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Scope of biopolymers in food industry: A review

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Plastics have significantly advanced the ever-demanding food industry since the last century. However, it has also induced ecological problems like threat to fragile ecosystems like coral reefs and aquatic life, pollution of air and land, as well as harm to animals through direct digestion due to its non-biodegradable nature. Owing to their extensive desirable properties, polymers as plastics are a fundamental part of the contemporary world. Biodegradable polymers have potential to contribute majorly to reduce the environmental impact of plastic production and processing especially in the food packaging industry. They can be a favourable option as packaging material due to their properties like availability, stability, flexibility, cost effectiveness, etc. It has been reported that certain edible films made of biopolymers such as cellulose, chitosan, pectin can not only be used for packaging of eatables but also improve their texture, flavour, and shelf life. The present review aims to highlight the approaches to replace plastic by biopolymers in food packaging industry and accentuate the research done in this field. This article emphasizes on the types of biopolymers, their sources, properties, assets, drawbacks along with trends of biodegradable packaging that may possibly be followed in the coming times.

Keywords: Biopolymers, Biodegradable packaging, Properties of biopolymers, Edible films, Food preservation

INTRODUCTION

Customer demands for assortments of food consistently, and inclination for comfort have empowered uncommon development of new advancements in packaging to guarantee accessibility of quality food. The essential capacity of foodstuff packaging is to isolate edibles from the general climate, limiting exposure to decay factors including the impacts of microbes, air, atmospheric conditions, and humidity to avoid nutrition loss therefore extending the service life. Thus, it plays a huge role in food safety [1]. Packaging safeguards the food product throughout its life cycle. All conventional methods like wrapping in paper, storing edibles in plastic, glass, and metal containers, have encountered difficulties in edible food packaging. Plastics like polyethylene and PETE are harmful to the environment. Most plastics used for food packaging can be used only once and end up in the ocean or landfill after use. They are acquired through petroleum and are called petroleum-based products. The burning of plastic has resulted in increased emissions of greenhouse gases with carbon dioxide being the most prominent [2].

Petrochemical industries manufacture most of the plastic material from non-renewable sources like synthetic plastics (around 95-99%). Synthetic plastic has a high resistance to physical, chemical, and biological disintegration, resulting in waste accumulation. Waste causes serious environmental and health issues. It builds up on the streets and highways, clogging the drain and causing it to overflow. Plastic waste is discarded in copious quantities into oceans and rivers, endangering marine life. Incineration releases harmful gases into the atmosphere, bringing down the air quality, increasing the risk of climate change, and posing various ailments. Moreover, some types of plastics are non-recyclable making them more vulnerable to single usage. The increasing challenge in discarding of wastes, as well as the negative consequences on the human health and environment caused by the non-degradability of many synthetic polymers, has sparked global alarm [3]. In many industrial applications, biodegradable polymers have evolved as a viable alternative to non-biodegradable plastics.

Biopolymers are not comparable to synthetic plastic in their physical and chemical properties. Hence, they need to be assessed carefully for modifications by blending with other materials. Biopolymers are naturally available. Some sources of biopolymers are shown in Figure 1. Derivatives of biopolymers may be synthesized for obtaining materials with more desirable properties (Table 1).

This article focuses on the types of biopolymers, their properties, and future biodegradable packaging trends. The purpose of this review is to emphasize the importance of using alternatives to plastic in the food packaging industry, as well as the research that has been conducted in this area.

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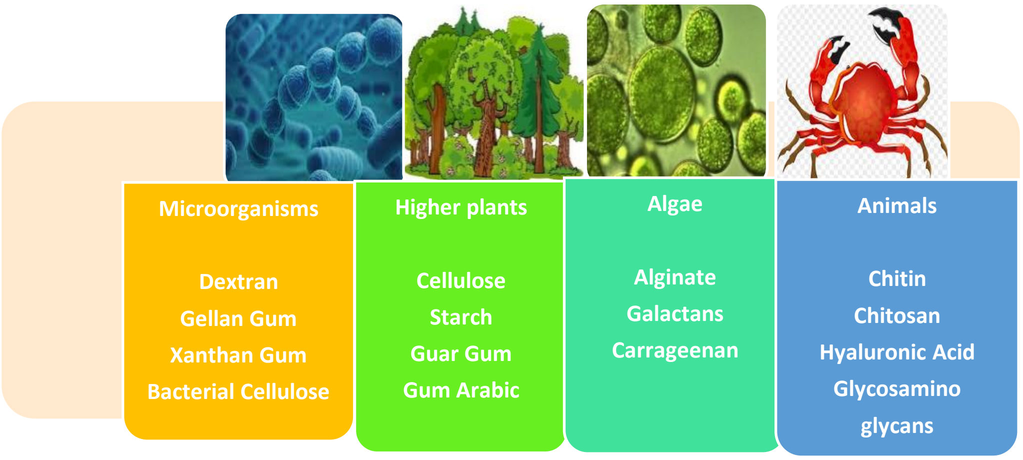
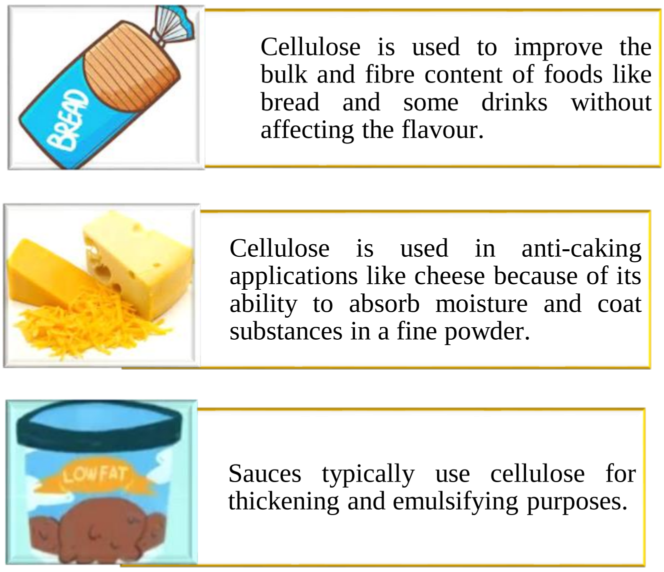


Figure 1. Sources of biopolymers ailments [4].

Table 1. Sources and derivatives of some biopolymers.

Biopolymer	Sources	Derivatives	Ref.
Cellulose	Wood Cotton Bran Plants Bacteria	Cellulose acetate Cellulose sulfate Cellulose nitrate Carboxylmethyl cellulose Ethyl cellulose Methyl cellulose Nanocellulose	[3]
Chitosan	Chitin (exoskeleton of marine invertebrates)	Alpha chitosan Beta chitosan	[1] [5]
Pectin	Citrus peels Apple pomace Sunflower head Sugar beet waste Mango waste	High methoxyl pectin Low methoxyl pectin	[6]
Proteins	Milk Milk products Animal origin Animal origin Corn Soybean	Whey Casein Collagen Gelatin Zein protein Soy protein	[2]
Polyhydroxyalkanoates (PHA)	Extracted from bacteria *via* fermentation of sugar or lipids	Poly(3-hydroxyalkanoate) PHA Poly(3-hydroxyvalerate) PHV Poly(3-hydroxyhexanoate) PHHex Poly(3-hydroxyoctanoate) PHO Poly(3-hydroxydecanoate) PHD	[7] [8]
Polylactic acid (PLA)	Fermented plant starch from corn, cassava, sugarcane	Poly-L-lactic acid (PLLA) Poly-D-lactic acid (PDLA) Poly-DL-lactic acid (PDLLA)	[9]
Alginate	Cell wall of Brown algae (*Phaeophyceae*)	Sodium alginate ($NaC_6H_7O_6$) Potassium alginate ($KC_6H_7O_6$) Calcium alginate ($CaC_6H_7O_6$)	[10] [11]
Thermoplastic starches (TPS)	Starches from plant materials heated with water and then mixed with plasticizers	Thermoplastic cassava starch Thermoplastic corn starch Thermoplastic sugar-palm starch	[12]



Cellulose is used to improve the bulk and fibre content of foods like bread and some drinks without affecting the flavour.

Cellulose is used in anti-caking applications like cheese because of its ability to absorb moisture and coat substances in a fine powder.

Sauces typically use cellulose for thickening and emulsifying purposes.

Figure 2. Uses of cellulose in food [19].

Types of biopolymers

Cellulose

Cellulose is a naturally occurring biodegradable polymer that is widely used as it contributes to the reduction of synthetic packaging and wastes. It is low in weight and helps to reduce packaging material weight. Cellulose and its derivatives can be found in a variety of natural settings. They are both bioavailable and cost effective due to the availability of sources. Wood is a key source of cellulose. Cellulose can be obtained from pulp of wood and utilised in a variety of applications. Cotton, which is commonly used for threads and garments, is another rich source; cotton blooms are composed of cellulose. Cellulose and its derivatives have high biocompatibility, material properties, heat capacity, moisture absorption, permeability, antimicrobial properties, crystallinity, hygroscopicity, and organoleptic attributes like smell, taste, colour. Despite cellulose's limited antioxidant and antibacterial capabilities, the addition of natural plant extracts fulfils this need. Antimicrobial properties of cellulose are limited. Therefore, derivatives of cellulose are preferable as they have enhanced antimicrobial properties like nanocellulose, methyl cellulose, CNC [13]. Cellulose and its derivatives are mechanically robust owing to its crystallinity [14].

It was reported that gallic acid-loaded nanofibers prevented oxidation of walnuts during storage [15]. Moreover, during the storage period, mangoes packed using CNC films were devoid of mango-associated postharvest deterioration [16]. Cellulose containing herbal extracts increased the storage period of button mushrooms with green tea extract incorporated bacterial cellulose being the most effective in preserving the colour of mushrooms [17]. It was observed that carboxymethyl cellulose increased the shelf life of white soft cheese and was effective against bacterial count, molds and yeast [18]. Cellulose is also used as a food additive for a variety of reasons as shown in Figure 2.

Chitosan

Chitosan is a N-deacetyl derivative of the polysaccharide chitin. This polymer has piqued the interest of researchers due to its potential as a natural antioxidant and its antimicrobial properties. Chitosan engages with pathogenic and decomposing bacteria's cell membrane, triggering structural and functional changes, as well as influencing cell wall permeability. Chitosan's unique properties make it ideal for film production, and chitosan-based films have a lot of potential as active packaging materials attributed to its antibacterial properties, non-toxicity, and reduced oxygen permeability. Chitosan-based films exhibit poor mechanical properties and lack of water resistance. Here arises the need to blend chitosan with other materials to improve its physical properties [20]. The tensile strength of chitosan films made using acetic acid is greater than that made with citric, lactic, or malic acids, and it rises over time. Plasticizers such as glycerol or sorbitol could be used to increase the coatings' elastic properties. Combining cellulose and its derivatives to chitosan films improves elasticity, structural rigidity, and optical clarity while retaining antibacterial property [21, 22].

It was reported that papaya fruit was longer preserved when stored with chitosan solutions at room temperature [23] and they also offered antioxidant mechanisms inhibiting guava ripening during storage at room temperature, prolonging the fruit's qualitative characteristics after harvest [24]. It was observed that phytochemical profiles of plum fruit were preserved with chitosan coatings [25]. Furthermore, the shelf life of carrots wrapped in composite films was up to nine days [26]. The chitosan layer altered tomato quality criteria by slowing down the ripening process [27].

Pectin

In many plants, pectin is a complex heteropolysaccharide that acts as a key multifunctional component of the cell wall [28]. Pectin is a robust molecule that can be employed in a variety of food applications, including stiffening and gelation agents, colloidal stabilisers, texturizers, and emulsifying agents. These major uses include packaging, coatings on fresh and cut fruits and vegetables, and microencapsulation agents. Pectin is water-soluble and insoluble in organic solvents. Pectin has been successfully produced as a natural organic biopolymer that may be derived from agricultural-waste products, aiding waste management. The final application of pectin composites is quite versatile yet very appealing in many domains associated with food packaging, especially when active formulations are sought, due to the variety in pectin structure. To better regulate the pectin-based products, more research on pectin composites and improvement of polymeric techniques would be required [6].

Antimicrobial substances are added to pectin edible films to obtain antimicrobial active packaging to prevent growth of microbial colonies and extend product shelf life [29].

It was reported that soybean oil can be kept from oxidizing for thirty days due to its bioactive pectin films [30]. The incorporation of halloysite nanotubes to modern food packaging materials provides significant benefits. Halloysite nanotubes containing peppermint [31], salicylic acid [32], and rosemary [33] essential oils have been shown to have an effect in pectin films. A greater compatibility of halloysite nanotubes enhances the mechanical, thermal, and moisture barrier qualities of pectin films. The antibacterial activity of these films can be upgraded with the increase in release rate of active constituents.

Proteins

A polymer made up of amino acids is referred to as a protein. The amino acids create peptide bonds between chains, indicating that they have polymerized into proteins [2]. Protein-based films are hydrophilic, which means they have relatively lower water barriers and lose their stability when exposed to elevated humidity. They serve as an excellent barrier against hydrophobic chemicals like oil and fragrance. Antimicrobial and antioxidant substances are also found in protein-based films [34]. The antimicrobial activity depends upon the variety of proteins, as well as additive compounds used in the edible coatings. For instance, lysosome can be used as an antimicrobial in pea protein or starch-based films and can be stored up to 15 days before use [35].

Milk protein films are ductile and transparent in nature with disinfectant properties. They also include strong antimicrobial and antioxidant compounds that serve to boost food quality. Whey and casein protein are two types of protein found in milk. Casein protein accounts for most of the milk protein. After casein precipitation, whey protein can be produced. After dissolving the casein protein in water, an alkali solution containing agents are added. When these substances bind with amino acids, calcium caseinate and sodium caseinate are produced. These ions improve the barrier properties and mechanical robustness of the film by increasing protein cross-linking. Whey protein films have better oxygen gas barrier properties than caseinate films. Animal muscles and tissues contain collagen protein. Gelatine is created when collagen is broken down with the assistance of water. Dry gelatine is flavourless and translucent. To make the film-forming solution, it is dissolved in hot water. Casting is used to create the film, which is then dried in the oven. Corn is also used to make zein protein. It is hydrophobic and can produce insoluble coatings in water. It can be utilised as an edible packaging material to preserve the standard and shelf life of food goods due to its inherent antibacterial and antioxidant capabilities. Soybeans are unique and the primary source of soy protein. Boiling soymilk initiates dehydration resulting in the formation of a soy protein film. This is followed by an air-drying procedure. When compared to lipid and polysaccharide-based films, soy protein films have a higher gas barrier [36]. It was reported that zein-based films containing monolaurin or eugenol had shown increase in elasticity and hydrophobicity [37]. It was observed that milk-based edible films showed difference in mechanical, optical, antioxidant and hydrodynamic properties depending upon the type of milk protein with casein being the most favourable [38]. It was observed that gelatine and gelatine mixed with papaya-based films showed bendability and lower moisture permeability [39].

Polyhydroxy alkanoate (PHA)

PHAs are made by a variety of bacteria that use agricultural waste as a carbon source. PHAs are employed in a variety of applications, including packaging, medicinal, and agricultural, due to their biodegradability and biocompatibility. The PHAs' inherent good gas barrier qualities make them appealing as a single-use packaging alternative to traditional plastics in order to reduce plastic pollution in the environment [16].

It has been discovered that a majority of short chain length-PHA copolymers with a minor fraction of medium chain length-PHA generate features similar to standard petroleum-based plastics such as polypropylene when generating PHAs with similarthermal and mechanical properties [40]. The advantages of PHA are that it is non-carcinogenic, non-toxic, and biodegradable. PHAs have good barrier properties against oxygen, carbon dioxide, and moisture, making them a better choice as food packaging materials [41, 42]. Its high production cost and short polymer chains that let through oxygen are the downsides which need to be focused on in future studies [43].

PHA lacks antimicrobial properties, thus there is a need to incorporate it with additives. Poly(3-hydroxybutyrate) or PHB is one of the most common forms of PHA. It has been reported that metal nanoparticles were used to create antibacterial PHB films [44].

It was observed that the PHAs including organic or inorganic fillers demonstrated useful water vapor barrier qualities, as well as improved crystallization behavior, thermal stability, mechanical properties, and lower production costs [45].

It was reported that drinking straws made from PHA were biodegradable and non-toxic, but the production cost was high [46].

Polylactic acid (PLA)

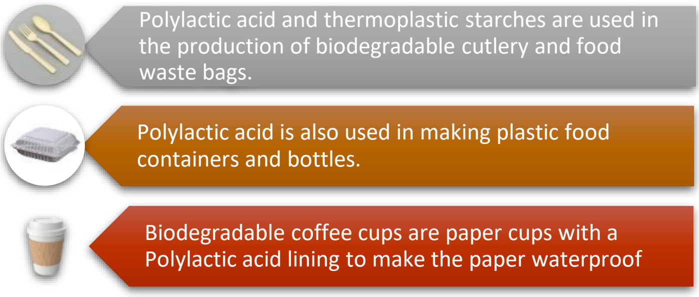
PLA is an acid-derived aliphatic linear poly(α-ester) or α-hydroxyalkanoic polyester. PLA is made from lactide that has been ionic-polymerized. Lactide is a cyclic chemical formed when two molecules of lactic acid are dehydrated and then condensed. As lactic acid is a chiral molecule possessing d-type and l-type isomers, it can be divided into three types of polylactic acid: poly-l-lactic acid (PLLA), poly-d-lactic acid (PDLA), and poly-d, l-lactic acid (PDLLA). In terms of optical activity, polylactic acid can be crystallized into three forms attributed to its two components (L and D enantiomers) [47, 48].

PLA has a low melt viscosity that is required for mould shaping. Yet there are some disadvantages. PLA, for example, has a low crystallisation rate during long moulding cycles and has poor gas characteristics. Furthermore, as compared to other synthetic polymers, PLA has low mechanical strength, as well as thermal resistance. PLA has been mixed with other polymers to circumvent these restrictions. PLA's glass transition temperature of 50–80 °C is relatively low to most polyesters, significantly limiting the applicability of this amorphous material in its pure state. PLA has low mechanical strength, as well as thermal resistance [44].

Plasticizers and fillers have also been introduced into PLA. In addition to the preparation of PLA nanocomposites, these technologies have proven successful in making PLA more commercially viable [9]. The films made from PLA are biodegradable, have good oxygen barrier properties, and have lower migration levels than those made from food contact materials [49].

Antimicrobial additives like nisin and ethylene oxide are needed to be introduced in PLA due to its lack of such properties [50]. Antibacterial food packaging made from PLA/PBS blends (90:10) was found to reduce both microorganisms (*S. aureus* and *E. coli*) and provide an effective barrier layer against water vapour transmission [51, 52].

Some applications of polylactic acid in food industry are shown in Figure 3.



Polylactic acid and thermoplastic starches are used in the production of biodegradable cutlery and food waste bags.

Polylactic acid is also used in making plastic food containers and bottles.

Biodegradable coffee cups are paper cups with a Polylactic acid lining to make the paper waterproof

Figure 3. Applications of polylactic acid in food industry [53].

Table 2. Possible applications of biopolymer food packaging

Biopolymer	Food item	Form of packaging	Function of the biopolymer	Ref.
Cellulose	Cheese	Film	Enhanced shelf life of cheese	[61]
	Chicken breast fillets	Film	Enhanced shelf life of meat due to decrease in microbial count	[62]
Chitosan	Bread	Film	Enhanced shelf life against aerobic bacteria and molds (up to 5 days and 7 days respectively)	[63]
PLA	Vegetable	Film and bag	Higher shelf life and antimicrobial activity was observed in composite bag as compared to the film	[64]
Zein	Pork sausages	Active film	Green tea extract was infused into chitosan film and utilized to package pork sausages that were preserved at 4^0C.	[65]
Gelatin	Melon	Container	Freshly cut melon stored in PLA container for 10 days was preserved well and no change in pH, stiffness was observed at 10^oC	[66]
Starch	Salad	Film	Antimicrobial properties observed during preservation of salad	[67]
Thermoplastic starch	Broccoli	Film	No change in broccoli was evident after 6 days of preservation at 5^oC	[68]
	Sea bass	Film	Antimicrobial and antioxidation properties were observed in sea bass stored in gelatin film at 4^oC for 12 days	
	Chicken breast fillets	Film	Antimicrobial activity observed in the food item. 1% SANAFOR incorporated tapioca starch film was used	[69]
	Sunflower oil	Active film	Films produced from cassava starch were used to encase wine grape pomace. Antioxidant activity was greater in the microencapsulated film with gum arabic.	[70]
	Pasta	Active film	TPS and PBAT were used to make active packaging films. The film inhibited the growth of germs, extending the pasta's storage period.	[71] [72]

Starch

Starch is a polysaccharide composed of 1,4 linkages between glucose monomers. The linear polymer amylose is the most basic type of starch, while amylopectin is the branched form. According to the FTIR test, the sago starch based biodegradable plastic was degradable after 14 days, with the primary chemical inside the sago starch-based biodegradable plastic disappearing. The sago starch-based biodegradable plastic was also shown to have strong acid resistance but low alkalis resistance [54]. Antimicrobial qualities must be imposed on starch because it does not have them naturally. For instance, cationic starch was also utilised in combination with starch and sodium alginate to create antibacterial polyelectrolyte films [40]. Mechanical integrity, thermal stability, and humidity absorption are some of the constraints of native starches. These drawbacks lead to starches being combined with other materials to improve their properties [55]. In addition to lowering production costs, blended starches improve barrier properties, dimensional stability, minimise hydrophilicity, and increase biodegradability. Various low molecular mass plasticizers, including glycerol, glucose, sorbitol, urea, and ethylene glycol, are blended with starches to enhance their properties [56]. By adding plasticizers, thermoplastic starch (TPS) is formed [57], which is characterized by the spontaneous breakdown of starch's semi-crystalline structure and the formation of hydrogen bonds between plasticizers and starch molecules [58]. TPS can be made in a variety of qualities depending on the plasticizer added to the starch. Plasticizers weaken the intermolecular chain connections, resulting in greater flexibility, extensibility, and fluidity. TPS is also an extremely hydrophilic compound. TPS and PLA combined provide significant benefits in terms of cost, property, and biodegradability [59].

It was reported that 1% SANAFOR incorporated polybutylene succinate/tapioca starch film for packaging of chicken breast fillet was the most successful in keeping the food item fresh and devoid of microbial activity [60].

Various experiments have been carried to use biopolymers for food packaging. Some of the possible applications are shown in Table 2.

CONCLUSION

Biodegradable polymers have an immense potential in turning the plastic industry upside down as they can reduce the negative impact on the environment. Biodegradable polymers such as cellulose, chitosan and starch are abundant in nature and can be used effectively for packaging of many food materials. Some of the biodegradable polymers such as polylactic acid (PLA) may be expensive to develop at the moment but future studies may help to synthesize them in more economical ways. Properties of biopolymers have been discussed to help understand the various aspects that can be advantageous or if disadvantageous may be modified to suit the needs. Cellulose, due to its abundance in nature and preferable properties, is the most widely assessed biopolymer. Some experiments have been mentioned in the form of examples to clarify how we might synthesize biopolymers for food packaging. Biodegradable polymers cannot replace plastic in the majority of the cases due to higher demand and lower availability. Researchers from all over the world are currently researching in this direction. Use of biodegradable polymers in food packaging including other industries has indeed started. Future studies need to focus on affordability and accessibility of some of the biodegradable polymers such as PHA and PLA as they can help in overall environmental sustainability.

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