Chapter 12
Sustainable and Biodegradable Active Films Based on Seaweed Compounds to Improve Shelf Life of Food Products

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Abbreviations

FAO Food and Agriculture Organization

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1 Introduction

Macroalgae or seaweeds are a diverse and ubiquitous group of predominantly marine photosynthetic organisms, chemically, physiologically, and morphologically different from land plants (Shama et al. 2019). Compounds like carrageenan, alginate, agar, fucose, fucoidan, laminarin, and mannitol distinguish them from microalgae and land plants (Wang et al. 2020). Macroalgae together with microalgae are responsible for the production of over 50% of the oxygen globally (Henriques et al. 2017; Gonçalves 2020) and consume most of the carbon dioxide in the atmosphere (Marine Biotechnology ERA-NET 2019). Different natural pigments like chlorophylls, carotenes and xantophylls give the thallus different colors leading to the division of seaweed in three distinct groups: the phyla Ochrophyta (class Phaeophyceae; brown algae), Chlorophyta (green algae) and Rhodophyta (red algae) (Marques 2017; Gonçalves 2020; Pacheco et al. 2020).

Seaweeds are pivotal in the cuisine of several Asian countries, especially in Japan, Korea, and China, but they are also present in some specialties in the island nations of the Pacific, and in Celtic nations (Brittany, Scotland and Ireland) (Pereira 2018). Its consumption is increasing in several Western countries, due to the growing interest in adopting healthier diets (Delaney et al. 2016; Marine Biotechnology ERA-NET 2019). Seaweeds are richer in minerals, vitamins, proteins, trace elements, iodine, omega-3 and in soluble and insoluble dietary fibers (FAO 2020; Pereira 2020), comparing with land plants, therefore, seaweeds can be a healthier alternative to conventional food products (Shama et al. 2019). These organisms can help in the effort to mitigate hunger in underdeveloped and emerging countries, as they are an abundant and highly nutritious food source that grow everywhere (Pereira 2020). An additional advantage is the seaweeds can be consumed without being in its fresh form. Although the several applications of seaweeds in the food industry there is the need for more studies on their toxicological profile to ensure consumers' safety (Rengasamy et al. 2020).

The decrease of arable land and the increase of the world population pushes the search for food alternatives that are more nutritious and eco-friendly. Macroalgae cultivation does not compete with agriculture as it uses resources that are not suitable for that purpose; they show a greater photosynthetic efficiency, faster growth rates, and higher production yields per unit area comparing with land crops. They are also easier to process because they do not have lignin (Baweja et al. 2016; Marques 2017; Raikova et al. 2019; Sedayu et al. 2019). Besides its use as food, macroalgae are collected and are cultivated for the production of bio-fertilizers, animal feed, hydrocolloids, wastewater treatment and biofuels (García-Poza et al. 2020; Wang et al. 2020).

Macroalgae are a sustainable and rich resource of bioactive compounds with broad-spectrum antimicrobial activity, antioxidant and anti-inflammatory properties, among other properties. Therefore its use in food, medical, pharmaceutical and cosmetic industries brings many advantages and opportunities in the development of new active products and supplements. Its exploitation results in the increase of research and development of new sustainable and efficient techniques of exploitation and production. As an industrial crop, seaweed cultivation is still a relatively recent activity, but has the potential to address the long-term issue of environmental sustainability (Abdul Khalil et al. 2017).

The industry around macroalgae is worth several millions of dollars (Pereira 2018; Marine Biotechnology ERA-NET 2019) as they are more productive than any land crop. In 2018 the trade in seaweed and other aquatic plants accounted for 63% of the USD 2 billion in exports according to the Food and Agriculture Organization (FAO 2020). Wang et al. (2020) reported that "China, Japan, Korea and the Philippines account for about 72% of the global annual production of macroalgae". Industries around seaweed create a large variety of jobs since the growers/farmers, all the way up to, researchers, engineers, and also create marketing and financial services (Marine Biotechnology ERA-NET 2019). Hence, macroalgae are an eco-friendly source of food and raw materials for different industries, and can be included in the concepts of blue and circular economies as its cultivation, production, and harvesting increases local employment at several levels and its byproducts can be used as raw materials for different industries.

This chapter aims to explore and summarize the uses of macroalgae and its most explored bioactive compounds in different industries, particularly in the food packaging industry; how seaweed-based packaging is produced and their effects on the shelf life of food products.

2 Macroalgae Bioactive Compounds and Its Application in Different Industries

Seaweed occupy habitats exposed to constantly changing conditions, consequently they are pressured towards metabolic evolution leading to the production of several secondary metabolites with important biological, ecological and economical value. Their essential amino acids, polysaccharides, essential fatty acids, sterols, terpenes, carotenoids, phenolic compounds and minerals provide them with the capability of reducing or stopping cell growth, eliminating parasitic worms, preventing the growth or spread of fungi and bacteria, and are effective against viruses (de Almeida et al. 2011). Seaweeds also provide antioxidant and anti-inflammatory properties as mentioned before, and are explored in the treatment of several diseases. Thickening, gelling, stabilizing, encapsulating, and dispersant agents (Abdul Khalil et al. 2017) used widely in the food industry are also found in seaweeds. The composition and quantity of these biomolecules change according with the species, the season, and the region where they grow due to differences in ecological parameters (Marine Biotechnology ERA-NET 2019; Pacheco et al. 2020). A more detailed and extensive description of the properties of macroalgae bioactive compounds and on research in the pharmaceutical and cosmetics industries can be read in the publication of Rengasamy et al. (2020). In the biomedical field seaweed-based polysaccharides are being explored due to their capacity to form hydrogels, their biocompatibility and for being hypoallergenic; their hydrophilic groups, like carboxyl, sulfate, and hydroxyl, can easily interact with biological tissues. It was reported that seaweeds are used as carriers of therapeutic macromolecules and other molecules, controlled delivery and release systems, bone tissue engineering, regeneration and implantation, hydrogel wound dressings, removal of heavy metals from the body (Abdul Khalil et al. 2017).

In the cosmetic industry, algae are advantageous because they can be resourced fast and at low prices, and also because of all the benefits for the skin and the variety of forms that they can be used as oils, powders, flakes (Marine Biotechnology ERA-NET 2019). In this industry, seaweeds are used as bioactive extracts, coloring agents, texturing stabilizers or emulsifiers; and as photosynthetic organisms that produce compounds that absorb UV rays, being used in the formulation of sunscreens (García-Poza et al. 2020).

Taking advantage of the bioaccumulation process, seaweeds can be used in the remediation of contaminated waters with the advantage of being more efficient and cost-effective, because they thrive in nutrient-rich waters and can remove toxic compounds, like metals, whilst capturing carbon dioxide emissions, reducing the use of chemicals for the same purpose and with lower energy costs (Henriques et al. 2017). Seaweed biosorption activity can also diminish the toxic effect of different pollutants and provide a promising approach for integrated energy production (Ungureanu et al. 2017; Wang et al. 2020). This approach provides several useful byproducts that can be utilized in the production of fertilizers, feed additives, and biofuels (bioethanol and biobutanol) (Marine Biotechnology ERA-NET 2019; Michalak 2020; Wang et al. 2020; Mohammad et al. 2019; Hessami et al. 2019). Algal biomass is a promising alternative to fossil resources not only to produce energy but also chemicals, enhancing energy security and contributing to the mitigation of climate change (Baweja et al. 2016; Marine Biotechnology ERA-NET 2019; García-Poza et al. 2020).

Polysaccharides are of the most researched seaweed bioactive compounds. Alginate, agaran, carrageenan, and fucoidan are some of the most significant polysaccharides found in seaweed, and except for fucoidan, their viscosity and poor solubility makes them inefficient for pharmaceutical applications, but it makes them perfect to use in cosmetics and food products.

Fucoidan is a brown seaweed sulfated polysaccharide applied industrially in cosmetics, diet supplements and animal feeding (Pacheco et al. 2020). This polysaccharide has strong antioxidant and antiaging properties, and also anticancer, anticoagulant, antimicrobial, anti-inflammatory and antidiabetic properties. It can also be used as an emulsifying agent. By itself it cannot form gels, but the mixture with other polymers may provide some advantages (Gomaa et al. 2018), however it is not common in the development of film matrices. Fucoidan is a promising natural compound targeted by the biomedical and pharmaceutical industries due to its promising therapeutic properties. Its low toxicity and wide range of biologically active ingredients have been confirmed in numerous *in vitro* and *in vivo* studies (Pacheco et al. 2020).

3 Macroalgae Polysaccharides in the Food Industry

Carrageenan, agar and alginate are the three major phycocolloids used in the food industry and due to its composition, structure, and consequent properties they are extensively used in the food industry. Table 12.1 summarizes their main properties and consequent applications in the food industry. Further information can be read in Alba and Kontogiorgos (2018), Ozilgen and Bucak (2018) and Skurtys et al. (2010).

Carrageenan is a linear sulfated polysaccharide composed of alternating and repeating disaccharides units of β-D-galactopyranose and α-D-galactopyranose or 3,6-anhydro-α-D-galactopyranose, linked with β-(1 → 4) and α-(1 → 3) glycosidic linkages, obtained from different red algae. Depending if it has one, two, or three sulfate groups per disaccharide unit, carrageenan can be differentiated as κ-, ι-, and λ-carrageenan, respectively, and these are the most relevant types industrially (Alba and Kontogiorgos 2018; Ozilgen and Bucak 2018). Although the different types of carrageenan are all soluble in water, factors like temperature, pH, ionic strength of the medium, and the presence of cations influence its aqueous solubility (Alba and Kontogiorgos 2018). Regardless of being technically considered a dietary fiber, carrageenan has gelling, thickening, and stabilizing properties, therefore, they are mainly used in dairy and meat products. λ-carrageenan does not form gels, but polyelectrolyte solutions used as thickening agents in dairy products.

Agar is also a linear polysaccharide composed of alternating and repeating disaccharide units of β-D-galactopyranose and 3,6-anhydro-α-L-galactopyranose, linked with β-(1 → 4) and α-(1 → 3) glycosidic linkages. These units are agarobiose and neoagarobiose. The hydrogen bonding between the 3,6-anhydro-*α*-L-galactopyranose residues stabilizes the gel. Agar has a fraction with high gelling capacity, the neutral, low sulphate/methoxyl substituted one, and a fraction with low gelling capacity, the charged, heterogeneous, highly substituted one (Alba and Kontogiorgos 2018). Usually the non-gelling fraction is removed during its extraction to obtain a powder with a higher gelling strength (Mostafavi and Zaeim 2020).

Alginate refers to alginic acid and all its derivatives and salts; it is the biopolymer with more commercial interest (Paixão et al. 2019). It is a linear polysaccharide consisting of β-D-mannuronic acid and α-L-guluronic acid linked with 1 → 4 glycosidic linkages. The higher the content in guluronic acid the stronger the gelling properties (Alba and Kontogiorgos 2018). The presence of ions in the solution, the pH and ionic strength of the solvent will determine the solubility of alginate, since it is a charged polysaccharide and have a wide range of molecular weight distribution. The selective binding of divalent and multivalent cations determines its ability to form gels, but they also gel following the cation-independent gelation mechanism.

Table 12.1 Source, properties and applications of the three major phycocolloids in the food industry—carrageenan, agar and alginate

Phycocolloid	Source	Properties	Applications
Carrageenan (κ-, ι-, λ-)	Rhodophyta	• Gelling, thickening and stabilizing properties. • Shear thinning flow. • Thermoreversible gels on cooling. • Kappa type: firm, brittle gel with potassium. • Iota type: soft shear thinning, elastic gel with calcium. • Kappa type gives lower viscosity compared to iota type.	• Confectionary: vegan alternative to gelatin. • Meat industry: texture improving agent; binding agent; stabilizer. • Desserts (water-based or dairy-based): thickening and stabilizing agent; binding agent. • Dairy products: stabilizer and texture improving agent. • Salad dressings: stabilizers. • Drink industry: stabilizers; thickening and flavor adding agent; flocculating agent. • Processed cheese: binding agent; texture improving agent • Bread making: dough proofing improving agent; formulation of gluten-free bread. • Foods with encapsulation technology: added components encapsulation agent; controlled release of encapsulated components.
Agar	Rhodophyta	• Major gelling agent, even at low concentrations. • Thermoreversible gels on cooling. • Heat resistant. • Brittle gels, but addition of sugars improves its elasticity. • Toleration to acids (pH 2.5–10).	• Confectionary: vegan gelatin substitute; jelly production; stabilizing agent. • Baking industry: preservative; moisture binding agent; dough proofing improving agent. • Meat industry: structuring and fat reducing agent of gelled canned meat products. • Frozen desserts: whey-binding agent. • Beverage industry: emulsion and foam stabilizing agent: flocculating agent.
Alginate	Ochrophyta - Phaeophyceae	• Major gelling agent. • Thermoreversible gel in the presence of calcium ions. • Clear and transparent gels resistant to heat. • Shear thinning. • Thickening properties in the absence of calcium. • In neutral solutions: low viscosity. • In lower pH (<5.5) solutions: high viscosity.	• Confectionary: jelly and bakery cream production. • Beverage industry: emulsion and foam stabilizing agent; flocculating agent. • Frozen desserts: whey-binding agent. • Food with encapsulation technology: added components encapsulation agent; controlled release of encapsulated components. • Edible coatings/films in meat products, fruits and vegetables.

3.1 Food Packaging Industry

The packaging industry is the largest market for plastic (Geyer et al. 2017), with food packaging having the bigger share in the total packaging sector (85%) (Silva et al. 2020). Petroleum-based synthetic polymers which are non-biodegradable polymers have been widely used in food packaging due to their low cost, durability and water resistance properties (Geyer et al. 2017; Karan et al. 2019; Farhan and Hani 2020; Silva et al. 2020). Because non-biodegradable plastic is cheap, resistant, and light, it is persistent in our lives, so it is challenging to reduce its use globally. Replacing traditional plastics with biodegradable materials could save the environment from a considerable amount of plastic waste, therefore, alternatives for single-use plastic packaging are being researched.

Bio-based plastics do not only have the advantages of traditional plastic but are also environmentally friendly, however, as they currently exist from crop plants, they compete for resources with crops used for food. This is where seaweed-based packaging enters in the effort of plastic pollution mitigation and for the innovation of new types of active packaging. As referred by Ozilgen and Bucak (2018) "Biopolymers are a group of molecules that are of natural resources and exhibit characteristic polymer properties". Food hydrocolloids are high molecular weight long-chain biopolymers commonly used as functional food additives. They are thickening, stabilizing, encapsulating, gelling and film forming agents, used in the food industry to produce films for packaging, maintain or improve the sensory properties of food and beverages, improve shelf life, make the production process easier and more effective, and produce functional foods (Skurtys et al. 2010; Ozilgen and Bucak 2018). Macroalgae can also be used indirectly as an alternative for largescale production of biopolymers, because its biomass can be the substrate to bacteria and *Archaea* capable of producing biopolymers like polyhydroxyalkanoate (Marques 2017; Ghosh et al. 2019).

Protecting food products during handling, storing, and transportation from physical, chemical and biological damage are the main roles of food packaging. By delaying food deterioration and keeping its integrity, the packaging maintains the quality and safety of food and increases its shelf life (Parreidt et al. 2018). Biofilms can exercise these functions, and the production of new biodegradable and edible biofilms consists in a matrix of hydrocolloids, lipids or a combination of both (a composite) (Skurtys et al. 2010; Paixão et al. 2019). Composites are a hybrid material with different properties from the ones of their individual components. Its mechanical and barrier properties depend on the properties of the individual polymers and their compatibility. Composite films made from polysaccharides and lipids, for example, have good mechanical and water barrier properties.

Consumers demand for environmentally friendly packaging, longer shelf life products, and better quality of fresh food has been growing, consequently the research and development of edible films for foodstuff are also growing. Edible films can be a solution for the environmental problems created by plastic packaging, and because they prevent moisture loss, oxidative rancidity and microbial spoilage, they extend the products' shelf life. Moreover, these films can be incorporated with antioxidant and other nutraceuticals supplementing the nutritional value of the food (Tavassoli-Kafrani et al. 2016; Gomaa et al. 2018).

3.2 Macroalgae Polysaccharide-Based Films for Food Packaging

Seaweed polysaccharides are an obvious choice material for edible films. The characteristics of the polysaccharides selected to produce a film will influence the disintegration rate, taste, and mechanical properties of the obtained film (Ozilgen and Bucak 2018).

Edible films need to be a selective barrier to gases and an effective barrier to water, water vapor, moisture, and temperature (Tavassoli-Kafrani et al. 2016). Films developed from algae polysaccharides have good oxygen vapor barrier properties and are impermeable to fats and oils, however, the major drawbacks of using polysaccharides as packing material are their poor mechanical and barrier properties. The most frequently used method to overcome these limitations is to produce composite films by mixing a polymer with another one and/or a hydrophobic component and/or nanoparticles (Abdul Khalil et al. 2017). The different characteristics of every component is used to improve the mechanical and barrier properties.

Carrageenan, agar and alginate are widely used in several food industries namely in the production of films for packaging, because they are nontoxic, biodegradable, and are derived from a renewable natural source (Kanmani and Rhim 2014; Tavassoli-Kafrani et al. 2016; Abdul Khalil et al. 2017; Gomaa et al. 2018; Parreidt et al. 2018).

Carrageenan solutions at certain temperatures and cation concentrations show shear thinning flow behavior and gel. Coil-to-helix transition upon cooling and cation-induced aggregation of helices are the two steps involved in the formation of gels from κ- and ι-carrageenan, however, these will have different properties (Farhan and Hani 2020). The addition of other hydrocolloids can improve the texture of carrageenan gels and its applications (Alba and Kontogiorgos 2018). However, the hydrophilic nature of carrageenan is a disadvantage for the manufacturing of packaging, because they would be susceptible to moisture transfer and have low water resistance, but blending carrageenan with hydrophobic compounds can solve this (Sedayu et al. 2019).

Agar films are biologically inert and can easily interact with different bioactive substances (Mostafavi and Zaeim 2020). Gels produced from agar are usually transparent and stiff, but the addition of sugars can increase its strength through the promotion of helices formation; the addition of other polysaccharides can expand the variety of textures of agar gels (Alba and Kontogiorgos 2018). Photodegradation and fluctuations in temperature and humidity in the surrounding environment promote formation of microfractures and embrittlement, therefore, agar has mainly been used in the development of edible films when mixed with film-forming emulsions, for example, to improve barrier performance (Skurtys et al. 2010). In the agar gel a network of agarose double helices is formed, as they aggregate by their external hydroxyl groups, and are stabilized by water molecules. During the casting, the temperature of the agar solution and casting surface needs to be higher than the agar gelling temperature to prevent the premature gelation of the solution. While drying the agarose structure allows its molecules to interact through hydrogen bonds, creating a continuous film network. Type and origin of agar, the film production method and the components incorporated in the matrix influence the needed concentration to produce an agar-based film.

Edible films prepared from alginate show poor water resistance due to its hydrophilic nature, but they are appropriate for loading additives and antibacterial compounds. Its mechanical properties can be improved mixing other polysaccharides in the alginate matrix (Skurtys et al. 2010). The β-D-mannuronic acid/α-L-guluronic acid ratio and the length of the blocks in the alginate structure impacts the mechanical properties of the gels; high ratios result in more elastic gels with good freeze-thaw stability, while low ratios result in strong and brittle gels with good heat stability but that shows syneresis after freeze-thaw processing (Alba and Kontogiorgos 2018). Alginate films have good oxygen barrier properties, prevent lipid oxidation, and improve food flavor and texture (Oussalah et al. 2007).

Comparing with carrageenan and alginate, agar has a less hygroscopic nature, which is an advantage in the production of packaging since one of its main functions is to reduce moisture transfer between the product and the surrounding environment (Sousa et al. 2010). The relatively high production cost of agar and its brittleness are drawbacks to its commercialization as food packaging, but the addition of plasticizers or the use of unpurified agar can be a way to overcome this. The plasticizers help to form softer and elastic gels, as well as the presence of proteins, polyphenols and other polysaccharides, considered as impurities in the agar extract, that additionally can give antioxidant properties to the gels (Martínez-Sanz et al. 2019). Alginate and carrageenan are highly hydrophilic, hence their weak moisture barrier properties. However, they are good barriers to fats and oils. These polysaccharides can prevent microbial proliferation in meat products and fruits. Additionally, films formulated with alginate or carrageenan prevent shrinkage and surface discoloration of meat products, and delay ripening of fruits, increasing its shelf life.

4 Processing of Macroalgae Polysaccharide-Based Films and Shelf Life Durability of Food Products

In the development of films for food packaging purposes the most common method is solvent casting; the biopolymer is dissolved in a constantly stirred solution (Abdul Khalil et al. 2017) and then casted. Figure 12.1 shows the general process of solvent casting. Extrusion is another method used, but usually in the production of synthetic polymer films. Even though this method is more applied to other non-seaweed hydrocolloids, some authors reported its use for the manufacturing of edible films (Skurtys et al. 2010).

Solvent casting is one of the most used methods for manufacturing films for food packaging. The chosen polymer is dissolved in a suitable solvent, centrifuged, or for a better result, filtered and degassed through vaccum, to remove any trapped air bubbles, poured into a mold, dried, and conditioned at a specific relative humidity environment, and then a film is obtained for analysis (Abdul Khalil et al. 2017; Ozilgen and Bucak 2018). When choosing a solvent for the manufacturing of an edible film, the preference is given to water-based solvents or to organic solvents listed safe, avoiding hazardous solvents not only to the environment but also to human health (Ozilgen and Bucak 2018). For analysis the American Society of Testing and Materials standard method is commonly utilized. The solvent casting method, or a similar one with the same principles, is the most recurrent in several studies on the development of edible seaweed-based packages.

The drying conditions influence the film structure as well as the wet casting thickness and the composition of the film solution. During the drying step the solubility of the polymer decreases and the film is formed when the polymer chains align themselves, therefore, the drying process cannot be fast. In the dried film a moisture content of 5–10% w/v is desirable (Skurtys et al. 2010).

The intrinsic properties of the food product (that determine their perishability), extrinsic factors (such as the storage conditions), and required shelf life are factors to be considered for the development of packaging for any type of food (Silva et al. 2020). In a general way, when these films are produced certain characteristics need to be evaluated to determine if and how they influence its efficiency. The characteristics are generally the following: physical properties (thickness, color, opacity), morphology, moisture barrier and water resistance properties, mechanical properties (tensile strength, Young's modulus, elongation at break), thermal properties, structural properties (X-ray diffraction patterns, Fourier-transform infrared spectra), diffusion of compounds (e.g., antimicrobial agents). In food packaging water resistance is important to prevent its disintegration when in contact with high moisture content food. Adequate mechanical properties also prevent the cracking or tears during the films' manufacture, when it is applied to the food product, handling, and storage. Uniformity, not only in its general aspect but also in the structure, is also important for its functionality, and the appearance important for the consumer. Thermal properties determine how the films react to heat fluctuations.

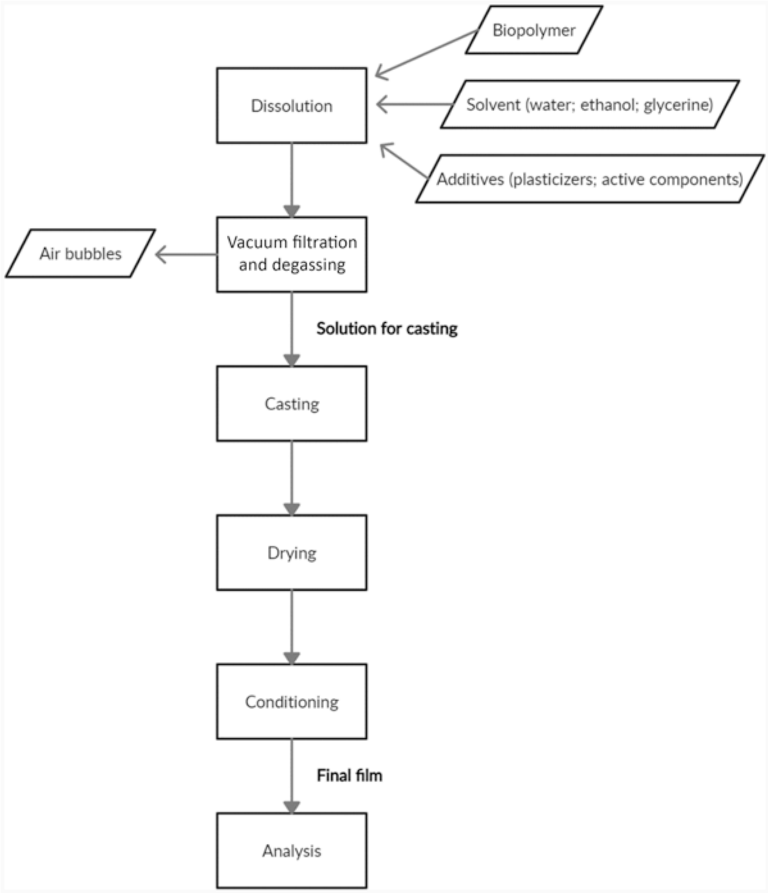

Fig. 12.1 Flowchart describing the general steps of the solvent casting method using a biopolymer as the main component of the matrix

The biological properties and the shelf life of food products are affected by the thickness of the film, that in turn is influenced by the concentrations of the polymer and additives, the spreading of the film solution, and its density, viscosity, and surface tension. A critical thickness must not be exceeded to avoid the decrease of oxygen and increase of carbon dioxide concentrations resulting from microbial activity. The food surface is dynamic and it modifies the film composition throughout storage time. The chemical composition and structure of the films, the characteristics of the products and the storage conditions depend on the barrier properties to gas, water vapor, aroma and oil which will influence the efficiency of the films (Skurtys et al. 2010). More detailed and extensive information on the properties of hydrocolloid edible films has been provided by Skurtys et al. (2010).

Films made of algae polysaccharides are usually brittle, they lack flexibility and toughness, therefore, they do not meet the criteria for commercial use edible films.

To overcome this problem plasticizers are added to improve its mechanical properties which in turn are affected by the type and concentration of plasticizer used. The most utilized plasticizers are polyols, like glycerol and sorbitol, sugars and water. What they do is increase the free volume in the matrix, intercalating between the biopolymer chains spreading them apart and disrupting hydrogen bonds, increasing flexibility, and water vapor and gas permeabilities (Skurtys et al. 2010). Although its advantages, the addition of plasticizers may alter the barrier properties of the films, decrease the ability of the film to attract water or decrease tensile strength (Oussalah et al. 2007; Skurtys et al. 2010). The elongation at break values is increased with the addition of plasticizers, however its increase in concentration decreases the tensile strength of the films. Therefore, the concentration of plasticizer added needs to be in accordance with the characteristics wanted/defined for the final package.

Active packaging has been one of the main areas of research in food packaging development to improve shelf life, add nutritional value, and improve sensory quality (Skurtys et al. 2010). Comparing to traditional packaging, it has several advantages because they can incorporate antimicrobial agents, antioxidants, enzymes, probiotics, minerals and vitamins (Skurtys et al. 2010). The addition of antioxidant and antimicrobial agents in the coatings or films makes their effect more efficient than when applied directly on the product, because its diffusion is slow.

Natural bio-preservatives are favored in the formulation of edible films, the most frequently used are essential oils, nisin and lysozyme. The incorporation of the enzyme lactoperoxidase in edible films has also been studied and showed bactericidal effects on Gram-negative bacteria, bacteriostatic effect on Gram-positive bacteria, and antifungal and antiviral activities. Oxidative rancidity, degradation, and discoloration can be avoided by the incorporation of antioxidant agents in the matrix, increasing the product shelf life as well. Most antimicrobial compounds have antioxidant properties, like the case of essential oils, phenolic compounds, vitamins E and C, that are some of the natural compounds used in the formulation of edible films (Oussalah et al. 2007; Raybaudi-Massilia et al. 2008; Alboofetileh et al. 2014; Azarakhsh et al. 2014; Kazemi and Rezaei 2015; Jalali et al. 2016).

The incorporation of essential oils of different spices and herbs provides a high antimicrobial activity to the composite material, expanding its application of food packaging. Rather than the type, the concentration of the essential oil is the factor that determines its antimicrobial efficiency. Several studies show the extension of shelf life and reduction on microbial counts in food products when these compounds are incorporated (Alboofetileh et al. 2014). Savory essential oil can act as a plasticizer as well as an antimicrobial agent, especially against Gram-positive ones. Because of their hydrophobicity and richness in fatty acids they improve water barrier properties and elongation at break values of the composites (Reboleira et al. 2020). Despite the advantages of integrating essential oils on food packaging films, they are usually extracted with toxic organic solvents implying the need for additional purification steps, thus the need for less toxic extraction techniques that can also reduce the production cost and increase the safety and sustainability of the product (Alboofetileh et al. 2014).

The formation of nanocomposites is currently one of the most effective ways to improve the properties of biopolymer films (Abdul Khalil et al. 2017). The most common types of inorganic nanomaterials used to develop seaweed-based nanocomposites are nanoclays and silver nanoparticles; and the most common organic nanomaterials are organically modified nanoclays, cellulose, carbon nanotubes and chitin nanofibers.

Several authors reported an improvement in mechanical strength and antimicrobial activity when films were reinforced with nanoclays, which are one of the most used additives in the development of seaweed-based nanocomposites. Mechanical strength of the films is improved as the stress is transferred to the nanoclay sheets, and these create a tortuous path in the matrix improving the barrier properties as well. The incorporation of nanoclays also decreases the rapid loss of other added components like essential oils. Chitin nanofibers can hypothetically be an allergen, so it might not be the best option to be incorporated in food packaging. On the other hand, silver in different chemical forms is toxic to several microorganisms. Nanocellulose can be added to food packaging to improve mechanical and barrier properties, and to serve as support for active compounds in active packaging. Its features include high crystallinity, high capacity of polymerization, high mechanical strength, low density, biocompatibility, non-toxicity and biodegradability. However, its use in food packaging, like the use of any other nanomaterial, raises potential safety concerns regarding their size, allergenicity and behavior, thus the need for more studies to demonstrate its safety.

Table 12.2 summarizes the main applications of several composites formulated with seaweed polysaccharides specifically in the food packaging industry. More detailed information, like concentrations and several examples of seaweed-based composites, and specifically for agar, alginate and carrageenan-based edible films and coatings for food packaging applications has been dealt with by Tavassoli-Kafrani et al. (2016) and Mostafavi and Zaeim (2020).

Several authors, like Jiang et al. (2013), Jalali et al. (2016), and Farhan and Hani (2020), to name a few, have reported for the use of different edible active films formulations where the characteristics of the food products were maintained for several days and at the end of the testing period the product was still good for consumption. The packaging reduced microbial spoilage, prevented moisture loss and maintained a good enough flavor, smell and color of the product. Oussalah et al. (2007) reported a controlled growth of foodborne pathogens (*Listeria monocytogenes* and *Salmonella Typhimurium*) in meat products packed in alginate-based films incorporated with essential oils. Other authors also report the decrease of microbial spoilage and maintenance of the organoleptic characteristics for several fruits (Rojas-Graü et al. 2007; Sipahi et al. 2013; Parreidt et al. 2018), mushrooms (Jiang et al. 2013), meat products (Oussalah et al. 2007; Parreidt et al. 2018; Surendhiran et al. 2019; Farhan and Hani 2020; Reboleira et al. 2020), and fish/seafood products (Kazemi and Rezaei 2015; Jalali et al. 2016; Albertos et al. 2019).

Table 12.2 Main seaweed-based polysaccharides composites and its applications in food packaging industry

Composite	Application
Alginate/nanocellulose	Films for packaging
Alginate/polysaccharides	Packaging of pre-cooked food
Alginate/polysaccharides/essential oils	Edible active films
Alginate/essential oils	Preservative coatings
	Shelf-life extension and quality retention of fresh cut fruits
Carrageenan/nanoclays	Shelf-life extension
Carrageenan/essential oils	Active packaging
Carrageenan/nanoclays/essential oils	Antimicrobial packaging
Agar/nanoclays	Biodegradable packaging
Agar/nanocellulose/essential oils	Active packaging for improving the safety and shelf-life of foodstuff

5 Conclusions and Future Perspectives

Macroalgae have been used for centuries, especially in Asian countries, however, its popularity and use have been increasing in several Western countries, mostly due to its reputation as a superfood. Macroalgae farming, aquaculture, and all the industries related to it are worth several millions of dollars and create jobs, especially on a local level. Seaweeds are a sustainable resource of several products and byproducts for the food, pharmaceutical, biomedical, cosmetic, and other industries; they can be used for wastewater treatment and production of biofuels. Therefore, it is a marine resource that can be included in sustainable economic models.

Seaweed-based polysaccharides can have several purposes on the industry previously mentioned due to its physical and chemical properties. One of its main uses is for the development of sustainable and biodegradable packaging for food, since traditional plastic packaging is the biggest contributor for plastic waste. Agar, carrageenan and alginate are the main phycocolloids used for the development of food packaging, since they have good gelling capacity and relatively good barrier properties. However, on their own these films are not commercially viable and do not have the properties that a good food packaging should have, like moisture and selective gases barrier, and resistance during handling. Therefore, they must be mixed with other components to improve these characteristics, and also with active components, like antioxidant, antimicrobial and nutraceuticals, to add some advantages comparing to traditional packaging. Nevertheless, the formulation of these composites need to be made suitable to the type of product, and the shelf life needed, since adding too much of one component to fix a problem can affect or create another one. Although the integration on the seaweed-based polysaccharide matrix of different components like plasticizers, biopolymers, lipids, nanoparticles, natural extracts, probiotic bacteria and bacteriocins, can improve its mechanical and chemical properties it also has some drawbacks affecting transparency, permeability, thermal stability or even mechanical strength. Therefore, further research to optimize the manufacturing of edible, biodegradable, nontoxic, seaweed-based packaging is needed. The probable toxicity and allergic effects of some additives like nanomaterials or natural extracts needs to be addressed as well. So, it is also important to study the synergy between components and the characteristics of each individual main component.

Although all the benefits of using seaweed polysaccharides to produce edible films, its commercial applications are still very limited. As there is still the need to optimize the production methods. Moreover, there is a need for guidelines and regulations in the packaging industry for these new types of packaging.

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