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Carrageenan-based edible biodegradable food packaging: A review

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Abstract
As traditional food packaging materials show shortcomings in terms of their environmental pollution impact and in their manufacturing requirements for non-renewable resources, the need for alternative packaging materials and packaging formats is now required more than ever. In the packaging industry, various approaches are being studied to look for bio-based polymers which could potentially replace the plastics due to the rising demands of food being safe and free from synthetic preservatives and non-toxic. Biodegradable, plant based, ecofriendly and sustainable approach is the need of an hour. Carrageenan is a well-known polysaccharide extracted from seaweeds of the Rhodophyceae family. This review explicates the chemical structure and properties of Carrageenan. The Carrageenan films produced are hard, flexible and soft, meeting the industrial requirements. The seaweed-based biopolymer which is also a renewable resource and is commercially available at low cost has a potential significance due to its worthy barrier and mechanical properties. This review not only focuses on the prospect and future of edible biodegradable packaging; various physical and chemical properties, the uptake and degradation profile, and the effect of carrageenan on humans but also explores the various carrageenan production methods. This review throws light on the various applications and future prospects of carrageenan and carrageenan-based products.

Keywords: carrageenan, edible film and coatings, additives, biodegradable packaging, food packaging

1. Introduction

In the present era of packaged foods, the packaging industry has seen a tremendous boost in the last 2-3 decades. Consumers have a preference for ready-to-eat packaged foods and hence the demand for desired packaging material is increasing day-by-day. To meet the present demand, the packaging industry solely runs on petroleum-based, synthetic, non-biodegradable materials. The manufacturing process of these products is highly chemical intensive and hence these products rank low on the green index. Due to their non-degradability, they pose an environmental problem leading to water, land and air pollution. Due to these shortcomings, there was a shift towards the trend of biodegradable packaging materials. They are biodegradable, natural and safer than their synthetic counterparts. The biodegradable packaging materials meet the desired requirements of a sustainable process and product as they present desirable features such as softness, lightness and transparency. There are various types of biodegradable packaging materials that are commercially being produced. The common types include Starch-based polymers, Cellulose-based polymers, Chitosan-based polymers, Carrageenan based films, Polyesters, Polylactic acid and derivatives, etc. Due to the increased interest in the field of biodegradable packaging, another sub-field that is gaining popularity is the development of edible biodegradable packaging. These are considered to be more eco-friendly than the non-edible biodegradable films because of the absence of the need of a disposal, leading to lower carbon prints. Researchers have made several efforts in the current year to enhance the shelf life and quality of food products by creating bio-based antimicrobial packaging materials. There are various biomolecules that are used for edible packaging like Wheat gluten, Soy protein, Corn zein, Collagen, Gelatin, Casein, Whey protein, Cellulose, Starch, Chitosan, Pectin, Alginate, Carrageenan, Seed gum, Glycerol esters, Waxes, and Resins [34].

For the development of edible packaging material, Carrageenan stands out as one of the most accepted biopolymers within industrial standards. Carrageenan is a water-soluble polysaccharide, containing sulphate groups, which is extracted from cell walls within seaweeds of the Rhodophyceae family. They are present in the voids formed from the cellulose network in the plant system. Carrageenan is found in two forms- native and degraded. Carrageenan is generally administered as an additive in the native form. The other form is the degraded form, also called Poligeenan. Poligeenan is known to produce certain ulceration and tumors. It is also responsible for suppression of immune response causing immune system toxicity [28]. The initial usage of seaweeds as food dates back to 600 BC in China. The Irish used it as a component of milk puddings, whereas in the Eastern countries, they were mostly used in salads. During the 1930s, the United States patented carrageenan as a commercial food additive. Carrageenan was declared as GRAS [1] in the United States in 1959 [25]. Carrageenan does not contain any nutritional value to the body and is also not assimilated inside the human digestive system but they possess water gelling and sulphate group-milk protein interaction properties which in turn is responsible in thickening and stabilization of the food.

The use of carrageenan as an additive has been well established in the food industry finding various applications. Due to the increasing popularity of carrageenan in the

[1] GRAS: Generally regarded as Safe

production of biodegradable packaging, there have been advancements in using carrageenan to produce an edible coating or film. A very thin level of consumable material is coated on a food product forming an edible coating, whereas an edible film is held among food components being made of edible material [15]. The various advantages of edible films are such as enhancing sensory properties and nutritive value of food products, reducing moisture loss, and environmental pollution. Due to delay in the process of ripening, edible coatings have the capability to enhance the shelf life of food products.

In general, processed foods are prone to microbial attack. The spoilage of such food products can be controlled due to the application of edible coatings which helps in delaying respiration or arresting microbial growth. This review primarily focuses on the current development in carrageenan based edible biodegradable films and coatings, their fabrication and the various applications of carrageenan-based products.

2. Carrageenan and its properties

2.1. Source and Structure

Carrageenan denotes a class of sulfated polysaccharide which is obtained from the cell walls of red seaweed species. The polysaccharides primary source is the red seaweed, Chondrus crispus which is also called by names such as Carrageen Moss or Irish Moss in different countries [1]. A temperate seaweed Kappaphycus alvarezii, also called as Eucheuma cottonii is the main source for producing k-carrageenan. ι-carrageenan is obtained from the species Eucheuma denticulum which is also known as Eucheuma spinosum. Many species of Gigartina and Chondrus genera are used to produce λ-carrageenan [23]. Several factors such as the source of species, development conditions, and treatment during the process affect the structure and properties of these polysaccharide preparations [32]. In general, there are two ways of producing this polysaccharide. First method involves the removal of carrageenan to an aqueous solution and then carrageenan can be obtained once the filtrate comprising seaweed residue is removed. This technique was only used until 1980 as it was costly. Second method consists of washing the seaweed to obtain the polysaccharide by getting rid of dense impurities in advance to reacting it with a basic salt solution. A pulpy mass will be obtained once the polysaccharide extracts are clarified, aggregated, and treated with alcohol such as isopropanol. To obtain particular dimensions of the particle, the fibrous mass is processed, cleaned, dried, and crushed [18].

The structure of Carrageenan is divided into 3 units. The G unit is made up of alternating 3-linked β-D-galactopyranose, the D unit consists of 4-linked α-D-galactopyranose, and the DA unit consists of 4-linked 3, 6-anhydro-α-D-galactopyranose [16]. There are various types of Carrageenan categorised depending on the occurrence of DA units and the number and position of sulphate groups. There are 3 principal types of Carrageenan (Figure 1) available in the market - mono-sulphated kappa carrageenan (κ-carrageenan), di-sulphated iota carrageenan (ι-carrageenan) and tri-sulphated lambda carrageenan (λ-carrageenan). κ-carrageenan and ι-carrageenan contain the 3,6-anhydro bridges, whereas λ-carrageenan lacks this bridge. (Table 1)

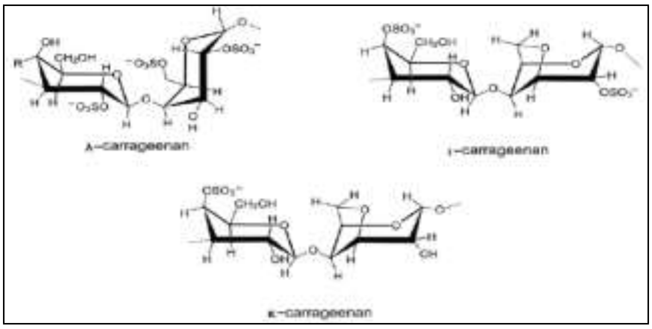

Fig 1: Structures of *Kappa*, *iota* and *lambda* carrageenan [16]

The properties of the 3 types of carrageenan depend upon the amount and location of the ester sulfate clusters that are present on the repeating glycosidic linkages [31]. Due to these varied chemical structural changes, the physicochemical property of the 3 types of Carrageenan varies. The gel formed by κ-carrageenan is firm, strong, and fragile, while ι-carrageenan gels are soft, flexible, and weak. Comparing these, κ-carrageenan proves to be the best candidate for edible biodegradable packaging [32].

Table 1: Characteristics of carrageenan [1]

Chemical composition	**A sulfated polygalactan compound containing α-d-1,3 and β-d-1,4 glycosidic linkages; linked to different salts such as potassium, sodium, calcium, magnesium etc.,**
Source	Red seaweed species of Gigartina, Chondrus, and Eucheuma genera are the primary sources for the polysaccharide's extraction.
Solubility of various carrageenan	λ can dissolve easily in hot or cold solutions; κ can dissolve in hot solutions; ι can solubilize in hot water.
Molecular weight	200,000 to 800,000 Da is the molecular weight range for the native polysaccharide; 20,000 to 40,000 Da is the weight range for degraded carrageenan; 10,000-20,000 Da is the average molecular weight range for poligeenan which is the highly degraded version of the polysaccharide.
Gel formation	κ type forms a firm, brittle gel; λ is non-gelling; ι forms a soft, elastic gel
Viscosity	All carrageenan products are highly viscous; As concentration increases, logarithmic rise of this property also takes place; At 75°C, 5-800 cps is the range of viscosity for 1.5% solutions.
Metabolism and stability	κ and ι is stable above pH 7 and undergoes hydrolysis in acidic systems; desulfation by sulfatases;
Properties of various carrageenan	λ and κ type of carrageenan acts as a stabiliser, thickener, and emulsifier in various food products; Enhance the solubility and texture as they can readily blend with milk proteins.
Synergism effects	In κ, syneresis of gel is high; ι has low synergistic effects; λ is non-gelling.
Concentration of polysaccharide	In food products, their concentration by weight usually ranges from 0.005- 2.0%.
Key applications	It's used in dairy and meat products, cosmetic industry, baby formula, chemical pesticides, food additive industry, pharmaceutical industry etc.,

2.2. Solubility

In general, most of the carrageenan products can soften in water to form highly viscous solutions with semi-plastic behavior [32]. In cold or hot water conditions, λ-carrageenan can readily dissolve. When κ-carrageenan is treated with an aqueous solution of potassium ions, it solubilizes and precipitates in hot water. The polysaccharides have the ability to swell; it is variable and relies on particle density. The temperature is a significant parameter that helps in determining which carrageenan to be used in a food system [23].

2.3. Carrageenan gel formation mechanism

The gelation process takes place when the first polysaccharide (carrageenan) molecule's helix comes in close contact to another matching single polysaccharide helix that results in forming a double helix. The ion double helices will have to cluster together to form a 3-dimensional network which will subsequently form a film. Gelling carrageenans are both kappa and iota (Figure 2). The mechanism shown in the below figure shows that the thermo-reversible gels are both kappa and iota. Upon heating above the melting temperature, the gel will get converted to fluid and will reorganize upon cooling with negligible to no loss of their original strength [23].

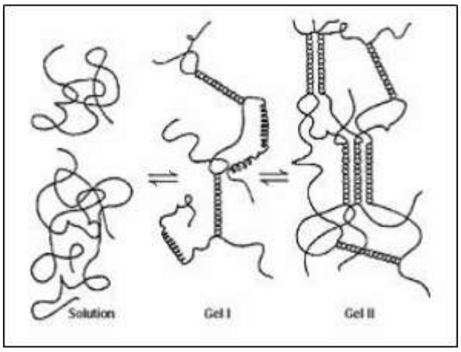

Fig 2: Thermal Reversibility of carrageenan gels [24]

2.4. Protein reactivity

In general, almost all carrageenans are protein reactive in nature. Reactivity depends on lot of factors such as pI [2] of the protein, type of protein, weight ratio protein to polysaccharide, and molar mass. The processes like divalent bridging and ionic bonding cause for the reaction to take place among the polysaccharide and protein. The carboxylic acid group of the protein gets ionized when it is above the pI of protein. Thus, the interaction between carrageenan and the protein is not due to negative- negative repulsions [23].

2.5. Carrageenan uptake studies

The uptake of carrageenan into other tissue and organs were studied on rats [1]. It was observed that the carrageenan was excreted in the faeces containing the same gel distribution pattern as the administered material. A small amount of carrageenan was observed to be absorbed by the Peyer's patches, intestinal wall, mesenteric and caecal lymph nodes, and serum. When administered into pigs, no retention in the caecum was observed. In new-born rabbits, the carrageenan was documented to be present in the small intestine, stomach and liver. When tested on *Rhesus* monkey, there was no evidence of storage in any of the tissues.

2.6. Degradation in gastrointestinal tract

Carrageenan can be found in two forms- native and degraded. The native form is mostly administered in the additive form. The molecular weight of the native carrageenan lies within the range of 200,000 – 800,000 Da. The molecular weight of the carrageenan, after being degraded in the tract, is present in the range of 20,000 to 40,000 Da. Highly degraded carrageenan or also called as Poligeenan is known to have an average molecular weight of 10,000 – 20,000 Da [28]. Carrageenan is partially degraded in the stomach, without any evidence of uptake into the stomach walls. The incubation of κ- / λ-carrageenan mixture in a simulated gastric juice mixture at pH 12.0 and 37ºC, 0.1% degradation was observed even after keeping it for several hours. Incubation of caecal content of rats and carrageenan mixture at 37ºC for a few hours did not produce any alteration in the viscosity of the solution proving that the gut microbes do not degrade carrageenan present. There has been documentation of presence of degraded carrageenan in the faeces of monkeys, pigs, and rats but concrete evidence of the site of breakdown was not found.

3. Production Process

Raw carrageenan is extracted from seaweeds. The raw form cannot be used for industrial production. Hence, processing of the raw carrageenan is required to produce usable forms of the polysaccharide. The carrageenan can be converted into 2 forms - refined and semi-refined carrageenan [20]. Research work in this field has led to the development of other advanced carrageenan products like edible films, edible coatings, among others. The procedure used to produce these are briefed below -

3.1. Refined Carrageenan process

Refined carrageenan is generally produced from seaweed *Chondrus crispus*. First, the seaweeds are washed Then are heated in water containing an alkali like sodium hydroxide for a predetermined time period leading to desulphurization for formation of 3, 6 anhydro bridges, thereby improving the gel strength. The filtration process of the obtained solution is conducted in a pressure filter using a filter aid for prevention of blockage due to fine gelatinous particles. The solution is concentrated using ultrafiltration or vacuum distillation. To obtain refined carrageenan in the solid form, two different methods can be used - the gel method and the alcohol method. (Figure 3)

3.1.1. Alcohol method

In this method, isopropanol is used for precipitation of carrageenan as a fibrous coagulum. The coagulum is centrifuged to separate it from the solution. The coagulum is further dehydrated by washing with alcohol. Then, it is dried and passed through a mill to obtain uniform sized solid carrageenan of desired size. The alcohol is recovered and recycled.

3.1.2. Gel method

In this method, the solution of carrageenan is poured into a potassium chloride solution. The coagulum obtained is washed with more potassium chloride to remove water. Surplus liquid is removed by pressing and it is frozen. When the mixture is thawed, separation of water occurs through

[2] pI: Isoelectric point

synaeresis and several hours of applying pressure accelerates the process. The gel sheets are chopped into smaller pieces and completely dried in a hot air dryer. The particles are milled to obtain carrageenan of desired size [30].

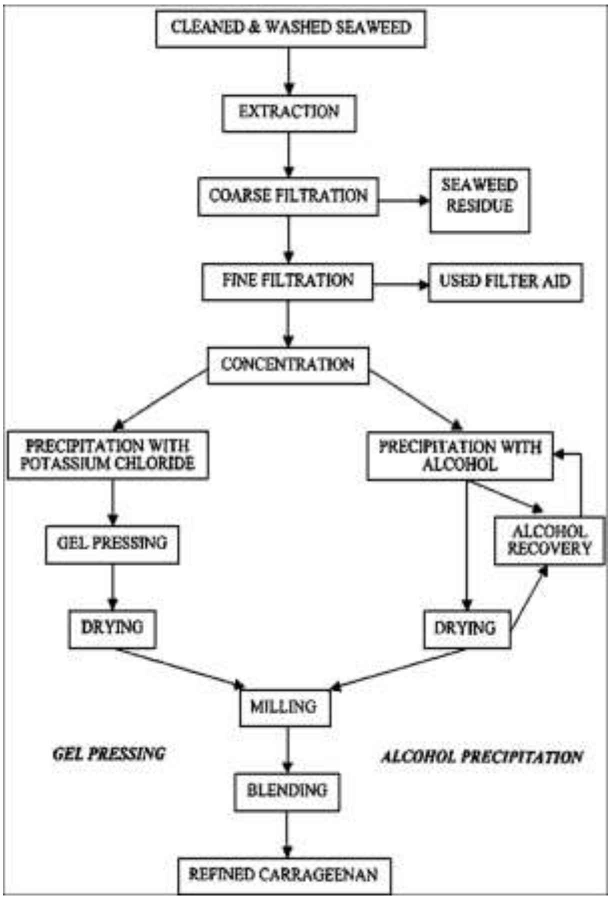

Fig 3: Flowchart of production of Refined Carrageenan [30]

3.2. Semi-refined Carrageenan
Semi-refined carrageenan is generally produced from *Kappaphycus alvarezii*. The seaweeds are heated in a metal container containing an alkaline solution of potassium hydroxide for around 2 hours. The potassium ion reacts with carrageenan forming a precipitate. The solution containing soluble carbohydrates, salts and proteins is separated from the precipitate. The precipitate which still resembles the seaweed is washed to remove the alkali. The residue is allowed to sun dry for about 2 days on a flat concrete slab. It is then chopped and milled to obtain optimal sized semi-refined carrageenan or seaweed flour [27].

3.3. Edible film formation methods
Edible films are those which act as a skinny protective layer over the packaged food product that can be consumed. There are two processes involved in producing a film.

The first process is named wet process/solution casting within which the edible biomaterials are solubilized in a solvent solution and then the solvent is removed by evaporation. Due to this, a reduction in solubility of the polymer is observed and as a result the polymer chain aligns itself to create a film. Factors such as drying rate and environmental conditions need to be maintained as it can affect the film's thickness and structural properties.

The other method is called a dry process that depends on the thermoplastic behavior of proteins and polysaccharides at low moisture range of compression molding and extrusion [18].

3.4. Edible coating creation methods
Food products containing edible coatings consists of a layer of polysaccharide that is present over the topmost surface. Edible coatings can be obtained by using the following methods -

3.4.1. Spraying method
This method involves a spray system that increases the surface area by the formulation of droplets and allocates them over the food surface area with the help of a set of nozzles. The advantages of this method include uniform coating, thickness control and therefore the possibility of multilayer applications [5].

3.4.2. Dipping method
This is the only method that can form high thick coating [13]. This method involves dipping the food product in a coating solution, draining the excess coating material on the product surface, formation of a thin membranous film followed by drying at room conditions or in a dryer. κ-carrageenan has been utilised to coat papaya fruit by this method [10].

3.4.3. Spreading method
The spreading/brushing method involves spreading the coating solution onto the food product using a brush to form a thin layer [16].

4. Applications of Carrageenan
4.1. Applications in food industry
In the continuous production of acetic acid, κ-carrageenan gel beads are used as carriers in a bubble-mixed reactor using *Acetobacter* species. Fermentation of milk products is done using κ-carrageenan gel immobilised bacterial cultures of three different strains of *Lactococcus lactis* and one strain of *Leuconostoc mesenteroides* in a 2 L stirred reactor. κ-carrageenan beads immobilised system of *Saccharomyces cerevisiae* cells is used for beer production by a static mixer. The research has further been extended to study the production of ethanol from glucose using immobilized cells of *Zymomonas mobilis* in a fluidized bed fermenter. Continuous ethanol production was also obtained using immobilized yeast cells on pineapple cannery waste. It is seen that in milk products like ice cream and gels, the combination of ι-carrageenan and calcium salts can be used as a thickener or stabilizer [18]. The polysaccharide is used as an emulsifier and has the EU additive E-number E407 when used in food products [1]. Carrageenan maintains the stability and consistency of various dairy products like chocolate, soymilk, infant formulations, and nutritional supplements, among others [26]. It plays a major role in suspending cocoa uniformly in chocolate milk. In various dessert gel formulations, ι-carrageenan is utilized because it can maintain the soft texture even after aging, finding immense applications in ready-to-eat desserts. The suitable rheological characteristics can be transferred to the paste by using carrageenan as a potential binder in toothpastes [29]. Carrageenan is used as a vegan alternative to gelatin which is used for gelation.

To fulfill the consumers' product acceptability, there is a need for the edible coating and film components to comply certain properties such as sensory and physicochemical [17]. Composites are hybrid materials which utilize certain physical or chemical treatments to enhance the edible film or coatings properties. Composite carrageenan products have been used to improve various properties. Composite films of carrageenan and grapefruit seed extracts have shown good antimicrobial properties, UV barrier properties, high transparency and improvement of shelf-life [21]. Rosemary extracts have been added to the carrageenan-nanoclay matrix improving anti-bacterial properties, tensile strength, elongation properties, and barrier properties, with reduced light transition at visible range and reduced water permeability [9].

The application of edible coatings with carrageenan and another polysaccharide such as alginate in pears resulted in the conservation of the fruit by lowering its water permeability and greater tensile strength [3]. To study the film structure and functional characteristics, κ-carrageenan was applied as an edible film coating along with plasticizers and carnauba wax emulsion into HPMC [3] for fresh blueberries. Carrageenan was added to delay the moisture loss and to avoid oxidations. As a result, the film structure and functionality had improved [4]. A study conducted to test the effects of chitosan/carrageenan and glycerol based edible coatings for the preservation of fruits stored at ambient temperatures provided positive results concluding that an increase in concentration of chitosan/carrageenan led to a decrease in water loss, weight loss and respiratory rate in the coated fruits [2]. Blending of carrageenan and clay, with Polylactic acid lamination improved the film properties such as thermal stability, mechanical barrier properties and optical transparency [6]. Carrageenan was blended with zein prolamine and mica clay by using glycerol as plasticizer. The film obtained had reduced water permeability and higher flexibility [7]. The incorporation of Chitin nano-fibrils into carrageenan films showed excellent antimicrobial properties as well as improved mechanical properties [8]. κ-carrageenan films reinforced with *Satureja hortensis* essential oil produced less rigid, more flexible films. The films had reduced water vapour permeability with excellent antimicrobial activity [12]. In another paper, many different antimicrobial agents were like nisin, sodium lactate, Novagard CB 1, sodium diacetate, among others, were incorporated into edible coatings of alginate and carrageenan, which gave high antimicrobial activity against *Listeria monocytogenes* in poached turkey products [14]. Various antioxidant compounds like Vitamin E, Citric acid, Essential oils, Vitamin C, sodium ascorbate, among others, are incorporated into edible coatings to reduce the chemical spoilage, reduced water loss, and enhancing overall sensory characteristics of the food product [19]. Research also shows the reinforcement of edible coatings with antibrowning agents such as Citric acid, Cysteine, Ascorbic acid [22]. Inclusion of mica flakes into κ-carrageenan and pectin matrices led to reduced water permeability and CO_2 and O_2 permeability [24].

4.2. Other Applications

Carrageenan finds various applications in other industries like pharmaceuticals, textile, among others. It's also used in air freshener gels, cosmetics and pesticides. Semi-refined carrageenan has been used in pet food formulations [29]. One of the special uses of this polysaccharide is for testing anti-inflammatory drugs in the domain of experimental medicine. For the production of tetracycline and chlortetracycline, κ-carrageenan immobilized cells of *Streptomyces aureofaciens* through fermentation. Carrageenan is used in the production of Penicillin. κ-carrageenan acts as a support to 6-Aminopenicillanic acid side chain which reacts with the β-lactam core to produce Penicillin G by fermentation. For over 40 years, κ-carrageenan immobilized cells of *P. dacunhae* have been used in the production of D-aspartic acid and L-alanine. The same immobilization technique has been used to produce other pharmaceutical products like L-tryptophan, L-malic acid, L-malic acid, 1, 5-dimethyl-2-piperidone, etc [33]. κ-carrageenan immobilized cells of Nitrosomonas europaea and Pseudomonas sp. have been used to develop nitrogen removal systems. K-carrageenan immobilized cells find applications in morpholine, 2, 4, 6-trichlorophenol, and 4-chlorophenol degradation. κ-carrageenan when blended with locust bean gum in the ratio of 40:60 (w/w) shows improved film barrier properties like decreased water permeability, improved elongation at break, and improved tensile strength [11].

5. Conclusion

A lot of research has been carried out regarding biopolymers to be used as a potential material in food packaging industry. The commercially produced edible packaging includes Alginates, Starch-based, Carrageenan, Seed gums, Pectin, Proteins, among others. Carrageenan is one such polysaccharide that can enhance the shelf life and maintain quality of food products. The native carrageenan films are known to produce hard, strong and flexible films which have applications in various fields. The films have properties such as aroma barrier, oil barrier, moisture barrier, barrier to mass transfer, oxygen barrier, acts as a carrier for food additives (antimicrobial, antioxidant, anti-browning, probiotics, minerals, etc.), product structural integrity enhancer, product appearance enhancer, food ingredients dispenser.

For the production of composite edible film or coatings, carrageenan can be combined with other polysaccharides such as chitosan, pectin, alginate, etc., Carrageenan films have also been reinforced with food additives having antimicrobial, antioxidant, anti-browning and plasticizing properties, which helps in the overall enhancement of chemical and mechanical properties of the film. Carrageenan has the raw potential to be an attractive biopolymer that can be used in food packaging applications and also minimize plastics. This area offers wide scope for future research by overlooking these parameters and studying the involvement of incorporation of nanomaterials, natural antimicrobials as edible coatings into the food products. It can aid in developing and large scale commercialization of carrageenan edible based biodegradable food packaging at later stages to replace the synthetic plastics that are harmful for society and environment.

6. Acknowledgment

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[3] HPMC: hydroxypropyl methyl cellulose

7. References

1. Necas J, Bartosikova L. Carrageenan: a review, Veterinarni Medicina. 2013; 58(4):187-205.
2. Mee Gie Lin, Ola Lasekan, Nazamid Saari, Siti Khairunniza-Bejo, Effect of chitosan and carrageenan-based edible coatings on post-harvested longan (Dimocarpus longan) fruits, CyTA - Journal of Food. 2018; 16(1):490-497.
3. Kessiane Silva de Moraes, Cristiane Fagundes, Maria Carolina Melo, Pamela Andreani, Alcilene Rodriguez Monteiro, Conservation of Williams pear using edible coating with alginate and carrageenan, Ciênc. Tecnol. Aliment., Campinas. 2012; 32(4):679-684.
4. Fernando A Osorioa, Paulina Molinaa, Silvia Matiacevicha, Javier Enrionea, Olivier Skurtys, Characteristics of hydroxypropyl methyl cellulose (HPMC) based edible film developed for blueberry coatings, Procedia Food Science, 2011; 1:287-293.
5. Ricardo D Andrade, Olivier Skurtys, Fernando A. Osorio, Atomizing Spray Systems for Application of Edible Coatings, Comprehensive Reviews in Food Science and Food Safety, 2012, 11.
6. Jong-Whan Rhim. Effect of PLA lamination on performance characteristics of agar/κ-carrageenan/clay bio-nanocomposite film, Food Research International, 2013; 51:714-722.
7. Maria D Sanchez-Garcia, Loic Hilliou, Jose M Lagaron. Nano-biocomposites of Carrageenan, Zein, and Mica of Interest in Food Packaging and Coating Applications, J Agric. Food Chem, 2010; 58:6884-6894.
8. Shiv Shankar, Jeevan Prasad Reddy, Jong Whan-Rhim, Hee-Yun Kim. Preparation, characterisation, and antimicrobial activity of chitin nanofibrils reinforced carrageenan nanocomposite films, Carbohydrate Polymers, 2015; 117:468-475.
9. Afsaneh Nouri, Mohammad Tavakkoli Yaraki, Mohammad Ghorbanpour, Shaobin Wang, Biodegradable κ-carrageenan/nanoclay nanocomposite films containing *Rosmarinus officinalis* L. extract for improved strength and antibacterial performance, International Journal of Biological Macromolecules, 2018; 115:227-235.
10. Hanisah Mustaffa Hamzah, Azizah Osman, Chin Ping Tan, Farinazleen Mohamad Ghazali, Carrageerean as an alternative for Papaya coating, Postharvest Biology and Technology, 2013; 75:142-146.
11. Martins JT, Cerqueira MA, Bourbon AI, Pinheiro AC, Souza BWS, Vicente AA, *et al*. Synergistic effects between κ-carrageenan and locust bean gum on physicochemical properties of edible films made thereof, Food Hydrocolloids. 2013; 29(2):901 280-289.
12. Saeedeh Shojaee-Aliabadi, Hedayat Hosseini, Mohammad Amin Mohammadifar, Abdorreza Mohammadi, Mehran Ghasemlou, Seyed Mahdi Ojagh, *et al*. Characterisation of antioxidant-antimicrobial κ-carrageenan films containing Satureja hortensis essential oil, International Journal of Biological Macromolecules, 2013; 52:116-124.
13. Dhanapal A, Sasikala P, Rajamani L, Kavitha V, Yazhini G, Banu MS, *et al*. Edible films from polysaccharides, Food Science and Quality Management, 2012; 3: 9-18.
14. Juck G, Neetoo H, Chen H. Application of an active alginate coating to control the growth of Listeria monocytogenes on poached and deli turkey products, International Journal of Food Microbiology. 2010; 142(3):302-308.
15. Beyza H Ulusoy, Fatma K Yildirim, Canan Hecer, Edible films and coatings: A good idea from past to future technology, Journal of Food Technology Research. 2018; 5(1):28-23.
16. Abdulaal Farhan, Norziah Mohd Hani. Characterization of edible packaging films based on semi-refined kappa carrageenan plasticized with glycerol and sorbitol, Food Hydrocolloids, 2016, 64.
17. Wang S, Marcone MF, Barbut S, Lim LT. Fortification of dietary biopolymers- based packaging material with bioactive plant extracts, Food Research International. 2012; 49(1):80-91.
18. Elham Tavassoli-Kafrani, Hajar Shekarchizadeh, Mahdieh Masoudpour-Behabadi. Development of edible films and coatings from alginates and carrageenans, Carbohydrate Polymers, 2016; 137:360-374.
19. Song Y, Liu L, Shen H, You J, Luo Y. Effect of sodium alginate-based edible coating containing different antioxidants on quality and shelf life of refrigerated bream (*Megalobrama amblycephala*). Food Control. 2011; 22(3-4):608-615.
20. Christopher S. Rideout, Richmond Hill, Method of extracting semi-refined carrageenan from seaweed, US Patent 5801240, 1998.
21. Paulraj Kanmani, Jong-Whan Rhim. Development and Characterization of carrageenan/grapefruit seed extract composite films for active packaging, International Journal of Biological Macromolecules, 2010; 68:258-266.
22. Robles-Sánchez RM, Rojas-Graü MA, Odriozola-Serrano I, González-Aguilar G, Martin-Belloso O. Influence of alginate-based edible coating as carrier of antibrowning agents on bioactive compounds and antioxidant activity in fresh-cut Kent mangoes, LWT - Food Science and Technology. 2010; 50(1):240-246.
23. Corina Popescu, Maria Iordan, Boscornea Cristian, Structure and properties of carrageenan, Fascicle VIII, 2007.
24. Vítor D Alves, Nuno Costa, Isabel M Coelhoso. Barrier properties of biodegradable composite films based on kappa-carrageenan/pectin blends and mica flakes, Carbohydrate Polymers, 2010; 79:269-276.
25. Joanne K Tobacman. Review of Harmful Gastrointestinal Effects of Carrageenan in Animal Experiments, Environmental Health Perspective, 2009, 109.
26. Thomas WR. Thickening and Gelling Agents for Food, Chapman & Hall, A. Imeson, Edition 1, US, 1997, 25-39.
27. Harris J Bixler. Recent developments in manufacturing and marketing carrageenan, Fifteenth International Seaweed Symposium, Hydrobiologia, S. C. Lindstrom & D. J. Chapman, Edition, 1996; 326/327:35-57
28. James M McKim, Jamin A Willoughby Sr, William R Blakemore, Myra L Weiner, *et al*. Clarifying the confusion between poligeenan, degraded carrageenan, and carrageenan: A review of the chemistry, nomenclature, and in vivo toxicology by the oral route, Critical Reviews in Food Science and Nutrition. 2018;

59(19):3054-3073.

29. Sarah Hotchkiss, Mariel Brooks, Ross Campbell, Kevin Philp and Angie Trius, The use of carrageenan in food, Carrigaline, Co. Cork, Ireland, ISBN: 978-1-63485-503-7, Chapter 10, 2016.
30. Porse H, Global seaweed market trends, Sixteenth International seaweed symposium, Cebu City, Philippines, 1998, 12-17.
31. Mahadevappa Y Kariduraganavar, Arjumand A Kittur, Ravindra R, Polymer synthesis and processing, Natural and Synthetic Biomedical Polymers, 2014, 1-31.
32. James N BeMiller, Carrageenans, Carbohydrate Chemistry for Food Scientists, West Lafayette, Indiana, Third Edition, 2019, 279-291.
33. Van de Velde F, Lourenco ND, Pinheiro HM, Bakkerd M, Carrageenan: a food-grade and biocompatible support for immobilisation techniques. Advanced Synthesis and Catalysis, 2002; 344:815-835.
34. Theeranun Janjarasskul, John M Krochta. Edible Packaging Materials, Annual Review of Food Science and Technology, 2010; 1:415-448.