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Emerging Trends in Biopolymers for Food Packaging

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1.1 Introduction to Polymers in Packaging

According to the Food and Agriculture Organization of the United Nations (FAO), approximately one-third of all food produced globally is lost or wasted [1]. Food waste is produced throughout the whole food value chain, from the household to manufacturing, distribution, retail, and food service activities. Taking into consideration the limited natural resources available, it is more effective to reduce food waste than to increase food production. For this reason, several efforts have been put for the development of more effective food packaging strategies [2, 3]. Packaging items have become essential to protect food from different environmental conditions. Depending on the type of food, the packaging article can be customized to prevent or inhibit microbial growth, avoid food decomposition by removing the entrance of light, oxygen, and moisture, or even to prevent spoilage from small insects. Additionally, novel packaging items can be monitored to give information about the quality of the packaged food, ultimately diminishing food waste during distribution and transport [4].

Common materials utilized for food packaging include glass, paper, metal, and plastic. The latter are nowadays more frequently used since they have a large availability at a relatively low cost and can display good characteristics for packaging items, such as mechanical strength, barrier properties, and transparency [4, 5]. The most commonly used petrochemical materials for packaging applications can be divided into various families:

- Polyolefins and substitutes of olefins, such as low-density polyethylene (LDPE) and linear low-density polyethylene (LLDPE), polypropylene (PP), polystyrene (PS), oriented polystyrene (OPS), polyvinyl alcohol (PVOH), polyvinyl chloride (PVC), and polyvinylidene chloride (PVDC). Polyolefins are frequently used in reusable bags, paper cups, and stand-up pouches, while substitutes of olefins such as PVC are popularly used in cling films and in some prepackaged meals.

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- Copolymers of ethylene, such as ethylene-vinyl acetate (EVA) and ethylene-vinyl alcohol (EVOH), are typically used to make lid films for trays and barrier interlayers.
- Polyesters, such as polyethylene terephthalate (PET) and other aliphatic and aromatic polyesters, are mainly used to make water bottles.
- Polyamides (PAs) are commonly employed in films or trays for food products that are very sensitive to oxygen.

Most of these materials are made by condensation or addition polymerization of monomers of hydrocarbon or hydrocarbon-like raw materials, which means that due to their fossil-based nature and high chemical stability, they are not biodegradable and will accumulate in landfills over the years, causing a negative impact on the environment. Although several recycling strategies are currently being carried out, packaging materials are often contaminated with leftover food, making recycling economically inconvenient and thus unviable. In 2010, primary plastic production was 270 million tons, yet plastic waste was 275 million tons since plastics produced in previous years entered the waste stream, where the sector of packaging was the highest producer of plastics, that is, 146 million in 2015. This has led to an increase in the number of campaigns requesting the removal of single-use plastics, with the European parliament aiming to ban single-use plastic cutlery, cotton buds, straws, and stirrers by 2021. Such environmental awareness and implementation of stringent environmental regulations are leading to research for alternatives to food packaging materials and, thus, efforts are being directed, at both academic and industrial levels, at the use of bioplastics in a variety of consumer products.

1.2 Classification of Biopolymers

The above-described environmental issues, together with the scarcity of oil sources, are the main drivers behind the interest for the development of new materials for food packaging applications. Although bioplastics only account for 1% of the approximately 350 million tons of plastics produced annually, being mostly applied as packaging materials [6, 7], including high-performance thermoplastic materials and foams, they represent an important part of the Bioeconomy and will undoubtedly shape the future of the plastic industry [8]. As a result, the use of biopolymers in packaging has increased considerably over the past few years due to their sustainable feedstock, biodegradability, and similar processing characteristics as existing thermoplastics [9].

Biopolymers comprise of a whole family of materials with different properties and applications. They include polymers with a “bio-based” origin and “biodegradable” polymers or polymers featuring both properties. Bio-based polymers refer to any kind of polymer that is produced from renewable resources, which include both naturally occurring polymers and synthetic polymers produced by means of monomers obtained from biological sources [10]. Naturally occurring polymers are biomacromolecules, that is, molecules of large molecular weights (M_W) produced in nature by living organisms and

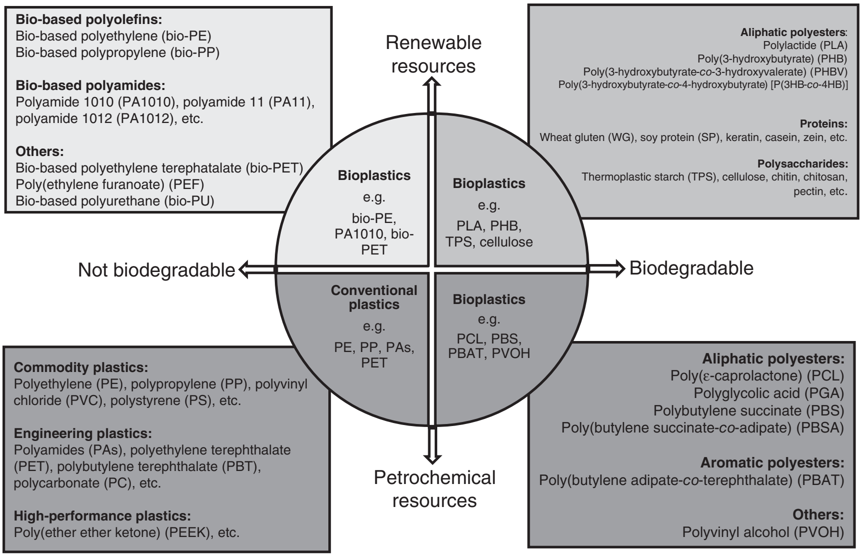

Figure 1.1 Classification of biopolymers widely used in packaging.

plants. Biodegradable polymers are defined as those polymer materials whose physical and chemical properties undergo deterioration and completely degrade, when exposed to the enzymatic action of microorganisms, to carbon dioxide (aerobic process), methane (anaerobic process), water (aerobic and anaerobic processes), inorganic compounds, and biomass [11]. Bio-based polymers can be biodegradable but not all biodegradable polymers are bio-based. Additionally, some synthetic biodegradable polymers could be in a near future partially or fully developed from bio-based monomers. Bio-based polymers offer the advantage of conservation of fossil resources by using biomass that regenerates (annually) and the unique potential of carbon neutrality whereas biodegradability is an add-on property of certain types of polymers that offers additional means of recovery at the end of a product's life [12, 13].

Figure 1.1 summarizes the classification of biopolymers grouped according to their origin and biodegradability characteristics. On the top right of the figure, bio-based and biodegradable polymers are gathered. Nature produces over 170 billion metric tons per year of biomass, yet only 3–4% of this material is being used by humans for food and nonfood purposes [14]. Biomass derived carbohydrates are the most abundant renewable resources available, representing approximately 75% of this biomass, which are currently regarded as the basis for the green chemistry of the future. Most of these biopolymers are mainly made from carbohydrate-rich plants such as corn or sugarcane, that is, the so-called food crops, which are also currently referred to as the "first generation feedstock" of bioplastics. This currently represents the most efficient feedstock for the production of bioplastics, as it requires the least amount of land to grow and produce the highest yields. Biomass derived polyesters such as polylactide (PLA) and thermoplastic starch (TPS) are among the most promising biodegradable polymers and they contribute to up to 65% of the family of this type of biopolymers.

The same durability properties that have made traditional petroleum derived plastics ideal for many applications, such as those found in packaging, are leading to terrible waste-disposal problems as these materials are resistant to microbial degradation and plastics accumulate in the environment. For this reason, some biodegradable polymers, yet based on petrochemical polymers, have been developed in the last few years. The most frequently studied polymers are included in the bottom-right group, which are aliphatic or aliphatic–aromatic polyesters since neat aromatic polyesters based on terephthalic acid are generally insensitive to hydrolytic degradation and to enzymatic or microbial attack due to their high stability. Indeed, the biodegradation rate increases rapidly when the concentration of terephthalic acid becomes lower than 55 mol%. These petrochemical biodegradable polymers can find several uses in both flexible and rigid packaging applications.

Bio-based but not biodegradable polymers, which are shown at the top-left of the figure, currently offer important contributions by reducing the dependence on fossil fuels and through the related positive environmental impact, that is, reduced carbon dioxide emissions. New approaches go toward the complete or partial substitution of conventional plastics by renewable resources such as biomass [15]. Conventional polymers from feedstock routes are being explored for well-known applications, including the packaging industry [16]. These are generally based on monomers derived from agricultural and food-based resources such as corn, potatoes, and other carbohydrate feedstock. The new branch of these “green polymers” reflects the “biorefinery” concept [17]. The monomers to produce these bio-based polymers can be obtained from natural resources, for example catalytic dehydration of bioethanol obtained by microbial fermentation. Although these biopolymers are not biodegradable, they have the same processing and performance as conventional polymers made from natural gas or oil feedstocks. Such developments have recently led to the new paradigm for sustainable food packaging: “Bio-based but not biodegradable” [18]. This is further evidenced by the recent development of fully bio-based polyethylene terephthalate (bio-PET), where the ethylene glycol and the terephthalic acid are both derived from plant-based sugars and agricultural residues.

The discussion about the use of biomass for industrial purposes is still often linked to the question about whether the conversion of potential food and feed into materials is ethically justifiable. Although the surface required to grow sufficient feedstock for current bioplastics production is only about 0.01% of the global agricultural area of a total of 5 billion hectares (bioplastics), the bioplastics industry is also researching the use of nonfood crops and agricultural residues, the so-called “second generation feedstock,” with a view to its further use. Innovative technologies are focusing on nonedible by-products as the source for bioplastics, which includes large amounts of cellulosic by-products and wastes such as straw, corn stover, or bagasse. This leaves significant potential for using biotechnological processes to create platform chemicals for industrial purposes, among them the production of bioplastics. Therefore, the trend for the development of next generation of bioplastics is currently led by the emergence of conventional polymers made from renewable and nonfood sources.

1.3 Food Packaging Materials Based on Biopolymers

The development of different kinds of packaging materials from biopolymers has seen an increase in the last few years [19]. The use of biopolymers in food packaging can provide physical protection during storage and transportation, and create proper physicochemical conditions for maintaining quality and safety and for extending the shelf life of food [20]. All subsections in Section 1.3 summarize the most important trends in biopolymers for food packaging applications.

1.3.1 Polylactide

The commercialization of PLA began in 1990 though it was known since 1845. PLA is mostly obtained from bacterial fermentation of carbohydrates that can come from renewable resources such as corn or sugar. Fermentation turns the sugar into lactic acid, which is the building block for PLA, but most industrial applications make use of its dimer lactide. NatureWorks LLC (previously Cargill Dow LLC) and, more recently, Corbion (former Purac Bioplastics) are the major suppliers of PLA with a production capacity of over 100 ktons per year, in which this biopolymer is produced in a continuous efficient synthetic process via ring-opening polymerization (ROP) of the lactide dimer [21]. There are two optical forms: L-lactide, the natural isomer, and D-lactide, the synthetic one [22]. The production of the different isomers depends on the microbial strain used during the fermentation process. The polymer crystallinity and the properties of PLA can significantly vary depending on the ratio and stereochemical nature of the monomer [23].

Nowadays, PLA is one of the most researched and commercialized biopolymers and it is seen as a potential substitute for conventional polymers as packaging materials since it is bio-based and compostable [24]. It has similar properties to traditional polymers such as PET, PS, and polycarbonate (PC) [25]. The most relevant characteristics of this biopolymer are high rigidity, good transparency, heat sealability, printability, and melt processability. Also, it can be processed on large-scale production lines such as injection molding, blow molding, thermoforming, and extrusion [26]. It is classified as generally recognized as safe (GRAS) by the United States Food and Drug Administration (FDA) and is safe for all food packaging applications [27]. However, it also has limiting properties for its use in packaging applications. For example, its low glass transition temperature (T_g) limits its utilization above 55 °C and it also shows low toughness and ductility [28]. Nevertheless, these narrow circumstances can be improved by varying the ratio of L/D isomers, modifying its stereochemistry, or mixing with other polymers and fillers to improve the mechanical and thermomechanical properties [29].

In the field of food packaging, PLA is ideal for fresh products and those that do not require protection against oxygen, but also it can be used in food trays, bottles, candy wraps, and cups [30]. Accordingly, its high permeation to water makes it suitable for some packaging applications such as extension of the life period of fresh fruit and bread. Some coatings are used as a kind of barrier layer

(a) (b)

Figure 1.2 Commercial food packaging articles made of polylactide (PLA): (a) Coffee capsules. (b) Yogurt cups. Source: Courtesy of Danone (Paris, France).

to reduce permeability of this biopolymer [31, 32]. Figure 1.2 shows some commercial packaging articles made of PLA to contain food products.

1.3.2 Polyhydroxyalkanoates

Polyhydroxyalkanoates (PHAs) currently represent one of the most important alternatives to fossil derived polymers in the frame of the Circular Economy [33], showing the highest potential to replace polyolefins in packaging applications due to their biocompatibility and physical properties [34]. PHAs are a family of biopolyesters synthesized by a wide range of microorganisms as carbon storage material. Although they have suitable characteristics such as biodegradability, thermoplasticity, and similar mechanical strength and water resistance to other polymers such as PP and PS [35], their production is expensive due to the high costs of the fermentation and downstream processes. The use of industrial by-products and waste or mixed microbial cultures (MMCs) represents a viable option to reduce the production costs of PHAs [36].

Among PHAs, the most widely studied and first bacterial member of this family identified was poly(3-hydroxybutyrate) (PHB). This isotactic homopolyester is biodegradable not only in composting conditions but also in other environments such as marine water and it presents similar thermal and mechanical properties with some petrochemical polymers. However, its use is limited due to its poor impact-strength resistance and a narrow processing temperature window [37]. To improve these shortcomings, its copolymers such as poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate) (PHBV) and poly(3-hydroxybutyrate-*co*-4-hydroxybutyrate) [P(3HB-*co*-4HB)] have been explored. Particularly, PHBV is a good candidate since it has a much lower crystallinity and melting temperature, decreased stiffness and brittleness, and

Figure 1.3 Biodegradable food tray made of poly(3-hydroxybutyrate) (PHB) obtained by injection molding.

higher ductility. The T_g of these PHA copolymers varies from −40 to 5 °C, and the melting temperature (T_m) also range from 50 to 180 °C, depending on their chemical composition [38].

Biomer (Krailling, Germany) and Tianan Biologic Materials (Ningbo, China) are the main producers of microbial PHB and PHBV, respectively. PHAs can be processed by common methods such as extrusion, injection molding, thermoforming, film blowing, and so on [39]. These materials are suitable for very different areas of food and cosmetic packaging, for instance blow-molded bottles, milk cartons, cosmetic containers, feminine hygiene products, adhesives, paper coatings, waxes, paints, and so on [40]. Figure 1.3 depicts, as an example, a tray made of PHA. Moreover, the use of nanofillers or active substances, such as antimicrobial and/or antioxidant substances, incorporated into a PHA-based packaging material can change the packed food condition extending the shelf life and improving the protection and/or sensory properties, adding an extra value to the final product [41, 42].

1.3.3 Poly(butylene adipate-*co*-terephthalate)

Poly(butylene adipate-*co*-terephtalate) (PBAT) is a biodegradable aliphatic–aromatic copolymer, synthetized by the reactions of the monomer 1,4-butanediol, adipic acid, and terephthalic acid. It is biocompatible and biodegradable, being degraded in a few weeks by lipases from *Pseudomonas cepacia* and *Candida cylindracea* [43]. Also, it is highly amorphous, it has high ductility and thermomechanical properties comparable with LDPE, and is compostable [44, 45]. Despite these suitable characteristics, PBAT shows a high permeability to water, that is, a poor water barrier property, and fails to achieve the mechanical strength required for some applications [46]. Different approaches have been considered to overcome these disadvantages, such as surface modifications, use of polymer blends, and reinforcement by fillers [47]. For instance, blends of PBAT with PLA can result in a biodegradable article with balanced mechanical properties, though the use of a chain extender or a cross-linking agent to enhance the interfacial adhesion is usually necessary [48]. Also, the use of nanocomposites based on PBAT and layered silicates have yielded materials with improved mechanical properties [49].

PBAT films can be prepared using cast film extrusion, blown film extrusion, thermo-compression, and solvent casting methods [50] and they can be used for agriculture, food packaging, waste and compost bags, among others [51]. PBAT is sold commercially by the trade names of Ecoflex® by BASF (Ludwigshafen, Germany), Easter Bio® from Eastman Chemical (Kingsport, USA), and Origo-Bi® from Novamont (Novara, Italy). It is allowed for food packaging applications by the FDA [52, 53] and the incorporation of antimicrobial substances for active food packaging has recently shown very promising results to enhance food safety [54].

1.3.4 Polybutylene Succinate

Polybutylene succinate (PBS) is a biodegradable and compostable aliphatic polyester produced by polycondensation of succinic acid and 1,4-butanediol. PBS was exclusively derived from petroleum-based monomers, but since more recently the monomers can also be obtained by the bacterial fermentation route to produce fully bio-based polybutylene succinate (bio-PBS) [29, 55]. So far succinic acid has been mainly produced by electrochemical synthesis due to the high yield, low cost, high purity of the final product, and very low or no waste formation [56]. However, the production of succinic acid by bacterial fermentation uses renewable resources and consumes less energy compared to chemical process. For this reason, companies such as Corbion (Geleen, the Netherlands) and BASF are working on the scaling up of an economically feasible bio-based succinate production process, despite the fact that these processes have traditionally suffered from poor productivity and high downstream processing costs. Other examples are the development of a biomass-derived succinic acid production by Mitsubishi Chemical (Tokyo, Japan) in collaboration with Ajinomoto (Tokyo, Japan) to commercialize bio-PBS or the development of a commercially feasible fermentation process for the production of succinic acid, 1,4-butanediol, and the subsequent production of PBS by DSM (Heerlen, the Netherlands) and Roquette (Lestrem, France). Myriant (Quincy, USA) and Bioamber (Plymouth, USA) have also developed a fermentation technology to produce the monomers [57, 58]. Thus, in 2015, the annual production capacity of bio-based succinic acid reached 200 000 tons [59]. In the case of 1,4-butanediol, conventional production processes use fossil fuel feedstocks, such as acetylene and formaldehyde. Nevertheless, the bio-based process to obtain the diol involves the use of glucose from renewable resources to produce succinic acid followed by a chemical reduction to produce butanediol [29]. PBS with excellent mechanical properties and processing capabilities can be then produced from the renewable monomers by transesterification, direct polymerization, and condensation polymerization reactions followed by chain extension and lipase-catalyzed synthesis.

PBS is a semicrystalline aliphatic polyester with a good melt processability and balanced mechanical properties, closely comparable to those of PP. It is tougher than PLA and it shows similar thermal behavior than LDPE and a melting point lower than that of PLA [29, 60]. Its thermal and mechanical properties highly depend on the crystal structure and the degree of crystallinity [61]. The T_g and T_m are approximately −32 and 115 °C, respectively. In terms of mechanical properties, PBS has a good tensile and impact strength with moderate rigidity and hardness [29]. PBS has a wide processing window, which makes the resin suitable for extrusion, injection molding, thermoforming, fiber spinning, and film blowing. PBS has been employed as film, in foaming, and in food packaging containers [60]. However, the relatively poor mechanical flexibility of PBS limits the applications of 100% PBS-based products. This issue can be overcome by blending PBS with other biopolymers and fillers to improve the mechanical properties to suit the required application and biodegradation rate [62–65]. The development of PBS copolymers can also lead to biopolymers with a decreased degree of crystallinity, depressed heat distortion temperature, and improved elongation [56, 66]. Copolymerization is achieved by adding a third monomer such as sebacic acid, adipic acid, terephthalic acid, succinic acid with substituted side groups, 1,3-propanediol, and other substituted glycols, which can be also produced from renewable resources. Poly(butylene succinate-*co*-terephthalate) (PBST) and poly(butylene succinate-*co*-adipate) (PBSA) are the most employed copolymers, PBSA being the most common for flexible packaging applications. Additionally, the flexibility of the PBS backbone and the presence of readily hydrolyzable ester bonds, which are prone to catalytic degradation by microorganisms or enzymes, promote rapid degradation process of the PBS copolyesters [67]. Some studies have evaluated the biodegradability of biodegradable polymers in the mature compost soil and found that the biodegradability of PBS was slower than that of PBSA in compost soil [68]. However, the results of enzymatic hydrolysis as well as environmental degradation of PBS are highly dependent on the environment, the composition of the PBS grade, and its compound [55].

1.3.5 Bio-based Polyethylene

Bio-based polyethylene (bio-PE), also called “microbial” or “green” polyethylene, can be produced by the catalytic dehydration of bioethanol obtained by microbial fermentation, followed by normal polymerization to produce polyethylene (PE) [69, 70]. Bio-PE is not biodegradable and has the same properties as PE made from natural gas or oil feedstocks [29]. Conventional PE is manufactured by polymerization of ethylene under pressure, temperature, in the presence of a catalyst. Traditionally, ethylene is produced through steam cracking of naphtha or heavy oils or ethanol dehydration. However, the concept of producing PE from bioethanol is not particularly new. In the 1980s, Braskem (São Paulo, Brazil) had already made bio-PE from bioethanol, however, the limitations of the biotechnology processes made the technology unattractive at that time [71]. Currently, bio-PE produced on an industrial scale from bioethanol is derived from renewable feedstocks, including sugarcane and beet, starch crops such as maize, wood, wheat, corn, and other plant wastes through microbial strain and biological fermentation process. In a typical process, extracted sugarcane juice with high sucrose content is anaerobically fermented to produce ethanol. At the end of the fermentation process, ethanol is distilled in order to remove water

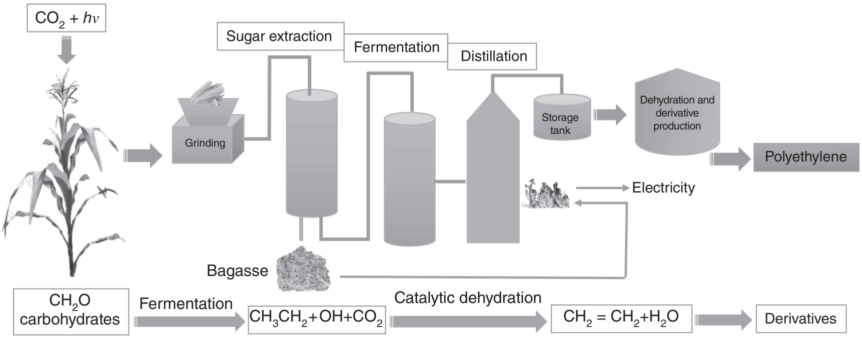

Figure 1.4 Schematic flow diagram of the production of bio-based polyethylene (bio-PE) from sugarcane via fermentation into ethanol and subsequent dehydration into ethylene. Source: From Koopmans [73]. © 2013, John Wiley & Sons.

and to yield an azeotropic mixture of hydrous ethanol. Ethanol is then dehydrated at high temperatures over a solid catalyst to produce ethylene and, subsequently, bio-PE [69, 72]. Figure 1.4 shows a schematic flow diagram of the bio-PE production.

Braskem is the largest producer of bio-PE, mainly bio-based high-density polyethylene (bio-HDPE), with 52% market share, with an annual production capacity of 200 000 tons per year made from ethanol obtained from sugarcane [71] and this is the first certified bio-PE in the world. Similarly, Braskem is developing other bio-based polymers such as bio-based polyvinyl chloride (bio-PVP), bio-based polypropylene (bio-PP), and their copolymers with similar industrial technologies. Braskem's current bio-based PE grades are mainly targeted toward food packaging, cosmetics, personal care, automotive parts, and toys. Dow Chemical (Midland, USA) in cooperation with Crystalsev (São Paulo, Brazil) is the second largest producer of bio-PE, having 12% market share. Solvay (Brussels, Belgium), another producer of bio-PE, has 10% share in the current market. However, Solvay is a leader in the production of bio-PVC with similar industrial technologies. China Petrochemical Corporation (Pekin, China) also plans to set up production facilities in China to produce bio-PE from bioethanol [74]. LyondellBasell (Rotterdam, The Netherlands) and Neste (Espoo, Finland) have recently announced the first parallel production of bio-PP and bio-based low-density polyethylene (bio-LDPE) at a commercial scale, being marketed under the trade names Circulen and Circulen Plus [75].

Bio-PE can replace all the packaging applications of current fossil derived PE because of its low price, good lifetime performance, and especially recyclability [75]. The price of bio-PE is currently about 50% higher as compared with petrochemical PE, but it will take advantage from the scale-economy. Current upcoming applications by multinationals include yogurt cups produced by Danone (Paris, France), fruit juice bottles by Odwalla (Atlanta, USA), and plastic caps and closures for aseptic paperboard cartons by Tetra Pak (Lund, Sweden) [76].

1.3.6 Bio-based Polyethylene Terephthalate

PET is a copolymer of monoethylene glycol (MEG) and terephthalic acid, and one of the most studied polymers to be transformed in commercial bio-based plastics, which can be derived from plant-based sugars and agricultural residues. This interest gave life to a technological collaboration between several companies, such as Coca-Cola (Atlanta, USA), Ford (Detroit, USA), Heinz (Sharpsburg, USA), Nike (Eugene, USA), Danone and Procter & Gamble (Cincinnati, USA), Avantium (Geleen, the Netherlands), and Micromidas (San Jose, CA), to develop commercial processes for the production of bio-PET. The source of petrochemical terephthalic acid is primarily from the oxidation of *p*-xylene, obtained from the catalytic reforming of naphtha. More than 98% of the *p*-xylene produced globally is converted to terephthalic acid and the global demand for purified terephthalic acid is expected to exceed 60 million tons by 2020, being most of it used for PET production. As a result of this cost-competitive demand, bio-based terephthalic acid made at equal purity and cost as the petroleum derived terephthalic acid would have a clear market advantage as well as a lower price volatility due to the non-dependence on petrochemical *p*-xylene [77]. However, bio-PET is currently produced from plant-based monoethylene glycol (bio-MEG) whereas terephthalic acid is still derived from petroleum. Toyota Tsusho (Nagoya, Japan) and China Manmade Fibers Corporation (Taipei, China) jointly founded a company in November 2010 that manufactures bio-MEG made from plant derived bioethanol [78]. Other companies such as SCG Chemicals (Bangkok, Thailand) also produce bio-MEG from residues of agricultural activities including molasses, hay, and bagasse [79]. The first partially bio-PET product was commercialized by The Coca-Cola Company (Atlanta, USA) under the trade name of PlantBottle™, where a 30 wt% of bio-MEG was used for the production of bio-PET (Company). At the moment, some researchers are working on the synthesis of bio-based terephthalic acid to obtain fully bio-PET. This process is based on an integrated method to convert forest residues to isobutanol [80], which can be processed into *p*-xylene [81], the precursor of terephthalic acid. Although the 100% bio-based bottle was released in Milan in June 2015, the so-called PlantBottle™, shown in Figure 1.5, has not reached yet the price parity to equal the price of producing current Coca-Cola PET bottles [82]. PepsiCo (New York, USA) also announced the use of a PET bottle made entirely with renewable resources coming from waste carbohydrate biomass obtained from the food industry such as orange peels, oat hulls, corn husks, and potato scraps [83].

Similar to bio-PE, bio-PET is not biodegradable but it has the same properties as conventional PET made from natural gas or oil feedstocks. Current partially bio-PET is used to make a number of products including drinking water and soda bottles, making them environmentally friendly and a new packaging alternative. Products made from bio-PET have the same qualities as regular PET in its distinctive functions, weight, appearance, and it can also be recycled and reused [79]. This material can be recycled, incinerated, or landfilled, but it can also be intended for disposal by composting, where it undergoes soil degradation to CO_2 and water [9]. Enzymatic hydrolysis of aromatic/aliphatic polyesters was first demonstrated in the 1990s for PET with several esterases, lipases, and especially

Figure 1.5 Image of the PlantBottle™ made up to 30% from biomass and 100% recyclable. Source: Courtesy of the Coca-Cola Company (Atlanta, USA).

cutinases [84, 85]. Nevertheless, PET hydrolysis by enzymes is a relatively slow process, since the biocatalysts are specialized to attack natural polyesters such as cutin and were not designed by nature for degrading manmade synthetic polyesters in the first instance [85].

1.3.7 Poly(ethylene furanoate)

A potential green substitute for terephthalic acid is 2,5-furandicarboxylic acid (FDCA), which is a bio-based building block that can be polymerized with bio-MEG to form a new 100% bio-based polyester called poly(ethylene furanoate) (PEF) [85]. PEF can be synthesized by polycondensation, ROP, and solid-state polymerization. Polycondensation is the most commercially relevant method but it results in long exposure times to high processing temperatures, around 200 °C, which increases the production cost and, even more importantly, leads to thermal degradation and discoloration of the biopolymer. Solid-state polymerization (SSP) is a milder process, though a bottle-grade PEF has not been achieved yet [86]. SSP involves heating of the starting partially crystalline polyester at a temperature between its T_g and T_m, which is used mainly for PET manufacturing to get over its relatively low M_W [87]. The company Avantium is developing PEF using bio-MEG and FDCA coming from the dehydration of carbohydrates [77]. In 2016, it was announced a new technology involving a highly efficient separation technology and catalyst that would result in economically feasible production of FDCA starting from 2016. The planned industrial production capacity is estimated to exceed 300 000 tons per year while the company has established collaborations with major endusers from the food and beverage industry [84].

PEF shows excellent thermal properties and lower T_m values than PET because of which it can be processed at lower temperatures. It has the ability to withstand high temperature due to its higher T_g as well as thermal stability up to 320 °C. PEF outperforms the barrier properties of PET. Specifically, PEF's O_2 barrier is more than ten times higher than that of PET, the CO_2 barrier is four times higher, and the water vapor barrier is two times higher [88]. Other attractive properties of PEF include excellent mechanical strength, reduced carbon footprint, and ability to formulate in films, fibers, and almost replace PET in water bottles [87]. PEF can be recycled in very similar ways to PET [88]. Recently, the enzymatic synthesis of FDCA-based polyesters was studied by the groups of Loos and Boeriu with *Candida antarctica* lipase B [89, 90]. However, apart from numerous reports around the emerging topic of PEF production and application, there is no information on enzymatic hydrolysis of PEF. Nevertheless, especially for bio-based PEF, biotechnological processing for functionalization and chemical recycling of monomers could have a large potential to replace harsh chemicals [84].

1.3.8 Poly(ε-caprolactone)

Poly(ε-caprolactone) (PCL) is a biodegradable aliphatic polyester derived from the chemical synthesis of crude petroleum [91]. It is obtained from ROP of ε-caprolactone in presence of metal alkoxides and also through the polycondensation of 6-hydroxyhexanoic acid. PCL is commercially available under the trade names CAPA (Solvay, Belgium), Tone (Union Carbide, USA), Celgreen (Daicel, Japan), and many others [92].

Some features of PCL include biodegradability, good solubility, flexibility, low T_m (approximately 60 °C) and a T_g of around −60 °C, and easy processing. PCL is used in flexible packaging materials in the form of films or coatings for extending the shelf life of food products. However, due to its high price and long biodegradability cycles, PCL is commonly blended with other biopolymers, such as chitosan and starch [93]. Among them, starch has been proposed as a reinforcing agent to improve the mechanical strength of PCL [94]. There are also several studies on the hydrolysis and biodegradability of PCL. The degradation process of PCL takes place through hydrolysis, thereby leading to molecular fragmentation or chain scission [94]. Moreover, enzymes and fungi easily biodegrade PCL. However, to improve the degradation rate, several copolymers with lactide or glycoside have been developed [94].

1.3.9 Thermoplastic Starch

Starch is a natural polysaccharide that can be obtained from a great variety of crops such as cassava and corn. It is considered as one of the most promising biopolymers for food packaging due to its availability, biodegradability, and low price [95]. Starch is composed of a mixture of two polymers, namely amylose and amylopectin. Amylose is a linear polysaccharide composed entirely of D-glucose units joined by α-1,4-glycosidic linkages. Amylopectin is a branched-chain polysaccharide composed of glucose units linked primarily by α-1,4-glycosidic bonds but with occasional α-1,6-glycosidic bonds, which are responsible for the branching. Relative percentages of amylose and amylopectin in starch are in the range 10–30% amylose and 70–90% amylopectin. The starch having a crystallinity between 20% and 40% is termed as semicrystalline in which the amorphous region of starch contains amylose and the branching points of amylopectin [96]. Native dry starch has a limited range of applications because of its high brittleness, high viscosity, retrogradation, insolubility in cold water, and poor melt processability because its T_g is probably above the decomposition point so it does not soften and flow [97]. BIOTEC® (Emmerich, Germany) has three product lines of TPS that include Bioplast® granules for injection molding, Bioflex® for film applications, and Biopur® as foamed starch [98]. In any case, films developed from native starch typically show moderate oxygen barrier properties but poor moisture barrier and mechanical properties, which limit their applications in food packaging [99].

Fortunately, starch can be modified by processing with plasticizers, grafting with vinyl monomers, and blending with other polymers. Plasticizers increase both the flexibility and processability of starch, which exhibits thermoplastic behavior and takes the name of TPS when plasticized by relatively low levels, in the 15–30 wt% range, of molecules that are capable of hydrogen bonding with the starch hydroxyl groups, mainly water, glycerol, and sorbitol. TPS can readily flow at elevated temperature and pressure and it can be extruded to give both foams or shaped into solid articles by injection molding. TPS products with different viscosity, water solubility, and water absorption have been prepared by altering the moisture/plasticizer content, amylose/amylopectin ratio of the raw material, and the temperature and pressure in the extruder [98]. A great deal of research has been performed on the plasticization of TPS using glycerol [100], sorbitol [101], urea or formamide [102], dimethyl sulfoxide [103], and low-M_W sugars [104]. Figure 1.6 shows different packaging articles obtained from starch, ranging from food trays to cups.

Unfortunately, the properties of neat TPS materials are not still good enough for most packaging applications. For example, the properties of films made of water- and glycerol-plasticized TPS are poor at high humidity, present poor dimensional stability, and become brittle as water is lost. Fortunately, TPS can be blended with other polymers and fillers to improve the mechanical properties and also attained water resistance [105]. For instance, TPS/PLA blends show chemical resistance, improved flexibility and toughness, and low cost [106]. The

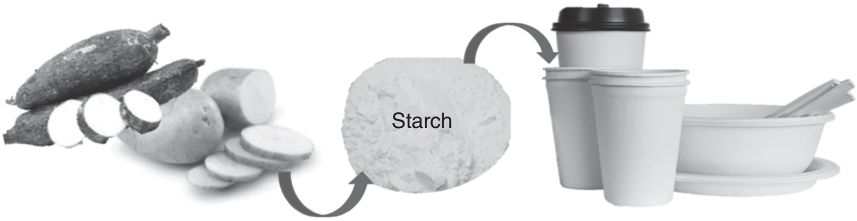

Figure 1.6 Biodegradable packaging articles based on starch.

use of TPS in biopolymer blends is particularly relevant to obtain materials with high elongation at break properties in food packaging [107].

1.3.10 Cellulose and Derivatives

Cellulose is the most abundant natural polymer on earth. The major source of cellulose is certainly wood, which contains 40–50 wt%, being the fundamental component of the cell walls of plants and natural fibers. Cellulose is a linear naturally occurring polymer composed of 1,4-linked-β-D-anhydroglucopyranose units that are covalently linked via acetal functions between the equatorial –OH group of C_4 and the C_1 carbon atom [108]. Neat cellulose is, however, unsuitable for film production because it is highly crystalline and also insoluble in water due to the strong intra- and intermolecular hydrogen bonding between the individual chains and its highly crystalline structure [109]. Therefore, cellulose is usually dissolved in a mixture of sodium hydroxide and carbon disulfide and recast into sulfuric acid. This chemical treatment results in the production of the so-called cellophane film, which has good mechanical properties. However, it is often coated with nitrocellulose wax or PVDC to improve its moisture sensitiveness. Coated cellophane is then used for baked goods, fresh products, processed meat, cheese, and candy though it is not heat sealable due to its non-thermoplastic nature [110].

Alternatively, cellulose can be chemically modified to produce water-soluble cellulose ester or ether derivatives by either esterification or etherification, respectively, of individual hydroxyl groups on the polysaccharide backbone. Commercial derivatives of cellulose include cellulose acetate, ethyl cellulose, hydroxylethylcellulose, and hydroxyl-propyl cellulose, among others [111]. Figure 1.7 summarizes some of the hydrophilic and hydrophobic cellulose derivatives categorized according to their pH-responsive behavior and chemistry. Steps involved in making these thermoplastic materials include, first, making cellulose derivatives biopolymers in powder form and, thereafter, extruding them in the presence of different additives and plasticizers such as citrates. Although the gas and moisture barrier properties of cellulose acetate are not optimal for food packaging, this film is excellent for products demanding high moisture as it allows respiration and reduces fogging [110]. Mazzucchelli (Castiglione Olona, Italy) and Planet Polymer (California, USA) manufacture biodegradable plastics under the trade names of BIOCETA® and EnviroPlastic® Z, respectively, based on cellulose acetate. BIOCETA® has been applied for the manufacture of biodegradable packaging films, retractable films, and tubes [98].

1.3.11 Proteins

Protein-based films have lately become a hot research topic due to their film-forming capacity and cohesiveness, low cost, and biodegradability features. Proteins present good barrier against oxygen and aroma, among others gases. However, they also show high water vapor permeability due to their hydrophilic

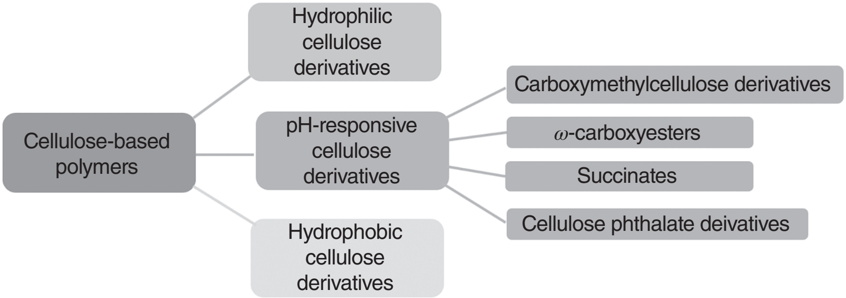

Figure 1.7 Cellulose derivatives categorized based on their pH-responsive behavior and chemistry.

nature [112, 113]. Protein films have been developed from gelatin, corn zein, wheat gluten (WG), soy protein (SP), casein, and whey protein [114–116].

1.3.11.1 Gelatin

Gelatin is a water-soluble protein that is prepared by thermal denaturation of collagen in the presence of dilute acid (gelatin type A) or alkali (gelatin type B). Collagen is found in animal skins and bones such as connective tissues, skin, and bones (see Figure 1.8) [117]. Its structure is triple helix, being stabilized by the formation of hydrogen bridges between the chains through amino and carboxyl groups. When collagen is denatured, the triple helix breaks and the polypeptide chains adopt a random configuration, forming gelatin composed mainly of glycine, proline, and 4-hydroxyproline residues [118–120]. Then, gelatin results in a heterogeneous mixture of single or multi-stranded polypeptides, each with extended left-handed proline helix conformations and containing between 300 and 4000 amino acids. Gelatin is primarily used as a gelling agent forming transparent elastic thermoreversible gels on cooling below 35 °C. It can be used as a valuable biopolymer in tissue engineering applications. Moreover, the gelification properties of gelatin, its capacity of forming and stabilizing emulsions, and its adhesive properties and dissolution behavior make this biopolymer a potential polymer for the manufacture of bio-based films [121]. However, its poor mechanical properties, especially in the wet conditions, limit its application as a packaging material, [122, 123]. Many techniques, including vapor cross-linking, orientation, and use of fillers such as hydroxyapatite nanoparticles (nHAs) and tricalcium phosphate (TCP), have been developed to reinforce gelatin-based films [124].

1.3.11.2 Wheat Gluten

WG is a protein complex having two major components, known as glutenin and gliadin. It is composed of proteins containing water-insoluble and ethanol-soluble prolamins and water- and ethanol-insoluble glutelins (70–80 wt%) in combination with small amounts of wheat oils, starch, and insoluble hemicellulose [125]. The gliadins are mainly monomeric single chain polypeptides, whereas the glutenins are polymeric and disulfide linked polymeric chains [126]. These components are responsible for the physical and chemical properties of WG and confer it with higher viscoelastic properties compared

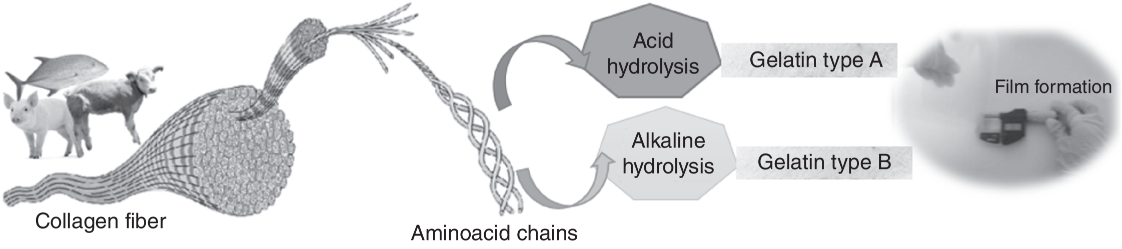

Figure 1.8 Scheme of the gelatin manufacturing from denaturation of collagen for film formation.

with other plant proteins [127, 128]. WG has been used for the production of sustainable food packaging because it is a renewable raw material, available in large quantities, fully biodegradable, and inexpensive. It has properties suitable for applications in edible films and biodegradable packaging. The methods used for processing WG-based bioplastics are casting, extrusion, and compression molding [129, 130]. WG-based films have exceptional oxygen and carbon dioxide barrier properties. However, they have lower water vapor barrier, mechanical strength, and thermal properties in comparison with conventional plastic films [131, 132]. Lignocellulosic reinforcement fillers have been used to improve the properties of WG since they can interact with proteins and lead to the formation of protein–polyphenol complexes, allowing a higher flexural strength, tensile strength, and modulus [133, 134]. Also, WG/montmorillonite (MMT) films were prepared by melt mixing and thermoforming [135]. The introduction of up to 5 wt% of MMT increased the mechanical properties in ways that were not possible by just the variation of the glycerol content and the processing temperature.

1.3.11.3 Soy Protein

Soy protein (SP) is an inexpensive renewable resource, sustainable, abundant, and functional, constituted by different globulins with mainly polar amino acids including acidic and basic amino acids and nonpolar amino acids fractions such as 2S, 7S, 11S, and 15S. The major components of SP are β-conglycinin (7S, nearly 35%) and glycinin (11S, nearly 52%) [136]. The protein with higher 11S fractions produces stronger films with lower water uptake than those richer in 7S, which is attributed to the presence of different sets of amino acids in 7S and 11S fractions [137]. Likewise, different chemical treatments and plasticizers have been explored to improve the intrinsic brittleness and low water resistance of SP-based films. Among them, glycerol, ethylene glycol, and propylene glycol have been found to outperform 1,3-propanediol. Glycerol and water can significantly increase the flexibility of films made of SP, but greatly decrease the tensile strength [138].

1.3.11.4 Corn Zein

Zein is a group of alcohol-soluble prolamin proteins found in the endosperm of corn. It is constituted by hydrophobic and neutral amino acids as well as some sulfur-containing amino acid [139]. Corn zein has a M_w ranging from 18 to 45 kDa and it is soluble in ethanol solutions in water at 60–70 wt% [140, 141]. Indeed, corn zein is produced commercially by extraction with aqueous alcohol and dried to a granular powder. The high proportion of nonpolar amino acid residues confers highly hydrophobic properties and solubility characteristics to zein, allowing its use in food packaging materials [142]. Zein films are formed by dissolving the protein into aqueous ethanol or isopropanol, heating to 65–85 °C, cooling down to 40–50 °C, and casting them by solvent evaporation. The resultant films are, however, translucid and present an intense yellow color (see Figure 1.9). Glycerol is often used to reduce the film brittleness though it tends to easily migrate through the film matrix because of the weak interaction between protein and plasticizer molecules. Migration of glycerol results in loss of flexibility in the film. Zein films have good oxygen barrier properties and

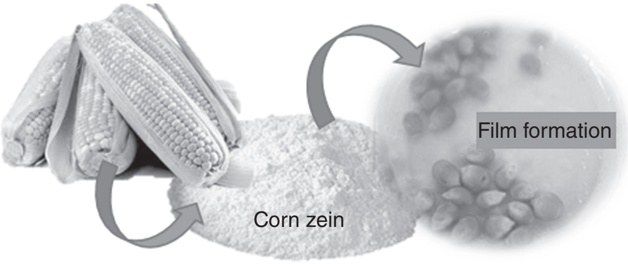

Figure 1.9 A zein film obtained from corn.

are greaseproof, which have been attributed to the helical conformation of the protein, but their mechanical properties and water resistance are low, similar to those of other protein films [143]. In order to overcome these deficiencies, blended films of zein with other biodegradable biopolymers have been widely studied [144–146].

1.3.11.5 Milk Proteins

Biodegradable films can also be formed from milk proteins. The two most important types in the packaging field are casein and whey protein [147]. Casein, comprising 80% of total milk protein, consists of three main components, α, β, and γ with *Mw*s in the 19–25 kDa range. It forms colloidal micelles in milk and is stabilized by calcium phosphate bridging. Casein precipitates when milk is acidified to the isoelectric point (pH = 4.6). Acidified casein is converted to functional soluble caseinates, that is, sodium and calcium caseinates, by neutralization through addition of alkali [148]. Biodegradable films based on caseinates can be obtained by solubilization in water followed by casting and drying. Film formation in water is feasible due to its emulsification capability [149]. Films from caseinates are transparent, with good mechanical and oxygen barrier properties but poor water vapor permeability in the range of WG- and SP-based films [150].

Whey protein is the milk protein that remains soluble in milk serum after casein is coagulated during cheese or casein production. It comprises around 20% of the total milk proteins, being based on a mixture of proteins β-lactoglobulin (approximately 57%, M_w of 18 kDa), α-lactalbumin (approximately 20%, M_w of 14 kDa), bovine serum albumin, and immunoglobulins, among others. Formation of whey protein films involves heat denaturation in aqueous solutions, breaks existing disulfide bonds, and forms new intermolecular disulfide and hydrophobic bonds [151]. Films based on whey protein isolate (WPI) have shown promising mechanical properties as well as moderate water vapor permeability and good oxygen barrier properties [152, 153]. Nevertheless, the properties of WPI films are highly affected by relative humidity (RH) and the type and concentration of plasticizer [154, 155].

1.4 Concluding Remarks

Due to their low cost and high-performance characteristics, fossil derived polymers have remained as the most preferable materials for packaging applications.

However, as mentioned throughout this chapter, serious environmental issues along with the limited natural resources have led to an increase in the development and use of biopolymers as potential strategies to generate novel packaging items. Currently, there are still challenges to overcome, since the material performance of biopolymers in terms of mechanical, thermal, and vapor and gas barrier properties still needs to be further improved to be able to compete with the current petrochemical plastics commonly found in the food packaging industry. Furthermore, ethical issues frequently arise when attempts are made to use biomass for industrial purposes.

According to the European Bioplastics, the global production capacities of bio-based plastics, biodegradable or not, amounted to 1.7 million tons in 2014. This translates to approximately 680 000 ha of land. Consequently, the surface required to grow sufficient feedstock for current bioplastics production is only about 0.01% of the global agricultural area of a total of 5 billion hectares. In any case, the bioplastics industry is also researching the use of nonfood crops and biomass derived from algae, that is, the “second and third generation feedstock”, respectively, with a view to its further use. Innovative technologies are currently being focused on nonedible by-products or waste materials as the source for bioplastics. In this regard, the trend for the development of the next generation of bioplastics is currently led by the emergence of conventional polymers made from renewable and nonfood sources. This generation feedstock is based on the production of plastics from cellulosic materials derived from food crop by-products such as straw, corn stover, or bagasse, which are usually left on the field where they biodegrade at a quantity far higher than necessary to restore the soil carbon pool. At best they are used to produce the energy for the conversion process to feedstock. This leaves significant potential for using biotechnological processes to create a platform to generate chemicals for industrial purposes, the so-called biorefinery concept, which includes the production of bioplastics. Indeed, the word “sustainable” means to maintain or keep going continuously and the word has been used in connection with forest management for over a century.

Although the renewable source may not be necessarily pursued in packaging applications, it can be still regarded as a remarkable plus, especially in times when oil prices are being increased markedly. However, it is also worthy to note that currently less than 6% of petroleum is addressed to produce polymers in the plastic industry. As a result, the real key property associated with biopolymers from an environmental point of view would be to develop polymers being readily biodegradable. Some plastic parts made of biodegradable polymers can additionally meet the requirements of harmonized standards for compostable materials. Today, a lot of different European and International Standards exist for biodegradable polymer-based materials (e.g. EN 13432 or ASTM D6400). They are mainly dealing with natural degradation under specific environmental conditions, particularly for packaging waste.

Looking at the end-of-life options for biopolymers, different recovery and disposal paths can coexist. In most countries, no separate collection system for biopolymers is established. In USA and Western Europe, highly developed separate collection systems for packaging waste exist and littering of plastic waste present a minor problem. However, waste disposal represents a serious problem for other countries where the recycling rates are still low and waste management is not properly working. Beside residual waste, the mixed plastic fraction from waste sorting can be supplied to waste incineration. During quaternary recycling, the resulting steam can be used in energy production, heating, and solid recovered fuel production. Secondary (mechanical) and, even, tertiary (chemical) recycling of biopolymers, particularly relevant if they are not biodegradable, is also possible. However, these processes would first require appropriate separate collection systems, which are difficult as biopolymers are still present in minor amounts and a wide range of bioplastics and their blends coexist on the market. At this moment, the mechanical recycling of biopolymers is at its beginning and the market penetration is not high enough to make recycling of biopolymers profitable. Furthermore, modern recycling processes, which are state of the art for commercial polymers, will have to be adapted to handle bioplastics properly. For instance, owners of recycling plants should make an effort to ensure that no mixed PLA- and PET-fractions are getting into bottle-to-bottle recycling.

Biodegradable packaging is expected to solve the solid waste problem as well as the litter problem. Nevertheless, the current situation indicates that only a few cities are able to collect and compost green waste. Converting a solid material to a gas via biodegradation or composting could not be sustainable if the collecting system is not prepared. In such cases, it is much better to recycle or recover the embodied energy through incineration. Therefore, there is a need to close the resource loop and make the most out of the material rather than simply use it once. Composting, both industrial or home types, is the expected option for biodegradable polymer-based packaging in a near future. This should be considered after material recycling and before thermal utilization. The production of humus-rich compost from different organic waste is a kind of material use. However, home composting rarely leads to success in terms of complete decomposition in an adequate period of time. Most of the biodegradable polymers are only usable for industrial composting. Nonbiodegradable biopolymers in addition to conventional fossil derived polymers can have a negative impact on the composting process. Additionally, owners of composting plants are not always pleased with the development and introduction of compostable articles either. In recent years, some labeling for compostable packaging materials has been developed, though they do not necessarily give information about the renewable material content.

Overall, although promising steps have been done in the area of biopolymers and new law regulations are pushing toward the use of such materials, more advances need to be carry not only to enhance material performance but also in terms of market possibilities. Current bioplastics should be in a near future more cost-effective, easier to process, and with enhanced performance so that food packaging users will fully benefit from their use and also, in terms of policy regulations, the use of such materials can be standardized in the food packaging industry.

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