Active Edible Films. Current State and Future Trends

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ABSTRACT

Active edible films represent one of the current and future trends in the development of new polymers for selected applications, particularly food packaging. Some biopolymers show excellent performance as carriers for active compounds extracted from natural sources and able to be released at controlled rate to the packaged food. This review aims to present in a comprehensive way the most recent advances and updates in this subject, where much research is currently on-going and new studies are reported very often. This review focuses on innovative biopolymer matrices, their processing to obtain edible active films and present and future applications.

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1. INTRODUCTION

The current increase in consumer demand for natural food has forced companies and researchers to explore different ways to improve their market penetration by offering products with improvement in quality, freshness and food safety.[1] One of the more fashionable trends consists of the development of innovative biopolymers obtained from agricultural commodities and/or of food-waste products.[2] The use of biopolymers in multiple food packaging applications has emerged as an alternative regarding their film-forming properties to produce edible films as an environmentally-friendly technology.[3]

Starches, cellulose derivatives, chitosan/chitin, gums, animal or plant-based proteins and lipids offer the possibility to obtain edible films in fresh or processed food packaging to extend shelf-life.[4-10] These polymers offer additional advantages in their commercial use, such as biocompatibility, barrier to moisture and/or gases, non-toxicity, non-polluting, mechanical integrity and relative low cost.[11-12] In addition, edible films can act as carriers for antioxidant/antimicrobial additives to extend food shelf-life, while maintaining mechanical integrity and handling characteristics.[10,13] Antioxidant edible films can prevent food oxidation, development of off-flavors and nutritional losses, while antimicrobials can avoid spoilage of food-borne bacteria and organoleptic deterioration by microorganisms' proliferation.[14-16] The introduction of natural active additives to packaging materials provides advantages compared to direct addition to food, such as the lower amount of active substances required, controlled release to food and elimination of additional steps on processing.[17]

Edible films are obtained from food-grade suspensions usually molded as solid sheets onto inert surfaces. They are dried and put in contact with food as wrapping, pouches, capsules, bags or casings through further processing.[18-19] However, sometimes the terms films and coatings are used interchangeably to note when food surface is covered by

relatively thin layers. Some authors distinguished both terms by the notion that coatings are applied directly onto food surface while films are stand-alone wrapping materials.[18-21]. For this reason, the current state in edible active matrices is summarized in this review, with emphasis on recent trends in protein-based and polysaccharides-based edible films. These matrices and processing methods used to obtain edible films and their role in active packaging are reviewed, while their industrial effectiveness in different applications is also discussed.

2. EDIBLE ACTIVE MATRICES

The use of edible films based on natural polymers and food-grade additives has been constantly increasing in the last few years. These films can be produced from a variety of products, such as polysaccharides, proteins, lipids and resins, with or without the addition of other components (e.g. plasticizers and surfactants), Figure 1 summarizes a general scheme for the classification of edible films.[22-23]

Polysaccharide-based films usually show poor moisture barrier, but selective permeability to O_2 and CO_2 and resistance to oils.[24] These films can be based on cellulose, starch (native and modified), pectins, seaweed extracts (alginates, carrageenan, agar), gums (acacia, tragacanth, guar), pullulan and chitosan. These compounds give hardness, crispness, compactness, viscosity, adhesiveness and gel-forming ability to films.[25] Marine organisms, such as seaweeds, bacteria and microalgae, have been considered other important sources of polysaccharide-based biomaterials.[26-27]

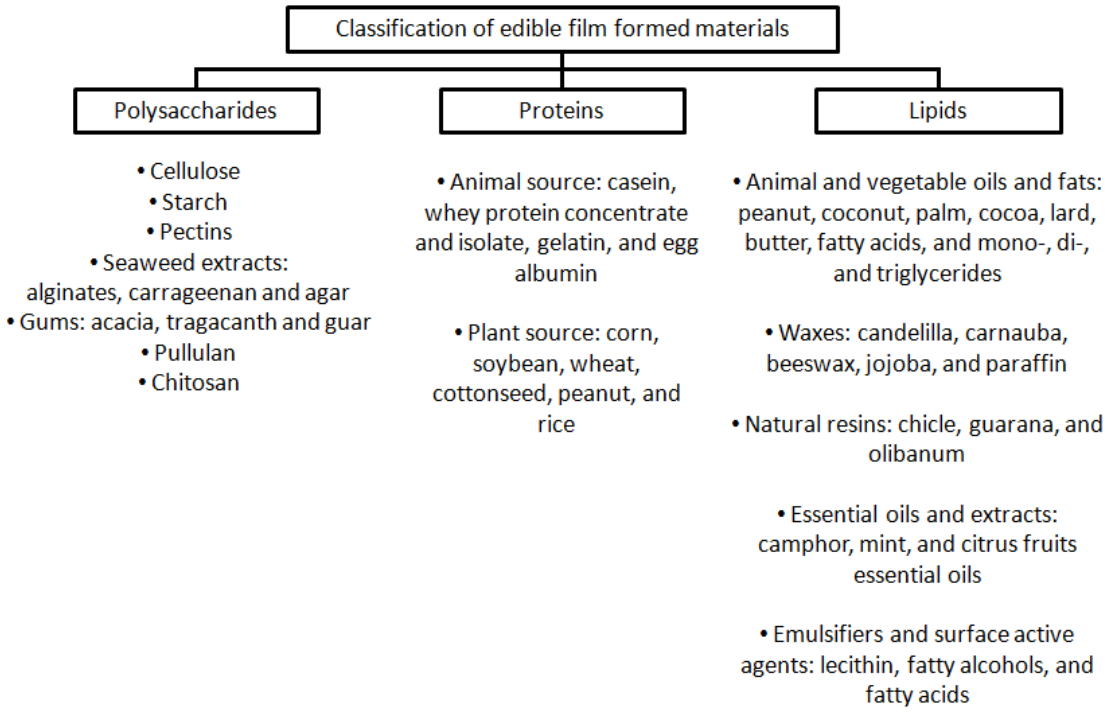

FIGURE 1. Classification of edible films according to their structural material.[23,28]

Film-forming proteins provide mechanical stability and can be derived from animals (casein, whey protein, gelatin and egg albumin) or plant sources (corn, soybean, wheat, cottonseed, peanut and rice). Plasticizers are added to improve flexibility of the protein network, whereas water permeability can be overcome by adding hydrophobic materials, such as beeswax or oils, to modify crystallinity, hydrophobicity, surface charge, and molecular size.[24] Protein-based films exhibit poor water resistance, but they are superior to polysaccharides in their ability to form films with high mechanical and barrier properties.

A wide range of hydrophobic compounds has been used to produce edible films, including animal and vegetable oils and fats (peanut, coconut, palm, cocoa, lard, butter, fatty acids, and mono-, di-, and triglycerides), waxes (candelilla, carnauba, beeswax, jojoba and paraffin), natural resins (chicle, guarana and olibanum), essential oils and extracts

(camphor, mint and essential oils). Lipids-based edible films are used to reduce water vapor permeability.[24]

The incorporation of active chemicals extracted from industrial wastes into edible films is a trending topic in materials research with a raising number of results.[29] It was found that edible films may serve as carriers of active compounds, such as antimicrobials, antioxidants and texture enhancers[13] and different ways to obtain them have been reported (Table 1). Some examples are discussed below.

New Trends in Polysaccharides-based edible films

Edible films produced from polysaccharides (cellulose, starch, pectins, seaweeds, gums, chitosan and pullulan) have been widely used in the food industry in the last few years, while lignocellulosic materials have been recently proved as suitable materials for edible films production. Slavutsky and Bertuzzi[29] reported the successful production of starch films reinforced with cellulose nanocrystals obtained from sugarcane bagasse. Translucent and transparent films were prepared by using hemicellulose fractions from leaves of *P. densiflora* by Shimokawa et al.[30] These authors obtained materials with properties similar to those of xylan, with high potential as edible films. Crystalline cellulose nanofibrils isolated from cotton linter by acid hydrolysis were used to prepare composite films with clear enhancement of optical and mechanical properties, water vapor barrier and thermal stability[31]. Composite alginate films were manufactured from alginate-carbohydrate solutions containing 5 wt% alginate and 0.25 wt% pectin, carrageenan (kappa or iota), potato starch (modified or unmodified), gellan gum or cellulose (extracted from soybean chaff or commercial)[32]. All those carbohydrates were able to form composite films with the alginate matrix. However, the cellulose extracted from soybean chaff could produce alginate-based composite films/casings with

mechanical strength similar to those produced from commercial microcrystalline cellulose.

Pectin extracted from different vegetal sources such as apple, carrot and hibiscus can be used to prepare active edible films with antioxidant and antimicrobial performance, obtained from natural additives, such as carvacrol and cinnamaldehyde[33] or lime essential oil[34]. In fact, lime is the most important citric fruit used for the extraction of essential oils while being a good source of pectin with antioxidant activity. Sánchez-Aldana et al.[34] studied the antibacterial activity against common food-borne bacteria of edible films based on extracts from Mexican limes pectin, increasing their value by providing an antibacterial effect. Citrus pectin was used to obtain one emulsion based on alginate-pectin-sunflower oil by spraying over a 2 % (w/w) calcium chloride solution at room temperature with a double fluid atomizer. Then, films could be fabricated in two different ways by cross-linking and hardening, like in the production of microparticles[35].

Carrageenan designs a family of polysaccharides produced by some red seaweed (*Rhodophyta*) as their main cell wall material. Paula et al.[26] studied the effects of the relative proportions of k-carrageenan, i-carrageenan and alginate on physical properties of glycerol-plasticized edible films. They reported that k-carrageenan was the component to improve the moisture barrier and overall tensile properties, while i-carrageenan was the component to impair them (Figure 2).

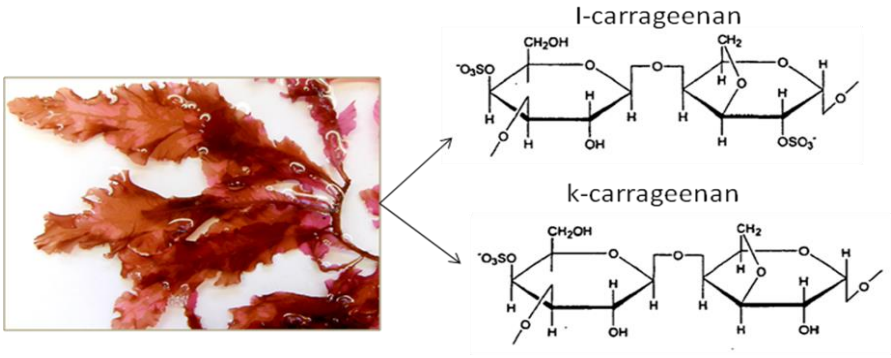

FIGURE 2. Structures of k-carrageenan and i-carrageenan extracted from the red algae *H. musciformis* and *S. filiformis.*

In this context, different authors have reported the use of hybrid carrageenan, extracted from *Mastocarpus stellatus* seaweeds, as an alternative to commercial k-carrageenan in new edible film formulations. These hybrid materials have shown their promising possibilities for the production of edible coatings and biodegradable films[36]. Other seaweed-based edible films obtained from several extracts have been recently studied[37,38,39,40] (Table 1).

Chitosan is produced by alkaline deacetylation of chitin, the material comprising the exo-skeleton of crustaceans and molluscs. Costa et al.[24] evaluated the properties of chitosan-based films with different fractions of arabinoxylans obtained through three different processes. In this sense, arabinoxylans can be obtained from the pre-treatment of low-cost agricultural residues such as cereal crops and wheat bran. The incorporation of 0.2 wt.% of arabinoxylans into the chitosan matrix enabled to obtain films with prebiotic and/or dietary fibre properties and potential health benefits. Arancibia et al.[41] used mild-processed chitosan and a protein concentrate obtained from shrimp (*Litopenaeus vannamei*) for the development of active edible films with antioxidant and antimicrobial properties. Different chitosan-based edible films in combination with several bio-polymers such as starch[42], fish gelatin[43-44] or proteins obtained from zein[45] have been recently reported.

Polysaccharide gums have been recently studied in their possibilities as edible films promoters due to their sustainable, biodegradable and bio-compatible characteristics. The term “gum” refers to polysaccharides that form gels, make viscous solutions or stabilize emulsion systems. Several plant gum exudates obtained from different agricultural wastes

have been recently used to obtain edible films. In this sense, Razavi et al.[9] reported that the gum extracted from sage (*Salvia macrosiphon*) seeds could be used to obtain edible films with increased thickness and ductility, moisture content and uptake, while decreasing surface hidrophilicity. Films with carvacrol exhibited higher antimicrobial activity than those with cinnamaldehyde, in particular in apple-based films. Pinto et al.[46] developed films from starch and cashew tree gum, a water soluble hetero-polysaccharide, with montmorillonite and they tested their application as coating to increase stability of cashew nut kernels, tensile properties and water vapour barrier. Smart thermos-sensitive poly(nisopropylacrylamide) nanohydrogels with or without acrylic acid incorporated into polysaccharide-based films obtained from k-carrageenan and locust bean gum have been recently reported by Fuciños et al[47]. These authors showed the possibilities of these biocomposites to transport natamycin and their controlled release as a response to environmental triggers. These results were promising, since this system makes possible to reduce natamycin concentrations in food products whilst improving their antifungal effect. The seeds of *Ocimum basilicum L.*, also known as basil, contain a considerable amount of gum composed by two major fractions of polysaccharides (43 % glucomannan and 24.3 % xylan) with outstanding functional properties in developed edible films[48-49]. Brea gum is the exudate obtained from the Brea tree (*Cercidium praecox*) which has been used to study the effect of montmorillonites incorporation into brea gum-based films through thermodynamic and phenomenological analysis[50-51]. The effect of the addition of plasticizers into edible films obtained from *Cordia myxa* gums with different effects has been also reported[52].

Finally, starch is the most important polysaccharide used in the formulation of biodegradable edible films. Different starch formulations may lead to the formation of edible films with particular characteristics and properties. For example, it was reported

that *Curcuma longa L.*, commonly known as turmeric, generates a residue that consists predominantly of starch and fibers that may present residual levels of curcuminoids with antioxidant properties[53] It was concluded that turmeric films could act as active packaging materials due to the presence of curcuminoids with antioxidant character. Among starches, cassava, corn and wheat have been recently proposed for the formulation of edible films thanks to their availability and relative low price. Starch is normally used in mixtures with different biomaterials, such as soybean protein concentrates[54], native and modified cush-cush yam and cassava starches[55-56], wax and normal starches[57], wheat starch and whey-protein isolates[58], wheat starch solution and rapeseed oil[59] or cassava starch, glycerol, carnauba wax and stearic acid[60], among others.

TABLE 1. New trends in edible film matrices with different matrices.

Edible matrix	Industry waste	Edible film	Reference
Polyssacharides	Sugarcane bagasse	Starch (4 %), glycerol (20 % dry weight), water, and an appropriate amount of cellulose nanocrystals obtained from sugarcane bagasse (3 % dry weight)	[29]
	Pinus densiflora leaves	Hemicellulose fractions of *Pinus densiflora* leaves with 1 % (w/w of polysaccharide) lecithin	[30]
	Cotton linter pulp	Crystalline cellulose nanofibrils from cotton linter pulp to reinforce sodium carboxymethyl cellulose films 2 % (w/v) and 0.9 g glycerol (30% of weight) to 150 mL distilled water	[31]
	Soybean chaff	Composite alginate films obtained from alginate-carbohydrate solutions containing 5 wt% alginate and 0.25 wt% cellulose extracted of soybean chaff	[32]
	Apple, carrot and hibiscus	Apple, carrot, and hibiscus-based pectin edible films	[33]
	Lime bagasse and lime pomace pectic extracts	Lime bagasse pectic extract and lime pomace pectic extract at 0.70, 0.85 and 1.00 % pectin equivalents with Mexican lime essential oil and 0.70 wt% glycerol plasticizer	[34]
	Pectin from citrus	Microparticles and films containing sunflower oil produced by ionic gelation using a 1:1 alginate:pectin mixture and electrostatically coated with whey and egg white proteins	[35]
	Mastocarpus stellatus seaweeds	Hybrid carrageenan, extracted from *Mastocarpus stellatus* seaweeds	[36]
	Pyropia columbina red algae	Carrageenans/porphyrans-based films obtained from *Pyropia columbina* aqueous fraction formed by casting from aqueous dispersions with different levels of glycerol	[37]
	Mastocarpus stellatus seaweed	Edible active films from different M. stellatus crude aqueous extracts	[38]
	Porphyra columbina seaweed	Antioxidant phycobiliproteins–phycocolloids-based films, obtained from mixtures of two aqueous fractions extracted from *Porphyra columbina* red seaweed	[39]
	Brown seaweeds *Laminaria digitata* and *Ascophyllum nodosum*	Film-forming carbohydrate-rich extracts from brown seaweeds *Laminaria digitata* and *Ascophyllum nodosum* obtained using Na_2CO_3 or NaOH at different temperatures and different acid pre-treatments (H_2SO_4 and HCl)	[40]
	Wheat bran arabinoxylans	1.5 % (w/v) of chitosan in 1 % (v/v) of lactic acid under agitation during 1 h at 25 ◦C. Glycerol (0.5 wt%) and tween 80 (0.1 wt%) were added at 60 ºC under agitation for 30 min. Then, arabinoxylans (0.2 %) were added and solution was stirred for 72 hours.	[24]
	Chitosan and protein concentrate from shrimp waste	Chitosan solution (2 % w/w) dissolved in 0.15 M lactic acid solution (pH 3.2) and sonicated.	[41]
	Chitosan and potato and cassava starches	Starch and chitosan films obtained by varying the starch source (potato and cassava starch), starch concentration (0.5 and 1.0 wt%) and type of plasticizer (glucose and glycerol)	[42]
	Marine industry by-products: chitosan and fish gelatin	Chitosan and fish gelatin (1:1 w:w), entrapping natural antioxidants (ferulic acid, quercetin and tyrosol (~50 mg/g)) were used to prepare edible active films by casting	[43-44]
	Chitosan and zein	Composite edible films fabricated with zein and chitosan and supplemented with phenolic compounds (ferulic acid or gallic acid) and dicarboxylic acids (adipic acid or succinic acid)	[45]

Proteins	Cashew tree gum	Starch-cashew tree gum nanocomposite films. Sage seed gum edible films with two different plasticizers (glycerol and sorbitol: 20, 40, 60, 80 and 100, w/w%)	[46]
	Locus bean gum	0.4 and 0.6 % (w/v) of κ-carrageenan and locust bean gum suspended in distilled water under agitation for1 h at 25 °C with 0.3 % (w/v) of glycerol (87 %, v/v) in solution, homogenised at 80 °C for 30 min	[47]
	Basil seed gum	Basil seed gum and different plasticizer concentrations added to deionized water and heated to 80 °C under mild stirring	[48-49]
	Brea gum	Brea gum (10 % w/v), glycerol (25 % w/w of Brea gum), water and montmorillonite (5 % w/w of Brea gum)	[50-51]
	Cordia myxa gum	Glycerol, sorbitol, polyethylene glycol 200 and polyethylene glycol 400 in the range of 0.1-0.3 g/g dry polymer weight basis dried at 40 °C for 48 h	[52]
	Turmeric dye solvent residue	Turmeric flour films and sorbitol (30 g sorbitol/100 g flour)	[53]
	Cassava starches	Cassava starch (5 % w/w) and soy protein concentrate with glycerol (20 %)	[54]
	Dark cush-cush yam and cassava starch	Edible films prepared from a film forming solution made by mixing 2 % w/v of starch and 1.9 % w/v of glycerol in distilled water	[55-56]
	Waxy and normal corn starches	2 % w/v of either native or modified starch, 1.9 % w/v glycerol and 500 mL distilled water	[57]
	Wheat starch	Wheat starch and whey-protein isolates (100-0, 75-25, 50-50, 25-75 and 0-100 %) ratios. Glycerol was used as a plasticizer at 50 wt%	[58]
	Wheat starch	Lamination of wheat starch solution and rapeseed oil	[59]
	Cassava starch, carnauba wax and stearic acid	Formulations containing cassava starch, glycerol, carnauba wax and stearic acid-based edible coatings/films	[60]
	Perilla seed oil residue	Perilla seed meal protein and different amounts of red algae 1.5 % (w/v) of chitosan	[61]
	Canola meal	Casted canola proteins isolate edible films (5.0 % and 7.5 %) and glycerol (30 % to 50 %)	[62]
	Chicken feet	Chicken feet protein films with 3:2 ratio (w/w) of glycerol-sorbitol	[63]
	Cold water fish skin	4 g gelatin in 100 mL distilled water with glycerol (0.3 g/g gelatin)	[64]
	Surimi and skin gelatin from silver carp	Surimi solution with gelatin solution (10:0, 8:2, 6:4, 5:5, 4:6, 2:8 and 0:10) 4 g gelatin in 100 mL distilled water with glycerol (0.3 g/g gelatin)	[65]
	Zein particles and fatty acid oleic acid	1.4 g of zein dissolved with 8.1 mL of ethanol (96 %), catechin and lysozyme	[66]

New Trends in Protein-based edible films

Several agricultural wastes have been reported as new sources of proteins to be used in edible films. For example, perilla seed consisting of 51 % fat and 17 % protein increasing this value up to approximately 40 % after oil extraction. Perilla seed is currently used as animal feed or fertilizer and would increase added value in edible films. Song et al.[61] reported that perilla seed protein combined with 3 wt.% of red algae resulted in suitable mechanical properties. Among the essential oils incorporated into the composite films, clove oil exhibited the highest level of antimicrobial performance. Canola (*Brassicaceae spp*.) proteins show functional attributes, but the oil is currently used for cooking and biodiesel synthesis with no further added-value applications. Once the oil is pressed, the remaining meal (high in proteins and fibers) is typically used in feeding animals. Canola proteins can be extracted from the meal as by-product for food and non-food applications, such as edible films[62]. Other proteins can be extracted from animal sources. For instance, Lee et al.[63] prepared antimicrobial and antioxidant films using proteins extracted from chicken feet and proposed their use in sliced cheddar cheese packaging.

Among all the protein sources, gelatin has been the most extensively studied by its high film forming capacity and application as outer coating to protect food against light and oxygen. Fish gelatin has gained interest in recent years as an alternative to bovine and porcine gelatin, due to social and health reasons, such as the bovine spongiform encephalopathy crisis. Furthermore, skin, a major by-product of the fish-processing industry, could provide a valuable source of gelatin. As consequence, the elaboration of edible films from fish gelatin has been recently studied by several authors.[64,65]

Zein has been used as supporting carrier of antimicrobial enzymes, including lysozyme (LYS), lactoperoxidase and glucose oxidase, bacteriocins, and natural antimicrobial and antioxidants, such as plant phenolics and essential oils. LYS-zein films showed high

performance in inhibition of Gram-positive pathogenic bacteria, such as *Listeria monocytogenes*, that might cause deadly infections. Zein-based edible films have recently gained interest, since (1) zein is a major co-product in bio-ethanol production, (2) it is one of the rare proteins soluble in organic solvents, and (3) it provides an effective delivery system for LYS. In this context, Arcan and Yemenicioglu[66] developed films by forming emulsions of zein with oleic acid in the presence of lecithin. Microspheres within these films were observed, increasing barrier against diffusion of encapsulated LYS.

3. ACTIVE EDIBLE FILMS PROCESSING

Traditionally, the methods used for the production of edible films have been divided in two main groups: wet and dry processes. The wet process needs solvents for the solution and dispersion of the polymer onto a flat surface, followed by drying in controlled conditions for the removal of the solvent and formation of the film. It is a high energy-consuming procedure, adequate for laboratories but not for the industrial scale-up. The production of edible films by dry methods includes the extrusion, injection, blow molding and heat pressing processes as those most commonly used.[12,67] The combination of efficiency and high productivity provided by these thermal processes have induced the increase of their application for active edible-films manufacturing.[68] But, the high temperatures used in the dry processes could affect the presence and concentration of some active compounds on the films[12], while the addition of plasticizers is sometimes necessary to decrease the glass transition temperature for polymer matrices. The method selected for the production of active edible films could affect and modify the final properties of the material.

Wet processing

Casting is a simple method for the production of edible films, but it is a batch procedure used in a very small-scale. Nevertheless, a continuous casting method (knife-coating or tape-casting) can be used at the industrial scale[3], since the film-forming suspension is prepared on continuous carrier-tapes with effective control of thickness. The formed film is dried by heat conduction, convection or radiation in short times. De Moraes et al.[69] showed that tape-casting is a suitable technology to scale-up the production of cassava starch-based edible films.

In general, the wet process could be divided into four steps: dispersion or gelatinization, homogenization (in the case of emulsions or mixtures), casting and drying. Several factors have influence and should be optimized depending on the polymer matrix: the solvent, plasticizer and/or other additives contents, method for the granules disruption, temperature and time.[70] If different hydrocolloids or other non-miscible components are added, a mixing step is also required to obtain stable emulsions and homogenous film-forming solutions. Homogenization is currently performed with new homogenizer devices, such as rotor-stator or Brabender viscographs, to induce high pressures that could enhance the disruption and interactions between all components.[53,71-76] Table 2 summarizes the recent trends in active edible films production following the wet method.

Since the final product should be edible and biodegradable, only water and ethanol, or their combinations, are suitable solvents.[67,77] Furthermore, all components of the film-forming solutions should be homogenously dispersed in the solvents to produce edible films without phase separation. Emulsifiers can be added to avoid this situation, even when using incompatible compounds.[72,74,76,78] The addition of food-grade plasticizers rich in hydroxyl groups, such as glycerol, sorbitol or polyethylene-glycol (PEG) in concentrations between 15 and 30 wt % reduce the polymers rigidity and glass transition temperature, enhancing the distribution of the film-forming solutions.

Essential oils (EO) extracted from plants have been used in the last years as active compounds for edible films manufacturing (Table 2). Different strategies to incorporate active components into water-soluble polymers, such as direct addition to the film-forming solution followed by casting method,[74,79-84], nanoemulsions through ultrasonication[85] or encapsulation in nanoliposomes through sonication of their aqueous dispersions[86-87] have been reported. Otoni et al.[85] prepared coarse emulsions (1.3-1.9 μm diameter) and nanoemulsions (180-250 nm) of clove EO through low-speed mixing and ultrasonication, respectively, using emulsifiers for homogenization in water. The incorporation of these emulsions into methyl-cellulose matrices plasticized with PEG showed that the droplet size reduction provided higher antimicrobial properties. In addition, lower EO contents might be used if encapsulated to keep the same antimicrobial efficiency. However, some negative effects on mechanical properties were observed by the addition of EO emulsions. Some increase in antimicrobial stability with a decrease in cinnamon EO release rate was observed for gelatin films with nanoliposomes.[86]

Casting is widely used for the direct incorporation of EO into film-forming solutions by the low temperatures used for the homogenization and drying steps. For example, cinnamon EO increased the antimicrobial activity of whey protein concentrate as well as the water vapor permeability and water solubility.[74] However, the addition of emulsifiers is necessary to help EO distribution in the film-forming solutions.[71,76,78,80] Other authors incorporated lignin to gelatin matrices by casting, resulting in films with excellent antioxidant and light barrier properties to prevent the ultraviolet-induced lipid oxidation in certain food applications.[88] They did not use emulsifiers, showing some microphase separation between gelatin and lignin. Maniglia et al.[53] developed turmeric flour films with antioxidant activity by casting, using the turmeric dye solvent extraction residue. But, air bubbles are frequently observed as a consequence of the homogenization step,

and vacuum[89-91] or ultrasound[78-79] devices are used to remove them, avoiding the presence of microholes in the film structures.

After homogenization, film-forming dispersions are cast on leveled dishes and allowed to dry under controlled conditions. The high difference in surface energy between the film and the dish surface is an important factor for an easy peeling after casting.[67] Therefore, depending on the polymer, different materials, such as polystyrene[76,82], polyethylene[73], polycarbonate[81], methacrylate[79,86] or glass[71,74,91] have been used to obtain films by casting. Other surfaces, such as stainless steel, silicone[69] or poly(tetra-fluoroethylene) (Teflon®)[92-93] have been also considered by their high inertness.

A great variation in drying temperatures and times has been reported, with times varying between 5 and 72 hours and temperatures between 20 and 45 ºC, being significantly lower for edible films with active volatile compounds to avoid their evaporation (Table 2).

TABLE 2. Recent trends in active edible films production (wet method).

Biopolymer	Solvents	Additives	Homogenization conditions	Drying	Reference
Chitosan	Acetic acid (1%)	Glycerol ,Tween 80, Clove oil	Chitosan solution stirred (40 ºC, 2 h). Mixing with additives by Ultra Turrax. Ultrasound for 30 min to remove bubbles	42 ºC for 15 h in a forced-air incubator	78
Chitosan	Acetic acid (1%)	Rosemary EO Tween 80	Chitosan solution stirred (90 ºC, 20 min). Cooling. Mixing with Tween 80 (40 ºC, 30 min) and EO (Ultra Turrax, 4000 rpm, 2 min). Cooling. Degassing under vacuum for 5 min.	72 h at 25 ºC in a Teflon-coated steel plate	93
Methycellulose	Water	PEG, Clove and oregano EO, Tween 80	Mixing EO with water and Tween (1000 rpm, 5 min) .Ultrasonication of coarse-emulsions (20 kHz, 400 W, 10 min). Homogenizing with MC and PEG (30 min, 6 rpm). Rested 2 h.	Overnight at 25 ºC in a glass plate	85
Whey protein isolate	Water	Glycerol, Cinnamon, cumin and thyme EO	pH 8 (NaOH). Stirring (90 ºC, 30 min). Cooling. Degassing under vacuum (30 min).	Overnight (35 ºC, 45 % RH) in a glass dish	91
Cassava starch	Water	Glycerol, Cellulose fibers	Hydration of fibers for 24 h. Stirring 10 min at 14000 rpm. Mixing with all components by stirring (71 ºC, 5 min, 90 rpm). Tape-casting at spreading speed of 40 cm min^{-1}.	Heat conduction (60 ºC), 5 h in PMMA protected by silicone coated PET film	69
Whey protein concentrate (WPC)	Water	Glycerol, Cinnamon EO, Tween 80	WPC solution (90 ºC, 30 min). Mixing with glycerol and Tween 80 for 30 min. Homogenization with CEO (25 ºC, 2 min, 7000 rpm). Kept overnight at 4 ºC.	72 h at 25 ºC in glass dish	74
Isolated Soy protein (ISP)	Water	Glycerol, Oregano and thyme EO	pH 10 (NaOH) of ISP solution with glycerol. Mixing with EO (90 ºC, 30 min). Cooling to 40 ºC.	Oven (30 ºC, 72 h) in polystyrene (PS) petri dish	94
Fish skin gelatin	Water	Glycerol, Natural extracts	Gelatin solution with glycerol and extracts mixing at 45 ºC, 30 min. Ultrasound for 15 min	Oven (22 ºC, 36 h) in methacrylate dish	79
Sodium alginate	Water	Glycerol, Essential oils Surfactant	Sodium alginate solution (100 ºC for 1 h). Cooling. Mixing with glycerol and EO (vortex).	Ambient conditions in glass dish	80
Sodium caseinate (NaCas)	Water	Glycerol, Naturally emulsified oil bodies (EOB)	NaCas solution with glycerol stirred for 2 h. Mixing with EOB (2 h). Homogenization at 700 bar for 5 min. Kept overnight at 4 ºC	37 ºC for 24 h in petri dish	75
Soybean polysaccharide (SSPS)	Water	Glycerol, Essential oils, Tween 80	SPSS solution (300 rpm, 40 min, hot plate). Mixing with glycerol (15 min, 82 ºC). Homogenization in a rotor-stator (20000 rpm, 3 min).	18 h, 25 ºC in PS petri dish	76
K-carrageenan	Water	Glycerol, Essential oils, Tween 80	K-carrageenan solution (15 min, 82 ºC). Mixing with glycerol (25 min, 82 ºC). Homogenizing in a rotor-stator (13500 rpm, 3 min, 80 ºC). Degassed at 65 ºC.	30 h at 30 ºC in glass dish	71
Chitosan	Acetic acid 1 %	Essential oils, Tween 80	Chitosan solution (250 rpm, 45 ºC) stirring overnight at room conditions. Homogenization in a Dual-Range Mixer (2500 rpm, 4 min). Vacuum.	48 h, 22 ºC, 30 %RH in PS dish	72
Cassava starch (CS)	Water Ethanol	Glycerol, clove and cinnamon EO, Emulsifier, Clay nanoparticles	Clay NP suspended in water (1 h, 500 rpm), resting for 24 h and blended with CS solution. Glycerol, EO and emulsifier (200 rpm). Both mixtures homogenized in a domestic microwave oven (until 69 ºC). Cooling and dilution with ethanol.	Forced-air oven at 35 ºC for 18-24 h in Teflon plate	84
Fish protein	Water	Glycerol, Clove, garlic and oregano EO	Protein concentrate and glycerol (stirred 30 min). Emulsifiying with EO in a homogenizer (13500 rpm, 2 min). Vacuum (20 min)	Ventilated drying chamber (30 ºC, 50 % RH, 20 h)	83

Fish gelatin	Water	Glycerol, Cinnamon EO nanoliposomes	Gelatin solution, glycerol and EO stirred 30 min at 45 ºC. Ultrasound	22 ºC, 50 % RH, 24-48 h in a methacrylate dish	86
Chitosan	Lactic acid (1 %)	Glycerol, Tween 80, Arabinoxylans (AX/AXOS)	Chitosan solution stirring (1 h, 25 ºC). Mixing with glycerol and Tween (60 ºC, 30 min). Mixing with AX/AXOS for 72 h.	30 ºC, 60 h in PS plate	95
Fish gelatin	Water	Glycerol:Sorbitol (1:1), Lignin	Gelatin solution at 40 ºC. Mixing with plasticizers and lignin at 40 ºC, 15 min and pH 11.	Forced-air oven at 45 ºC for 15 h	88
Sage seed gum (SSG)	Water	Glycerol, Sorbitol, PEG-400	Plasticizers in water (150 rpm, 80 ºC). Mixing with SSG (1200 rpm, 80 ºC, 10 min). Homogenization (3200 rpm, 1 min). Mixing on rotating roller-mixer (24 h, 25 ºC).	23 ºC, 53 % RH in polyethylene dish	73
Turmeric flour	Water	Sorbitol	Turmeric in water (30 min stirring). Adjusted different pH (6.5-9.5) and temperature (78-92 ºC) for 4 h. Homogenization cycles (12000 rpm, 2 min) every hour. Mixing with sorbitol (20 min heated). Sonication (20 min).	Oven with forced-air (35 ºC, 7 h) in acrylic plate	53

Blending

Blending of different macromolecules by either a direct way or associated with co-drying processes leads to edible films with good control of their final properties. The most recent studies on blending different matrices to yield edible films focused on the combination of polysaccharides with proteins, taking advantage of their synergistic effects.[87,89-90,96-97] Direct blending consists of an initial preparation stage of individual polymer solutions with the subsequent homogenization and casting. It shows some advantages, since the co-drying method requires strict conditions, such as narrow concentration range and good compatibility.[89]. Table 3 summarizes the production of active edible films by blending.

Chitosan is one of the most used biopolymers in the production of active edible films.[98] Direct mixing of chitosan with protein concentrate solutions changes significantly the film structures, leading to the reinforcement of the chitosan matrices, improving their barrier, antimicrobial and antioxidant properties.[96] Edible films of chitosan with gelatin[90,97] or methylcellulose[92] have been developed to improve mechanical and barrier properties, while showing antimicrobial activity against Gram-positive bacteria. In addition, chitosan/gelatin films exhibited antioxidant activity monitored by β-carotene bleaching and DPPH radical scavenging.[97]

TABLE 3. Recent trends in blending methods for the production of active edible films.

Biopolymer	Solvents	Additives	Homogenization	Drying	Reference
Corn starch/sodium caseinate	Water	Glycerol Orange EO and limonene encapsulated in nanoliposomes	Starch stirred in water (95 ºC, 30 min). Mixing with sodium caseinate solution, glycerol and nanoliposomes solution (1 h at 300 rpm).	48 h at 20 ºC and 45 % RH in PET petri dish	87
Chitosan/protein concentrate	Lactic acid (1 %)		Chitosan and protein solutions - direct mixing	Oven at 45 ºC, 12 h in methacrylate plate	96
Chitosan/gelatin	Water/ acetic acid (1 %)	Glycerol	Blend stirred at 40 ºC, 30 min	25 ºC, 12 h (air-blown) and 25 ºC, 50% RH, 48 h in silicone plate	97
Chitosan/methylcellulose (MC)	Water Acetic acid 0.25% Ethanol	Resveratrol	MC in water. Chitosan stirred with acetic acid (0.25 %) overnight at 25 ºC. Homogenization with resveratrol in ethanol in a rotor-stator (13500 rpm, 4 min). Vacuum (10 min)	Natural convection (48 h, 25 ºC, 60 % RH) in darkness	92
Chicken feather protein (CFP)/gelatin	Water	Clove oil cinnamaldehyde Tween 20	CFP solution with gelatin and sorbitol stirred 1 h. Ultrasonication 8 min. Hot water bath (75 ºC, 30 min). All components stirred 20 min, 40 ºC.	24 h, 25 ºC in Teflon-coated glass plate	99
Fish gelatin/chitosan	Water/ acetic acid (1%)	Glycerol	Gelatin in water stirred 30 min, 25 ºC and 30 min, 45 ºC. Chitosan and acetic acid (1%) stirred overnight at 25 ºC. Mixing both solutions at 45 ºC, 30 min. Glycerol addition (45 ºC, 15 min). Vacuum (15 min)	72 h at 23-25 ºC in PS dish	90

Composite edible films formed by blending different polysaccharides[92,100-101] or proteins[99] have been recently reported. For example, an active compound (resveratrol) was efficiently incorporated into chitosan and methylcellulose blends, providing antioxidant activity with physical changes that did not affect negatively to their handling and appearance.[92] The incorporation of clove EO into gelatin/CFP blended films improved their antimicrobial and antioxidant properties while the mechanical behavior was not affected.[99]

Spraying is a wet processing method mainly used for coating production, where a film-forming solution is sprayed onto the polymer surface and furthermore droplets are cast and dried. Solvent mainly evaporates after leaving the nozzle of the sprayer allowing short drying times.[3] Recently, Jindal et al.[102] used this method for the production of pectin-chitosan cross-linked films.

Dry processing

It is known that those materials with thermoplastic behavior can be processed into films by the application of different thermal/mechanical processing techniques. Therefore, it is essential to study the rheological properties and the effect of additives (plasticizers, emulsifiers, active agents) on the thermoplastic behavior of the film-forming materials to select the adequate processing parameters.

The most common dry processing methods for edible films include extrusion, injection, blow molding and heat pressing. Recent technical developments, in particular in twin-screw extrusion, have increased the application of this technique for edible-films production[103], where one or two rotating screws induce pressure and high temperature to disrupt the polymer granules and to mix the film components. This technique shows some

advantages, including the absence of solvents, the possibility to handle high viscosity polymers and multiple injections, the broad range of processing conditions (0-500 atm and 70-500 ºC), the control of the residence time and the mixing degree.[103] Other processing techniques, such as injection-molding, film-blown die,[104-106] or thermo-pressing,[68] are combined with extrusion to get the final edible films.

Belyamani et al.[106] reported the production of sodium caseinate films in large scale by using glycerol as plasticizer and twin screw extrusion to obtain homogeneous thermoplastic pellets, which were further processed into transparent films by using a classical film blowing machine. These films showed mechanical properties similar to those obtained by solution casting and they were highly sensitive to glycerol and environmental moisture contents. Colak et al.[105] prepared a mixture of sodium caseinate containing LYS (1 wt%) and converted in pellets by extrusion (between 65 and 100 ºC) with the addition of glycerol. These pellets were further blown by an industrial-like blown-film-extruder to obtain thermoplastic antimicrobial films. The incorporation of plasticized chitosan to thermoplastic starch in a twin-screw extruder improved the subsequent blown-film processability and properties (mechanical, thermal stability, water absorption and surface stickiness), although it caused some changes in color and transparency. Authors observed that LYS stability was mainly dependent on processing temperature and glycerol content.[104]

Thermo-compression efficiency was shown for thermoplastic corn starch with chitosan/chitin by using a thermo-hydraulic press with a previous melt mixing process with glycerol and water at 140 ºC. Films were homogeneous, with uniform thickness, good appearance and antimicrobial activity.[68]

Edible films modifications

Lamination is another method to improve films performance, consisting in the formulation of multi-layered structures, combining properties of different materials into one sheet. Multi-layered films usually show higher toughness and tensile strength than single-layer films. However, this technology is complex and solvent-consuming at high temperature and time, increasing the production costs. In addition, the high differences in surface energy between layers could result in their separation.[89,107] For example, three-layer films obtained by heat-compression of dialdehyde cross-linked starch and plasticized gelatin films as outer layers and plasticized gelatin-sodium montmorillonite composite films as inner layer, provided a new biodegradable multilayer material with a compact structure and modulated properties.[107] Individual films were obtained separately in a first step and layers were stacked together by heat-compression. Bioactive tri-layer films were also prepared with poly(ε-caprolactone) as external layers and methylcellulose with encapsulated EO as the internal film.[108-109] Other methods were proposed to improve properties in active edible films based on chitosan by the application of moderate electric fields during processing.[4,110]

4. INDUSTRIAL APPLICATIONS OF EDIBLE FILMS

Edible films and coatings offer practical advantages, such as aesthetics, barrier properties, non-toxicity, and low cost[4]. In addition, the high compatibility of edible films with multiple active compounds has resulted in many interesting studies on the development of active food packaging materials due to their ability to extend the food shelf-life. Some examples of these applications are summarized in Table 4.

TABLE 4. Recent trends in application of active edible films in food packaging.

Edible matrix	Active coumpond	Application	Reference
Carregeenan	Lemon EO	Trout	111
Whey protein	Oregano and clove EO	Chicken	112
Sunflower protein	Clove EO	Fish patties	82
Argentine anchovy protein	Sorbic and benzoic acids	Meat	113
Chitosan	Thyme EO	Cured ham	114
Whey protein	Cinnamon, cumin and thyme EO	Beef	91
Chitosan	Basil and thymus EO	Pork	115
Agar	Green tea extract and probiotic strains	Fish	116
Gelatin fish	Laurel leaf EO	Trout	117
Methylcellulose	Nanoemulsions of clove and oregano EO	Sliced bread	85
Whey protein	Oregano and clove EO	Poultry	118
Barley bran protein-gelatin	Grapefruit seed extract	Salmon	119
Soy-based protein	Oregano or thyme EO	Ground beef patties	120

Essential oils extracted from herbs and spices are the more usual active compounds in these formulations. In fact, the incorporation of natural extracts from plants, spices, and herbs represents a promising approach for the development of bioactive edible films/coatings with improved bioactive, mechanical and physico-chemical properties and applications[12]. For example, Pires et al.[121] studied the incorporation of different EO to protein edible films. They concluded that the addition of citronella, coriander, tarragon and thyme oils reduced the water vapour permeability and increased the solubility in water of the resulting films. The amount of protein released from these films upon water solubilisation was quite dependent on the EO composition.

Volpe et al.[111] studied the effect of lemon essential oil (ELO) on carrageenan matrices and reported the efficiency of ELO in slowing down the microbial growth and lipid oxidation in trout fillets. In addition, the carrageenan matrix showed good performance in keeping the shiny and fresh aspect of trout beyond 7 days of cold storage. Conservation

of fish patties was also studied by Salgado et al,[82] by addition of clove EO to sunflower protein concentrates to obtain edible and biodegradable films with *in vitro* antioxidant and antimicrobial properties. These sunflower protein films contributed to limit the lipid auto-oxidation and to delay the growth of total mesophiles when applied to refrigerated sardine patties.

Fernández-Pan et al,[112] studied the quality and extension of shelf-life of chicken breast, by using Whey Protein Isolate (WPI) edible coatings with oregano or clove EOs. These insoluble and homogeneous WPI coatings formed an imperceptible second skin covering the chicken breast and they were effective to control the release of the antimicrobial compounds onto the food surface throughout the storage period.

Biomedical applications are other future trend for the use of edible films. In fact, the use of biopolymers as effective carriers for drug delivery has been extensively reported and many reviews have been already published in the last few years[122]. For example, novel hydrogels were prepared by Chetouani et al by crosslinking gelatin with oxidized pectin.[123] The reaction of the aldehyde groups of the oxidized pectin with the amino groups of gelatin is responsible for the crosslinking. In comparison with pure gelatin, these edible films exhibited higher thermal stability and better blood compatibility, with potential uses in wound dressing, tissue engineering scaffolds, and other biomedical fields.

5. CONCLUSIONS.

The use of edible films has found a very important niche of applications, including food packaging, biomedical and others, by their good performance as carriers for active compounds. Research in this field has largely increased in the last few years, but some

drawbacks are still to be solved to permit their use in massive applications in packaging of consumer goods, in particular difficulties in processing since most of the current research has been performed by using wet methods. Nevertheless, this important bottle-neck, resulting in difficulties for the up-scaling from laboratory results to industrial production, is currently under study as shown in many of the most recent references in this review article, since the successful production of these active films at large scale will be possible soon. The most updated prospection for the use of edible films as a real sustainable alternative to conventional plastic formulations in active food packaging and/or biomedical systems reflects their high possibilities to be introduced in markets in the next few years.

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