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Biopolymers with Renewable Resources and Recyclable in Nature as a Promising Alternative for Synthetic Polymers in Food Packaging Applications: A Short Review

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Abstract

A large number of both biopolymers and synthetic polymers have been used as food coating packaging materials. In this manuscript, properties and applications of synthetic polymers and biopolymers with a particular attention on biopolymers for food coating and packaging were reviewed. The properties and applications of biopolymers were compared with synthetic polymers. Synthetic polymers are thermoplastic and have a high potential to process them for making different shapes of packaging for foods and drinks. Most synthetic polymers show excellent water vapor barriers compared with biopolymers. On the other hand, biopolymers are safe materials respecting environmentally concerns. Biodegradability, biocompatibility, non-toxic, green and renewable resources make biopolymers as excellent candidates for food coating and packaging. However, the use of biopolymers in food coating and packaging is limited, because of their hydrophilic characters, poor process abilities, high water vapor permeability, and limited mechanical properties. Most biopolymers are edible, thus biopolymer-based materials as coatings and packaging materials can be eaten with foods.

Keywords: Biopolymers; Synthetic polymers; Properties; Food Packaging.

Introduction

A large number of both natural and synthetic polymers have been used as food packaging materials. Packaging materials are used to protect foods from contaminants. Synthetic materials represent a major fraction of all packaging materials. Synthetic polymers as packaging materials are thermoplastic, i.e., reversibly fluid at high temperatures and solid at ambient temperatures [1-7]. Synthetic polymers with petrochemical-based such as polyethylene terephthalate (PET), polyvinylchloride (PVC), polyethylene (PE), polypropylene (PP), polystyrene (PS) and polyamide (PA) have been increasingly used as packaging materials, because their large availability at relatively low cost and their good mechanical performance such as tensile and tear strength, good barrier to oxygen (O_2), carbon dioxide, anhydride and aroma compounds, and heat seal-ability (Siracusaa, Rocculib, Romanib, & Dalla Rosab, 2008). Abbreviations and expressions are listed in Table 1 (Table 1).

Biopolymer-based packaging materials originated from naturally renewable resources such as polysaccharides, proteins, and lipids or combinations of them offer favorable environmental advantages of recyclability and utilization compared to conventional petroleum-based synthetic polymers. A wide variety of natural polymers are derived from plants and animals [8-10]. Proteins and polysaccharides have drawn attention for their film-forming ability and have been used to make edible films (EFs). Lipids and waxes were also used as edible coatings.

Table 1: Abbreviations and expressions appeared in this manuscript.

Abbreviation	Expression, Term	Abbreviation	Expression, Term
BP	Barrier Properties	O_2B	Oxygen barrier
BW	beeswax	PET	Polyethylene terephthalate
D	Diameter (size)	PA	polyamide
DNA	deoxyribonucleic acids	PP	Polypropylene
EF	Edible film	PS	polystyrene
EFs	Edible films	RH	Relative humidity
HDPE	high density polyethylene	RNA	Ribonucleic acids
HPMC	hydroxyl propyl methyl cellulose	UV	Ultraviolet
LDPE	low density polyethylene	a_w	water activity
M_w	molecular weight	WV	water vapor
MWD	Molecular weight distribution	WVB	Water vapor barrier
O_2	Oxygen	WVP	water vapor permeability

Use of synthetic packaging films has led to a serious environmental problem, due to their total non-biodegradability. The use of biopolymers with renewable resources instead of synthetic polymers for food coating and packaging applications is a subdivision of the global environmental demand. Despite their complete replacement of eco-friendly packaging films meet economical and research and development issues for specific applications like food packaging [11-14]. Partial replacement of synthetic materials with natural polymers would yield in a positive environmental impact. However, some of these derived materials are expensive and pose an economical problem for manufacturers. In order to reduce material costs of packaging systems, it is desirable to combine less expensive natural products such as food and agricultural wastes.

Cellulose being a major component of paper with a hydrophilic nature absorbs more WV at higher relative humidity (RH) in

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comparison with the lower RH. As the amounts of hydrophobic materials in the extracts increased, water barrier properties of the treated papers were improved [15,16]. Beeswax (BW) and stearic acid have been used as coating materials to improve water vapor barrier (WVB) properties of paper. Hydroxypropyl methylcellulose (HPMC), and BW have been used to improve physical properties and water vapor permeability (WVP) of coated papers). HPMC-based coated papers increased stretch and decreased in tensile index. HPMC-based coatings reduced WVP and further reduction was obtained when BW was incorporated into the HPMC-lipid composite coated paper.

Paper coated with HPMC and lipid yielded in packaging materials for food and medical applications. Synthetic plastic materials with a hydrophobic nature, such as PE have been used as coating layers for papers to improve their water barrier properties [17]. However, the addition of synthetic polymers as thin layers of the paper yield reduction in their susceptibility to degradation reported that the barrier properties of papers coated with chitosan were improved against moisture. However, the coated papers are not a good candidate for food applications, because of their hydrophilic nature. Water vapor (WV), O_2 and other gas barrier and mechanical properties and efficiencies of the biopolymer films can be improved via making polymer blends/ composites. Some reasons for using composite materials rather than the single polymers are: to increase stiffness, strength, and dimensional stability and to reduce permeability to WV, O_2 and carbon dioxide (CO_2) [18-20].

Biopolymers with renewable resources and potential for production of edible and biodegradable films can improve product quality and/or reduce waste disposal problems. Increasing environmental concerns caused by accumulation of plastic wastes, yielded in intensive attention for research and development on moisture barrier layers containing environmentally friendly materials [21-30]. The objectives of this study are: to describe the sources, properties and food applications of biopolymers and compare their properties and applications with synthetic polymers. Three main groups; polysaccharides, proteins and lipids, which play important roles in food coating and packaging are also discussed.

General Considerations

A macromolecule or a polymer is a chemical species composed of a long chain with regular repeating units, a high molecular weight (M_w) and a high molecular size (D). Macromolecules are divided into natural and man-made polymers. The natural polymers and man-made polymers also known as biopolymers and synthetic polymers, respectively [31-33]. Biopolymers are produced by biosynthesis in nature, whereas synthetic polymers are made and controlled by human beings (Mandelkern, 1983). Generally, biopolymers can be classified into carbohydrate polymers (polysaccharides), proteins, deoxyribonucleic acids (DNA), and ribonucleic acids (RNA). Macromolecules are also composed of semi-synthetic polymers. Semi-synthetic polymers can be prepared by chemical modification of either synthetic polymers using natural polymers including polysaccharides and proteins or preparation of functional derivatives of natural polymers. Lipid compounds such as long-chain fatty acids and waxes have been considered as natural polymers in some references [34-36]. Resources, properties, and applications of synthetic and natural polymers are presented in Table 2 (Table 2).

Properties of Biopolymers and Synthetic Polymers

In this section, properties of petroleum-based synthetic polymers are compared with properties of biopolymers. Advantages and disadvantages of biopolymers in comparison with synthetic polymers are also presented, in order to have a comparison view for food coatings and packaging applications. In general, the properties and applications of polymers depend on their M_w, D, and molecular weight distribution (MWD). Nearly all synthetic polymers and some biopolymers are polydisperse and can be described in terms of MWD (Kasaai, 2017). Advantages of petroleum- based synthetic polymers over biopolymers include: low cost, low density, inertness, flexibility, thermo-plastic, transparency, mechanical and WVB properties. Most synthetic polymers show excellent WVB properties compared with biopolymers [37-39]. Their applications in food packaging partially restricted, because most of them are not biodegradable and thus lead to negative impact to the environment. Biopolymers present a number of excellent and promising properties for a number of applications, including food and biomedical applications. Biopolymers are eco-friendly materials and play an important role in protecting the ecosystems. The natural packaging materials can also help to prevent the growth of foodborne pathogens and to reduce environmental waste. However, there are limitations on the utilization of biopolymer-based materials in food coating and packaging, due to their poor WVB and mechanical properties, which cause a shorter shelf life compared

Table 2: Resources, characteristics, properties, performances/advantages and limitations/ disadvantages for synthetic and natural polymers for food coating and packaging.

Item	Resources, Characteristics and Properties; Performances and Advantages	Limitations and Disadvantages	Function and Applications	References
Synthetic Polymers	Petroleum-based; hydrophobic nature; good WVB and mechanical properties; high efficiency for their production processes; the production in large scale is practical, economical and cost effective.	Environmentally are high toxic; toxic for human, animals, and plants species; adverse effects on humankinds, animals, and plants species; they do not degrade in nature; they are not biodegradable and cannot be recycled; harmful for environment; adverse effects on foodstuffs (migration of undesirable and toxic compounds including monomers, plasticizers, and other compounds from packaging materials into foods)	High potential to make different types of packaging systems for foods and drinks	Benning, 1983; Briston & Katan, 1983; Khwaldia et al., 2010; Osborn & Jenkins 199; Samanta et al., 2016; Schlegel,1985; Silvestre et al., 2011.
Natural Polymers	Biopolymers are naturally occurred with renewable resources; they are environmentally safe and friendly materials; renewable resources and reutilization of recycled materials compared to conventional petroleum-based synthetic polymers; non-toxic or low toxicity (with an acceptable level of toxicity); no need to purify; most of impurities are not toxic or posse low toxicity; no adverse effect on climate	Large scale production is a limitation due to their high cost; purification and extraction of active ingredient are expensive process; low WVB and mechanical properties.	Exhibit edible films for food coating packaging; a large spectrum of chemical functionalities and O_2 and CO_2 barrier properties	Al-Tayyar et al., 2020; Cha et al., 2002; Debeaufort et al., 1998; Dole et al., 2004; Gontard et al., 1996; Khwaldia et al., 2010; Samanta et al., 2016; Silvestre et al., 2011

to synthetic polymers (as conventional food packaging materials) [40-45]. Other important properties of biopolymers include transparency (some proteins and polysaccharides), and film- forming properties via casting method.

Most biopolymers are edible and thus food stuffs coated with EFs can be eaten without requiring to remove coating materials. Biopolymer films and coatings may also serve as gas and solute barriers and complement other types of packaging by minimizing food quality deterioration and extending the shelf life of foods [46-48]. Biodegradable materials (proteins and polysaccharides) are either strongly plasticized by sorption of moisture and exhibit somewhat oxygen barrier (O_2B) properties.

Lipids can be incorporated in polysaccharide or protein film or coating matrix to improve WVB properties, because of their hydro-repellency. Waxes are the most efficient substances to reduce moisture permeability. Their high hydrophobicity is a consequence of a high content in esters of long-chain fatty alcohols and acids, as well as long-chain alkanes (Kester & Fennema 1986; Donhowe 1992; Hagenmeier & Shaw 1992). The advantages of biopolymers in comparison with synthetic polymers forfood packaging applications have been identified and highlighted in Table 2 (Table 2).

Proteins with different amino acids in their backbones and hetero-polymeric structures offer them a large spectrum of chemical functionalities and a wide variety of polymer network structures leading to unique gas barrier properties [49-52].

Polysaccharides (chitosan, cellulose, sodium alginate, and carboxy methyl cellulose, guar gum, karya gum, carrageenan, locust bean gum, and gum Arabic), were used to improve mechanical, antimicrobial, antioxidant, and eco-friendly properties. WV, O_2, and other gases barrier and mechanical properties of a biopolymer can be improved via making a blend/ composite using another biopolymer and/or filler (Day, 2008; Khwaldia, Arab- Tehrany & Desobry, 2010). Lipid compounds such as long-chain fatty acids and waxes can be incorporated in biopolymer films or coating matrix to improve barrier properties, because of their hydro-repellency. Waxes are the most efficient substances to reduce WVP. The high hydrophobicity of lipids is a consequence of high content of long-chain fatty alcohols, fatty acids or esters (different types of glycerides) (Kester & Fennema 1986; Donhowe 1992; Hagenmeier and Shaw 1992). A large spectrum of chemical functionalities and a wide variety of polymer network structures leading to O_2 and CO_2 barrier properties (Gontard, Thibault, Cuq, & Guilbert, 1996; Khwaldia et al., 2010). Resources, characteristics, and properties of synthetic and natural polymers are presented in Table 2 (Table 2).

Plasticizers, antioxidants, antimicrobial agents, or fillers can be added to biopolymers to improve properties and performances of biopolymers [53-55]. Lipids provide good WV barrier, but they have certain disadvantages such as brittleness, lack of homogeneity, and presence of pinholes and cracks in the surface of the coatings. The WVP of coated biopolymers decreased as the amount of wax in the coating increased. The addition of hydrophobic substances (wax) to a hydrophilic matrix provides the moisture-barrier properties.

Food Packaging

The main purpose of food packaging is to protect food stuffs against attack from O_2, WV, light, particularly ultraviolet (UV) light, and chemical and microbiological contaminations. In addition, packaging protects foods from physical/ mechanical damage, facilitate transportation and distribution, minimize weight loss, and prolong shelf- life. Thus, packaging materials should possess sufficient WVB and O_2B capacity, and good mechanical properties. The shelf life of packaged foods depends on both the intrinsic and extrinsic factors. Intrinsic factors include pH, water activity (a_w), nutrient content, presence of antimicrobial compounds, redox potential, and respiratory rate, whereas extrinsic factors include storage temperature, RH, and the surrounding gas composition.

Synthetic polymers have been used to make thin films, bottles, jars, cups, tubs, and trays [56-59]. Low density polyethylene (LDPE), and PP for thin films, high density polyethylene (HDPE) for bottles, and polyesters for both films and bottles. PET has been widely used for bottles and packaging film.

Biopolymer films and coatings serve as gas and solute barriers and complement other types of packaging by minimizing food quality deterioration and extending the shelf life of foods.

Discussion

Despite biopolymers are environmentally friendly materials and they are alternative for synthetic polymers, but they have faced major problems, including poor mechanical properties, low degradation temperatures, high permeability to WV and gases. Several investigations have been performed to overcome some problems of biopolymers, enhance their properties, and to ensure food integrity. Research and development have been already started to replace biopolymers (proteins, polysaccharides, lipids) with conventional materials (synthetic polymers) in food packaging.

The hydrophilic nature of biopolymers yields in a loss of barrier properties and limits their industrial applications. Biopolymers can be mixed or blends with synthetic polymers to improve the functional properties of the finished product and finally expand the range of applications. The functional properties of synthetic or bio- polymers can be also improved by incorporation of additives and pigments into synthetic polymers or biopolymer matrix. The incorporation would yield in the expansion of their applications. Additives and pigments can be derived from renewable resources, and finally can be obtained food packaging materials with approximately 100% weight of biodegradation compounds. Development of edible and/or biodegradable coating materials for partially or totally substitution with synthetic polymers would be of great benefit to consumers and environmentalists, as they are safe and eco-friendly materials. Most of bio polymers are edible, thus bio polymer-based materials as coatings and packaging materials can be eaten with foods.

Conclusions

In this manuscript, properties and applications of synthetic and bio polymers with a particular attention on bio polymers for food coating and packaging were reviewed. The properties and applications of bio polymers were compared with synthetic polymer. A large number of both biopolymers and synthetic polymers have been used as food packaging materials. Packaging prevents food from pathogens and other environmental attack prolongs storage and shelf-life and reduces food waste.

Synthetic polymers are thermoplastic and thus have a high potential to process them for making films, bottles, jars, cups, and tubs for packaging of foods and drinks. Most synthetic polymers show excellent WV barrier properties compared with biopolymers. Synthetic polymers are not recyclable and yield in a negative impact on the environment. Biopolymers exhibit interesting properties such as biodegradability, biocompatibility, biological activity, and non-toxic properties. Thus, they have high potential for various applications in the food industry. Biopolymers such as proteins and polysaccharides have drawn attention for their film-forming ability and have been used to make edible and biodegradable films. Biopolymers are safe materials respecting environmentally concerns. Biodegradability, biocompatibility, non-toxic, green and renewable resources make biopolymers as excellent candidates for food coatings and packaging. The use of biopolymers in food coatings and packaging is limited, because of their hydrophilic characters, poor process abilities, high WVP, and limited mechanical properties. Biopolymers exhibit medium barrier properties to O_2 and antioxidants.

Biopolymers have the potential to be broadly applied and there is a growing market for biopolymers in food packaging. This is due to material properties, food safety, eco-friendly, and biological functionalities of biopolymers. Most biopolymers are edible, thus food stuffs coated by edible films can be eaten with foods.

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