ASTM D6691 (ASTM D7473 2012). The amount of plastic biodegradability is measured by the levels of organic carbon oxidation and carbon

dioxide recovered therefrom. There is no ISO equal to this procedure (ASTM D7473 2012).

15.5 Organization for Economic Cooperation and Development (OECD) Standards for Biodegradability of Bio-Based Plastics

The Organization for Economic Cooperation and Development is an intergovernmental organization which provided standards for responsible business conduct with 36 member countries. The methodology for the plastics' biodegradability has been taken from the guidelines of the OECD for the chemicals' degradability. Biodegradability test methods of OECD standards apply simple markers for measuring the biodegradation process of bio-based materials. The following standard test methods are common test methods which can be applied for measuring biodegradation rate and/or degree in the bioplastics. Test methods of OECD establish threshold criteria for the marketing and direct classification of matters or products under two terms ready and ultimate biodegradability. Table 15.3 shows OECD standards for biodegradable plastics.

- OECD 301A test procedure is used for determining the degree of ready or ultimate aerobic biodegradation of soluble and non-volatile substrates, which the degree of aerobic biodegradation of materials is measured using the change in dissolved organic carbon (DOC) during a 28-day period (OECD n.d.-a).
- OECD 301B presents an aerobic biodegradation test method for introducing a material to an inoculum in the closed environment (a liquid surrounding) which the biodegradation of the material is measured via CO_2 evolution using respirometry during 28 days. This test procedure can be used for poorly or highly soluble materials and insoluble materials at certain concentrations. For example, oil, fuels, lubricants, and personal care products can be assessed by this method. The OECD 301B can be used for liquid materials, and ASTM D6400 (ASTM D6400-19 2019) test method is used for solid material (OECD n.d.-b).
- OECD 301C is a suitable modified MITI (Ministry of International Trade and Industry, Japan) aerobic biodegradation test method, which is used for poorly materials or with volatile material samples and possesses particular parameters differentiating it from other methods (OECD n.d.-c).
- OECD 301D is a suitable aerobic biodegradation test procedure, which can be applied with poorly soluble materials and volatile and absorbing material samples and also measures ready, ultimate, or inherent biodegradation via dissolved oxygen using respirometry during minimum of 28-day period. In this method, many chemical and physical characteristics can influence biodegradability testing (OECD n.d.-d).
- OECD 301E is like OECD 301A test method, but OECD 301E is a modified aerobic biodegradation test method with the use of lower concentration of microorganism and measures the ready or ultimate biodegradation of materials

via the evaluation of dissolved organic carbon (DOC) during a 28-day period (OECD n.d.-e).

- OECD 301F is an aerobic biodegradation test method of solutions for the determination of the insoluble and volatile materials' biodegradability which are challenged in the OECD 301B test method. In this test method, the purity or major component proportions of sample is necessary for calculation of theoretical oxygen demand (ThOD). The duration of the test similar to other OECD tests is a minimum of 28 days and used for measuring ready or ultimate biodegradability (OECD n.d.-f).
- OECD 306 is more similar to the OECD 301 standards, but this standard test method needs to use a seawater inoculum and often use with the OECD 301/302 sludge inoculum protocol. The duration of test procedure is 30 days which can be extended to 60 days and is applied for evaluation of ready or ultimate biodegradation. This test procedure is useful for all test materials which are in contact with aquatic environments (OECD n.d.-g).
- OECD 311 is a screening test method for investigating the potential anaerobic biodegradability of organic compounds under conditions similar to an anaerobic digester which is a biological reactor applied to digest sewage sludge after treatment of water. OECD 311 test method applies for the residual organic materials' biodegradability before entering the environment (OECD n.d.-h).
- Another aerobic biodegradability test method is OECD 310 which measures ready biodegradability using the evaluation of inorganic carbon (IC) and CO_2, produced in sealed vessels. This method is in the basis of ISO 14593 and OECD 310. The duration of this test method is 28 days and is applied for water-soluble and insoluble test material (OECD 2014).

Table 15.3 List of OECD standards for biodegradation of bio-plastic

Standard no.	Title
OECD 301 A	Biodegradation Test-DOC
OECD 301 B	Biodegradation Test—CO_2 Evolution
OECD 301C	MITI Biodegradation Test
OECD 301D	Biodegradation Closed Bottle Test
OECD 301 E	Modified Biodegradation Test—DOC
OECD 301 F	Biodegradation Test—O_2 Consumption
OECD 311	Anaerobic Biodegradability of Organic Compounds in Digested Sludge : by Measurement of Gas Production
OECD 310	Ready Biodegradability—CO_2 in sealed vessels (Headspace Test)
OECD 306	Biodegradation Test—Seawater

15.6 European Standards for Biodegradability of Bio-Based Plastics

There are other national and international organizations which are producing standards relating to biodegradable plastics. European Committee for Standardization (CEN) is an international organization which develops, distributes, and develops standards with 34 member countries (Harrison et al. 2018).

Also, the British Standards Institution (BSI) is an organization for developing standards which contains over 50,000 standards and include standards of UK and European standards from CEN/CENELEC, ISO, and IEC standards. The British Composting Association tried to establish the industry standards for composts (Harrison et al. 2018). In addition, based on the new BSI standard, a plastic containing organic carbon (90%) needs to be converted to CO_2 within 730 days to be suitable. Table 15.4 shows a list of European standards for biodegradable plastics or bio-based products, including bio-based plastics. Descriptions of European standards for biodegradable plastics or bio-based plastics present as follows:

- BS EN 17033 describes the necessities for biodegradable films made up from thermoplastic matters, which are used for mulch applications in horticulture and agriculture without causing any adverse effect on the surroundings (BS EN 17033 2018).
- BS EN 13432 specifies necessities and test procedures for measuring the anaerobic treatability and compostability of packaging and packaging materials with regard to four properties, including impact on the biological treatment process, biodegradability, impact on the quality of obtained compost, and disintegration during biological treatment (BS EN 13432 2000).
- BS EN 14046 covers a test method for determining the ultimate aerobic biodegradability of packaging substances based on organic materials under laboratory controlled composting situations (including aeration, temperature and humidity) by determining released CO_2 at ending test (BS EN 14046 2003).
- BS EN 14995 specifies the necessities and procedures for plastic substances which are organically recoverable. This standard determines the compostability or anaerobic treatability of plastic matters regarding four characteristics, including disintegration during biological treatment, effect on the quality of the resulting compost, effect on the biological treatment process, and biodegradability. This standard can be applied to support claims plastics' compostability. Also, the procedure of this standard is comparable with that of EN 13432 (BS EN 13432 2000) in which the necessities for packaging matters are defined (BS EN 14995 2006).
- BS 8472 specifies procedures for the evaluation of the oxo-biodegradation of plastic matters and the phytotoxicity of the residues in controlled laboratory situations when plastics are subjected to artificial weathering or heat exposure. This standard test method is useful to characterize the degradation mechanism based on possible oxidation followed by biodegradation (BS 8472 2011).

Table 15.4 List of European standards for biodegradation of bio-plastic

Standard no.	Title
BS EN 17033	Plastics—Biodegradable mulch films for use in agriculture and horticulture. Requirements and test methods
BS EN 13432	Packaging—Requirements for packaging recoverable through composting and biodegradation. Test scheme and evaluation criteria for the final acceptance of packaging
BS EN 14046	Packaging-Evaluation of the ultimate aerobic biodegradability and disintegration of packaging materials under controlled composting conditions. Method by analysis of released carbon dioxide
BS EN 14995	Plastics- Evaluation of compostability. Test scheme and specifications
BS 8472	Methods for the assessment of the oxo-biodegradation of plastics and of the phyto-toxicity of the residues in controlled laboratory conditions
BS EN 17417	Determination of the ultimate biodegradation of plastics materials in an aqueous system under anoxic (denitrifying) conditions. Method by measurement of pressure increase
BS PAS 100	Specification for composted materials
BS EN 14987	Plastics. Evaluation of disposability in waste water treatment plants. Test scheme for final acceptance and specifications
BS EN 16785-1	Bio-based products. Bio-based content. Determination of the bio-based content using the radiocarbon analysis and elemental analysis
BS EN 16785-2	Bio-based products—Bio-based content—Part 2: Determination of the bio-based content using the material balance method
BS EN 16640	Bio-based products. Bio-based carbon content. Determination of the bio-based carbon content using the radiocarbon method
BS EN 16760	Bio-based products. Life Cycle Assessment
BS EN 16935	Bio-based products. Requirements for Business-to-Consumer communication and claims
EN 13655	Plastics—Thermoplastic mulch films recoverable after use, for use in agriculture and horticulture
EN 17228	Terminology, Characteristics and Communication for Bio-based Polymers & Plastics
EN 16751	Bio-based products. Sustainability criteria
PD CEN/TR 17219	Plastics. Biodegradable thermoplastic mulch films for use in agriculture and horticulture. Guide for the quantification of alteration of films
UNE-CEN/TR 15822	Plastics—Biodegradable plastics in or on soil—Recovery, disposal and related environmental issues
UNE-CEN/TR 15351	Plastics—Guide for vocabulary in the field of degradable and biodegradable polymers and plastic items
DIN EN 13592	Plastics sacks for household waste collection—Types, requirements and test methods
DIN EN 17427	Packaging—Requirements and test scheme for carrier bags suitable for treatment in well-managed home composting installations
DIN EN 14045	Packaging—Evaluation of the disintegration of packaging materials in practical oriented tests under defined composting conditions
AS 5810	Biodegradable plastics—Biodegradable plastics suitable for home composting

(continued)

Table 15.4 (continued)

Standard no.	Title
AS 4736	Biodegradable Plastic-Biodegradable Plastics Suitable for Composting and other Microbial Treatment
CSA Z218.0-93	Test Method for Determining the Anaerobic Biodegradability of Plastic Materials
PD CEN/TR 17219	Plastics. Biodegradable thermoplastic mulch films for use in agriculture and horticulture. Guide for the quantification of alteration of films

- BS EN 17417 describes a test procedure under laboratory situations for determining the ultimate plastics' anoxic biodegradation manufactured from organic compounds by quantifying the produced carbon dioxide and nitrogen at ending test method (BS EN 17417 2020).
- BS PAS 100 describes requirements for the composting process, the minimum quality of composted materials, choice of input materials and labeling, and traceability and storage of compost materials which these requirements are for a quality management system (QMS) of the compost production assure that they are consistently fit for their intended uses (PAS 100 2018).
- BS EN 14987 defines criteria and test methods for verification that if a solid plastic material considered is disposable in wastewater treatment plants, it means that these plastics do not make problems for drainage and surrounding. For this purpose, it needs to be verified that the plastic material is under evaluation of aerobic condition for its biodegradability (e.g., susceptible to mineralization) and dispersibility and solubility in water. These plastics which are in compliance with this standard can be disposed in industrial or municipal wastewater treatment plants through the sewage (BS EN 14987 2006).
- This document (BS 07/30111991 DC, BS 8472) defines a laboratory test method to characterize the degradation mechanism based on oxidation followed by biodegradation in which the plastics' behaviors subjected to heat exposure or artificial weathering are specified. These two mechanisms together (photodegradation and heat—degradation) are referred to as "oxo-degradation" (BS 07/30111991 DC, BS 8472 1991).
- EN 16640 describes three test methods for determining radiocarbon content liquid scintillation counting (LSC), beta-ionization (BI), and accelerator mass spectrometry (AMS) of bio-based products (BS EN 16640 2017).
- European standard EN 16785-1 describes the requirements for measuring bio-based (derived from biomass) content of a product by radiocarbon (carbon-14) and elemental analyses. This standard is used for solid, gaseous, and liquid products containing carbon. The carbon content of bio-based products is determined according to EN 16640 (BS EN 16785-1 2015).
- EN 16785-2 defines a test method for measuring the bio-based content in the products by the material balance used for the representative product batch in a unit of production. This standard is usable for any solid, gaseous, and liquid bio-based product containing carbon, gained using chemical synthesis,

assembling, or mixing, provided: for the product batch, the product composition and the bio-based content of each input and loss and output in the production unit are recognized. The bio-based content of the product using analysis is verified (BS EN 16785-2 2018).

- EN 16760 (BS EN 16760 2015) specifies particular life cycle assessment (LCA) guidance and requirements for bio-based products derived partly or wholly from biomass, excluding feed, energy, and food according to EN ISO 14040 (BS EN ISO 14040+A1 2020) and EN ISO 14044 (BS EN ISO 14044+A1 2018) with focus on how to apply the specificities of the bio-based part of the product (BS EN 16760 2015).
- BS EN 16935 defines requirements for non-misleading and transparent business-to-consumer relationship of characteristics of bio-based products via labeling and claims. This standard is used as a tool to create and transfer data to the consumer and/or as an input for product-specific standards and certification schemes (BS EN 16935 2017).
- EN 17228 defines test methods, terminology, and templates for reporting on bio-based plastics and polymers, including semifinished composites and products, aside from bio-based carbon content of the products. This standard includes life cycle assessment and sustainability, but this document does not cover biocompatible plastics and polymers for medical application (EN 17228 2019).
- EN 16751 defines horizontal sustainability criteria usable for the bio-based part of all bio-based products, excluding energy, feed, and food, which covers all three pillars of sustainability and social, economic, and environmental aspects. This standard is not applicable for non-bio-based materials such as fossil or mineral part of a product. This standard can be applied for two cases, including sustainability information about biomass production only or sustainability information in the supply chain for the bio-based part of the bio-based product (BS EN 16751 2016).
- PD CEN/TR 17219 is a technical report or informative document which presents guidance for the quantification of conversion of biodegradable thermoplastic mulch films for application in horticulture and agriculture and can be applied for biodegradable thermoplastic mulch films in adaptation with BS EN 17033 (PD CEN/TR 17219 2018a).
- UNE-CEN/TR 15822 is a technical report and presents experience and science in the field of biodegradable plastics that are applied end up in soil or on soil. It considered the linkages between degradation mechanisms, use, disposal after use, and the environment. This document can be used for providing a basis for the development of future standards (UNE-CEN/TR 15822 2011).
- UNE-CEN/TR 15351defines a guidance of the vocabulary in the field of polymers and plastic products and items, which they are derived from the technical analysis of the different steps and mechanisms involved in the plastics' conversion up to polymer products, bioaccumulation and biorecycling of macromolecular compounds, and also mineralization (UNE-CEN/TR 15351 2006).

- DIN EN 13592 defines the common properties, requirements, and test methods for bags and bin liners, which are made from plastic films and applied for household selective waste collection and household waste collection. Therefore, biodegradable or compostable sacks should be complied with EN 13432 (DIN EN 13592 2017).
- DIN EN 17427 defines a requirement and test method for carrier bags appropriate for application in well-managed home composting plants under specified environmental situations. The five characteristics, including biodegradation, compost quality and recognizability, typing, and decay during composting, are considered in this standard, which are useful for evaluation and the influence on the biological treatment process. This standard covers the basis for the carrier bags' labeling which are appropriate for home composting (DIN EN 17427 2020).
- The standard of DIN EN 14045 is applied for the evaluation and the disintegration of packaging matters in the pilot-scale composting test method under controlled conditions. In this standard, packaging matters are mixed with biowaste and then spontaneously composted for 12 weeks under practical-oriented composting situations (DIN EN 14045 2003). At the end of the composting cycle, the disintegration is determined using sieving of the compost and the mass balance calculation. The impact of the tested sample on the compost quality can be investigated by applying the obtained compost at the end of the composting process for more measurement including ecotoxicity and chemical analyses. In addition, this test method can be applied for photographic documentation and visual perception of the packaging materials' disintegration and also for evaluation of the impact of their addition on the composting process (DIN EN 14045 2003).
- AS 5810 covers test methods and requirements to specify the biodegradability of a plastic material under home composting and assigns the basis for allowance labeling of products and material produced from plastics as home compostable (Australian Standard AS 5810 2010).
- Also, in AS 4736, the test methods and requirements for determining the compostability or anaerobic biodegradation of plastic materials regarding biodegradability, influence on the biological treatment process, disintegration during biological treatment, and influence on the quality of the resulted compost are specified (Australian Standard AS 4736 2006).
- CSA Z218.0-93 standard describes a laboratory test method condition for the evaluation of the anaerobic biodegradability of plastic substances on subject to primary anaerobic digester sludge resulted from the treatment of preliminary clarifier sludge at urban wastewater treatment plant. The degree of anaerobic biodegradability of the plastic materials is specified by measuring carbon dioxide and methane as a function of time (CSA Z218.0-93 1999).
- This document (PD CEN/TR 17219) presents a guidance for the conversion quantification of biodegradable mulch films, which are used in horticulture and agriculture, but they are applied for biodegradable thermoplastic mulch films in agreement with EN 17033 (PD CEN/TR 17219 2018b).

– EN 13655 defines the requirements relating to dimensional, optical, dimensional, and thermal characteristics of thermoplastic films for the application of mulching in horticulture and agriculture. These films are based on polyethylene and/or ethylene copolymers and are intended to be removed after their applications (EN 13655 2018).

15.7 Certification and Labeling

The producer can use standard quality control test methods to present a consistent, quality product; the end-customer are confident that they are buying the high-quality product which will meet the market requirements and regulatory time again. For consumers, it is difficult to differentiate bioplastics from conventional plastics. It is well known that quality assurance without valid testing has not worth. The compostability performance claims require to be substantiated and backed up using valid results of test (Horvat and Kržan 2012).

For this reason, a certification label scheme provides the suitable use of biodegradable plastics by consumers and makes consumers informed about discrimination between compostable products appropriate for application in home composting and large-scale industrial plants and facilitates the waste collection activities and recycling programs (if the recycle of biodegradable plastics is treated by biological process) (Horvat and Kržan 2012).

A certificate is used to guarantee a particular characteristic. Therefore, for biodegradable plastics, a certificate is an evidence for confirmation biodegradability of a plastic under specified conditions in the standard. The most significant certification organizations in Europe are included such as DIN Certco and Vincotte which both of them issue certificates for bioplastic materials. DIN CERTCO covers certificates for all products which are manufactured from compostable plastics or compostable materials made from renewable resources based on standards (including ASTM D 6866) related to these products.

In addition, the Biodegradable Products Institute (BPI) from the United States, the Japan BioPlastics Association in Japan, and other organizations are issued certification organizations for bioplastics (Horvat and Kržan 2012; Hann et al. 2020). Table 15.5 shows main certification organizations and their label logo for bio-based plastics.

15.8 Certification Process

Figure 15.3 shows stages of gaining the certificate process. Obtaining a certificate for biodegradable plastics is optional. For this purpose, a producer contacts with a certification organization by an application comprising information about the production (a kind of biodegradable plastic) which it wishes to be certified. Then, certification organization gives a list of accredited laboratories confirmed based on the EN ISO/IEC 17025 standard (ISO/IEC 17025 2017) to perform test methods

Table 15.5 Major certification organizations and their certificate labels for bioplastics

Country	Organization	Norm/standard	Certification label
Belgian and German	TÜV Austria Belgium and DIN CERTCO	EN 13432 / 14995 /ISO ASTM D 6400 standards	
Germany	DIN CERTCO	EN 13432/ASTMD 6400/ ISO17088/EN 14995/AS 4736	
Belgian	TÜV Austria Belgium	EU standard CEN/TS 16137:2011	
German	DIN CERTCO	EU standard CEN/TS 16137:2011	
USDA	RTP Company	ASTM D6866	
German	DIN CERTCO	EN 17033	
Belgian	TÜV Austria Belgium	EN 17033	
German	DIN CERTCO	PrEN 17427 EN 13432	
Belgian	TÜV Austria Belgium	PrEN 17427 EN 13432	
German	DIN CERTCO	EN 13432	
Belgian	TÜV Austria Belgium	EN 13432	

(continued)

Table 15.5 (continued)

Country	Organization	Norm/standard	Certification label
Belgium	Vincotte	EN 13432/EN14995	
Belgium	Vincotte	Special Vincotte process based on EN 13432 (at low temperature)	
United States	Biodegradable products Institute	ASTM D6400	
Belgium	Vincotte	Special Vincotte process based on ISO 14851/ISO 14852	
Belgium	Vincotte	Special Vincotte process based on ISO	
Japan	The Japan BioPlastics Association (JBPA)	Green PLA certification scheme	
America	Biodegradable Products Institute (BPI)	ASTMD 6868/ASTM D6400	
America	Cedar Grove	ASTM D6400 and ASTM D6868 with additionally mandatory full scale test	
Italy	Consorzio Italiano Compostatori (CIC)	Based on EN 13432 with additionally mandatory full scale test	
Finland	Jatelaitosyhdistys	EN 13432	
Sweden	SP Technical Research Institute of Sweden	SPCR 141	

(continued)

Table 15.5 (continued)

Country	Organization	Norm/standard	Certification label
Spain	Department de Medi i Ambient Habitatge	EN 17033 and EN 14995, 13432	

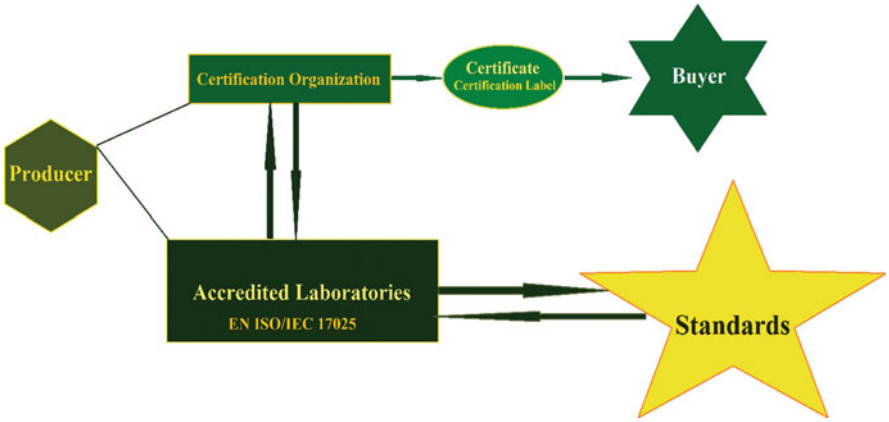

Fig. 15.3 Certification Process

according to the specified standards. The results of product analysis are sent to the certification organization for the issuance of certificates if the results were positive. The valid certificate must include the label of the certification authority that it should remark the standard on which the certificate is based and also a certificate number. In addition, the validity of the certificate can be verified on the website of the certification organization (Horvat and Kržan 2012).

15.9 Conclusions

Valid test methods to determine the biodegradability of bio-based plastics in nature are essentially needed for the whole assessment of the biodegradability and recoverability of bio-based plastics entering the various environments including soil, marine, etc.

In different standard test methods, the biodegradation rate for bioplastic materials or bio-based products can be measured on the basis of the evaluation of dissolved oxygen, oxygen consumption or inorganic carbon, dissolved organic carbon, carbon dioxide production, or oxygen release in the environment. Standards specify the requirements and test methods for produced bio-based plastics in order to control and validate these products before entering to the market or environment. These

standards give the choice to consumers for the correct handling of the products. In addition, standards prescribe test methods to analyze threshold values for particular parameters which help to validate the bio-based products. In addition, certification logo is the proof of a product based on the related standard which shows a product validation based on the specific requirements of standard, although various improvements are needed for enhancing the reproducibility of the validity of the testing methods.

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ASTM D5929 (2018) Standard test method for determining biodegradability of materials exposed to source-separated organic municipal solid waste mesophilic composting conditions by Respirometry. ASTM International, West Conshohocken, PA, https://www.astm.org

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ASTM D6868 (2021) Standard specification for labeling of end items that incorporate plastics and polymers as coatings or additives with paper and other substrates designed to be aerobically composted in municipal or industrial facilities. ASTM International, West Conshohocken, PA, https://www.astm.org

ASTM D6954 (2018) Standard guide for exposing and testing plastics that degrade in the environment by a combination of oxidation and biodegradation. ASTM International, West Conshohocken, PA, https://www.astm.org

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Future Prospects of Biodegradable Polymers with Potential Application in Food Industry

16

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Abstract

Enormous plastic production and its consumption and accumulation are a global concern. Although the solution to this issue is "reuse, recycle, and reduce plastic," it is not quite enough, and therefore biodegradable packaging material is gaining acceptability in the agriculture and food industry for packaging purposes. This chapter summarizes recent approaches and innovations in the field of biodegradable polymers and future prospects. Here, biodegradable polymers and natural polymers with their properties, their applicability, and their degradation are discussed. Also, improvements in properties of natural polymers by using technologies have been discussed. Biodegradable polymers reduce the burden of greenhouse gases on Earth.

Keywords

Biodegradable polymers · Food packaging · Properties · Degradation · Future prospects

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16.1 Introduction

Modern life cannot be imagined without polymers as they play the biggest role in packaging. Despite all these things, plastic possesses unique features like lightness, inexpensive, high specific strength, non-permeability, and flexibility and therefore is most commonly used in packaging material. About 26% of plastic from overall plastic production is used for packaging purposes (Ellen MacArthur Foundation and McKinsey and Company 2016). In 2018, the Nova Research Institute, which studies chemical and material transition, had concluded that worldwide plastic production will be 2.62 million tons up to 2023 from 2.11 million tons in 2018 (Bioplastics Market Data n.d.). There are some polymers which are not decomposed by action of microorganisms like polyethylene, polypropylene, polyethylene terephthalate, polyvinyl chloride (PVC), nylon and polyurethane (PU or PUR), etc. Aluminum foil is used in the center of multilayer packaging material to improve barrier properties (European Plastics Recycling and Recovery Organisations Statistics 2014).

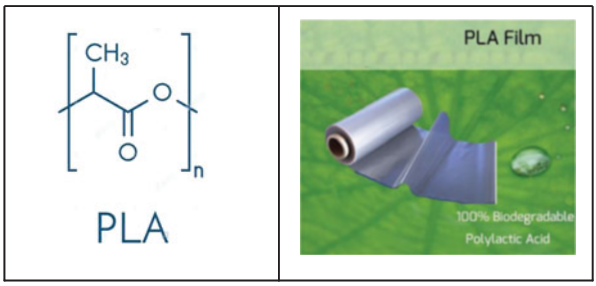
These high molar mass polymers having a very stable C-C (carbon-carbon) backbone remain in the environment for a very long period from several 10–1000 years. Nonbiodegradable polymers have many drawbacks. They accumulate in the body and cause toxicity (Guo et al. 2012). In order to reduce ecological pollution due to landfilling of plastic waste after use, biodegradable packages or other forms should be utilized for various short-term applications. As biodegradable polymers have relatively high cost and very low mechanical properties compared to nonbiodegradable synthetic polymers, therefore they are confined for use in some applications (Fortunati et al. 2017).

16.2 Biodegradable Polymers

Biodegradable polymers are those polymers under biodegradation either by enzymatically or nonenzymatically yielding biocompatible or less harmful components. Improvement in drug pharmacokinetics is achieved and side effects are reduced due to these polymers (Zhao et al. 2016). There are natural, synthetic, and microbial plastics available which can be degraded naturally. One of the most promising biodegradable polymers is **polylactic acid (PLA)**, which is used in drug delivery devices, preparation of tissue engineering scaffolds, biosensors, and food packaging materials. PLA is highly transparent (as shown in Fig. 16.1b) with high molecular weight and very good barrier properties to water, but besides its mechanical properties like strength, stiffness, and thermal properties are inferior (Gupta et al. 2017).

Polylactide films formed were similar in appearance and properties to oriented polystyrene films. In 2010, it was second most bioplastic used in the world. PLA possesses those mechanical properties which lie between polystyrene and polyethylene terephthalate (PET).

Blends: PLLA (poly-L-lactide) can be blended with PDLA (poly-D-lactide) physically to enhance its melting point by 40–50 °C. Also, its heat distortion



(a) (b)

Fig. 16.1 (**a**) Chemical structure of PLA. (**b**) PLA film available in market

temperature (i.e., temperature at which polymer deforms) rose from 60 °C to 190 °C. At 1:1 proportion, temperature stability can be maximized, but even at very low concentration like 3–10% of poly-D-lactic acid, properties of the blend improved significantly. Increased crystallinity is due to PDLA. Due to its higher crystalline structure, the biodegradation rate of PDLA is slower than PLLA.

Properties of PLA are improved by various technologies like annealing, preparing blends, and forming nanocomposites. Chain extension and introduction of cross-linked structures are some processes used to improve properties. Packaging films and fibers are formed from PLA in the same way from thermoplastic.

Degradation of PLA:

PLA degradation is carried out by hydrolysis, thermal degradation, and photodegradation to organic compounds. PLA degradation at room temperatures is deliberate. In 2017, a study was conducted to check the loss of PLA mass over some period of time. Negligible loss of mass over a year appeared at 25 °C in seawater, but change in structure of polymer chains or water intake by PLA mass was not observed. Therefore, we can say that degradation of PLA is effectively carried out in industrial composting. Home composting and landfilling are not effective methods for its degradation (Bagheri et al. 2017).

Polybutylene adipate-co-terephthalate (PBAT) is an environment-friendly polymer with high ductility and used in food and agricultural produce packaging. It is widely used for blending purposes in order to improve properties of PLA (Xing et al. 2019). Generally, PBAT is marketed as an alternative to nonbiodegradable polymer LDPE, as it possesses many similar properties like flexibility and resilience; therefore, it is used for making bags and wraps.

Properties of PBAT

- Due to its random structure, it is impossible to crystallize.
- It requires a high melting temperature and less stiffness.
- It has great flexible nature and is tough (it will not be strong and rigid); therefore it is not suitable for rigid containers.
- Adipate groups present in the butylenes make it fully biodegradable, and mechanical properties of PBAT are due to terephthalate portion (La Mantia et al. 2018).

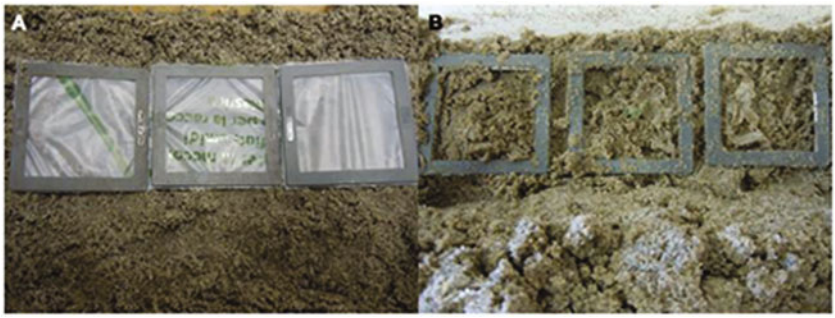


Fig. 16.2 Mater-Bi specimen degradation before (**a**) and after (**b**) nine months of treatment period

Sustainable end-of-life options for PBAT and PBAT blends are industrial composting and chemical/catalytic recycling (Hatti-Kaul et al. 2020). Another biodegradable polymer is the MaterBi® originated from modification of starch (as shown in Fig. 16.2 below); it can be also synthesized from synthetic but biodegradable polyester. It possesses fine mechanical and barrier properties, and it has satisfactory thermal equilibrium. Another biodegradable polymer is **Bioflex®** which is better than the MaterBi® family (La Mantia et al. 2018). Home composting, industrial composting, and anaerobic digestion are good ways for degradation of TPS (thermoplastic starch), cellulose, and its derivatives like cellulose acetate and polymers based on starch blending (Hatti-Kaul et al. 2020).

Polyglycolic acid or PGA is also a biodegradable polymer widely used along with these some other degradable polymers such as polybutylene succinate (PBT) which is insoluble in water. Polyhydroxyalkanoate produced by different kinds of microorganisms is biodegradable in nature. Biocompatible and ductile nature of PLA is enhanced by blending with polyglycolide. PBS is typically used in film packaging when combined with chitosan. Sustainable end-of-life options for PHA, PHB, and PHO are home composting, industrial composting, anaerobic digestion, and chemical/catalytic recycling and for PBS are chemical/catalytic recycling and enzymatic depolymerization (Hatti-Kaul et al. 2020).

16.3 Classification of Biopolymers

16.3.1 Biopolymers (Renewable Sources)

1. Polymers which are produced using biomass:
   (a) Starch, cellulose, carrageenan, and galactomannans like some polysaccharides
   (b) Casein, zein, silk fibroin, and gluten and whey proteins like some proteins
2. Chemically synthesized sustainable bio-based monomers, like polylactic acid.
3. Microbiologically obtained polymer:

(a) Polysaccharide: gellan gum and pullulan
(b) Polyhydroxyalkanoate (PHA)
(c) Fucopol

16.3.2 Polymers (Fossil Sources)

- PCL—polycaprolactone
- PGA—polyglycolide
- PBSA—polybutylene succinate (Galgano 2015)

16.4 Polysaccharides in Food Packaging

16.4.1 Animal-Derived Polysaccharides

16.4.1.1 Chitin

Chitin polysaccharide is the prime constituent of exoskeleton prawns, crabs, arthropods, etc. (as shown in Fig. 16.3) wasted by chemical extraction processes. It has different properties which are mentioned in Table 16.1 given below than other polysaccharides due to backbone structure and cationic groups on it. Chitin is not favorable for microorganisms as in fungi it suppresses sporulation and germination of spores. Chitin is degraded naturally by microorganisms, not toxic to humans, sustainable, and biocompatible. It is mostly used to pack coffee in the form of bags

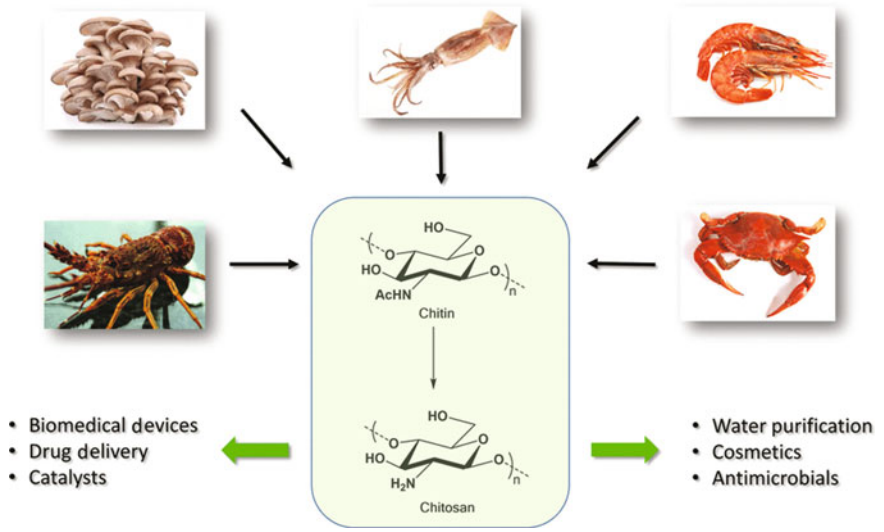


Fig. 16.3 Sources and structure of chitin and chitosan

Table 16.1 Properties and application of different kinds of polymers available in market (Galgano 2015; Prajapati et al. 2013; Duan et al. 2016; Tavassoli-Kafrani et al. 2016; Quoc et al. 2015)

Polymers	Properties of polymer	Applications in food industry
Polysaccharides (chitin, starch, carrageenan, etc.)	Most are biocompatible. All are biodegradable. They are mostly transparent in nature. All are nontoxic. Most of them have antimicrobial properties.	They can be used as edible film or membrane on fruits and vegetables. Also, they are used to protect from hazardous conditions, chemicals, vibrations, and microorganisms in order to increase shelf life.
Proteins (gluten, zein, etc.)	They improve barrier and mechanical properties of packaging film as they are tough in nature. They are very good barrier properties to gases and water vapor.	Edible proteins are used for coating purposes, and nonedible proteins like gelatin and keratin are used in the formation of bags and containers.
Synthetic (nylon, Teflon, etc.)	They are tough and have great structural properties. They can be added in natural polymers to increase strength.	They are used in film and package manufacturing. These are used in manufacturing of pipes, bags, and paint also.
Bio-based (PHA, PLA, etc.)	They possess good mechanical properties. They are mostly used for blending purpose with natural biodegradable polymers.	They are used in disposable food packaging like bags and containers.
Nonbiodegradable (polystyrene, polyethylene, etc.)	They have great mechanical strength. They are commonly used in plastic production for permanent use. They have good gas barrier properties.	They are used in pipes, bags, and containers. They are also used in manufacture of food packaging cans and others.

and films for coating as it has fine transparency (Kerch 2015; Tavassoli-Kafrani et al. 2016).

16.4.1.2 Chitosan

Being semipermeable chitosans are essentially used in preservation of some food as they have low oxygen permeability and moderate water vapor barrier. Thermoplastic films can be produced from glycerol and chitosan and thermal treatment is given (Thakur and Thakur 2016). They are not toxic to humans and bioabsorbable. They are effective against microorganisms and have good barrier properties to gases. Some plasticizers are added to reduce their brittle nature which is due to polymer-polymer interaction. They are used to coat vegetables and fruits like mangoes, cherries, and strawberries to increase their shelf life (Kerch 2015; Tavassoli-Kafrani et al. 2016).

Other polysaccharides like starch, pectin, and alginate and proteins are added to improve properties like water solubility and water vapor permeability (Luo and Wang 2014). Also to impart hydrophobicity lipids like beeswax, carnauba wax like naturally produced waxes, plant resins, oleic acid, or vegetable oils are added

to membranes or films, and moisture transfer is reduced (Galus, and Kadzinska, J. 2015).

16.4.2 Polysaccharides Obtained from Plants

16.4.2.1 Starch

Starch is a polysaccharide found in plants abundantly and can be degraded biologically. It has thermoplastic behavior. Packaging films and coatings made from starch polysaccharide have very low oxygen permeability and limited mechanical strength. It has no odor and taste but has hydrophilicity and ability to retrograde over time which gives brittle nature. To make starch-based coating or membrane with strengthened mechanical properties like polyolefin, polyols, glycerol, and glycol, and sorbitol-like plasticizers are used to overcome these drawbacks which increase chain mobility and improve the flexibility. In order to increase stretchability, water barrier properties, and appropriate mechanical strength, starch is blended with greater hydrophobic polymer, and its composites are made and chemical modification of starch is carried out (Duan et al. 2016).

Starch is used in packaging like to form extruded bags and films and nets for fruit and vegetable packaging. Starch-based trays are formed by the thermoforming process and also used in food packaging applications.

16.4.2.2 Galactomannans

Edible membranes and coatings made from these gums possess good mechanical and barrier properties which make galactomannans suitable for use to enhance lifespan. The use of galactomannans is safe and increases the overall quality of food (Galgano 2015). Also these coatings and membranes are used in fruit and cheese coatings. Studies showed that when apple is coated by these coatings, internal oxygen concentration is decreased and the firmness, crispiness, and juiciness are maintained (Prajapati et al. 2013).

Cellulose

Cellulose can form powerful hydrogen bonds to make crystalline structure or fibrous structure. Cellulose has low density, great mechanical properties, less production expenditure, good film forming property, and chemical stability. It is durable, nontoxic, renewable, biodegradable, and biocompatible in nature; besides these properties, it cannot be used directly for packaging purposes as it possesses water absorption capacity (Duan et al. 2016).

16.4.3 Polysaccharides Obtained from Algae

Carrageenan and alginate are the polysaccharides obtained from algae. They have good properties due to which they can be used in the packaging application. Alginate is not toxic to humans and biodegradable and biocompatible, and it has low

production cost. Sodium alginate (E401) is obtained from brown seaweed, and it is most widely used in industrial application like in packaging of food products, in paper manufacturing, and in pharmaceuticals. Membrane is strong because of its linear structure, and therefore it can be used as film for packaging purposes (Tavassoli-Kafrani et al. 2016).

16.4.4 Polysaccharides Obtained from Microorganisms

Many polysaccharides obtained from microorganisms are used for film and coating formation as they possess some properties like biodegradability, biocompatibility, etc. Properties and applications of important microbial polysaccharide in the food industry are given in the diagram below except bacterial alginate and cellulose as they are already discussed.

16.4.4.1 Pullulan

Pullulan is produced from *Aureobasidium pullulan*, and film produced from it has great transparency and can be degraded biologically to simpler by-products. It is soluble in water and can resist entry and exit of oils and fats; therefore it can be used to package seasoning bags and instant coffee. Heat can be applied to seal the bags to keep the product fresh.

16.4.4.2 Gellan Gum

Sphingomonas elodea produces this polysaccharide. Lipid-resistant films produced from this degradable polymer are used for coating and wrapping purposes for chicken, cheese, fruits, etc. This is also used for flavor and other plant-derived ingredient encapsulations.

16.4.4.3 Xanthan Gum

It is a common food additive produced from *Xanthomonas campestris* used as a thickener. Also, films and coatings are produced from this polysaccharide used for meat and fruit covering to increase their shelf life.

16.4.4.4 Fucopol

Enterobacter A47 bacterium produces this polysaccharide which is degradable in nature. It has excellent gas resistance properties and can be used in multilayer packaging film (Quoc et al. 2015; Ferreira et al. 2016).

16.5 Degradation of Biodegradable Polymer-Based Systems

There are several biodegradable polymer degradation mechanisms depending on the processing conditions, for example, PLA and its production and degradation shown in the figure below (Fig. 16.4). PCL degrades in the same way followed by PBAT and PLA, but it has excellent crystalline nature which is responsible for slowly

Fig. 16.4 Life cycle of biodegradable polylactic acid (PLA)

degrading by nature. Study showed that pecan (*Carya illinoinensis*) NSE (nut shell extract) contains antioxidants which causes poor degradation of polylactic acid and polyethylene films over period, when exposed to thermal and oxidative photodegradation, that is, combined action of light and oxygen. Under ultraviolet protection, NSE protects PE and not PLA. This happens due to peroxy radical scavenging effect and inhibition of Norrish-type photolytic breakdown. Scientists studied and reported that PCL has a semicrystalline structure and has hydrophobicity; therefore, it is stable against abiotic hydrolysis while poly-D,L-lactic acid degradation is accelerated as it does not possess crystallinity (Agustin-Salazar et al. 2017).

Nanocomposite formed from polylactic acid is blended with PCA and titanium dioxide. It has concluded that when exposed to degradation with temperature, the rate of degradation is more as many degradation processes like chain cleavage and reformation which are good in the presence of temperature. Blending of PLA and PCL after sometime showed lowered heat stability and TiO_2 nanoparticles improved stability (Mofokeng and Luyt 2015).

When different conditions are provided to decompose PBAT, rates of decomposition of plastic were different in "on the soil" and "immersed in the soil" condition. PBAT requires UV radiation to start the process of degradation. Enzyme-based process of hydrolysis of PBAT is carried by UV radiations or surface phenomenon and not by microorganisms. Many blends are observed over a period of time; it is found that when blends like PBAT with PLA, PBAT with polypropylene carbonate,

Table 16.2 Factors concerned with biodegradation of polymers (Agustin-Salazar et al. 2017; Mofokeng and Luyt 2015; Touchaleaume et al. 2018; Sangroniz et al. 2018; Müller et al. 2012)

Sr. no.	Factors related to degradation	Biodegradation of polymer
1	Agent	Microorganisms
2	Heat requirement	No need of heat treatment
3	Degradation rate	Slower
4	Effect on environment	It is environment friendly
5	Global advantage	Low cost and available everywhere and cheap
6	By-products	Not harmful and toxic

and PBAT with starch are immersed in the soil degradation, they could occur but UV radiations play a vital role in the decomposition of blends in initial steps (Touchaleaume et al. 2018).

When nonbiodegradable agent like phenoxy resins is added to degradable polymer to form complete mixed and partially mixed blends, its degradation rate was analyzed. Then, it is found that PBAT with phenoxy resins take longer time to degrade, like 400 days which are required for hydrolysis of adipate reaction. Adipate degrades in early stages without any blending of nondegradable polymers. Phenoxy resins are used to improve properties like toughness, flexibility, and impact resistance, mostly in other polymers like PU, polyamide, polyester, etc. (Sangroniz et al. 2018).

Biodegradable polymers and their rate of degradation by microorganisms depend on many external conditions which are mentioned in Table 16.2. Rate of degradation of starch-based MaterBi® compostable bioplastic is examined in aquatic conditions along with two other HDPE and polyethylene or polypropylene plastic. Bags made from these three materials are placed in the intestinal tract of sea turtles, in order to check the effect of hydrolytic fluids and enzymes present in the intestines of turtles. Over a period of around 49 days, it was found that there was no loss of mass in standard bags of HDPE and degradable bags produced from polyethylene or polypropylene. As expected, 9% degradation is found in biodegradable starch-based plastic, which is very much less than the rate of degradation in industrial composting (Müller et al. 2012).

16.6 Case Studies on Biodegradable Polymers

A 60-μm-thick flexible film produced from the polyethylene and hydrolyzed collagen, that is, HC content about 10–50%, is used. Ethylene elastomer based on maleic anhydride is used as stabilizer to strengthen the properties of parent polymer. Then, it is found that the mechanical effect and heat stability of the parent polymer are increased by the addition of ethylene elastomer, therefore suggesting that it is suitable for use in packaging and agriculture (Puccini et al. 2015).

A packaging film is produced by blending PBAT with PLA in order to enhance the properties. Epoxy-functionalized chain extender is used mostly in case of PBAT.

Chain extenders are low molecular weight diols or diamines. It is found that under the influence of multifunctional chain extender, molecular weight of PBAT initially increases and then decreases as cross-linking is formed. Rate of degradation is dependent on the amount of the chain extender; upon increasing the amount of chain extender, the rate of decomposition of PBAT increases. SEM analysis showed that chain extenders improved the stability of structure also, which means that overall properties of PBAT like tensile strength and heat stability are enhanced, so it is suitable for shopping bag applications (Li et al. 2018a).

One more experiment was carried out in which films are prepared by blending PLA with PBAT and PLA with PBS. Polypropylene glycol diglycidyl ether is used to increase its plasticity and compatibility. It is found that tensile strength is increased and showed maximum fracture strain up to 150–260% (Mallegni et al. 2018).

Organically modified montmorillonite (OMMT)-embedded nanocomposites are used to overcome disappointing water vapor resistance of PBAT membrane. Water vapor resistance is raised upon addition, and it is directly proportional to OMMT percentage (Li et al. 2018b).

Also, to increase the fracture strain of PLA, palm oil deodorizer distillate (PODD) is used. Overall properties of final blended film are examined, and it is found that fracture strain of film is increased significantly but other properties like toughness and glass transition are not changed (Ruellan et al. 2016).

Blown films from PLA and PBAT are produced by using EF-PLA for modification in the stability and compatibility. Melting point of blend increases due to this modifier to some extent as compared to virgin PLA and PBAT blend (Schneider et al. 2016).

Poly(hydroxybutyrate-co-valerate) (PHBV) has substandard processing behavior while in film blowing process. PBAT is blended with this substandard processable polymer to improve its behavior. After examination, they concluded that the combination of these two polymers greatly extended the bubble stability and processing ability (Cunha et al. 2016).

When hydroxypropyl distarch phosphate (HPDSP) is blended with PHA by film blowing process, the presence of PHA alters properties of HPDSP. As PHA content raised, the crystalline nature of film also enhanced. Also, greatest light transmissivity is achieved along with its tearing strength by using 12% PHA. Apart from these improvements, water vapor permeability, elastic modulus, and heat stability lowered due to higher amount of PHA (Sun et al. 2017).

16.7 Characteristics of Multilayer Biologically Degradable Polymer Film

Blending of starch recovered from sugar palm and PLA is used to produce double-layered film. Solvent casting method is used to produce this bilayered film. After examining overall properties of bilayered film, it is concluded that adherence in

starch and PLA layer was defective and of abysmal quality. Mechanical strength and tear strength of bilayered film were also disappointing (Sanyang et al. 2016).

Two-layered film produced by solvent-based process from PLA and soy protein isolate (SPI) showed great characteristics as adherence in two layers was also fine. Another film produced from chitosan and whey protein had a fine visual appearance and was transparent. Its strength is also enhanced, and water resistance capacity is also great as compared to single layer film. Adherence in two layers is found superior. Electrospinning is a technology used to produce nanomaterials. By using this technique, a multilayered film from zein (in one case, cinnamaldehyde is used but in another case, it is not used) and PHBV is prepared. After this, another layer of PHBV or polysaccharide such as alginate is applied on initially produced two-layered film by using solvent-based method. This three-layered final film is pressed using heat. When this adherence of three layers is viewed under SEM, it is concluded that these three layers are bounded very tightly. But initially two layers were more transparent than three-layered film. This opaque appearance was due to the addition of a third layer and cinnamaldehyde (Cerqueira et al. 2016).

Multilayered film is prepared from five layers of different polymers. Outer two layers are made up of polylactic acid, and the middle layer is made up of graphene oxide (GO). Layer of PVP is sandwiched between PLA and GO. By applying heat, these layers are fixed in a single film. Polyvinylpyrrolidone is used here as binding material. After examining the overall structure and properties of multilayered film, it appears that gas resistance properties of film are enhanced (Lee et al. 2020).

Another two layered film is prepared by applying a layer of PHBV on the primary layer of PBAT. Adherence between two layers was disappointing but mechanical properties were improved significantly. Film under the influence of strain of 10% leads to separation of two layers (Messin et al. 2017).

16.8 Recent Advances in Commercial Bioplastic

Polyhydroxyalkanoate (PHA) receives great interest next to PLA. Market report of 2019 shows that the worldwide production of polyhydroxyalkanoate is about 25,320 tons, which is 1.2%, while worldwide manufacture of PBAT is 13.4% and manufacture of PBS is 4.3% (European Bioplastics n.d.).

When PLA is blended with PCL, it possessed the same properties as standard hydrocarbon plastic. Another main advantage of this blend is that it can be degraded naturally by microorganisms in household composting or domestic conditions of composting (Narancic et al. 2018).

Biodegradability and functionality of PEF film can be obtained by blending this polymer with another degradable polymer. Polyhydroxyalkanoate or polylactic acid is used in order to enhance properties. Therefore biodegradable packaging with excellent properties can be used for coating and food packing purposes (Wu et al. 2015).

16.9 Reinforcement of Nanocellulose in a Polymer Matrix

Cellulose nanocrystals (CNCs) are reinforced into polymer matrix to form nanocomposites (as shown in Fig. 16.5). Greenhouse coating is made by forming nanocomposite from polyethylene and CNCs, zinc oxide, and silicon dioxide. This nanocomposite forms blocks and absorbs harmful UV rays (Xie et al. 2018).

When CNFs (cellulose nanofibers) were reinforced in PLA polymer matrix, their mechanical properties and tensile strength increased to greater extent than virgin PLA film. Also, morphological characteristics, water vapor, and oxygen permeability improved (Kumar et al. 2019).

Also, film can be obtained from tartaric acid, and nanofibrillated cellulose are embedded in natural PU or PUR to improve its tensile strength (Hormaiztegui et al. 2019).

To enhance the water resistance property, nanocellulose is reinforced into cellulose matrix, and periodic oxidation is used as a treatment of nanocellulose and further reinforced into polyvinyl alcohol (PVA) matrix (Lee et al. 2020).

Composite semi-IPN (interpenetrating polymer network) films are prepared by reinforcing nanocellulose up to 5% by wt into PVA and polyacrylamide matrix. Mechanical properties and structural properties are enhanced as compared to virgin PVA and polyacrylamide (Zhong et al. 2020).

Nanofibrils are obtained from leaf fibers of pineapple reinforced into degradable polyurethane to form nanocomposites for medical application. Film stacking technique is used to prepare these nanocomposite films obtained by placing film of

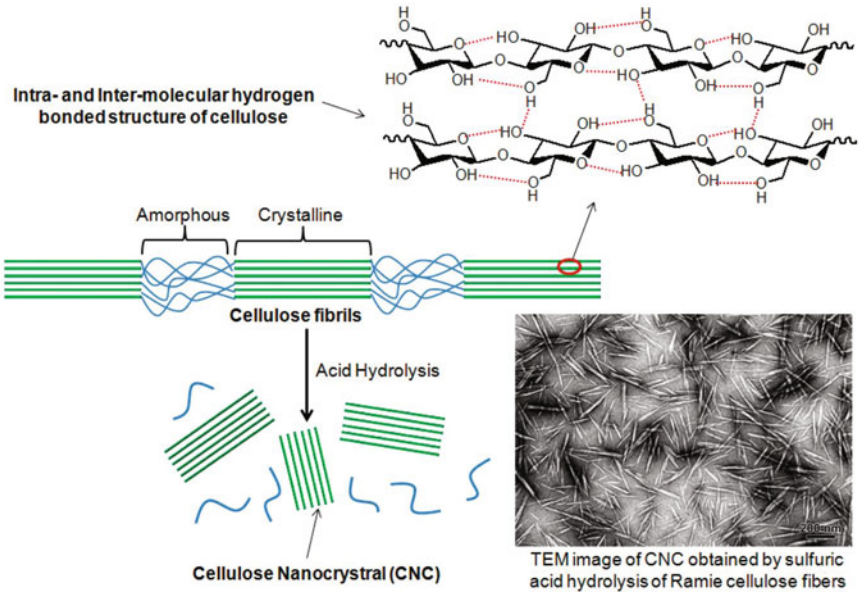


Fig. 16.5 Nanocellulose composites with polymers

polyurethane and nano-sized fibers. These composites are formed by compressing (Cherian et al. 2011).

When nanocomposite starch film is prepared from bacteriocin-immobilized CNCs, it showed biodegradable behavior upon testing (Bagde and Nadanathangam 2019).

16.10 Future Concerns

Multifunctional food packaging film is made via embedding nano-TiO_2 into polysaccharide like chitosan. Black plum peel extract (BPPE) which is rich in anthocyanin phytonutrients is added in chitosan. Physical and mechanical properties of chitosan greatly improved by addition of TiO_2 and black plum peel extract. TiO_2 addition leads to increment in structural and physical properties. Ultraviolet-visible light is blocked and gas barriers like water vapor permeability are also enhanced by TiO_2 and BPPE. Intermolecular interaction among chitosan, glycerol, TiO_2, and BPPE causes a great strengthening effect. SEM (scanning electron microscopy), FT-IR (Fourier transform infrared spectroscopy), and XRD (X-ray diffraction) analytical techniques confirmed the improvement of the structure and intermolecular bonding.

BPPE contains an abundant quantity of anthocyanin phytonutrients. Anthocyanin is a good antioxidant and prevents the oxidation of food products when applied as film or coating. Anthocyanin is also effective against microorganisms and can change color with change in pH of the environment due to the great number of phenols. Incorporation of TiO_2 acts as an ethylene scavenger and helps to maintain the quality of food products. Therefore, CS-TiO_2-BPPL membranes can be applied as multifunctional packing on food in the future (Zhang et al. 2019).

Active packaging film can be produced by adding plant extracts from plant sources to biodegradable polymers. Incorporation of plant extracts can enhance mechanical, physical, and structural properties to some extent. Antimicrobial and antioxidant properties can be enhanced by incorporating plant extract, and deterioration of food quality can be prevented or reduced. Apart from great results reported in chapter, further studies are needed to increase the functional properties; therefore, in the future, it can be used in food packaging application worldwide. Also, more research are needed on stability and compatibility of film with food products by considering color and transparency of film. Growth of microorganisms and reservation of flavor which leads to the quality of food should be taken into consideration before practicing on biodegradable film. Furthermore, there are tremendous natural plant extracts available with bioactive properties to be used in food packaging to preserve and add value to foods (Mira et al. 2018).

In order to improve optical, morphological, photocatalytic, and antimicrobial properties of three different TiO_2 nanoparticles (NPs), incorporated biodegradable polymer films were produced. However, less compatibility is present between TiO_2 NPs and PCL polymer; scanning electron microscopy images of this film showed good uniformity for TiO_2-embedded cellulose acetate and PLA films. TiO_2

nanoparticles embedded in film produced show great transparency, good photocatalytic activity, and antimicrobial properties. But future study is needed to check the compatibility of this film with food, so that it can be used as antimicrobial food packaging (Xie and Hung 2018).

16.11 Potential Problems

First, the weight capacity property of biodegradable packaging is a major problem as compared to conventional synthetic packaging. Biodegradable polymers are mostly organic compounds as they are produced from plant materials and may contain pesticide residues and chemicals which can directly enter into finished products when applied to food products. They have a low biodegradation rate compared to traditional deposition because biodegradation takes much time. PHA has a biodegradation period of 3–6 months. Also, the cost of these biodegradable polymers is high enough than conventional packaging materials as production technology is still immature and cost of resources like labor and raw material is also high (Bagde and Nadanathangam 2019; Galgano 2015).

16.12 Conclusion

Nowadays, various biodegradable polymers with different amazing properties are present for application in different areas. Previously discussed biodegradable polymers can be used in food packaging, agriculture, and automotive and medicine industries. Biodegradable plastics can be degraded by many ways like home composting, industrial composting, chemical/catalytic recycling, enzymatic biodegradation, and anaerobic degradation. Nanoparticles or fibers are embedded into another polymer matrix to strengthen the overall property of film. Multilayer film packaging and other several strategies are there to enhance the quality of biodegradable polymers. Currently, there is a great demand for plant extract-based bioactive biodegradable films. As plants contain many important phytonutrients which have antibacterial and functional properties, therefore, it is gaining attraction.

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