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Formulation of secondary compounds as additives of biopolymer-based food packaging: A review

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ABSTRACT

Background: Biopolymers can be considered a valid alternative to synthetic polymers in the food packaging industry since their biodegradability, biocompatibility, easy renewability, and generally good mechanical properties, comparable with the ones of conventional polymers.

Natural secondary metabolites derived from plants and fungi have attracted much attention in the food packaging industry because of their both antimicrobial and antioxidant activity and positive effect on biofilm mechanical performances.

Scope and approach: Food packaging aims to preserve food quality and safety as well as to extend food shelf-life. Due to the environmental impact of synthetic polymers used in the food packaging industry, academic and industrial research focused the attention on the exploitation of biopolymer-based package systems. Active packaging is a new food packaging path, concentrating on generating a multifunctional system via formulating active agents into the packaging polymer matrices. Secondary compounds of plants and fungal are promising natural additives for active packaging since they can act as antioxidants, antimicrobial, and plasticizer agents.

In this review, the antimicrobial, antioxidant, and plasticizing effect of secondary metabolites included in biopolymer-based food packaging materials are described, highlighting their main impact on bioplastics properties.

Key findings and conclusions: Secondary metabolites (SMs) evidenced antimicrobial and antioxidant activity by inhibiting the growth of pathogenic microorganisms and protect food from oxidation. Besides, depending on the specific formulation, preparation methodology, and physical or chemical interaction occurring between the polymer and additive functional groups, they could provide peculiar effects on the mechanical performances of the biofilms.

1. Introduction

Food packaging has been widely used to protect food from chemical and biological contaminations and physical damage and extend the food shelf-life by preserving its quality and safety. The first food package was glass bottles with a cork seal, made by Nicolas Appert during the Napoleon Bonaparte era in France (Risch, 2009). However, the first application of plastic in the food packaging industry backs to the Second World War when plastic materials developed for the army's aims (Risch, 2009).

The big concern of food packaging, however, is the synthetic polymers massive impact on the environment. Indeed, data revealed that plastic consumptions have considerably increased over time and one-third of all plastic usage is due to the packaging materials (Schwarzböck, Van Eygen, Rechberger, & Fellner, 2016). Hence, the food packaging industry plays a crucial role in the production of plastic wastes. It seems necessary to find an alternative for the replacement of synthetic polymer in this segment. So far, petroleum-based plastics such as polyethylene terephthalate, high-density polyethylene, polyvinyl chloride, low-density polyethylene, polypropylene, and polystyrene have been commonly used in the packaging industry because of their wide range of benefits, such as low cost, long-lasting, lightweight, excellent resistance to chemicals and water and suitable mechanical properties. Although, concerning environmental pollution,

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petroleum-based plastics are not biodegradable or compostable, thus generating a tremendous mass of plastic waste worldwide. According to the European Commission report, only about 25% of used plastics can be recycled, which is two times less than the spread amount of plastic on the land surface and oceans (An EU action plan for the Circular Economy COM/2015/0614 final, Brussels, Belgium: European Commission. (2015)). On the other side, the European Sustainable Development Goals mainly focused on the reduction of plastic pollution within 2030 by paying attention to the replacement of oil-based polymers with biodegradable polymers coming from renewable resources (An EU action plan for the Circular Economy COM/2015/0614 final, Brussels, Belgium: European Commission. (2015)). All these reasons made researchers, institutions, and packaging companies shifting their investments to agriculturally based (biobased) products in the packaging industry. According to the standards EN 13432 and ASTMD, 6400, biopolymers are biodegradable and compostable polymers synthesized from renewable resources. Biopolymers are widely available; being non-toxic and biocompatible can be potentially used in various applications such as packaging, paper coating, biomedical, food science, and agriculture. The importance of renewability and compostability in the packaging sector drastically influenced the usage of petroleum-derived polymers.

The biopolymers can be obtained from two sources; the first is represented by renewable raw resources (microorganisms, vegetables, animals, and proteins). Among them, Polyhydroxyalkanoates (PHA), polysaccharides (cellulose, starch, alginate, chitosan, pectin), and poly (lactic acid) (PLA) are the most important. The second group of biopolymers is the so-called oil-derived biodegradable biopolymers, deriving from petroleum. Polycaprolactone, poly(butylenesuccinate) (PBS), and some aliphatic-aromatic copolyesters deserve to be mentioned since they are already used for industrial applications (Salerno, Cesarelli, Pedram, & Netti, 2019).

1.1. *Towards the bioactive packaging*

The traditional food preservation techniques such as salting and heat application altered the foods' flavor, odor, color, and textural properties (Domínguez et al., 2018). For these reasons, scientists and food industries paid their attention to developing new packaging materials in which the package systems could extend the food shelf-life by keeping the food quality and tastes (Battisti et al., 2017). Also, the increase in consumer demands for healthy and safe food resulted in developing a new food packaging approach based on "active packaging" (Valerio et al., 2017). The main idea was to formulate new multifunctional active compounds in the polymer-based packaging to exploit their essential functions, including food containment and protection, by preserving food sensorial quality and safety, extending shelf-life, and retaining the beneficial effects of food products. This novel food packaging concept started to develop in the second half of twenty century by using natural and artificial additives in the package system (De Paoli, Aurelio, & Waldman, 2019). Over recent years, the new packaging trend has been designed to both using natural additives and ensuring maximum food safety also during transport, thus filling in the blanks of food protection. Actually, the bioactive additives, such as antioxidants, antimicrobials, flavors, and probiotics, represent an upcoming technological challenge for the food industry since their exploitation in polymer matrices avoids food deteriorations due to microbial proliferation and physical senescence. In this review, the antimicrobial, antioxidant, and plasticizing effects of natural additives in classified biopolymers for food packaging applications have been overviewed. Particular attention will be devoted to a detailed analysis of the secondary compounds by exploiting their bioactive and plasticizing action. Finally, a focus will be turned to novel plant metabolites evidencing excellent antimicrobial and plasticizing properties.

1.2. *Secondary compounds in food packaging polymers: functionalities and inclusion methods*

Generally, the natural additives used for food packaging improve the food properties by acting as antimicrobial, antifungal, and antioxidant agents able to preserve and extend the shelf-life of food exposed to the spoilage of several microbial strains. Simultaneously, the natural compounds affect the package physicochemical properties and functionality by acting as plasticizers, lubricants, nucleating and blowing agents, optical brighteners, ultra-violet light stabilizers, and flame retardants.

Based on the specific polymer systems used as the carrier of the bioactive compounds, different inclusion methodologies can be exploited:

a . Casting from solvent

This method consists of the solubilization of both biopolymer and natural additive in a common solvent and on the following casting, drying, and recovery of the doped film. Usually, the process occurs at room temperature and is particularly suitable for volatile and thermally unstable active compounds, such as essential oils and natural extracts (Ribeiro-Santos, Andrade, Melo, & Sanches-Silva, 2017). The above method can also be applied to obtain multilayer films or to develop coatings on preformed films obtained with different techniques.

b . Coating

In the coating technique, an active agent is immobilized on the surface of the biofilm. The main privilege of this technique is that the active agents can cover the inner layer of the package without interfering with the thermal or mechanical process, which results in preserving their highest activity in contact with the food surface (Santagata et al., 2018; Valerio et al., 2020). The coating solutions can be deposited through different techniques; the gravure coating technique affords several advantages. For instance, in this technique, the solvent is quickly removed by hot air and infrared lamps, thus supporting the formation of thin coatings (usually ranged between 0.2 and 2 μm). Biopolymer-based coatings deposited on a plastic substrate represent an efficient technique and a sustainable approach for the development of innovative packaging and a reasonable alternative solution to the plastic waste disposal issue, a crucial point at a European level.

c . Extrusion/blending

Extrusion is the most common and scalable method for incorporating the natural additive into the suitable biopolymer matrices for the industrial production of active packages. In this method, the active agent is mixed with a thermoplastic biopolymer inside an extruder. The active biofilms can be obtained by compression molding, or by film blowing process, or by casting from the melt. The foremost drawback of this technique is the high processing temperature, often not compatible with the thermal instability and high volatility of the natural compounds. Therefore, developing formulations able to protect them within an enclosed environment is considered an essential task.

To this aim, several strategies have been experienced, generally consisting of the encapsulation or physical protection of active additives in inorganic compounds like clay minerals. However, the addition of these compounds might affect the mechanical, optical, or barrier properties of the formulated films. Subsequently, in section (2.1.1), several examples related to thermoplastic bioactive biodegradable polymers will be detailed.

2. Secondary compounds effect in food packaging

2.1. Antimicrobial and antioxidants activity

The natural compounds, commonly used as antimicrobial, antifungal, and antioxidants additives in active food packaging, are mainly secondary metabolites and essential oils (EOs) isolated from plants and fungi. The natural compounds have potential applications in a wide range of fields such as agriculture (Johnson et al., 2018; Moeini et al., 2019), medicine (Mathieu et al., 2015), food packaging (Masi et al., 2017; Valerio et al., 2017), wound healing (Moeini, Pedram, Makvandi, Malinconico, & Gomez d'Ayala, 2020), cosmetic (Kusumawati & Indrayanto, 2013), pharmaceutical, and tissue engineering to develop skin scaffold (Ambekar & Kandasubramanian, 2019). However, most natural compounds cannot be used as they are in direct contact with food substrate to exploit their bioactivity, because of their low concentration, high volatility, tasting, smell. A valid and already investigated alternative is their incorporation in the packaging system. Many studies have recently focused attention on the formulation of active natural metabolites and essential oils (EOs) in biodegradable and edible active packaging. The inclusion can occur through physical interaction with the polymer matrix via blending or chemical immobilization via reactive processing. Thus, the antibacterial action can be obtained by a controlled release from the packaged materials to the food surface or by the action of the whole package system; in the last case, to the tuned antimicrobial effect, also joins the outstanding benefit of the hindering of additive migration into the food products, responsible of undesirable effects. Anyway, both methods are assumed to control the growth of undesirable microorganisms by modulating kinetics and mechanism (Huang, Qian, Wei, & Zhou, 2019). Among the common microorganisms that contaminate food and beverage products, *E. coli*, *Staphylococcus aureus*, *Campylobacter*, *Salmonella*, *Clostridium perfringens*, and *Bacillus cereus* are the widely diffused.

Different kinds of compounds have been used as antimicrobial agents, such as bacteriocins, organic acids, thiosulphates, spice extracts, enzymes, proteins, isothiocyanates, antibiotics, chelating agents, fungicides, parabens, and metals. (Ramos, Valdés, Beltrán, & Garrigós, 2016).

The studies in this field concentrate on exploiting natural compounds from different sources, like plants, animals, bacteria, algae, fungi, and by-products generated during fruit and vegetable processing (Ramos et al., 2016). The main target of active food packaging is to preserve food from microbial contamination, extending the food shelf-life and the inhibition mechanisms. The active agents' functionality is based on the migration of active compounds from the package to the food. Different parameters influence the migration kinetics and releasing mechanism: firstly, the polymer macromolecular structure, film physicochemical properties and thickness, as well as environmental parameters, such as pH and temperature, and the different food substrates undergoing specific bacterial spoilage (Ribeiro-Santos, Sanches-Silva et al., 2017).

Thus, many studies concern the broad range of antimicrobial and antifungal agents against various pathogenic and food spoilage microorganisms (Gram-negative, Gram-positive, and molds). So far, the studies found many plant extracts with potential applications in food packaging like blueberry (*Vaccinium corymbosum* L.), grapeseed, and green tea extracts that showed inhibitory effect against major foodborne pathogens: *Listeriaponocytogenes, Staphylococcus, Salmonella Enteritidis, Salmonella Typhimurium*, *Escherichia coli*, and *Campylobacter Jejun* (Shen et al., 2014). Besides, several studies investigated the antifungal activity of plants and fungal metabolites against *Penicillium roqueforti* and *Aspergillus niger*, the leading bakery products contaminant (Moeini, Cimmino, Masi, Evidente, & Van Reenen, 2020; Moeini et al., 2018; Santagata et al., 2017).

The essential oils (EOs) are oily aromatic secondary plant metabolites with low molecular weight, usually monoterpenes and sesquiterpenes. Because of presenting different active natural metabolites with different functional groups, EOs have various properties (antifungal, antioxidant, and antimicrobial). The most common essential oils with broad applications as active agents in food packaging are rosemary, cinnamon (cinnamaldehyde), tea tree, lavender, thyme oil (thymol and carvacrol), lemon, and citrus.

The cinnamon essential oil has the highest number of studies among other EOs in food packaging applications. The main compound in the cinnamon essential oil is cinnamaldehyde (CAL) or (2E)-3-Phenylprop-2-enal (55–76%), which is isolated from cinnamon trees, camphor, and cassia and used as an antibacterial and antifungal agent (Kenawy, Omer, Tamer, Elmeligy, & Eldin, 2019; Wasupalli & Verma, 2018). In this regard, Mohammadi et al. designed an active packaging system by incorporating chitosan nanofibers and cinnamon essential oil into whey protein films (Mohammadi, Mirabzadeh, Shahvalizadeh, & Hamishehkar, 2020). Both films (formulated by chitosan nanofibers and cinnamon essential oil) showed an inhibitory effect against *E. coli*, *S. aureus*, and *S. fluorescence* as a common psychrophilic bacterium (Mohammadi et al., 2020).

The other common EOs used in active packaging is rosemary essential oil isolated from Salvia rosmarinus or Rosmarinus officinalis, an evergreen native Mediterranean perennial plant. Since the potent antioxidant and antimicrobial properties against gram-positive and gram-negative bacterial strained, rosemary is widely applied as an active agent of food packaging. Choulitoudi et al. entrapped rosemary essential oil and its extracts in carboxyl methylcellulose (Choulitoudi et al., 2017). They evaluated the antioxidant and antimicrobial properties of this coating system for smoked eel. The antimicrobial test proved the activity of rosemary essential oil and its extracts in decreasing the rate of *Pseudomonas* spp. and lactic acid bacteria growth (Choulitoudi et al., 2017). Besides, the entrapped rosemary and extract in carboxyl methylcellulose confirmed the antioxidant protection to smoked eel (Choulitoudi et al., 2017).

Like the antimicrobial effect, the antioxidant action mechanism involves the releasing inside the package medium followed by absorption of undesirable compounds like oxygen, food-derived chemicals, and radical oxidative species by scavengers from the food surface and package environment. The mechanisms of natural antioxidants action are correlated to lipid oxidation reactions. Indeed, hydrogen peroxyl radicals, produced in the early stages, could react with atoms from phenol hydroxyl groups of the oxidation mechanisms to produce stable phenoxyl radicals able to avoid the lipid peroxidation chain reactions. However, phenolic compounds antioxidant activity mechanisms are strongly related to other vital factors, such as the electronic and steric effects of the strength of hydrogen-bonding interactions between the phenol and the solvent in the essential oil, ring substituents, as well as the interactions with matrix and food (Ramos et al., 2016).

Aimed at protecting additives from temperature or light, they are encapsulated in a protective polymer based structure and then incorporated in the biopolymer matrix (Ngamakeue & Chitprasert, 2016).

Natural antioxidants are mainly used for fresh foods like meat, fish, fruits, and processed and raw food (Domínguez et al., 2018). A wide range of literature data is recently related to the development of bioactive antioxidant food packaging materials (Han, Yu, & Wang, 2018; Li et al., 2016). In this regard, Catarino et al. prepared active packaging by formulating *Origanumvirens* essential oil in whey protein concentrate and coated two traditional Portuguese sausages (*paínhos* and *alheiras*) (Catarino et al., 2017). The treated samples inhibited microbial growth and significantly reduced the lipid peroxidation in *alheiras,* thus acting as antioxidants and antimicrobial agents (Catarino et al., 2017).

2.2. Secondary compounds as natural plasticizers

In this section, the different behavior of secondary compounds as plasticizers in active biofilms will be discussed. The food packages are strongly characterized by mechanical, optical, and gas barrier properties. Biopolymers are usually fragile and brittle with poor mechanical properties. These drawbacks strongly limited biopolymers' application in the food packaging industry. Therefore, plasticizers play a vital role in enhancing the biopolymers mechanical performance. The package mechanical properties are evaluated by means of the tensile test (ASTM D882, 2001), through evaluation of elastic modulus, stress, and strain at break (Atarés & Chiralt, 2016). Plasticizers are a class of low molecular weight non-volatile compounds widely used in polymer industries as additives able to improve both the flexibility and processability of polymers. The council of the IUPAC defines (International Union of Pure and Applied Chemistry) a plasticizer as "a substance or material incorporated in plastic or elastomer able to increase its flexibility, workability, or distensibility''. These substances reduce the tension of deformation, hardness, density, viscosity, and the electrostatic charge of the polymer whilst increase the polymer chain flexibility, resistance to fracture, and dielectric constant. The plasticizers are able to interpose among the macromolecular chains by decreasing their secondary forces and increasing both their free volume and macromolecular mobility. Thus, they reduce the polymer inter-intramolecular interaction and facilitate the formation of hydrogen bonding between the macromolecules, leading to the improvement of polymer mechanical performance. This behavior is evidenced by a decrease in melt viscosity, glass transition temperature, and elastic modulus of the film without altering the fundamental chemical character of the plasticized material. The degree of plasticization is directly correlated to the plasticizer's chemical properties, such as molecular weight, functional groups, and chemical composition so that the flexibility of the final products can directly depend on the types of plasticizer.

The choice of a suitable plasticizer cannot disregard from the physical compatibility with the polymer, including polarity, hydrogen bonding, and solubility parameters, as plasticizers should have similar polymer solubility parameters; thus, less energy to melt or solvate the polymer is required. The temperature of melting or gelation is linked to the plasticizer solvation strength and to the size of its molecule. Moreover, the plasticizers should not migrate or exudate from the polymer matrix. Hence, they should have low vapor pressure and low diffusion rate in the polymer. Besides, above a critical concentration, the plasticizer can exceed the compatibility limit with the biopolymer, and phase separation is usually detected in the form of exudate drops on the surface of the polymer, right after its blending or during final product application (Turco, Tesser, et al., 2019).

Thus, the amount of plasticizer, the structural properties of additives and biopolymers, and their functional groups are responsible for the goodness of their physical interaction. Thus, they should be strictly tuned in the plasticizer selection.

Plasticizers commonly used for biopolymers can be hydrophilic, such as glycerol, sorbitol, polyethylene glycol, and hydrophobic, such as fatty acids and essential oils (EOs) (Gómez-Estaca, Gavara, Catalá, & Hernández-Muñoz, 2016). Natural metabolites and essential oils from plants can be used as plasticizers for biopolymer-based films and coatings production since they can improve flexibility and handling of films, preserve their integrity by avoiding pores and cracks in the polymeric matrix. However, in comparison with conventional plasticizers, natural compounds may have an unpredictable impact on the package structure and the mechanical properties since their complex composition (Atarés & Chiralt, 2016). Actually, the mechanical properties of plasticized films depend on different parameters, such as the polymer matrix structure, the preparation technique, and the physical interactions occurring between polymer and plasticizer functional groups. In some cases, in a particular polysaccharide-based biopolymer, the tensile strength is decreased because of the replacement of strong polymer-polymer bonds with hydrogen bonding between polymer and plasticizers (Atarés & Chiralt, 2016). In this concern, Hosseini et al. formulated *Origanum vulgare* L. essential oil in the fish gelatin-chitosan blend by casting method (Hosseini, Rezaei, Zandi, & Farahmandghavi, 2015). The tensile test showed a noteworthy decrease in tensile strength (TS) and elastic modulus (EM) in favor of elongation at break increasing (Hosseini et al., 2015). In another study, Otoni et al. incorporated carvacrol and cinnamaldehyde into soy protein by casting method. Tensile tests evidenced a strong plasticizing effect exploited by EOs as shown by the reduction in tensile strength and increase in their strain at break (Otoni, Avena-Bustillos, Olsen, Bilbao-Sáinz, & McHugh, 2016). Shojaee-Aliabadi et al. showed that the inclusion of Satureja Hortensis EO extracted from the savory genus in k-carrageenan films improved their mechanical properties plasticization (Shojaee-Aliabadi et al., 2013).

On the other hand, some studies proved that secondary compounds and EOs could increase the tensile strength of the biofilms, probably due to the development of crosslinking junction points (Bonilla & Sobral, 2016).

In these cases, EOs act as reinforcement agents that can increase the intermolecular binding resulting in improved mechanical strength (Garavand, Rouhi, Razavi, Cacciotti, & Mohammadi, 2017). Similarly, EOs with phenolic compounds could act as crosslinkers in protein-made films. Likewise, *Citrus aurantifolia* incorporated in starch/gelatin blends evidenced an improvement of mechanical properties because of the presence of citric acid acting as a cross-linker agent in the blend (Kanatt, 2020).

3. Biopolymers in food packaging

According to the European Bioplastics, biopolymers are biodegradable, biocompatible, and compostable polymers derived from renewable resources (Santagata et al., 2017). They can be considered the most promising alternative for synthetic polymers in the food packaging industry and can be classified as thermoplastic and hydroplastic biopolymers (Fig. 1). In general, working with biopolymers is always a challenge for researchers since their concern in optimizing the physicochemical and mechanical properties. In the following sub-sections, a brief description of the most common biopolymers has been detailed.

3.1. Thermoplastic polymers in food packaging

3.1.1. Thermoplastic starch

Thermoplastic starch (TPS) is a hydrophilic biopolymer obtained from the gelatinization process of starch. It results from the physical modification of native starch into a thermoplastic polymer. Indeed, starch granules exhibit hydrophilic properties and strong intermolecular association via hydrogen bonding formed by the hydroxyl groups on the granule surface. Moreover, starch granules cannot be processed by conventional processing techniques due to the thermal decomposition of starch before its melting point. Thus, it is necessary to use plasticizers to transform starch into a thermoplastic polymer. Indeed, when it is mixed with some water and/or plasticizers such as glycerol and subjected to heat and shearing action, the intermolecular and intramolecular hydrogen bonds in the starch break down and undergo a spontaneous destructuring. The thermal process leads to a homogeneous melt evidencing typical thermoplastic and amorphous behavior. This process, known as gelatinization of starch, leads to the final upgraded thermoplastic starch (TPS), whose processing methodologies fit with those of conventional thermoplastic polymers. The structural modification of starch induces strong hydrophilicity responsible for TPS fast degradation via hydrolysis. Hence, the potential applications severely confine to a few sectors (Turco, Ortega-Toro et al., 2019). To overcome this drawback, Novamont company (Novamont S.p.A.), under the Mater-Bi trademark, manufactured TPS blend with the polyesters or vinyl alcohol copolymers by targeting the new products to the packaging market, such as packaging materials, disposable cutlery, consumer goods.

3.1.2. Poly (lactic acid) (PLA)

Poly (lactic acid) PLA is obtained from lactic acid (2-

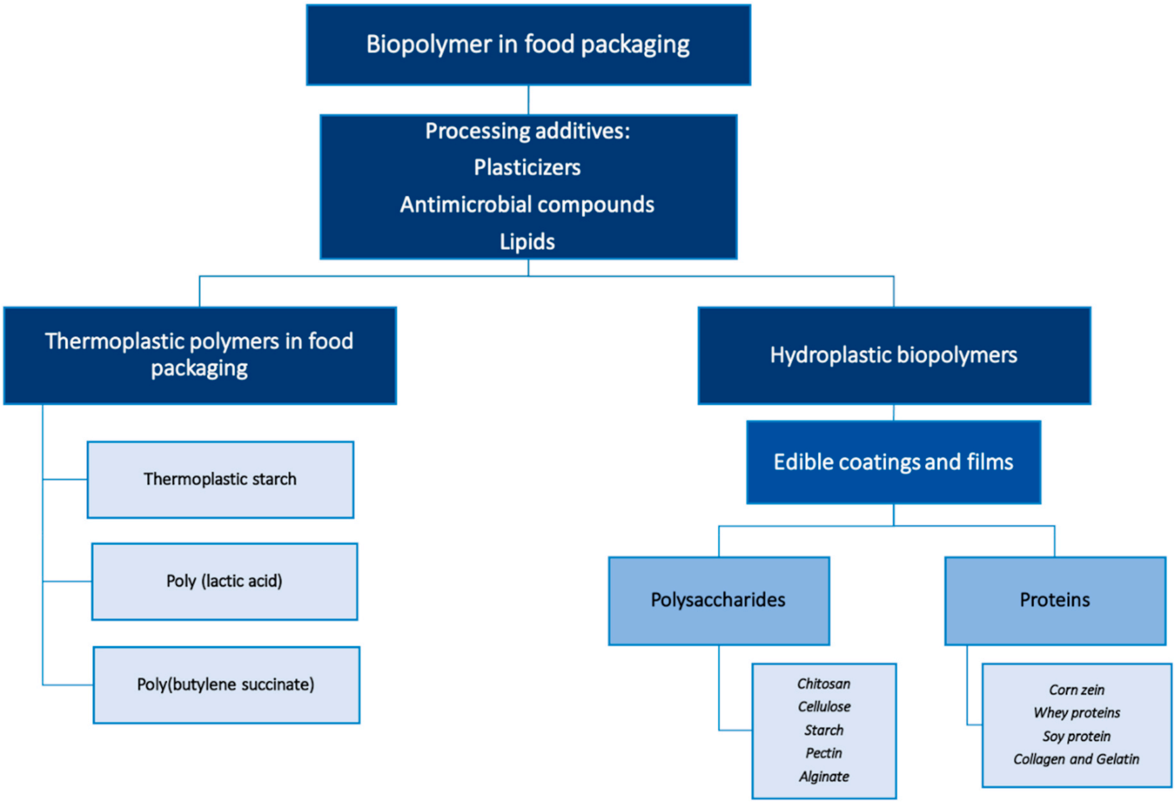

Fig. 1. The classification of biopolymers in food packaging.

hydroxypropanoic acid) (LA), a monomer existing in two enantiomeric forms, L-lactic acid and D-lactic acid, and mainly produced by the process of microbial fermentation of starch plants, such as maize, cassava, sugarcane, and sugar beet. Although 90% of total LA is obtained by bacterial fermentation, the other 10% is synthetically produced by hydrolysis of lactonitrile.

From lactic acid, chemical treatments link up the molecules into long chains or polymers, thus providing biodegradable aliphatic polyesters with three stereoisomers (poly(L-lactide) (PLLA), poly(D-lactide) (PDLA), and poly (DL-lactide or Meso-lactide)) (Fig. 2).

PLA properties, such as stiffness, tensile strength, stability, transparency, and gas permeability are comparable to those of synthetic polymers from fossil fuels, such as polyethylene (PE), polypropylene (PP), polystyrene (PS), and polyethylene terephthalate (PET) (Turco, Tesser, et al., 2019). Moreover, PLA can be processed by using the existing equipment of the conventional plastics manufacturing industry. PLA safety for food packaging application was approved by the United States Food and Drug Administration (FDA) (Moeini, Cimmino, et al., 2020; Moeini, van Reenen et al., 2020). Therefore, the application of PLA in the food packaging industry has developed as disposable cutlery, drinking cups, salad cups, plates, overwrap and lamination film, straws, stirrers, lids and cups, plates, and containers for food dispensed at a grocery to fast-food establishments. However, the high cost and drawbacks, such as brittleness, low flexibility, and low degradation rate, sharply reduce PLA use in engineering. Considerable efforts have made to improve PLA performance; the blending with other natural polymers, such as thermoplastic starch (TPS), could represent strong support to both obtain cost-effective biopolymer-based systems and enhance biodegradability without compromising environmental and carbon management benefits, but reaching improved mechanical properties (Turco, Ortega-Toro et al., 2019). The addition of plasticizers to improve PLA mechanical performances is a widely spread method in the plastics industry; nevertheless, it should meet several requirements when food packaging materials are concerned. Indeed, it should be compatible with the polymer, non-toxic, and biodegradable. The enormous demand for new “green” plasticizers shifted the focus on natural-based resources, such as vegetable oils, eco-sustainable, biodegradable, non-toxic plasticizers from readily renewable sources (Moeini, van Reenen et al., 2020; Turco, Ortega-Toro et al., 2019).

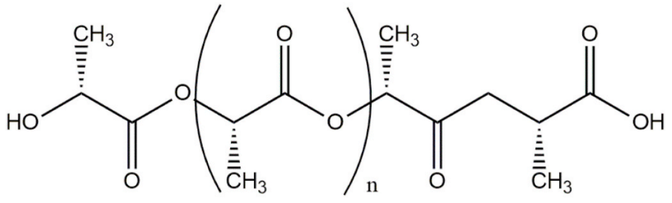

Fig. 2. High molecular weight PLA.

3.1.3. *Polybutylene succinate (PBS)*

Among available biodegradable polymers, poly(butylene succinate) (PBS), a semi-crystalline aliphatic thermoplastic polyester, represents one of the most exploited bioplastics material due to its relatively good melt processability, thermal and chemical resistance, biodegradability, and excellent mechanical properties, strictly comparable to those of the widely-used polyethylene (PE) and polypropylene (PP) (Gumede, Luyt, & Müller, 2018). It is synthesized via polycondensation of succinic acid and 1,4- butanediol, i.e., from monomers currently obtainable from renewable resources, in this way providing up to 100% bio-based improved carbon footprint polyester (Fig. 3). Different methods can be employed for processing thermoplastic PBS, such as blown films, fibers spinning, injection molding, and blow molding, which make this biopolymer suitable for a wide range of applications from electronics, agricultural mulching films to packaging materials. As concerning the packaging applications, PBS is commonly used as packaging bags, netting, foam trays for fresh food (meat, fish, vegetables, and fruits), and cutlery, filaments, blown bottles, hygiene commodities (Mallardo et al.,

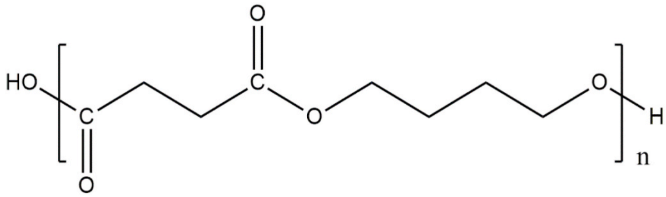

Fig. 3. Poly (butylene succinate) structure.

2016).

Furthermore, the use of PBS as a bioactive packaging film, including antimicrobial and antifungal compounds, is widely reported (de Matos Costa et al., 2020; Mallardo et al., 2016; Santagata et al., 2017).

3.2. Hydroplastic polymers in food packaging: edible coating and films

A novel approach exploited in the frame of the food packaging material can be represented by edible coatings. They are defined as thin layers of edible polymer applied to the surface of the food to improve the quality of products via shielding them from natural deterioration processes due to oxidation, moisture absorption/desorption, microbial growth, and chemical reactions. Moreover, they act as barriers against oils, gas, or vapors and as carriers of bioactive compounds like antioxidants, antimicrobials, and plasticizers able to tune the physical strength of the food products by reducing the particle clustering and enhancing the visual and tactile features of food surfaces (colors, and flavors). Thus, edible coatings improve the quality of food products, resulting in their extended shelf-life. Since the edible coatings must eat as part of the total product, their composition must conform to the regulation applied to the food product; for this reason, edible biopolymers, such as polysaccharides, protein, lipids, and food-grade additives, as antimicrobial agents and plasticizers, are the main constituents of the coating packages. Direct contact with the food and the edible coating requires protection against microbial activity. Hence, most of the time, an antimicrobial agent is incorporated inside coating formulations, providing self-protection against the bacterial load on the food surface and preserving the outer surface of the food with antimicrobial properties. Thus, the edible coatings can be considered an application of active food packaging because their edibility and biodegradability are functions beyond the package's necessity.

Therefore, active secondary compounds can be formulated into edible coating; nonetheless, the function and performance of edible films depend on the specific preparation method (temperature, pH, cross-linking or enzymatic reactions, drying process) and on the kind of interaction (covalent bonds, disulfide bond cross-linking, ionic bonds, and H-bonding) occurring between biopolymer, food substrate and active agents (Salgado, Ortiz, Musso, Di Giorgio, & Mauri, 2015).

The control of these parameters is crucial since any changes in treatment conditions can alter kinetics and reaction mechanisms. Generally, bioactive edible coatings are dry, even if wet coatings are used when functional agents as probiotics are included (Valerio et al., 2020).

However, wet systems need another wrapper. Thus, it couples with a secondary external packaging, which improves both the efficiency of kinetics bioactivity and the food preservation from external contamination. Nevertheless, the multilayer packaging complexity should be overcome by optimizing the properties of single-layer package properties.

Numerous studies concern the film-forming ability of biopolymers to be exploited as food packaging materials; they are mainly based on polysaccharides and proteins (Moghadam, Salami, Mohammadian, Khodadadi, & Emam-Djomeh, 2020). The most edible biopolymers for packaging applications are polysaccharides, proteins, and lipids. Different classes of edible biopolymers, along with the well-known examples of each group with film-forming ability, will be discussed in the following part.

3.2.1. Polysaccharides

Polysaccharides are the earliest and most extensively investigated biopolymers for packaging. Several studies reported that polysaccharides from different sources are promising materials for preparing films and coatings with tailored behavior (Gao, Pollet, & Avérous, 2017). It is not surprising to consider that they are natural, non-toxic, easily accessible, and renewable biodegradable polymers. Different kinds of polysaccharides and their derivatives have been potentially used as biodegradable/edible films, including alginate, chitosan, cellulose, starch pectin, alginate, and carrageenan (Santagata et al., 2018).

Polysaccharides are biopolymers with saccharides units linked via glycosidic bonds. The hydroxyl groups in polysaccharides lead to their hydrophilic nature and hydrogen bonding, responsible for the inter-intra macromolecular association and film-forming properties. Due to the plenty amount, low cost, fair mechanical, and gas barrier properties, polysaccharides could be considered a valid alternative to synthetic polymers, especially for short-term bioactive, biodegradable food packaging materials.

3.2.1.1. Chitosan (CH). Chitosan or β-(l-4)-2-amino-2-deoxy-D-glucopyranose, a cationic linear polysaccharide, consists of N-acetyl-glucosamine and N-glucosamine units; it derives from N-deacetylation of chitin, the second abundant polysaccharides present in nature after the cellulose. The primary sources of chitin are the shrimp shell wastes, lobsters, crabs peritrophic membranes, and cocoons of insects (Moeini, Pedram, et al., 2020; Nesic, Moeini, & Santagata, 2020). The chitin synthesis follows a common pathway that ended by enzymatic polymerization of N-acetylglucosamine. Due to the abundance, low cost, and good chemical and biological properties, chitosan is widely used in medicine, cosmetics (Straccia, Romano, Oliva, Santagata, & Laurienzo, 2014), agriculture (Malinconico, Cerruti, Santagata, & Immirzi, 2014), nutrition (Moeini et al., 2018), and several other application. The US Food and Drug Administration (FDA) has considered chitosan a safe material for foods since 2001 (Bellich, D'Agostino, Semeraro, Gamini, & Cesàro, 2016). The CH film-forming ability and antimicrobial activity against food-borne filamentous fungi, yeast, and gram-negative and gram-positive bacteria, were proved in many studies (Cazón, Velazquez, Ramírez, & Vázquez, 2017). For example, edible chitosan coatings provide more inhibitory effects against spoilage and pathogenic bacteria on fresh food substrate, such as fruit (Rayees, Maqsood, Shaeel, & Muneer, 2013). Thus, chitosan can be a potential natural fungicide in pre-harvest fruit control and an effective preservative edible coating material to improve post-harvest fruit quality and shelf life. Indeed, the suitable combination of chitosan pre-harvest spray with post-harvest chitosan coating can significantly reduce grapes decay than pre-harvest treatment alone. Hence, chitosan can be a challenging edible coating in commercial pre-post-harvest applications for prolonging the shelf-life of fruits before and during cold storage. It is able to provide excellent mechanical properties by improving the firmness of post-harvested fruit (Romanazzi, Feliziani, Baños, & Sivakumar, 2017). The homogeneous distribution of chitosan coating and its mechanical resistance on food substrate can be supported by improving physical interaction between chitosan macromolecules and food substrate. In particular, the inclusion of oily antibacterial compounds in chitosan solution could enhance the surface adhesive properties of the edible coating on lipophilic surfaces, such as peel fruits. In addition, bioactive oils can prolong the safety and quality of fresh fruits. For example, bergamot oil enhanced chitosan antimicrobial activity and evidenced the proper O_2 and CO_2 gas barriers (Sánchez-González, Cháfer, Hernández, Chiralt, & González-Martínez, 2011). Several studies investigated the natural metabolite effects in chitosan as a polymer matrix for active food packaging application (Moeini et al., 2018; Moeini, Mallardo, et al., 2020).

3.2.1.2. *Cellulose.*

Cellulose or (1 → 4)-β-ᴅ-glucopyranosyl is a water-insoluble linear chain polysaccharide. The esterification can enhance water solubility. The leading cellulose derivatives with film-forming ability are carboxymethyl cellulose, hydroxypropyl methylcellulose, hydroxypropyl cellulose, and methylcellulose (Han et al., 2018). Carboxymethyl cellulose films are tasteless, odorless, transparent, and show excellent gas barriers (Chiumarelli & Hubinger, 2012). In this regard, Dashipour et al. evaluated the antimicrobial and antioxidant activity and film-forming ability of carboxymethyl cellulose by formulating *Zataria multiflora* essential oil into the polysaccharide (Dashipour et al., 2015). The bioactive films evidenced antimicrobial inhibition against *P. aeruginosa, S. typhimurium, E. coli, B. cereus,* S. aureus, and antioxidant activity evaluated phenolic content in the films (Dashipour et al., 2015).

3.2.1.3. *Starch.*

Starch, a wholly biodegradable polysaccharide biosynthesized by numerous plants, like maize, wheat, potato, rice, pea, etc., is one of the most plentiful renewable feedstock resources known to man and the primary energy reserve of the plant kingdom. The native starch consists of a mixture of amylose, a linear polysaccharide with (1 → 4)-α-ᴅ-glucopyranosyl units, and high molecular weight amylopectin, branched amylose with (1 → 6)-α- ᴅ-glucopyranosyl side units (Samsudin & Hani, 2017). Thanks to its biodegradability, renewability, and easy availability, starch has been extensively studied as a low-cost biodegradable plastic and food hydrocolloid component. Also, starch is helpful for food preservation purposes due to its extensive versatility and functionality, relatively low cost, and high ability to form transparent, odorless films with excellent oxygen barrier properties. Thus, starch-based coatings can increase the shelf life of fruits, vegetables, and other products. Actually, of the two starch polymers, amylose shows a tight and packed crystalline structure with the ability to form films and coatings (Acosta, Jiménez, Cháfer, González-Martínez, & Chiralt, 2015). Moreover, Nawab et al. showed that sorbitol inclusion in the starch-based formulation played a crucial role in water loss restriction and mechanical firmness preservation (Nawab, Alam, & Hasnain, 2017).

Actually, due to the high hydrophilicity, starch-based coatings exhibit poor water vapor barrier properties (Hassan, Chatha, Hussain, Zia, & Akhtar, 2018). In order to overcome this drawback, hydrophobic substances can be incorporated into the coating formulation (Cazón et al., 2017). Usually, lipids inclusion in polysaccharide-based coatings supports the decreasing water evolution from the coating and, if opportunely tuned, positively affects the gas exchange (Perdones, Chiralt, & Vargas, 2016).

During storage, perishable food, such as fruit and vegetable, are often subjected to microbial attack, mainly due to phytopathogenic fungi. The inclusion of antifungal compounds, such as organic acids and various plant extracts or essential oils in the starch-based coating, creates a natural barrier against bacterial flora, prolonging the postharvest shelf-life of fruit and vegetable (Sapper & Chiralt, 2018). The active essential oils, such as carvacrol, thyme oil, cinnamon, eugenol, lemon essential oil, enhance the antimicrobial activity while reducing starch both hygroscopic behavior and cost (Marín, Atarés, & Chiralt, 2017). Finally, edible coatings based on starch derivatives, such as hydroxypropylated high amylose starch, have been used to protect bakery products (Galus, Arik Kibar, Gniewosz, & Kraśniewska, 2020). However, starch films are usually employed in confectionery, batters, and meat products as well.

3.2.1.4. *Pectin.*

Pectin is the main component of the plant cell wall, contributing to tissue integrity and rigidity. Structurally, pectin is poly α 1-4-galacturonic acids, showing some modification of carboxyl groups in methoxylated residues, occurring by esterification with methanol of carboxyl groups, and/or amidated carboxyl group obtained when some of the galacturonic acids convert with ammonia to a carboxylic acid amide (Nešić et al., 2017). According to the esterification degree (DE), i.e., the ratio between esterified galacturonic acid groups to total galacturonic acid groups, pectin can be classified as high methoxyl pectin (HMP) with more than 50% of methoxylated residues (DE > 50) and low methoxyl pectin (LMP) showing DE < 50 (Ye et al., 2020). DE strongly affects pectin gelling properties. The main natural and industrial sources of pectin are apple pomace and citrus peels (Zannini, Dal Poggetto, Malinconico, Santagata, & Immirzi, 2021). Pectin is widely used in the food industry as a gelling, stabilizing, and thickening agent of jams, yogurt drinks, fruity, milk drinks, and ice cream. Indeed, it is recognized as a safe ingredient (GRAS) by the FDA (Part 184: Direct food substances affirmed as generally recognized as safe). In general, edible films are developed with the specific aim of vehicle functional additives over the food. Among them, antimicrobial agents are commonly used. In their paper, Santagata et al. used pectin-honey-based coatings as a novel method to dehydrate the cut fruits and protect them from the microbial attach of Pseudomonas and Escherichia coli bacteria. Pectin-honey coating was tested on several fruits, such as apple, cantaloupe melon, mango, and pineapple, evidenced bioactive properties, enhanced dehydration percentage, enriched polyphenol and vitamin C contents, improved both antioxidant activity and volatile molecules profile (Santagata et al., 2018). In another paper, Valerio et al. developed a pectin-coated dehydrated apple snack containing probiotic cells of Lactobacillus paracasei IMPC 2.1. They morphologically evidenced the presence of the apple surface strain even after 30 days of storage at 4 °C; as concerning the antioxidant properties, the author demonstrated that pectin-coated apple slices preserved the color parameters of fresh fruit pieces and suitable radical scavenging activity. In addition, the enhancement of total phenol content was evidenced together with the ability of the strain to deliver bacterial cells in a viable form to the gastro-intestinal tract by surviving in the digestive process (Valerio et al., 2020). Several investigations have been performed to enhance pectin-based coating properties. In particular, to improve the mechanical stability of the film and its surface adhesion on the food substrate, food-grade plasticizers, and more flexible polymers are usually added in pectin water solutions before the coating development. Thus, plasticizers, such as glycerol, polyethylene glycol, and sucrose, are mainly used. The key role of the plasticizers is to reduce the intra-inter molecular interaction force of pectin chains in favor of macromolecular mobility rising and mechanical performance enhancement. Also, the introduction of plasticizers and flexible polymers, such as poly (vinyl alcohol) (PVOH), water-soluble cellulose derivatives, carboxymethylcellulose, starch, allowed to prepare pectin-based coating also by means of the extrusion process. Being hydrophilic and hygroscopic, pectin films evidence poor moisture barriers, which results in food dehydration. A valid alternative to overcome this drawback is developing pectin-based films, including hydrophobic compounds such as lipids. In contrast to polysaccharides and proteins, lipids are hydrophobic molecules usually employed for avoiding water permeability throughout hydrophilic membranes. Hence, lipids application aims to incorporate edible films to provide the required moisture barrier. However, the non-polymeric nature of lipids limits their homogeneous distribution inside the film. As a result, cohesive separated clusters form, which is responsible for hindering a suitable moisture barrier. Besides, lipids reduce the food sensorial quality by changing the flavor and the film optical performance by reducing transparency (Tavassoli-Kafrani, Shekarchizadeh, & Masoudpour-Behabadi, 2016). Finalized to develop functional pectin coating with high water barrier properties, bioactive hydrophobic compounds, such as natural antioxidant vegetable oils, natural flavoring food-grade substances, can be added to the pectin-based formulations (Otoni et al., 2017). Among them, oregano, cinnamon, or lemongrass essential oils are widely used, evidencing antimicrobial activity against several bacteria strains, such as *Escherichia coli* Salmonella enteric and *L. monocytogenes*. Du et al., found that the antimicrobial compounds were stable at 5 °C and 25 °C and active even over 98 days (Du et al., 2008). Nonetheless, like lipids, natural oils are inclined to coalesce in discrete macro-domains, in this way strongly worsening the moisture-barrier properties of the film. In both cases, the inclusion of an emulsifier, i.e., a surface-active compound with both polar and non-polar molecular structures, strongly improve oil and lipid dispersion, thus improving mechanical properties while reducing water permeability.

3.2.1.5. Alginate. Alginates are linear water-soluble polysaccharides comprising (1–4)-linked units of α-D-man uronate (M) and β-L-guluronate (G) at different proportions and different distributions in the chain. They mainly derive from brown algae belonging to the *Phaeophyceae* family but can also be recovered from the metabolic products of some bacteria. The chemical composition and sequence of the M and G residues depend on the biological source and the plant maturation. M/G ratio and sequential distribution are responsible for the physical and chemical properties of alginates, as well as of their application performances. Actually, alginates are well-known natural ionic polysaccharides mainly used as food additives, thickeners, gelling agents, and carriers in drug delivery. The high interest in this family of polysaccharides is strictly related to the gelling properties. Alginate solutions can form gels either by lowering the pH below the pKa value of the uronic residue or in the presence of divalent ions. The divalent ions cooperatively interact with blocks of guluronic units to form ionic bridges between different chains. The most popular model accounting for the chain-to-chain is the "egg-box model." In this model, the G-blocks form a three-dimensional arrangement in which Ca ions are embodied in cavities like eggs in a cardboard egg box (Straccia et al., 2014). Most of the chemico-physical properties of alginate-based films and coatings are strictly correlated to the crosslinking network formed in the presence of divalent cations (Nešić et al., 2017). Just to give an idea, Zactiti and Kieckbusch evidenced that by increasing the concentration of Ca^{+2}, alginate swelling degree and solubility decreased; as concerning mechanical properties, by increasing the crosslinking network, the elongation of the alginate films decreased while the tensile strength increased (Zactiti & Kieckbusch, 2009).

Sodium alginate-based edible films and coatings have been widely used for several food packaging applications. As an example, promising results have been achieved on fresh fruits coated with alginate solution; the coating was able to reduce the water permeability of fresh-cut fruits with high moisture surfaces (Campos, Gerschenson, & Flores, 2011). Further developments could be attained by incorporating antimicrobial compounds into the solution to protect against microbial contamination, thus enhancing food safety and stability. Moreover, several antimicrobial and antioxidant agents have been incorporated into alginate-based edible films and coatings in order to develop bioactive polymeric systems.

Bazargani-Gilani showed that sodium alginate-based edible coating, including resveratrol, a natural antimicrobial and antioxidant metabolite, provided a bioactive coating for increasing the shelf-life of trout fillet during refrigerated storage. Indeed, complete inhibition of *Enterobacteriaceae*, *Pseudomonas* spp., lactic acid bacteria, and yeasts was observed after 15 days of storage at 4 °C, in this way evidencing that sodium alginate-based edible coating in combination with resveratrol provided a kind of active coating, applicable as a safe preservative with extended health benefits for the fish under refrigerated storage (Bazargani-Gilani, 2018).

Peretto et al. used specific carvacrol and methyl cinnamate concentrations in alginate coatings to optimize their antibacterial activity against *Escherichia coli* and *Botrytis cinerea* bacteria of strawberry fruits. Indeed, the bioactive alginate-based coatings exploited on post-harvest crops were really effective in protecting strawberries from microbial spoilage, thus preserving their overall quality (Peretto et al., 2014).

3.2.2. Proteins

Proteins are promising edible biopolymers showing interesting properties, such as excellent mechanical, physicochemical, optical performances, and a selective and excellent gas barrier, quite similar to the ones of polyvinyl chloride (Ribeiro-Santos et al., 2018). Several proteins like corn-zein, whey protein, and gelatin are produced at low cost and are commonly used in the food industry; following a brief description of the above protein-based films and coating in the presence of natural antimicrobial additives are reported.

3.2.2.1. Corn zein. Zein is a natural protein of corn seeds. As a raw material, it contributes to the food packaging market through the protein fraction, adding more financial value to the milling industries and grain producers. The hydrophobic nature of zein is because of the presence of non-polar amino acids (Sahraee, Milani, Regenstein, & Kafil, 2019). This hydrophobic characteristic makes zein a good candidate for developing natural biopolymer edible films and coatings suitable for foods exposed to moisture. Indeed, the film formation is due to the hydrophobic, hydrogen, and disulfide bonds between zein chains during solvent evaporation.

For this reason, zein-based films could act as barriers to oxygen, carbon dioxide, and oils. There are several studies related to the use of corn zein as antibacterial edible and preformed films. Ghasemi et al. included *Zataria multiflora boiss* essential oil inside the protein films to preserve Feta cheese, usually affected by microbial spoilage. The inclusion of this bio preservative agent in corn zein-based films made them resistant against *S. enteritidis, L. monocytogenes*, *S. aureus,* and *E. coli* growth and to extend cheese shelf-life during 70 days of storage (Ghasemi, Haji Seyed Javadi, Moradi, & Khosravi, 2015).

Moreover, it is worthy of underlining that the fragile nature of zein films can compromise their wide application, making it necessary to add plasticizers. To this aim, the essential oils can provide suitable mechanical properties while guaranteeing food protection against microbial spoilage deterioration. This outcome was reported by Pereira et al. In their paper, the authors evaluated the antimicrobial and mechanical properties of thyme (Thymus vulgaris) and garlic (Allium sativum) essential oils on the zein films. Four bacteria (the same ones used by the previous authors) related to food contamination were chosen to evaluate the antimicrobial properties. The results indicated that the inclusion of the oil to the zein films showed inhibitory activity against all the tested bacteria; in addition, the essential oils acted as a suitable plasticizer, as evidenced by the decreasing of glass transition temperature and Young's Modulus of the films, increasing of the puncture resistance and decreasing of the mechanical cracks. Moreover, the addition of the oil also resulted in lower film solubility and water absorption. This study highlighted that thyme and garlic EOs could promote the biopolymer coating properties, contribute to the food quality, and extend the food shelf-life (Pereira et al., 2019).

3.2.2.2. Whey proteins. Cheese whey, produced in large amounts as a by-product in the cheese-making process, shows excellent functional properties and produces edible films and coatings. Utilization of whey excess in the form of whey protein concentrate could effectively support the whey disposal problem by the conversion of whey into value-added products, such as edible films and coatings. Based on the protein content, the powder is called either whey protein concentrate (25%–80%, WPC) or whey protein isolate (WPI), which contains >90% protein on a dry weight basis. Whey protein isolates (WPI) are the purer form of whey proteins and evidence excellent film-forming, producing transparent and flavorless films (Ozer, Uz, Oymaci, & Altinkaya, 2016). The hydrophobic amino acid content strongly influences the whey protein solubility. Protein-protein interaction in an aqueous medium is accelerated by hydrophobic interactions between the non-polar groups on the protein. The presence of hydrophobic groups as disulfide bonding increases film stiffness, water insolubility, and elasticity (Calva-Estrada, Jiménez-Fernández, & Lugo-Cervantes, 2019). WPI based films are excellent carriers of food additives as antimicrobials and spices to improve their functionality. In particular, whey protein films are good vehicles to incorporate antimicrobial compounds, for example, plant-derived essential oils and bacteriocins. Badr et al. used whey protein films containing essential oils of cinnamon, cumin, and thyme to wrap fresh beef cuts (Badr, Ahmed, & ElGamal, 2014). The effectiveness of these films against beef bacterial flora spoilage during storage at 5 °C for 12 days was investigated, and the results revealed that in some formulations containing 2.5 %w/w of essential oils, the shelf-life of the edible wrapping doubled the fresh beef cut preservation. In addition, the mechanical properties of oil-doped whey films strongly improved, as previously evidenced by the same authors (Badr, Ahmed, & Gamal, 2013).

3.2.2.3. Soy protein. Soy protein, isolated from soybean (SPI), is commercially produced in three different concentrations of soy flour (50–59%), (65–72%), and (>90%). It is widely applied as a food ingredient in almost all food products available for the consumer because of its high nutrition and excellent functional properties. In particular, soy protein films can be applied to all high water-permeable food, such as meat, fresh bakery products, vegetables, and cheese, due to its general both polar and non-polar side chains. Actually, the polar nature of soy protein results in the hydrogen bonding between side chains that limit the segmental rotation and molecular mobility, in this way increasing the stiffness, yield point, and tensile strength of soy protein films (Chen et al., 2019). Most of the soy protein films are based on highly refined soy protein containing 90% protein, at least obtained by removing the great mass of non-protein components, carbohydrates and fats through isoelectric precipitation (Tian et al., 2018).

The most common method used to prepare soy protein films is the casting from solvent. Since the specific hydrophobic interaction between the protein chains and disulfide bonds, soy protein films have many functional characteristics, such as adhesiveness, dough, emulsification, water, fat absorption, fiber formation, and texturizing capability (Chen et al., 2019). SPI films show moderate mechanical properties, good barrier properties against oxygen while being impermeable to lipids; thus, they can be used for food packaging (Gómez-Estaca et al., 2016). However, SPI is very easily contaminated by bacteria. Therefore, it is a key point to support SPI-based films with antibacterial properties to prolong food shelf-life. Liang and Wang prepared an active film in their study by incorporating different amounts of cortex Phellodendron extract, a natural antibacterial-antioxidant agent, into soybean protein isolate films. The films were active against Staphylococcus aureus (*S. aureus*, Gram-positive bacteria). They also analyzed the chemico-physical properties of the films following the physical interaction occurring between the natural additive molecules and protein chains, leading, by the way, to a slight increase of tensile strength and decrease of barrier properties (Liang & Wang, 2018).

In another study, the antibacterial activities of thyme (Thymus vulgaris L.) and oregano *(Oreganum heracleoticum* L.) essential oils incorporated in soy protein-based edible films were tested against Pseudomonas spp. and coliform bacteria of ground beef patties during refrigerated storage. It was shown that experimental conditions, such as low pH, high protein concentration, and moderate levels of simple sugars, positively influenced the antibacterial properties (Gutierrez, Barry-Ryan, & Bourke, 2009). In another paper, González-Estrada et al. investigated the potential application of SPI-coatings forming solutions incorporated with citral and limonene for post-harvest quality of Persian lime and evaluated the antifungal activity of these coatings against *P. italicum* in inoculated lime. The post-harvest protection analyses demonstrated the effectiveness of the SPI-coating as a carrier of antimicrobial compounds and the efficacy of the limonene against fungal growth (González-Estrada, Chalier, Ragazzo-Sánchez, Konuk, & Calderón-Santoyo, 2017).

3.2.2.4. Gelatin. Among biopolymers and hydrocolloids, gelatin is unique since it forms a thermo-reversible gel with a melting point close to body temperature. Therefore, gelatin widely applies in foods, dietary, and pharmaceuticals (Ramos et al., 2016), where protective coating and bioactive compound carriers are required (Nur Hanani, Roos, & Kerry, 2014).

Gelatin is widely found in nature as the major constituent of skin, bones, and connective tissue obtained by controlled hydrolysis from the fibrous insoluble protein and collagen (Shankar, Jaiswal, & Rhim, 2016). Gelatin with a hydrophilic character is a unique sequence of amino acids, such as glycine, proline, and hydroxyproline. Due to its peculiar structure, at approximately 40 °C, gelatin aqueous solutions are in the sol state while on cooling, the chains undergo a conformational disorder–order transition and tend to recover the collagen triple-helix structure because of the cross-linking process involving amino and carboxyl groups of amino acid and side residues. The formed gel is thermoreversible, and this behavior plays a key role in the widening applications of this protein for the encapsulation of oil and drugs. The encapsulation provides oxygen and light protection. In addition, gelatin films were formed as coatings on meats to reduce oxygen and water permeability and to vehicle the oil (Ramos et al., 2016). However, as occurring with most protein films, the edible application of gelatin films is still restricted because of a scarce water vapor barrier. The inclusion of antibacterial oils can support both bioactivities of gelatin-based films and their barrier properties. Several research investigations evaluated the effect of the addition of crosslinkers, strengthening agents, plasticizers, natural antimicrobial or antioxidant additives, in gelatin-based film coatings to improve the functional and chemico-physical performances of gelatin and the shelf-life of food products (Ortiz-Zarama, Jiménez-Aparicio, & Solorza-Feria, 2016).

Zhao et al. demonstrated that a natural extract could act as a crosslinker of gelatin by creating hydrogen bonding between water and free hydroxyl groups of amino or polyphenol groups. The results showed that the gel strength drastically increased if compared to the untreated gelatin (Zhao et al., 2016). In addition, the physical blend with other biopolymers represents a valuable strategy to improve gelatin-based films' mechanical and water barrier properties (Benbettaïeb et al., 2016).

Recently, the evaluation of food by-products as a natural antioxidant and an antimicrobial agent is gaining importance due to their economic and simple extraction processes. It is the case of garlic peel extract, evidencing both antioxidant and antibacterial activities.

The addition of this natural additive inside gelatin-based films massively improved the shelf-life of rainbow trout (Oncorhynchus mykiss) fillets during their storage at 4 °C by delaying the lipid oxidation and retarding the total mesophilic and total psychrophilic bacteria growth and Enterobacteriaceae counts during the storage period. Compared to control samples, the shelf-life of fillets lasted ten days more, preserving the sensorial and organoleptic values of the fresh fish. Thus, garlic peel extract can be an effective antioxidant and antimicrobial agent in gelatin-based edible films, and it can be used for the extension of fish and fish products' shelf-life (Ucak, 2019).

4. Industrial constraints

The innovative technological developments in the production of functional foods, whose packaging or coating materials are designed to contain the bioactive compounds, gives rise to a novel conceptual approach of a packaging technology known as bioactive packaging, in which the food impact the consumers' health is ruled only to the food package or coating. The outstanding target is reached by enclosing bioactive compounds within external package or coating materials, providing worthy industrial benefits over the direct inclusion in foods. Moreover, as widely overviewed, all bioactive compounds have excellent improvements or tuning of the polymer matrix. Mainly, active food packaging extends the lag period prolonging shelf-life and maintaining food quality and safety. The new packaging trend makes food packaging optimizable up to the food product. These features will induce producers to pay much more attention to manufacture active packaging to increase food safety and consumers' health.

Although a large number of antimicrobial and antioxidant agents have been tested, bioactive packaging is still confined to the laboratory scale and is not commercially available. Although many efforts have recently been devoted to developing bioactive packaging solutions, there is still a deep gap between laboratory-scale research and real-time applications and commercialization. For example, Malhotra et al. reported that the antimicrobial activity of essential oils depends on the pH, temperature, and level of microbial contamination in food (Malhotra, Keshwani, & Kharkwal, 2015). Thus, when foods are concerned, much higher concentrations of essential oils were required to achieve antimicrobial effects than those required at a laboratory scale. The use of essential oils may cause negative sensory effects because of their intense aroma, which partially limits their use as preservatives in food. Several authors reported that better results could be obtained by encapsulating the volatile components of essential oils in nanoemulsions or sachets, even if these approaches find economic restrictions since they are not cost-effective (Ozogul et al., 2017). Thus, although many bioactive secondary compounds evidence valuable properties like antioxidant, antimicrobial, and mechanical properties enhancers, they are still far from an industrial application.

Moreover, proper investigations need to be performed to assess the non-toxicity of the additives following their accidental package migration and contact with the food. Therefore, a complete profile of each active agent must be known as well as the suitable concentration, the possible products resulting from its degradation and last, but critically worthy, their influence on human health. Indeed, the migration rate and degree of the active agent depend on the intrinsic packaging material. To this aim, more in-depth analysis is required to know the biological interaction occurring between the food product and natural compounds in case of contact to avoid both any possible hazard for human health and to ensure the quality of the whole package.

In general, literature data related to natural metabolites exploitation as active agents in food packaging needs to be improved if compared to essential oil investigations (EOs). This outcome could be due to several reasons; in principle, the plant recovery and natural metabolites extraction is a more time and cost-consuming process, with a low mass yield if compared to the EOs. Indeed, since secondary components are mainly derived from plant materials, their availability represents an important issue, mostly if harvesting season and plant health conditions in terms of diseases and pests are considered.

Besides, if the production costs are concerned, the conventional extraction procedures are quite expensive since to recover small amounts of pure metabolites, many solvents and purification steps are required, making the whole process irksome also for time-consuming. In addition, several investigations are necessary to assess their non-toxicity, which is a crucial issue for food application in terms of regulatory issues. Finally, many natural metabolites, when exposed to high temperatures, undergo molecular degradation and lose their bioactive properties. In addition to these technical constraints, also regulatory issues strongly limit the commercialization of bioactive packaging systems. Indeed, the admission of the bioactive compounds follows severe legal food regulation since their release should not make any food spoilage. It is because, unlike the conventional packaging system, active packaging may change the packaged food texture and organoleptic characteristics. These concerns certainly set a significant drawback for the pilot and industrial exploitation as additives in novel upgraded bioactive food packaging materials.

Recently, many efforts are making to improve secondary compounds extraction and purification by exploiting greener approaches by reducing solvents and purification steps, where possible. This tendency could result in a more eco-sustainable and cost-effective approach. Work is in progress on this worthy topic.

5. Conclusions and future trends

Active food packaging is favorably used to increase the food shelf-life by protecting food from microbial attack and oxidation. Synthetic polymers are still the main used matrices for food packaging. The growing tendency of the producers and consumers towards natural biopolymers, resulting from the environmental impact of synthetic plastics, led to the development of bio-based food packaging materials. The application of biopolymers in the food packaging industry has increased since they come from natural and renewable sources. They are biodegradable, compostable, readily available, and show almost similar mechanical properties to conventional polymers. Biodegradable polymers in food packaging are categorized into three groups. The most common biopolymers with potential applications for incorporating active natural agents (PLA, PBS, Mater-Bi, chitosan, alginate, starch, cellulose, pectin, and proteins) have briefly been introduced in this review. Secondary compounds (EOs and metabolites) of plants and fungi act as antioxidants, antimicrobial agents and plasticizers, depending on their structure and functional groups. The secondary natural compounds, opportunely formulated into the biofilms, could successfully show antimicrobial and antioxidant activity by hindering the growth of pathogenic microorganisms and protecting food from oxidation. Besides, the tensile test of active biofilms showed the effectiveness of natural additives as plasticizers of the polymer matrices, as widely discussed.

Nonetheless, some drawbacks are severely limiting the scaling up production of active packaging from laboratory to industrial scale. More in-depth investigations are required to overcome the toxicity of the natural compounds and develop greener and cost-effective methods for their extraction.

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Declaration of competing interest

The authors declare no conflict of interest.

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Abbreviations

Polyhydroxyalkanoates	PHA
poly (lactic acid)	lactic acid PLA
poly(butylenesuccinate)	PBS
Secondary Metabolites	SMs
Thermoplastic starch	TPS
Chitosan	CH
The US Food and Drug Administration	FDA
esterification degree	DE
low methoxyl pectin	LMP
poly (vinyl alcohol)	PVOH
whey protein isolate	WPI
whey protein concentrate	WPC
Essential Oils	EOs
Soybean	SPI
Cinnamaldehyde	CAL

International Union of Pure and Applied Chemistry	IUPAC
tensile strength	TS
elastic modulus	EM
Polyethylene glycol	PEG

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