Biopolymers as Food Packaging Materials

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Abstract This review examines the recent trends, current technology and future challenges in applications of biopolymers as food packaging materials, together with potential solutions, as well as discussing the major safety concerns regarding food packaging materials produced from sustainable and renewable resources. As food contact materials, biopolymers are increasingly being utilized as alternatives to conventional plastics obtained from oil derivatives. This review covers most of the available polymers, focusing on the general principles of their production, properties, and analysis of the possibilities for potential use in food packaging. The use of biopolymers brings new opportunities, not only from the point of replacing conventional polymers and other materials that are widely used in food packaging (glass, paper, metals, etc.), but also in the way it opens up a whole new level of properties and characteristics. Bio-based resources are the base source for production of biopolymers in food application, while in practice, bioresource content may be different. Biopolymers can be produced by microorganisms through fermentative processes of different bioresources [e.g., polyhydroxyalkanoates (PHAs)] and biomass may be produced directly from different kind of plant (starch, cellulose, etc.). In the context of growing environmental and safety concerns, biopolymers have gained increased attention, related to concerns about conventional plastics traditionally produced from fossil fuel.

Keywords Biopolymers · Biomaterials · Food packaging · Sustainable resources

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E. Pellicer et al. (eds.), *Advances in Applications of Industrial Biomaterials*,
DOI 10.1007/978-3-319-62767-0_8

1 Introduction

Biopolymers are not new. In the 1850s, a British chemist created plastics from bio-cellulose. Henry Ford, in the early 20th century, experimented with the use of different polymers derived from soy proteins in his automobiles. After that, in the ’70s, biodegradable polymers gained wider interest in the USA during the great oil crisis. The 1980s brought items such as biodegradable films, sheets and mold-forming materials (Tim and Sylvana 2011). Nowadays, a different type of biomaterial is usually combined with glass, metals, board and an assortment of fuel-based plastic polymers, or used for food packaging as a pure biomaterial. These materials are applied in various combinations to provide unique properties that ensure the safety and quality of packed food products, from processing, handling, and storage to final use by consumers. Notably, these materials have to fulfill a significant task in the sense of preventing the quick deterioration of quality and safety, which provides long-term use of food products during their shelf-life and ultimately prevents massive commercial losses of valuable food products (Babu et al. 2013). When contemplating the principle of food packaging, the entire dynamic interaction between food, packaging material and the ambient condition has to be considered. Materials used for food packaging must be capable of providing specific optimal requirements during storage of different types of food product. The engineering and development of new biomaterials suitable for food packaging is a great challenge both in science and industry (Claus 2000).

On account of environmental change, biopolymers have been elevated to important roles by customers, financial specialists and worldwide producers in recent years. A few plastic materials with properties similar to those of petroleum-based polymers (frequently called biopolymers) are now available. Some of these materials are widely available on the market, such as bio-based polyethylene (PE), poly trimethylene terephthalate (PTT), polylactic acid (PLA), starch, thermo-plasticized starch, cellulose, chitosan, pectin, collagen, gelatin, caseins, zein, natural waxes, polybutylenes succinate (PBS), polyp-phenylene (PPP) and microbiological synthesized polyhydroxyalkanoates (PHAs). The afore-mentioned biomaterials and many others have already been successfully used for a long time as materials for packaging various food products (Chen 2010). Each of these biopolymers shows certain mechanical and synthetic properties that permit them to be utilized as a part of the food packaging industry. PHAs can be qualified by their manifold structural variations, resulting in numerous different properties and, subsequently, different spheres of application (Koller et al. 2013; Koller 2014).

According to their origin and production method, biopolymers may be roughly divided into four fundamental classes:

Class 1 Biopolymers obtained by concentrate from biomass (polysaccharides, for instance, starch, pectin, Chitosan, cellulose, etc., proteins like collagen, casein and gluten, etc.);

Class 2 Biopolymers obtained through the usual chemical synthesis from biobased monomers (polylactic acid, a bio-polyester). The fermentation of carbohydrates is the most common way of obtaining such a monomer;
Class 3 Biopolymers produced by microorganism activity. The main representative of this group of biobased polymers mostly consists of polyhydroxyalkanoates (PHAs), however, materials based on bacterial cellulose are currently being advanced;
Class 4 Biopolymers produced through chemical synthesis from both bio-derived monomers and petroleum-based monomers, polybutylene succinate (PBS), bio-based terephthalic acid (TPA) poly trimethylene terephthalate (PTT), biobased PP and PE, etc. (Claus 2000; Robertson 2008; Mittal 2012; Babu et al. 2013).

In this big family, the most common biopolymers used for food packaging applications are: polymer based on starch or cellulose, polylactic acid (PLA), especially, more recently, multilayer (ML) PLA films, polyvinyl alcohol (PVOH), polyhydroxyalkanoates (PHAs) biopolymers, aliphatic-aromatic copolyesters and polyethylene (PE), and polyethylene terephthalate (PET) partially or completely obtained from renewable sources (Bio-PE and/or Bio-PET, Bio PP and Bio PTT) (Timothy 2010; Tim and Sylvana 2011; Babu et al. 2013; Youngjae and Young 2014a, b; Benetto et al. 2015).

2 Biopolymers Based on Starch

Starch is the most plenteous and ordinarily utilized of the renewable crude materials. Starch is comprised of rehashed units of glucose and involved amylose and amylopectin (Gallant et al. 1997). Its unique chemical and physical characteristics and qualities can be recognized apart from all different carbohydrates. Starch is acquired from seeds, legumes, cereals, potatoes and fruits (acorns and chestnuts), among other items (Whistler and BeMiller 2007). Starch polymers are highly sensitive to moisture, with high water vapor permeability and poor mechanical properties that limit their packaging application. Different vegetal source provide the starch used in the form of biodegradable polymers in food application. The characteristic form of natural starch is a crystalline molecular structure, which is not a plastic material. It is necessary that this crystalline form be changed throughout the process of plasticization. During this process, the molecular structure loses its crystalline form and an amorphous material is obtained. The most interesting starch derivative for the food industry is thermoplastic starch (TPS), as it is the most convenient for obtaining various materials. The type and quantity of plasticizer used during production of thermoplastic starch (TPS) strongly determine the physical, chemical and thermal properties of the final products. Its primary application in the food industry is in the sector of production of flexible and solid packaging (bio-films, bags, laminates, etc.). Polymer films produced from starch are biodegradable and possess good properties as an oxygen barrier. The plasticizer, moisture, and amylose content are strongly limiting factors, related to the mechanical properties of TPS (de Vileger 2000; Youngjae and Young 2014a, b). In many cases, in order to modify the properties of TPS, other ingredients or different structural enhancers have been added to the starch-polymer matrix, such as microcrystalline cellulose (MC), fibers, nano-clays, carboxymethylcellulose (CMC), carbon nanotubes, etc., (Ma et al. 2008; Muller et al. 2011; Girones et al. 2012). Sisal and hemp fiber reinforced with TPS through melt processing have been produced very successfully. In this way, TPS enhances their mechanical properties. Beside this combination, starch mixed with PE and PP in the amount of 5% significantly improves their properties. If used in parallel with applied and advanced shaping techniques such as extrusion with supercritical gases, the obtained biopolymer exceeds the conventional polymer properties. Different kinds of this reinforced starch are already being evaluated in the packaging of bread, vegetables and meat products stored under standard conditions (Girones et al. 2012; Chauvet et al. 2017).

Figure 1 depicts the different commercial starch products used for the packaging of processed and fresh food products, as well as dishes. The following table shows the commercial products, the world's largest producers of said products, and examples of products based on starch biopolymers (Table 1).

Fig. 1 Biodegradable starch cups, plates, and cutlery

Table 1 The world's largest manufacturer of commercial starch products for food packaging (Biomass Packaging 2011; Glenn 2014)

Product	Brand Name	Sample products
PSM (Plastarch material), a highly heat resistant biopolymer made from plant starch and polypropylene, with natural modifying agents for a range of applications	PSM is a biobased thermoplastic resin, highly water and oil proof, similar to conventional plastic. It has a high resistance to low and high temperatures	SpudWare cutlery resistant to high heat
Mater-Bi, obtained mainly from starch	Italian-based Novamont is a manufacturer of a Genetically Modified Organism (GMO)-free, starch-based plastic called Mater-Bi used to make BioBag branded certified compostable bags BioBag® is the world's largest brand of certified compostable bags and films made from Mater-Bi	The main products are shopping and waste bags, food service items (plates and cutlery)
TPS (Thermoplastic starch) Made of the cornstarch-derived amylose molecule, whose special chemical properties allow for a wide range of applications in product manufacture	Australian-based Plantic Technologies uses non-GMO corn starch to produce their biopolymer resin. The main area of application is food, cosmetic and pharmaceutical packaging	BioMass Packaging® uses TPS to manufacture water-soluble packing

During 2008, in the UK, the first biodegradable cereal bag was produced by Jordans Organic Cereals and Alcan. The packaging uses two dissimilar types of biopolymer film. The outer layer is made from Innovia Film's clear NatureFlex film. The inside layer is made from Novamont's Mater-Bi film (Hill 2010). In 2009, Novamont launched an improved version of Mater-Bi. This new Mater-Bi integrates Novamont's starch-based technology with the technology of bio-polyesters from vegetable oil. In 2014, Novamont increased their production capacity of their fourth generation of Mater-Bi by more than 120,000 tons per year. This is a good model for the current movement in the food packaging industry towards transitioning from starch to bio-polyester or starch-polyester composites as acceptable food packaging materials (Biomass Packaging 2011; Tim and Sylvana 2011; Youngjae and Young 2014a, b). Figure 2 shows an example of BioBag® commercial product.

Fig. 2 Biodegradable thermoplastic starch food pack bags

3 Biopolymers Based on Cellulose

A number of cellulose derivatives are produced commercially, most commonly methylcellulose (MC), carboxymethyl cellulose (CMC), ethyl cellulose (EC), hydroxyl propyl cellulose (HPC), hydroxyethyl cellulose (HEC) (Sanchez et al. 2011) and cellulose acetate (CA). In relation to the derivatives mentioned, only CA is widely used for food packaging (baked goods and fresh produce). CA is characterized by low resistance to gasses and moisture and must be conducted through a plastification process if used for the development of film. This is a direct consequence of the crystalline structure of cellulose, which makes the initial steps of derivatization difficult and costly (Claus 2000; Jafarizadeh et al. 2011). Emulsified cellulose-based biofilm composed of corn starch, microcrystalline cellulose (MCC), and soybean oil extended the shelf-life of wrapped crackers stored in different RH values, compared to unwrapped ones, by reducing moisture loss. The excellent film-forming properties possess many cellulose derivatives, but they are just too expensive for wider industrial usage. To change this situation and produce lower-cost cellulose packaging materials, we will be obliged to create effective processing technologies for the production of cellulose derivatives (Bravin et al. 2006; Sauperl et al. 2009). Table 2 shows the largest commercial producers of cellulose products around the world.

Figure 3 shows the oxygen permeable cellulose commercial films for packaging various kinds of food.

Table 2 The world's largest manufacturers of commercial cellulose products for food packaging (Biomass Packaging 2011)

Product	Brand Name	Sample Products
Cellophane: natural biopolymer obtained from wood	BioMass Packaging® carries cellophane products made with Nature Works LLC, a 100% cellulose biopolymer with excellent oxygen, grease, oil, and moisture barrier characteristics	Used as a packaging film for bakery product wraps, confectionery product wraps, other food wraps, and food-grade transparent bags
Cellophane is one of the first ever biopolymers made from cellulose, the main component of trees and plants	Nature Flex bags generally compost in several weeks in a home compost pile or a commercial compost facility	
It is produced from renewable resources	Nature Flex™, Innovia Films (U.K.)	

Fig. 3 Cellulose films for packaging of different kinds of food

4 Biopolymers Based on Chitosan

Chitosan biopolymer films are strong and difficult to break. They are also flexible, with mechanical properties similar to those of commercial polymers traditionally produced from petroleum-based derivatives. They are sensitive to humidity and have a low moisture barrier, which has limited their wider use in food applications. Because of that, as with other biopolymers based on polysaccharides, special attention must be paid to a moist environment. In order to reduce the water vapor permeability (WVP) of the chitosan coatings and polymer films, various other biopolymers may be incorporated into chitosan to form stable and mechanically compact films such as, e.g., lipids and other polysaccharides (Bonilla et al. 2012). Emulsion films based on caseinates or chitosan have been successfully applied to dried fruit products (partially-dehydrated pineapple) and different types of cereal products. Chitosan films are poorly resistant to moisture and water vapor. During the storage of cereals treated with chitosan-based films, the critical moisture content for cereal products was reached (Talens et al. 2012). New techniques of chitosan synthesis in many ways solved these problems. Advanced catalytic systems, such as pincer-type PdII, produce chitosan-based polymers with significantly improved properties and durability (Baran and Menteş 2017).

At Harvard, Wyss Institute researchers have developed fully degradable biopolymers isolated from shrimp shells. This new material can be very well molded into different shapes, as much as conventional plastics, but without any environmental hazards. As a cheap and environmentally friendly alternative to conventionally produced plastic based on petroleum derivatives, the chitosan biopolymers could be used as a base for production of different kind of bags, food packaging in different shapes, and diapers that decompose in just a few weeks while releasing rich nutrients that are suitable for cultivation and growth of plants.

5 Polylactic (PLA)-Based Biopolymers

Polylactic acid (PLA) is a biodegradable, thermoplastic, renewable biopolymer obtained through the polymerization of the lactic acid monomer. Lactic acid (LA), as a basic monomer, is obtained from the bacterial fermentation of polysaccharides or through chemical synthesis. The biopolymer's production can be roughly divided and considered through the production of lactic acid (LA) as a basic monomer in the first stage and polymerization of the lactic acid in the second final stage. PLA has a high potential for application as a hygiene and packaging material in the food industry. The most commonly used polymer for food packaging applications may be 90% L-lactide and 10% racemic D, L-lactide. This material is reported to be readily polymerized, easily melt processable and easily oriented (Linnemann et al. 2003; Wang et al. 2005; Rasal et al. 2010).

The PLA composite obtained through polymer modification with 2-methacryloyloxyethyl isocyanate (MOI) significantly improved the physicomechanical and thermal properties of the final biopolymer (Chen et al. 2012). The MOI-PLA composite had a 20 times higher percentage of stretching than the pure PLA. Copolymerized PLA with other bio-polyesters significantly improved its physical properties (Sodergard and Stolt 2002). There are also synthesized polylactide-polyisoprene-polylactide thermoplastic elastomers with various compositions, and the excellent stretching and elastomeric copolymers (Frick et al. 2003; Youngjae and Young 2014a, b).

PLA polymers are GRAS (Generally Recognised As Safe), permitting their use in direct food contact with aqueous, acidic and fatty foods under 60 °C and aqueous and acidic drinks served under 90 °C. Therefore, PLA polymers are designed for direct food contact (Yokesahachart and Yoksan 2011). In Europe, lactic acid is listed as an approved monomer for food contact applications in Amendment 4 of the Monomers Directive, 96/11/EC (1996). The high elastic modulus and low hardness are characteristic physical features of PLA that are similar to polystyrene (PS). PLA in its amorphous form is clearly transparent, with excellent thermal and physical properties. It is a very versatile polymer, suitable for a large number of applications, flexible (for labels, composites, etc.), or rigid and foaming (for food use) packaging (Chen 2010; Chen et al. 2012).

For example, from NatureWorks PLA, Wilkinson Industries produces various thermoformed dishes and biofilms. This kind of PLA material provides an optimal aroma barrier and high strength. Mighty Leaf Tea launched 100% bio-pouches, while Revolution T Organics presented PLA tea bags. College Farm Organic Candy uses individual packages made from PLA for organic candy products. Similarly, Noble launched a line of PLA bottles and labels in 2008. It was one of the first "all renewable" bottles to be used for juice packaging (Raithatha 2009).

In 2010, Walmart began utilizing Nature Works Ingeo as packaging materials for organic salad, salsa, spinach, fresh-cut fruit, vegetables, and tomatoes, while in 2011, Danone introduced the Ingeo cup for yogurt on the EU market. Compared to previous packaging, by introducing the Ingeo PLA packaging, the company's carbon footprint was reduced by around 25%, which resulted in a decrease in the use of fossil raw materials of more than 40% (Sanjay and Ackmez 2011; Youngjae and Young 2014a, b). Figures 4 and 5 show a common example of commercial PLA products.

Although PLA is not a commonly used material, some companies have found specific uses for it, such as:

- **Bags for salads**. Salad bags and similar promotional materials for new food applications accounted for more than 40% of PLA use in 2006. It is reckoned that the food service industry is the most probable source of growth for this material, and it is proposed that the use of PLA could have a 24% annual increase rate. The use of PLA in the packaging of processed and fresh food is generally preferred by companies promoting a sustainable and organic life culture (Casey 2010).

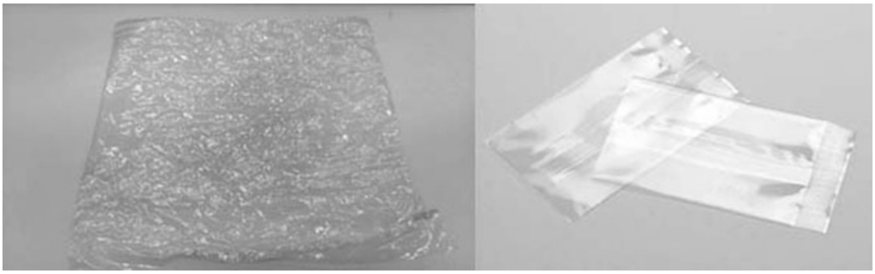

Fig. 4 Polylactic Acid (PLA) bags from corn

Fig. 5 PLA cup and bowl

- **Coca-Cola** is another company that is looking to implement PLA into its operation. They are currently developing a PET "Plant Bottle" that will contain 25% PLA. This, however, could make an existing recyclable PET bottle no longer recyclable, as well as non-bio-degradable (Youngjae and Young 2014a, b). Combining the two ingredients in concert would make separation at a recycling level impossible, which could push the bottles into the landfill. This is the type of critical thinking that is necessary when assessing a new idea (Sanjay and Ackmez 2011).

Some of the problems with PLA are in its production. A vast amount of corn is needed to produce commercially-used PLA. According to projections, calculated by the 116,000 metric tons of PLA in use by 2011, the demand for corn can be estimated using the conversion of 2.5 kg of corn needed to get 1 kg of PLA. Separating the portion of the grain used for PLA production from that utilized for human and animal food could affect the marketplace by increasing the cost of corn, which would mostly impact the poorest countries already suffering due to a lack of basic foodstuffs. Additionally, taking into account the fact that only two countries produce the majority of the world's corn could create inflated prices as well (Casey 2010). Table 3 shows the largest commercial PLA products producer around the world.

Table 3 The world's largest manufacturers of commercial PLA (Polylactic Acid) products for food packaging (Biomass Packaging 2011)

Product	Brand Name	Sample Products
PLA (Polylactic Acid) is plastic made from vegetable starch A clear alternative to petrochemical-based plastic, such as PET (polyethylene terephthalate) and PS (polystyrene)	Most PLA is marketed as Ingeo™ by the U.S. company Nature Works, LLC Nature Works, LLC ferments animal-feed corn dextrose into lactic acid	Takeout containers, coated paper and cold drink cups, various other cups, and fresh produce packaging

6 Polyhydroxyalkanoate (PHA) Biopolymers

PHAs are very suitable for food packaging applications because their moisture barrier is comparable to conventional packaging materials. Generally, PHAs are bio-polyesters of alkanoic acids, containing a hydroxyl group and at least one functional group attached to the carboxyl group. PHAs polymers could be different in their properties according to their chemical composition (homo or co-polyester, contained hydroxyl fatty acids, etc.) (Lee 1996). They are water-insoluble, being based on a thermoplastic biopolymer with high surface energy. Because of that, PHAs are very suitable for printing and dye. PHAs possess oxygen UV resistance in their level of commercial ethyl vinyl alcohol (EVOH). Poly (3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) is suitable for heat-shaping and producing a flexible plastic used in the food packaging sector, where biodegradable materials are desirable. PHAs are currently mostly used as flexible food packaging with high oil content (marinated olives, cheese, nuts and others), and for frozen foods and food that is declared as organic (Innocentini et al. 2003; Shen et al. 2009).

PHAs can be embedded in a matrix of biomaterials, such as bio-coatings, laminates, and biodegradable dye printing. Additionally, PHA structures can include different kinds of thermoplastic elastomer, waxes, adhesives, different binders and others. Depending on the type and relationship of different inclusions, mechanical properties vary from elastomeric to resins as stiff as nylon or polycarbonate. PHAs are most commonly shaped via film extrusion, injection, hollow bodies, etc. The first two commercial PHA products launched on the market were extrusion coating and cast films. Other current potential applications are as mulch films, stretch films, different kinds of bag, and surfactant soluble packagings. An injection molding procedure is also under continuing development by academia and industry, with new methods and techniques for obtaining cheaper and more suitable packaging materials being studied. Currently, Metabolix alone is developing and commercializing PHAs for film and bag applications, such as PHA Latex Barrier Coating for Paper and Cardboard. Other major worldwide PHA-based product producers with main world market shares are the Kaneka Corporation (Japan), GreenBio (China), Tianan Biologic Material Co. (China), and Meridian

Fig. 6 Different kinds of PHA bags used in food packaging

Fig. 7 PHA thermoformed cups

(Bainbridge, GA). GreenBio built a PHA production plant in Tianjin, China, that began operation in 2009 and has the capacity to produce 10,000 tons of PHA per year (Modi et al. 2011). The basic requirement which is imposed if PHAs are used for food packaging is that they should not be in direct contact with the food. PHAs are a natural material whose life cycle is completely renewable, produced by microorganisms and completely decomposed by microorganisms (Doi et al. 1994; Bugnicourt et al. 2014) (Fig. 6).

Mirel's thermoformed cups. Mainly produced from PHA resins. These resins are known as aliphatic polyesters, made biologically by converting products of photosynthesis using microbial or plant biofactories. The main raw materials for the microbial production of PHA are corn and various sugars (different carbohydrates). The resins obtained in this way have mainly been used for the production of thermoformed cups. The properties of the PHA cups are noted as being comparable to polypropylenes, offering good stiffness and tensile strength (Casey 2010; Koller et al. 2013; Koller 2014). Figure 7 illustrates an example of a PHA thermoformed cups commercially used in food packaging.

7 Other Biopolymers Used in Food Packaging

Biopolymers, for example, poly trimethylene terephthalate (PTT), are a kind of bio-polyester which have extraordinary mechanical properties, processability, and thermal steadiness. The 1,3-propanediol (PDO) and pure terephthalic acid (PTA) or dimethyl terephthalate (DMT) are the main compounds for PTT production. Succinic acid can be synthesized through bacterial fermentation from either a bioresource or oil-based resources (Shen et al. 2009). Monomers produced in this way can be used for the synthesis of polybutylenes succinate (PBS). The mechanical properties of PBS are similar to those of PP and PE. That kind of bio-polyester has a relatively high melting temperature (T_m), around 113 °C (Kabasci and Bretz 2012). The main chemical composition of polyethylene terephthalate (PET) includes around 30% ethylene glycol (EG) and 70% terephthalic acid (TPA) (Shen et al. 2009). Biobased TPA can additionally be produced by the bio-route from isobutanol, n-butanol, isobutylene, muconic acid, limonene, terpenes, and carbohydrates, while commercial TPA is still being produced from oil resources (Berti et al. 2010). In polyethylene (PE) production, ethylene represents a basic monomer. It can be produced from ethanol obtained via fermentation of a different kind of sugar, sugarcane or corn. PE and PP obtained in this way are mechanically and physically identical to the traditionally produced plastic packaging materials. PE and PP produced from bioresources are not biodegradable; in any case, they can be recycled like conventional PE and PP (Timothy 2010).

Basically, fully biodegradable polymers are not recyclable from the aspect of currently applied technologies used in the recycling of conventional petroleum-based polymers. In 2009, Coca-Cola launched "PlantBottle," bottles made out of up to 30% of plant-based monomers with the same mechanical, chemical physical, and functional properties as conventional PET plastics. One of the most important advantages of this new bottle is a recyclability performance as full as a conventional one. In the conventional PET, ethylene glycol (EG) and terephthalic acid (TPA) are irreplaceable base components. To produce a PlantBottle, a monomer of EG is bio-produced from sugarcane through the fermentation process. Coca-Cola is currently trying to produce fully bio-based terephthalic acid (TPA) from natural resources such as stems, fruit peels, and bark. In this way, they will achieve their goal of fully bio-based bottles (Hill 2010; Ying 2014).

In 2011, Heinz introduced the PlantBottle for their ketchup sold in the retail markets of U.S. and Canada. In 2012, Heinz, Nike, Coca-Cola, Ford Motor, and Proctor & Gamble founded the Plant PET Technology Collaborative (PTC), a strategic working group with the mission of accelerating and promoting research of bio-PET. In 2011, PepsiCo produced the world's first 100% bio-based PET made from pine bark, switchgrass, and corn husks, with the same structure and physical and mechanical properties as conventional PET. They are also researching and developing technology for the production of bio-based PET from other natural resources, such as oat hulls, orange peels, and potato scraps (Youngjae and Young 2014a, b; Ying 2014).

Changes in retail patterns, such as the globalization of markets resulting in longer distribution distances, present major challenges for the food-packaging industry, which ultimately act as driving forces for the growth of novel and improved packaging concepts that extend shelf-life while sustaining the safety and defined quality of the packed food. Novel active and bioactive packaging technologies, combined with bio-packaging and nanotechnology, can best help in achieving the goals of both the food industry and consumers. Therefore, the proper combination of these three technological concepts will provide the driving force towards innovation in the food sector over the next few years (Biopolymers Market Forecast 2014).

The use of polymeric packages for food applications has increased considerably over recent decades. Apart from the intrinsic benefits associated with polymers, significant improvements in their physicochemical characteristics,specifically regarding barrier, mechanical, and thermal properties, have been attained as a consequence of extensive research work. Furthermore, due to the deficit of petroleum resources and waste management issues, the focus of the research is switching from synthetic oil-based plastics to biomass-derived biodegradable and non-environmentally harmful polymers. The main drawbacks of biopolymers in regard to wide industrial and commercial application stem from their poor barrier properties and high instability. The progress of research is in novel applications, making polymers an ideal partner for active and bioactive packaging,in which the package is no longer a passive barrier,but actively contributes to the preservation of food. Biopolymers have an ideal structural matrix for the incorporation and controlled release of a number of substances to be added to foods (Sanjay and Ackmez 2011; Ying 2014).

8 Biopolymers Used in Paper Packaging

Paper biopolymers, besides making for rigid packaging, could be used for wrapping food products (e.g., flexible paper). In this way, non-biodegradable plastic materials would no longer be required. According to Khwaldia et al. (2010), the association of biopolymers to paper provides an interesting functionality while maintaining the environmentally-friendly characteristic of the material. Caseinates (Khwaldia 2010; Khwaldia et al. 2010), whey protein isolate (Lin and Krochta 2003), isolated soy protein (Rhim et al. 2006), wheat gluten (Gallstedt et al. 2005), corn zein (Trezza et al. 1998), chitosan (Despond et al. 2005; Ham-Pichavant et al. 2005), carrageenan (Rhim et al. 1998), starch (Matsui et al. 2004), and alginate (Rhim et al. 2006) have been the usual substances researched and applied as biomaterials for the coating of various kind of papers. Han and Krochta (2001) have found that use of paper for food packaging shows significant performance improvement (reducing moisture permeability and resisting oil oxidation) when the paper biopolymer film is made based on whey protein. Despond et al. (2005) write about packaging products in paper covered with a film of chitin/carnauba wax that gets great results, owing to the paper having improved barrier properties in regard to water and gasses.

In addition, it is necessary that any given biopolymer packaging material fulfill all requirements pertaining to conventional packaging materials. This refers to the properties of permeability (permeability to water vapor and gases, aroma substances, and light) and mechanical and optical properties (e.g., transparency) (Debeaufort et al. 1998; Chan and Krochta 2001; Weber et al. 2002; Hong et al. 2004; Gallstedt et al. 2005; Kjellgren et al. 2006; Bordenave et al. 2007; Khwaldia 2010). Figure 8 shows examples of lined paper bags and cups commercially used products.

Fig. 8 PLA, PHAs, Cellulose, Chitosan-Lined Paper Bags and cups

Tetra Pak has launched the industry's first entirely plant-based, renewable packaging materials. This was the first packaging to have 100% bio-low-density polyethylene (LDPE) films and caps made from 100% bio-high-density polyethylene (HDPE). All of these products were obtained from sugar and laminated on paperboard certified by the Forest Stewardship Council (FSC™). This kind of package has been commercially available starting in 2015.

The Table 4 presents an overview of the use of biopolymers for the production of packaging materials.

Table 4 Properties of biopolymers used in paper coating (Khaoula et al. 2010)

Type of commercial biopolymers	Main functions/properties	Reference
WPI	Suitable for printing with water-based ink	Han and Krochta (1999)
	Fat and oil barrier/resistant	Han and Krochta (2001)
		Chan and Krochta (2001)
NaCAS	Oxygen barrier	Khwaldia (2004)
NaCAS/paraffin wax bilayer	Water vapor barrier	Khwaldia (2010)
Corn zein	Grease barrier	Trezza and Vergano (1994)
	Prevention of drying/brittleness	
Corn zein/paraffin wax bilayer	Water vapor barrier	Parris et al. (1998)
	Grease barrier	
SPI	Gas and lipid barrier	Park et al. (2000)
SPI with $CaCl_2$ posttreatment	Water vapor barrier	Rhim et al. (2006)
WG	Oxygen barrier	Gällstedt et al. (2005)
Carrageenan	Grease barrier	Rhim et al. (1998)
HPMC/beeswax	Water vapor barrier	Sothornvit (2009)
Chitosan	Fat barrier	Ham-Pichavant et al. (2005)
	Gas barrier	Kjellgren et al. (2006)
Chitosan/sodium alginate bilayer	Fat barrier	Ham-Pichavant et al. (2005)
Chitosan/carnauba wax bilayer	Gas barrier	Despond et al. (2005)
Chitosan/sodium alginate bilayer	Fat barrier	Ham-Pichavant et al. (2005)
Paraffin wax	Water vapor barrier	Parris et al. (1998)

9 Advantages of Biopolymers

Packaging is a system of preparing goods for transport, distribution, storage, retailing and end use. It means that a product must be safely shipped to the final retail market in a defined condition at reasonable cost. All conventional polymers used for the production of different kinds of food package could be roughly categorized according to their application, functional properties in packaging, and contents of containment in the package. The presence of various contaminants in conventional plastics, as well as their possible migration into the food, is one of the main reasons they need to be replaced with biopolymers. Another key reason is the environmental issue and lack of biodegradability, a byproduct of the use of plastic produced from petroleum derivatives. Production of 1 kg of conventional plastics requires 65% more energy than does the same amount of biopolymers. Conventional plastic has an unreasonably long degradation period, resulting in huge environmental impact and contamination. In spite of all this, for a long period of time, using conventional plastic was considered as viable concept, regardless of all the benefits of use sustainable materials such as biopolymers. More or less all conventional plastics are toxic due to the need to use different ingredients and, as such, limited in terms of their safe use in the food packaging industry. Biopolymers save 30–80% in greenhouse gas emissions and provide longer shelf-life than normal plastic (Chen 2010; Raiand and Roy 2011; Sanjay and Ackmez 2011; Babu et al. 2013).

Most of the materials obtained on the basis of biopolymers are biodegradable and suitable for the production of compost, which carries nutrients and organic material to the soil. The result of this is an increase in water and nutrient retention, reduction in chemical input and prevention of plant diseases. Starch-based biopolymers have been shown to degrade 10–20 times quicker than conventional plastics (Liu et al. 2009). Incineration of conventional plastics generates smoke and fumes that are toxic to humans, wildlife, and the environment. It was not necessary to investigate the Incineration of biopolymers in regard to their biodegradability over a short period of time, but were such incineration to happen, the fumes released would not be hazardous to the environment. Biopolymers have a more diversified structure, chemical composition and architecture, which permits researchers a vast number of opportunities to customize the properties of the final packaging material (Tokiwa et al. 2009; Wei et al. 2011; Mittal 2012). The great advantage of the use of biopolymers is the possibility of incorporating nanoparticles that carry a number of positive characteristics, such as heat and cold stability, impermeability to gasses, strength, firmness, antimicrobial properties, impermeability to oxygen, etc. (Huang et al. 2015; Cazóna et al. 2016; Van Long 2016).

10 Toxicity Concerns Related to Biopolymers in Food Applications

The monomers of cellulose and starch-based biopolymers, as well as those of poly3-hydroxybutyrate (PHB) and PLA, have been estimated not to cause health problems. The main concerns associated with the use of PHAs as materials for food packaging refer to microorganisms, considering that some strains used in their production could be potentially hazardous (Conn et al. 1995; Zhu et al. 2014). Different kinds of additive are usually used in biopolymer material production than those used in conventional plastics. The physicochemical properties of biopolymers and their environmental condition determine the potential migration rate of their ingredients. The pure biopolymers (additive-free) usually have fewer properties than conventional ones. The additive migration rate from PLA and starch-based biopolymers was reported to be very low (Avella et al. 2005; Clarke et al. 2012). The most common source of chemical migrants is oxo-biodegradable plastics. Ammala (2011) and colleagues gave a detailed overview of potential additives for commercial use, including dithiocarbamates and benzophenones. Related to bio-nano-composites, the studies viewed demonstrated the cytotoxic effects of nano-clays consolidated into nano-bio-composite polymers. Nonetheless, these studies did not take into consideration a conclusion reached on the poisonous capability of bio-nano-composites, because of the incredible variety of nanomaterials, even those obtained from the same batch, and an absence of accepted standardized testing conditions (Maisanaba et al. 2013; Houtman et al. 2014).

11 Conclusion

Biopolymer materials are already widely used in developed countries, having practically replaced conventional polymers as food packaging materials, especially in the packaging of organic, natural and functional foods. Biopolymers have been set up in many applications, from food packaging to hi-tech. Despite the benefits that biopolymers possess, there are a number of drawbacks that prevent the widespread commercial use of these materials, particularly in the field of food packaging. This is usually because of performance and price when compared with their conventional doublets. In accordance with the method of production and use in the food industry, biopolymers can be classified into different categories and quality groups. The widest commercial use in the food packaging sector is occupied by cellulose-based biopolymers; with the exception of these, very few other biobased materials have commercial use in the packaging of conventional food products. Advancements are taking place at increasing speed in the development of commercial products using starch- and PLA-based biomaterials for a different kind of food packaging that has already been created. In this way, biopolymers have increasing significance in food application. The primary reason for this is that they are created from renewable resources, and the fact that they can be reused through the recycling process. The researchers focused on applications of biopolymers have demonstrated not only that they have suitable properties for wider use in the food industry, but also that they could achieve an acceptable commercial price in the future. If we compare them with petroleum recyclable products, packaging materials made from renewable bioresources could very soon have a low cost and suitable properties for food packaging applications.

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