

1     **A Review of Property Enhancement Techniques for Carrageenan-**  
2                                   **based Films and Coatings**

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10    **Abstract**

11           Carrageenan, a polysaccharide extracted from marine algae, is becoming  
12    increasingly regarded as a promising renewable biomaterial that has strong potential as  
13    a substitute for conventional synthetic plastics. Materials derived from carrageenans  
14    have been widely investigated over the recent decades for use in pharmaceutical and  
15    biomedical applications through to edible films and coatings. In the area of flexible  
16    films, carrageenans suffer from limitations that are primarily a result of their inherent  
17    hydrophilicity. Considerable research efforts have been devoted to the improvement of  
18    the properties of carrageenan films in order to extend the range of suitable applications.  
19    These include blending with other polymers, the use of plasticizers, and reinforcements  
20    with nanomaterials. This review comprehensively assesses the current status of  
21    carrageenan-based film development including material characteristics and strategies  
22    to obtain desirable film properties with particular regard to real applications.

23    **Keywords:** Carrageenan, polysaccharides, bioplastics, film, material properties

## 24 **1 Introduction**

25         The extensive use of plastic materials over the years has indisputably  
26 contributed to increasing environmental pollution (Thompson, Moore, vom Saal &  
27 Swan, 2009; Woodall et al., 2014). In 2014, it was estimated that more than 310 million  
28 tons of plastics were used worldwide, with more than 99% of these derived from  
29 petrochemicals (Plastic Europe, 2014). These conventional plastics are resistant to  
30 degradation in nature, and this is particularly evident in the oceans and on sea beds  
31 where vast quantities of plastic wastes accumulate (Andrades, Martins, Fardim, Ferreira  
32 & Santos, 2016; Enders, Lenz, Stedmon & Nielsen, 2015). As a result, such materials  
33 can lead to serious environmental problems and can be harmful not only to wildlife  
34 (Bond et al., 2013; Neves, Sobral, Ferreira & Pereira, 2015; Rummel et al., 2016) but  
35 also to human health, particularly in form of microplastics which can enter the food  
36 chain (Efferth & Paul, 2017; Prata, 2018; The Lancet Planetary Health, 2017).

37         In recent decades, this environmental issue has drawn considerable attention  
38 from governments, industry and researchers in order to find sustainable, biodegradable  
39 alternatives to synthetic plastics. This is particularly the case in packaging applications  
40 that represent the largest proportion of the overall plastic usage. Approximately one-  
41 third of plastics manufactured worldwide are transformed into packaging materials,  
42 with the majority converted into single-use applications such as flexible and rigid food  
43 packaging, plastic bags and film, among numerous others (Siracusa, Rocculi, Romani  
44 & Dalla Rosa, 2008).

45         Extensive research has been conducted to produce bioplastics from many  
46 different sources including plants, microbes, and animals (Pathak, Sneha & Mathew,  
47 2014). Some are now commercially available in the global market such as poly(lactic  
48 acid) (PLA), poly(hydroxyalkanoates) (PHAs) and starch-based polymers, with new

49 materials frequently investigated for various uses (Accinelli, Sacca, Mencarelli &  
50 Vicari, 2012; Yates & Barlow, 2013). Even though these materials can be produced  
51 from many renewable sources, there are still challenges to be addressed due to their  
52 limited biomass-availability and also their cultivation or synthesis. Seaweed is one such  
53 material that can offer a source of raw materials from which packaging materials can  
54 be produced. Compared with terrestrial plant sources, seaweed offers some  
55 considerable advantages including its low cost and abundance in nature. Moreover, as  
56 a non-terrestrial plant material, it is unnecessary to clear valuable land to plant crops or  
57 compete with food production. Additionally, seaweeds are purported to lessen impacts  
58 on the food chain and are generally safe from exposure to chemicals or fertilizers  
59 (Rajendran, Puppala, Sneha, Ruth & Rajam, 2012).

60         Amongst several polysaccharides extracted from seaweeds, carrageenan is one  
61 of the most promising phycocolloids that demonstrates excellent film-forming ability  
62 (Blanco-Pascual, Montero & Gómez-Guillén, 2014; Paula et al., 2015; Siah, Aminah  
63 & Ishak, 2015). Carrageenan, obtained from red seaweeds of the class *Rhodophyceae*,  
64 is a sulfated polygalactan with 15-40% ester sulfate content and with an average  
65 molecular weight above 100 kDa. Its polymer chains are formed by alternate units of  
66 D-galactose and 3,6-anhydrogalactose joined by  $\alpha$ -1,3- and  $\beta$ -1,4-glycosidic linkages  
67 (Necas & Bartosikova, 2013).

68         Recent studies have reported the transformation of carrageenan into packaging  
69 films for a range of different applications (Kanmani & Rhim, 2014a; Martins, Cerqueira,  
70 et al., 2012; Setha, Mailoa & Gaspersz, 2016; Shojaee-Aliabadi, Mohammadifar, et al.,  
71 2014). However, these polymer films still exhibit limitations with particular regard to  
72 their water vapour permeability (WVP) and water resistance since they are naturally  
73 hydrophilic (Alves et al., 2011), as well as being brittle (Larotonda, 2007; Shojaee-

74 Aliabadi, Hosseini, et al., 2014). As a consequence, such inherent weaknesses may limit  
75 the widespread packaging applications of these materials. Many approaches have been  
76 investigated to overcome these shortcomings such as blending with natural or synthetic  
77 polymers (Martins, Bourbon, et al., 2012; Rhim, 2012), reinforcing with hydrophobic  
78 fillers (Alves, Costa & Coelho, 2010), or cross-linking (Xu, Bartley & Johnson, 2003).  
79 Moreover, the utility of these materials may be improved by the inclusion of natural  
80 antimicrobial (AM) compounds as well as nanoparticles, among other measures (Rhim  
81 & Wang, 2014; Shojaee-Aliabadi, Hosseini, et al., 2014; Soni, Kandeepan, Mendiratta,  
82 Shukla & Kumar, 2016).

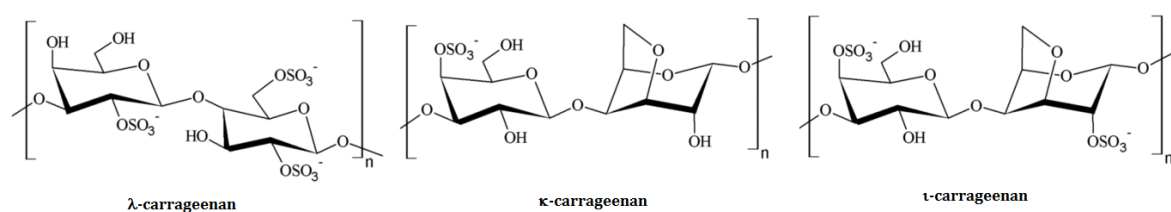
83         The development of carrageenan-based films for packaging purposes is a  
84 relatively new and emerging research area. Consequently, there are a limited number  
85 of articles in the literature that review the current status of this topic although some  
86 previous reviews have described the potential applications and some general  
87 preparations of seaweed polysaccharides-based composites (Abdul Khalil, Saurabh, et  
88 al., 2017; Tavassoli-Kafrani, Shekarchizadeh & Masoudpour-Behabadi, 2016).  
89 However, these reviews have not provided insight on the development of specific  
90 carrageenan-based film composites and, in particular, the techniques that are available  
91 to improve the physico-mechanical properties of such material. This review therefore  
92 considers the fundamental knowledge and current state of research into strategies to  
93 enhance the properties of carrageenan-based films with a focus on food packaging  
94 applications.

## 95 2 Carrageenan

### 96 2.1 Chemical Structures and Characteristics

97 Carrageenan is a type of hydrophilic linear sulfated galactan found specifically  
98 in the cell walls of red marine algae (*Rhodophyceae*), which is primarily extracted from  
99 the genus *Chondrus*, *Eucheuma*, *Gigartina* and *Iridaea* (Jouanneau et al., 2010; Nanaki,  
100 Karavas, Kalantzi & Bikiaris, 2010). Carrageenan is of typically high molecular weight  
101 with an average molecular mass of around 100 to 1000 kDa. In addition to the ester  
102 sulfate and galactose groups as the main backbone in its structure, other polysaccharide  
103 residues and substituents are also present including glucose, xylose, uronic acids,  
104 methyl ethers, and pyruvate groups (Aldalbahi, 2012).

105 The sulfate groups on the disaccharide repeating unit determine the  
106 classification into one of three major carrageenan types: lambda ( $\lambda$ ), kappa ( $\kappa$ ), and iota  
107 ( $\iota$ ) (Al-Alawi, Al-Marhubi, Al-Belushi & Soussi, 2011) as depicted in Figure 1. In  
108 general,  $\kappa$ -carrageenan containing about 25-30% of ester sulfate groups with 28-35%  
109 of 3,6-AG exhibits the strongest gelling ability followed by  $\iota$ -carrageenan (28-30% of  
110 ester sulfate groups and 25-30% of 3,6-AG), and  $\lambda$ -carrageenan (32-39% of ester sulfate  
111 groups and no 3,6-AG content) (Barbeyron, Michel, Potin, Henrissat & Kloareg, 2000).



112

$\lambda$ -carrageenan

$\kappa$ -carrageenan

$\iota$ -carrageenan

113 **Figure 1.** Chemical structures of carrageenans (Cunha & Grenha, 2016)

114 In addition to the specific types of carrageenan described above, there are also  
115 some hybrid types. In nature, seaweeds generally do not produce pure carrageenan but

116 more likely mixtures of different sulfated polysaccharides in their structures including  
117 hybrid carrageenans (van de Velde, 2008). The composition of carrageenans in a given  
118 seaweed is determined by several factors, such as its biological stage (Gómez-Ordóñez  
119 & Rupérez, 2011), gender of the gametophyte, environmental condition (Hilliou, 2014),  
120 as well as the extraction method used in carrageenan recovery (Larotonda, Torres,  
121 Goncalves, Sereno & Hilliou, 2016; Souza, Hilliou, Bastos & Gonçalves, 2011). Hilliou  
122 (2014) reported that the vegetative phase of the *Gigartinales* seaweed order produces  
123 highly sulfated forms of  $\mu$ -carrageenan, which is a non-gelling type, whereas in the  
124 reproductive life stage,  $\kappa$ - and  $\iota$ - types of gelling carrageenan together with  $\nu$ - and  $\eta$ -  
125 carrageenans are produced. Furthermore, in *Kappaphycus striatum* seaweed the young-  
126 age seaweed contains less-gelling carrageenan types than the matured seaweed (Hilliou,  
127 2014).

## 128 **2.2 Carrageenan Sources**

129 The name carrageenan is derived from the Gaelic word, *carraigín* or “little rock”  
130 that has been used as early as 400 A.D. in Ireland. The first types of carrageenans were  
131 obtained from the “Irish moss” seaweed (*Chondus crispus*) which was used for animal  
132 feed and medicinal purposes (Loureiro, Cornish & Neish, 2017; Loureiro, Hurtado &  
133 Critchley, 2017). During World War II, the world’s demand for carrageenan noticeably  
134 increased particularly in relation to the food processing industries, with *Chondus*  
135 *crispus* and *Gigartina* seaweeds harvested from natural stock being the major sources.  
136 *Chondus crispus* grows naturally in Canada, Ireland, France, Spain and Portugal, and  
137 *Gigartina* beds are found in Southern Europe and South America (Valderrama, Cai,  
138 Hishamunda & Ridler, 2013). In the 1940’s, Canada with its abundant natural beds of  
139 *Chondus crispus* had become the world’s largest carrageenan-seaweed supplier which

140 continued for almost three decades. However, the discovery of alternative carrageenan-  
141 seaweed species, *Eucheuma sp.* in the Philippines, followed by the success of its  
142 cultivation for large-scale farming production, has made this species a major source for  
143 carrageenan with the Philippines displacing Canada as the largest supplier of  
144 carrageenans. Indonesia soon followed and adopted successful seaweed farming from  
145 its neighboring country such that in the last few decades it has surpassed the Philippines'  
146 carrageenan-seaweed production to become the leading global supplier of carrageenan,  
147 predominantly derived from the *Kappaphycus* and *Eucheuma* seaweeds (Hurtado,  
148 Neish & Critchley, 2015; Valderrama et al., 2013). To date, around 90% of world's  
149 carrageenan is derived from these two species and their farming is now spreading  
150 worldwide including regions of South-east Asia, Pacific Islands, mainland of East  
151 Africa, South America, and the Central Americas (Hurtado et al., 2015). The success  
152 of carrageenan seaweed farming worldwide may also denote a sustainable resource of  
153 raw material stocks for future industrial production of carrageenan-based plastics.

154         Similar to land-based crops, however, carrageenan seaweed farming is also  
155 subjected to the challenges of nature *i.e.* herbivorous fish predation, stormy weather,  
156 parasite epiphyte, and outbreaks of the “ice-ice” disease. This disease, which presents  
157 as a white bleaching of the seaweed's thalli, is one of the biggest problems associated  
158 carrageenan seaweed farming. Outbreaks have been reported since the early years of  
159 *Kappaphycus* farming development in the Philippines and since then, the disease has  
160 been reported in almost all carrageenan seaweed farms worldwide (Hafting et al., 2015).  
161 This outbreak is recognized as the seaweed's physiological stress in responding to its  
162 surrounding environmental changes such as temperature and salinity fluctuations.  
163 However, it is commonly followed by pathogenic microbial infestations which cause  
164 complete necrosis and fragmentation of the infected thalli (Loureiro, Hurtado, et al.,

165 2017). This, in turn, can cause a tremendous drop in seaweed production, as well as the  
166 quality of the carrageenan (Mendoza, Montaña, Gazon-Fortes & Villanueva, 2002).  
167 To respond to this challenge, there is an urgent need to develop seaweed strains that are  
168 tolerant to fluctuations in marine environmental conditions, resistant to disease and  
169 produce greater carrageenan yields (Hayashi et al., 2017; Kim, Yarish, Hwang, Park &  
170 Kim, 2017).

### 171 **2.3 Production of Carrageenan**

172 The extraction and processing of the three main types of carrageenan is very  
173 similar in principle. It invariably involves the removal of impurities, separation of the  
174 carrageenan from the aqueous extraction medium and other constituents, followed by  
175 drying. For the production of  $\kappa$ -carrageenan, raw material can be obtained from  
176 seaweed species including *Eucheuma*, *Chondrus*, *Hypnea*, *Iridaea* and *Furcellaria*  
177 (McHugh, 2003; Prajapati, Maheriya, Jani & Solanki, 2014). For these species, the  
178 dried mass of seaweed is washed to remove all the impurities and other particulates  
179 attached to the surface of its thalli followed by a hot alkali treatment using solutions of  
180 NaOH or KOH to remove any remaining impurities. This treatment also increases the  
181 3,6-AG content which subsequently increases the gel strength (Haug, 1967). The  
182 carrageenan is then boiled in water until it forms a slurry, after which the volume of the  
183 solution is reduced by evaporation before it is cooled and allowed to gel. Next, the  
184 gelled carrageenan is pressed to remove most of the water before it is further dried and  
185 milled into carrageenan powder.

186 Additional steps are performed for the *Eucheuma* and *Furcellaria* seaweed  
187 species, whereby precipitation using KCl solution is applied (Stanley, 1987). Following  
188 the hot water extraction step, the carrageenan slurry is extruded through spinnerets and



189 collected in a container of cold KCl solution to form a gel before it is dehydrated, dried  
190 and powdered (Minghou, 1990). For the production of  $\lambda$ -carrageenan, *Gigartina* and  
191 *Chondrus* (Irish moss) seaweeds are commonly used (van de Velde & De Ruiter, 2002)  
192 and since  $\lambda$ -carrageenan does not characteristically form a gel, the dehydration process  
193 is usually performed using a drum dryer and/or alcohol precipitation with propanol or  
194 ethanol. However, thermal processing using a drum dryer may adversely impact the  
195 carrageenan quality, so alcohol precipitation is the more common industrial practice  
196 (Prajapati et al., 2014).

197 As the gelling strength of  $\iota$ -carrageenan is not as high as  $\kappa$ -carrageenan, the  
198 filtrate of  $\iota$ -carrageenan is not suitable for dehydration through the gel-pressing  
199 technique, thus precipitation in alcohol solution has been shown to be the best practice  
200 for its production (Prajapati et al., 2014). After hot extraction, the liquor extract is  
201 filtered through a fine filter, evaporated, and precipitated with isopropanol to get a  
202 fibrous carrageenan coagulum. This material is then pressed to remove the alcohol  
203 solvent before it is washed with water, dried, and milled to the required particle size  
204 (McHugh, 2003; Tavassoli-Kafrani et al., 2016).

#### 205 **2.4 Semi-Refined Carrageenan**

206 The aforementioned methods describe the production of refined carrageenan,  
207 but in addition to these materials, semi-processed/semi-refined carrageenans are also  
208 extensively produced for various industries including use as additives in pet foods and  
209 dairy products (Dewi, Darmanto & Ambariyanto, 2012). According to the US Food and  
210 Drug Administration (US Food and Drug Administration, 2017), semi-refined  
211 carrageenan (SRC) can be acceptably referred to as carrageenan and there is no legal  
212 distinction between these two materials. However, in the European Union (EU), these

213 materials are recognized as different substances and are thus regulated separately. In  
214 this case, the SRC is regulated under the name "Processed Eucheuma Seaweed (PES)"  
215 with the trade "E" number of E407a, whereas pure carrageenan is registered with the  
216 number E407 (EUR Lex, 2004).

217 During the production of SRC using *Eucheuma cottonii*, the seaweed is  
218 subjected to alkali treatment before it is dried and powdered (Anisuzzaman, Bono,  
219 Samiran, Ariffin & Farm, 2013). In addition to removing the pigments, some proteins,  
220 and other impurities during the alkali treatment, the hydroxide ions penetrate the thallus  
221 and reduce the amount of ester sulfate groups in the structure. The 3,6-AG content is  
222 also increased, and this subsequently improves the gel strength (Anisuzzaman et al.,  
223 2013; Mustapha, Chandar, Abidin, Saghravani & Harun, 2011).

224 Compared with the refined carrageenan, SRC has a significantly lower price  
225 due the reduced number of processing steps required in its production. Fewer resources  
226 are therefore required including significantly less water in order to produce the final  
227 SRC product. In addition, the alcohol precipitation and filtration of impurities steps are  
228 not required and there is also no need for a refrigeration process to freeze the gel as in  
229 the case of refined-carrageenan production (Dewi et al., 2012; Farhan & Hani, 2017).  
230 The water-soluble component in SRC is primarily  $\kappa$ -carrageenan (Jurasek & Phillips,  
231 1998) and although this chemical species forms the main part of the physical structure,  
232 an insoluble cellulose component originating from the algae cell walls is retained  
233 (Gunning et al., 1998; Phillips, 1996). The cellulosic content together with other  
234 residual plant debris constitutes around 20-30% of the SRC, and this can impart  
235 undesirable optical properties to any films formed using this material (Ghosh,  
236 Siddhanta, Prasad, Meena & Bhattacharya, 2006).

## 237 **2.5 Economic Perspectives**

238 It is evident that seaweed-based film can offer many advantages that  
239 demonstrate its potential to be developed further into high-end commodities (Rajendran  
240 et al., 2012). However, the pathway of carrageenan film development for commercial  
241 applications is still in its infancy with issues such as quality and economic feasibility  
242 of the end-products compared with conventional plastics or other available bio-based  
243 plastics in the market the main barriers to wider development and acceptance.

244 In general, cost effectiveness is the main hurdle to be overcome for the  
245 development of bio-based plastic materials through to the commercialization stage  
246 (Mekonnen, Mussone, Khalil & Bressler, 2013) since production costs are generally  
247 more expensive than those of petroleum-based plastics (Changwichan, Silalertruksa &  
248 Gheewala, 2018; Song, Murphy, Narayan & Davies, 2009). Nonetheless, some unique  
249 properties of bio-based plastic materials may allow for future cost reductions,  
250 particularly in the end-of-life phase where bio-based materials can be more cost  
251 effective with regard to waste disposal management (van den Oever, Molenveld, van  
252 der Zee & Bos, 2017). There are also examples of other bio-polymer resins such as PLA  
253 and PHAs that are becoming more competitive in price compared to their petroleum-  
254 based counterparts in the global market. Additionally, the bio-based plastic price is  
255 relatively more stable than fossil-based plastics because biomass prices typically  
256 fluctuate much less than the oil price (van den Oever et al., 2017).

257 In comparison with other sources of bio-based plastic materials such as those  
258 derived from corn, cassava, sugarcane, and other terrestrial crops, seaweed may be a  
259 less expensive material since it does not require the use of arable lands, fresh water, and  
260 fertilizer or chemicals (Konda, Singh, Simmons & Klein-Marcuschamer, 2015).  
261 However, the extraction process of carrageenan does require a large amount of

262 chemicals and energy (Abdul Khalil, Tye, et al., 2017) which is the key drawback that  
263 must be overcome to achieve economic feasibility for industrial implementation.  
264 Nonetheless, it has been previously observed that the price of bio-based plastics  
265 becomes more competitive with its synthetic counterparts whenever the economics of  
266 large-scale production, conversion into products, and logistics become more favorable  
267 (van den Oever et al., 2017). For example, various single use-plastic products such as  
268 bottles, food tray and lid containers, overwraps, cups, and some flexible films made  
269 from PLA are now widely available in the market with competitive prices to those made  
270 from conventional plastics. This is because PLA and its end-products are currently  
271 manufactured on a large industrial scale with similar product processing technologies  
272 that are utilized for synthetic plastics (Muller, Gonzalez-Martinez & Chiralt, 2017).  
273 Similarly, the price of bio-poly(butylene succinate) (bio-PBS) has dropped from 4.00  
274 €/kg to *ca.* 2.50 €/kg due to the production of succinic acid from biomass becoming  
275 more efficient with larger production volumes (van den Oever et al., 2017).

276         To achieve successful commercial production of carrageenan films in a way  
277 similar to PLA, bio-PBS, and other commercial bio-based polymers, significant  
278 innovative breakthroughs are needed across the whole production chain, starting from  
279 seaweed cultivation and harvesting, transport, carrageenan extraction, through to the  
280 manufacture and marketing of products. Another important consideration that  
281 compensates in part for the higher production costs is that carrageenan-based plastics  
282 can offer consumers significant overall environmental benefits compared with some  
283 other materials and such perspectives have previously been associated with growing  
284 market demands (DeGruson, 2016). End-products derived from carrageenan may also  
285 be developed for niche markets where slightly higher production costs may be more

286 acceptable. Moreover, utilization of less expensive semi-refined carrageenan may also  
287 reduce production costs of films for various uses (Sedayu, Cran & Bigger, 2018).

### 288 **3 Carrageenan-Based Films**

#### 289 **3.1 Gel Formation**

290 In an aqueous solution,  $\kappa$ - and  $\iota$ -carrageenan demonstrate a thermo-reversible  
291 sol-gel transition, whereas no gel state occurs in  $\lambda$ -carrageenan solutions (Yuguchi, Thu  
292 Thuy, Urakawa & Kajiwara, 2002). Gelation of carrageenan has been described as a  
293 conformational transition of random coils into helical structures which aggregate during  
294 low temperature and/or by the presence of cations in the solution (Piculell, 1995; Rees,  
295 Scott & Williamson, 1970). In the sol-phase, carrageenan conformation adopts a  
296 random coil formation whereby the anhydro-galactose sequences twist into a double  
297 helix at low temperature. Further aggregation also occurs among the twisted double  
298 helical parts, and these subsequently form a cross-linked domain creating an infinite  
299 network structure to accomplish gelation (Yuguchi et al., 2002). Moreover, since the  
300 repeating units of the ester sulfate groups are electrically charged, the cations have been  
301 found to contribute in the gelation process by mediating between the double helices  
302 (Morris, Rees & Robinson, 1980). During this process, the transition kinetics are driven  
303 by the amount and molecular weight of the galactan, the types of cations involved, and  
304 the temperature of the solution (Piculell, 1995). In an aqueous solution, the transition  
305 of molecular conformation from random coils to double helices of  $\kappa$ - and  $\iota$ -carrageenan  
306 occurs at 38°C and 45°C, respectively, which is well known as the coil-helix transition  
307 temperature (Nanaki et al., 2010; van de Velde & De Ruiter, 2005).

308 To generate a helical structure in  $\kappa$ - or  $\iota$ -carrageenan solutions, a minimum  
309 degree of polymerization of around one hundred is required (Hjerde, Smidsrød, Stokke

310 & Christensen, 1998). Partially de-sulfated  $\kappa$ -carrageenan shows similar structural  
311 behavior to fully sulfated  $\kappa$ -carrageenan, except that its coil helix transition temperature  
312 is higher than that of the latter (Zhang, Piculell & Nilsson, 1991; Zhang, Piculell,  
313 Nilsson & Knutsen, 1994). By selecting the appropriate type and concentrations of salts  
314 in solution, various carrageenan helical behaviors can be manipulated, ranging from  
315 liquid-nematic crystals to double-helical rods and super-helical rods in gels (Piculell,  
316 Borgström, Chronakis, Quist & Viebke, 1997).

317 Iota-carrageenan is unable to form a liquid crystal structure which again reflects  
318 the difference in molecular behavior among the carrageenans (Lahaye, 2001). In  
319 general,  $\kappa$ - and  $\iota$ -carrageenan are comprised of alternating 1,3 linked  $\beta$ -D-  
320 galactopyranose-4-sulfate and 1,4-linked 3,6-anhydro-D-galactopyranose units with  
321 different amounts of ester sulfate groups. The sulfate groups are positioned at the  
322 outside of the helix chains during conformational changes and the subsequent  
323 stabilization of this helix conformation depends on the hydrogen bonds formed between  
324 the chains (Makino, Idenuma, Murakami & Ohshima, 2001). A hydrogel is then formed  
325 when surrounding water molecules penetrate the matrix (Nanaki et al., 2010).

326 Hybrid carrageenan structures possess properties that are distinct from those of  
327 the single polymeric counterparts (Souza et al., 2011). However, because of the  
328 profound gelling ability among the hybrid groups, most studies have focused on the  $\kappa/\iota$ -  
329 hybrid carrageenans (Larotonda et al., 2016; Sánchez-García, Hilliou & Lagarón, 2010;  
330 Souza et al., 2011; van de Velde, 2008). Kappa/iota-hybrid carrageenans are sulfated  
331 polysaccharide structures consisting of blocks of  $\kappa$ - or  $\iota$ -carrageenan disaccharide units  
332 distributed in their molecular chain (van de Velde, 2008; van de Velde & De Ruiter,  
333 2005), and are usually found together with small amounts of non-gelling disaccharide  
334 units, such as  $\mu$ - and/or  $\nu$ -carrageenans (Souza et al., 2011). The structure and

335 composition of the disaccharide units determines the conformational transition from the  
336 random coil state to the helical state of the polymer during gel formation as well as the  
337 functional polymer properties (Larotonda et al., 2016; van de Velde, 2008). It has been  
338 reported that  $\kappa/\iota$ -hybrid carrageenans extracted from *Martocarpus stellatus* seaweed  
339 exhibit a gelling property which is intermediate between those of single  $\kappa$ - and  $\iota$ -  
340 carrageenans gels. In contrast,  $\lambda$ -carrageenan produces only viscous solutions, without  
341 gel formation (de Araújo et al., 2011; Gu, Decker & McClements, 2005).

### 342 **3.2 Film Formation and Characteristics**

343 Compared to other bio-based films, the development of carrageenan-based films  
344 is still in its infancy. As such, the only reported film fabrication method to date is  
345 solvent casting which involves casting carrageenan gel then evaporating the solvent  
346 (water) to form a solid film. Typically,  $\iota$ -carrageenan forms a clear, elastic, soft gel with  
347 no syneresis in the presence of calcium salts, whereas  $\kappa$ -carrageenan forms a strong,  
348 hard, brittle gel (Farhan & Hani, 2017; McHugh, 2003). The differences in gelling  
349 properties contribute to the properties of films or composites produced using these  
350 different types of carrageenan. For example, the three-dimensional structure of  $\iota$ -  
351 carrageenan exhibits a dense, compact, and organized film structure (Hambleton,  
352 Perpiñan-Saiz, Fabra, Voilley & Debeaufort, 2012). Edible films made of  $\iota$ -carrageenan  
353 demonstrated good mechanical properties with the carrageenan stabilizing the emulsion  
354 in the polymer matrix (Hambleton et al., 2012). In packaging applications, such films  
355 may also exhibit decreased gas permeability to potentially impede surface dehydration  
356 and maintain the taste attributes of certain products such as fruits and cheeses.

357 Similarly, as in the case of  $\iota$ -carrageenan,  $\kappa$ -carrageenan polymers exhibit a  
358 compact film structure (El-Fawal, 2014; Nanaki et al., 2010), and the high gelling

359 ability of  $\kappa$ -carrageenan imparts excellent film-forming properties (Wu & Imai, 2012)  
 360 with higher mechanical and water barrier properties, as well as greater transparency  
 361 (Park, 1996; Paula et al., 2015). Table 1 lists various functional properties of  
 362 carrageenan-based films in comparison with other bio-based and synthetic films used  
 363 in food packaging applications. These basic properties are amongst the most important  
 364 properties that are commonly considered when developing materials for industrial  
 365 applications and include the physico-mechanical properties of tensile strength (TS) and  
 366 elongation at break (EAB), along with the functional properties of water vapor  
 367 permeability (WVP) and gas permeability. Clearly, the development of novel  
 368 packaging films requires the optimization of these properties to ensure the material can  
 369 adequately protect the product quality and safety during storage until it is delivered to  
 370 consumers (Lagaron, 2011).

371

372 **Table 1.** Comparison of carrageenan-based films physico-mechanical and functional  
 373 properties with other bio-based and synthetic films

Film	TS /MPa	EAB /%	WVP /10 <sup>11</sup> g m <sup>-1</sup> Pa <sup>-1</sup> s <sup>-1</sup>	OP /10 <sup>12</sup> cm <sup>3</sup> m <sup>-1</sup> Pa <sup>-1</sup> s <sup>-1</sup>	References
$\kappa$ -carrageenan	42.5	3.9	7.5	5.2	Larotonda et al. (2016)
$\iota$ -carrageenan	2.5	1.04	36	-	Paula et al. (2015)
$\kappa/\iota$ -hybrid carrageenan	55.2	3.4	6.7	3.3	Larotonda et al. (2016)
SR $\kappa$ -carrageenan	35.43 <sup>a</sup>	10.14 <sup>a</sup>	27.8 <sup>a</sup>	1.67 <sup>b</sup>	<sup>a</sup> Sedayu et al. (2018) <sup>b</sup> Farhan & Hani (2017)
SR $\iota$ -carrageenan	8.9	12.05	-	-	Aji, Praseptiangga, Rochima, Joni & Panatarani (2018)
PLA	15.2 <sup>a</sup>	40.4 <sup>a</sup>	2.47 <sup>a</sup>	62 <sup>b</sup>	<sup>a</sup> Li et al. (2017) <sup>b</sup> Tee et al. (2015)
PHB	35-50	2-4	0.79-0.95	-	Arrieta, Samper, Aldas & López (2017)
Cellophane	85.8	14.4	8.4	2.9	Larotonda et al. (2016)
Chitosan	60.7	3.3	4.5	10.4	Larotonda et al. (2016)
Whey protein	2.2	20	1,380	1.7	Larotonda et al. (2016)
Corn starch	47.4	3.6	18	0.15	Larotonda et al. (2016)
LDPE	7.85-34.5 <sup>a</sup>	100-1330 <sup>a</sup>	0.091 <sup>b</sup>	21.6 <sup>b</sup>	<sup>a</sup> MatWeb (2019) <sup>b</sup> Larotonda et al. (2016)
HDPE	11.6-228 <sup>a</sup>	160-1010 <sup>a</sup>	0.023 <sup>b</sup>	4.9 <sup>b</sup>	<sup>a</sup> MatWeb (2019) <sup>b</sup> Larotonda et al. (2016)

374 OP: Oxygen permeability; SR: semi-refined; LDPE: Low-density polyethylene; HDPE: High-density  
 375 polyethylene



376           The data in Table 1 shows that films produced from refined  $\kappa$ - or  $\kappa/\iota$ -hybrid  
377 carrageenan exhibit superior properties among the other carrageenan films with higher  
378 TS and lower WVP values. Larotonda et al. (2016) reported that hybrid  $\kappa/\iota$ -carrageenan  
379 films are less hygroscopic with higher oxygen and UV barrier performance than films  
380 made of  $\kappa$ -carrageenan. Moreover, SRC films show higher stretchability than those that  
381 are made of refined carrageenan. The overall TS of carrageenan films, with the  
382 exception of the  $\iota$ - type, is also comparable with other commercial bio-based films and  
383 is in fact higher than those of PLA and synthetic plastic films, LDPE and HDPE.  
384 Nonetheless, carrageenan films have lower flexibility, particularly in comparison with  
385 the synthetic films and in the case of  $\kappa$ -carrageenan, a brittle film structure has also  
386 been reported (Cian, Salgado, Drago & Mauri, 2014; Zarina & Ahmad, 2015). This  
387 characteristic may limit the use of these materials for wider applications such as flexible  
388 thin films although  $\kappa$ -carrageenan may be suitable to be developed as a rigid packaging  
389 material.

390           High film barrier properties are vital for many food packaging  
391 applications, particularly in order to prevent the migration of low molecular weight  
392 chemical compounds such as gases and vapors (Lagaron, 2011). Similar to almost all  
393 bio-based films, carrageenan films have poor WVP which is a result of the large number  
394 of hydroxyl and sulfate groups in their structures rendering carrageenan films highly  
395 hydrophilic (Cunha & Grenha, 2016; Distantina, Rochmadi, Fahrurrozi & Wiratni,  
396 2013; Roh & Shin, 2006), and this consequently imparts poor moisture barrier  
397 properties and a poor water resistance (Fabra, Talens & Chiralt, 2008). In contrast,  
398 carrageenan-based films have excellent oxygen barrier properties, which are superior  
399 to those of PLA and LDPE films.

400

401 **4 Property Enhancement of Carrageenan-Based Films**

402 Attempts to improve or manipulate carrageenan-based film properties have  
 403 been investigated encompassing physical and/or chemical processes. For food  
 404 packaging purposes, barrier property enhancement of the carrageenan films is the major  
 405 motivation in addition to the enhancement of other functional properties such as  
 406 mechanical, optical and AM properties. Various technical approaches have been used  
 407 to obtain desirable properties of carrageenan-based film including blending,  
 408 plasticizing and nanoparticle incorporation as described in the following section and  
 409 summarized in Table 2.

410 **Table 2.** Property modifications of carrageenan-based films.

<b>Carrageenan and other components</b>	<b>Property Enhancements</b>	<b>Disadvantages</b>	<b>Reference(s)</b>
$\kappa$ -carrageenan, alginate	Increased mechanical properties, thermal stability, optical properties		Ye et al. (2017)
$\kappa$ -carrageenan, alginate	Improved water resistance, thermal stability		Xu et al. (2003)
$\kappa$ -carrageenan, alginate	AM activity		Cha, Choi, Chinnan & Park (2002)
$\kappa$ -carrageenan, cassava starch, LDPE	Increased Young's modulus, hardness		Prachayawarakorn & Pomdage (2014)
Carrageenan, starch	Increased shear stress, EAB, decreased WVP	Decreased TS	Abdou & Sorour (2014)
$\kappa$ -carrageenan, rice starch	Improved barrier properties, increased $T_g$ , mechanical properties		Larotonda, Hilliou, Sereno & Gonçalves (2005)
$\kappa$ -carrageenan, agar	Increased EAB, water resistance, decreased WVP	Decreased TS	Rhim (2012)
$\kappa$ -carrageenan, agar, konjac glucomannan	Agar increased barrier properties, water resistance; konjac improved EAB, hydrophobicity	Agar, konjac glucomannan decreased optical properties, TS, konjac glucomannan decreased barrier properties	Rhim & Wang (2013)
Carboxymethyl $\kappa$ -carrageenan, carboxymethyl cellulose	Increased mechanical properties		Rudhziah, Rani, Ahmad, Mohamed & Kaddami (2015)
$\kappa$ -carrageenan, pea starch	Increased EAB	Decreased TS, thermal stability	Lafargue, Lourdin & Doublier (2007)
$\kappa$ -, $\iota$ -, $\lambda$ -carrageenan blends			Nanaki et al. (2010)

<b>Carrageenan and other components</b>	<b>Property Enhancements</b>	<b>Disadvantages</b>	<b>Reference(s)</b>
$\kappa$ -carrageenan, locust bean gum	Increased thermal stability, mechanical properties	Increased WVP	Martins, Cerqueira, et al. (2012)
$\kappa$ -carrageenan, pectin, mica flakes	Increased hydrophobicity, mica flakes alone specifically increased WVP and gas barrier properties		Alves et al. (2010); Alves et al. (2011)
$\kappa$ -carrageenan, chitosan	Increased EAB	Rougher surface, increased WVP, decreased TS, water resistance	Shahbazi, Rajabzadeh, Ettelaie & Rafe (2016)
$\kappa$ -carrageenan, chitosan	Increased water resistance		
$\kappa$ -carrageenan, plant essential oils ( <i>Zataria multiflora</i> Boiss, <i>Mentha pulegium</i> , <i>Satureja hortensis</i> )	Decreased WVP, higher stretchability, water resistance, and EAB, AM activity	Decreased transparency, TS	Shojaee-Aliabadi et al. (2013) Shojaee-Aliabadi, Hosseini, et al. (2014) Shojaee-Aliabadi, Mohammadifar, et al. (2014)
$\kappa$ -carrageenan, essential oils (oregano & thyme)	Decreased WVP, increased water resistance, EAB, AM activity	Decreased transparency, TS	Soni et al. (2016)
$\iota$ -carrageenan, fat, aroma compounds	Decreased permeability of aroma compounds, increased surface hydrophobicity	Rough microstructure, morphology	Hambleton, Fabra, Debeaufort, Dury-Brun & Voilley (2009)
$\iota$ -carrageenan, fat, emulsifier	Increased surface hydrophobicity	Rough microstructure, morphology	Karbowiak, Debeaufort, Champion & Voilley (2006)
$\kappa$ -carrageenan, latex	Increased TS, energy absorption		Machmud, Fahmi, Abdullah & Kokarkin (2013)
$\kappa$ -carrageenan, cinnamon oil	Decreased WVP	Decreased mechanical properties	Praseptiangga, Fatmala, Manuhara, Utami & Khasanah (2016)
$\kappa$ -carrageenan, various plant oils (corn, soybean, olive, sunflower)	Decreased WVP, increased water resistance	Increased opacity, yellowish color, decreased TS	Rekemin & Abedin (2017)
$\kappa$ -carrageenan, palmitic acid	Increased water resistance	Decreased mechanical properties	Wibowo, Listiyawati & Purnawan (2016)
$\kappa/\iota$ hybrid carrageenan, zein prolamine	Reduced WVP, improved TS, stretchability	Decreased water resistance, EAB	Sanchez-Garcia, Hilliou & Lagaron (2010)
$\kappa$ -carrageenan, potassium sorbate	AM activity		Choi et al. (2005)
$\kappa$ -carrageenan, citric acid	AM activity against <i>E. coli</i> , <i>P. mirabilis</i> , <i>D. chrysanthemi</i> , <i>S. aureus</i> , but not <i>P. aeruginosa</i>	Decreased mechanical properties, hydrophobicity	El-Fawal (2014)
$\kappa$ -carrageenan, nano-silver	Fungicidal activity to <i>Fusarium</i> , <i>penicillium spp.</i> & <i>Aspergillus niger</i> , higher thermal stability, increased TS	Decreased transparency, hydrophobicity	Fouda et al. (2015)
$\kappa$ -carrageenan, grapefruit seed extract	AM activity, decreased UV light transmittance, increased EAB	Decreased barrier properties, optical properties,	Kanmani & Rhim (2014a)

Carrageenan and other components	Property Enhancements	Disadvantages	Reference(s)
$\kappa$ -carrageenan/alginate, nisin, lysozyme, EDTA, grapefruit seed extract	AM activity	hydrophobicity, mechanical properties Decreased TS, EAB	Cha et al. (2002)
$\kappa$ -carrageenan, zinc oxide	AM activity, increased hydrophobicity, EAB	Reduced optical properties, mechanical properties	Kanmani & Rhim (2014b)
Carrageenan, nanoparticles (zinc oxide, copper oxide)	Increased EAB, thermal stability, AM activity against <i>E. coli</i> , <i>L. monocytogenes</i>	Decreased TS	Oun & Rhim (2017)
Carrageenan, chitin nanofibrils	AM activity against <i>L. monocytogenes</i> , increased TS, EAB, thermal stability	Increased opacity, hydrophilicity	Shankar, Reddy, Rhim & Kim (2015)
$\kappa$ -carrageenan, essential oils	AM activity, increased flexibility, improved water barrier properties	Decreased TS, optical properties	
$\kappa$ -carrageenan, nanoclay, silver	Reduced WVP, increased TS, EAB, thermal stability, hydrophobicity and AM activity		Rhim & Wang (2014) Rhim & Wang (2013)
$\kappa$ -carrageenan, nanocellulose fibers	Reduced WVP and gas barrier properties, increased TS		Savadekar, Karande, Vigneshwaran, Bharimalla & Mhaske (2012)
$\kappa$ -carrageenan, chitin nanofibrils	Increased WVP, TS, AM activity, stiffness, hydrophobicity	Decreased EAB, transparency	Shankar et al. (2015)
$\kappa$ -carrageenan, cellulose nano-crystals, nanoclay	Increased TS		Zakuwan, Ahmad & Ramli (2013)
$\kappa$ -carrageenan, nanoclay	Increased TS, EAB, thermal stability, AM activity against <i>L. monocytogenes</i>	Rougher microstructure	Martins, Bourbon, et al. (2012)
$\kappa$ -carrageenan, nanosilica	Increased mechanical properties, hydrophobicity, decreased WVP		Rane, Savadekar, Kadam & Mhaske (2014)
$\kappa$ -carrageenan, nanoclay	Improved mechanical properties, barrier properties, hydrophobicity		Rhim (2012)
$\kappa/\lambda$ hybrid carrageenan, cellulose nano whiskers	Increased water barrier properties, water resistance		Sánchez-García et al. (2010)
Carrageenan, agar, poly(lactic acid)	Increased WVP, TS, water resistance	Decreased gas barrier properties, EAB	Rhim (2013)

## 412 **4.1 Blending Carrageenans**

413 Blending carrageenans or hydrogel polymers with other polymeric materials is  
414 among the more simple and effective methods to obtain desirable film properties  
415 (Makhijani, Kumar & Sharma, 2015). The compatibility of the component polymers is  
416 a significant factor since the final properties of the film will be influenced by the  
417 conformational arrangement of the polymer chains. An ordered conformational  
418 structure creates a compact and stable network in the blended matrix, whereas disorder  
419 results in chain interactions with a greater level of space-occupancy by the chain coils.  
420 In this regard, the compatibility of blended materials with carrageenan polymers can be  
421 determined by investigating the miscibility and thermodynamic behavior (Shahbazi,  
422 Rajabzadeh, Rafe, Ettelaie & Ahmadi, 2017). However, the final properties of blended  
423 films comprised of carrageenan and other materials will vary depending on the types of  
424 materials added, the ratio of the polymers, and the degree of miscibility. Carrageenan  
425 polymers have been blended with a range of different polymers including starch, lipids,  
426 proteins, and other materials to obtain desired film properties (Fabra et al., 2008;  
427 Prachayawarakorn & Pomdage, 2014; Sanchez-Garcia et al., 2010).

### 428 **4.1.1 Polysaccharides**

429 Polysaccharides have been extensively explored for various film applications,  
430 and these are considered to be the most widely used biomaterials for both food and non-  
431 food purposes. A wide range of film properties can be obtained by combining different  
432 types of polysaccharides since these can demonstrate various intrinsic properties  
433 (Nisperos-Carriedo, 1994). Among the biopolymers, starch is the most popular resource  
434 used as a filler in polymer blending since it is less expensive than many other materials  
435 and is abundant in nature (Fakhouri et al., 2013). Starch consists of two main  
436 components: amylose and amylopectin, whereby the first structure is primarily linear

437 and is crystalline with an average molecular weight around 500,000 Dalton, whereas  
438 the second is highly branched with very high molecular weight (Chandra & Rustgi,  
439 1998; Hyang Aee, Nam Hie & Nishinari, 1998; Rosa, Lopes & Calil, 2005).

440 The properties of carrageenan-starch films are inherently influenced by the  
441 origin and specific properties of the starch such as the source material from which the  
442 starch was derived (rice, pea, cassava, etc.). Combining carrageenan with starch may  
443 improve the moisture sensitivity of the film and increase certain mechanical properties  
444 such as the elongation at break (EAB) and the shear stress, however, these increases  
445 only occur within a certain range of mixing ratios (Abdou & Sorour, 2014; Lafargue et  
446 al., 2007). The amount of starch in the mixture plays an important role in determining  
447 the mechanical properties since its native crystalline structure is disrupted and  
448 irreversibly swells to a remarkably larger size when it undergoes gelatinization (Ali  
449 Akbari Ghavimi, Ebrahimzadeh, Solati-Hashjin & Abu Osman, 2015). This  
450 phenomenon affects the film texture rendering it more brittle and may consequently  
451 decrease the tensile strength of the film (Abdou & Sorour, 2014; Prachayawarakorn &  
452 Pomdage, 2014).

453 In addition to starch, combining carrageenan with various sulfated  
454 polysaccharide polymers such as agar and alginate, or combining the different types of  
455 carrageenan ( $\kappa$ ,  $\lambda$  and  $\iota$ ) have also been investigated considering these polymers are  
456 very similar in their chemical structure and also demonstrate a good degree of  
457 miscibility (Nanaki et al., 2010). Combining carrageenan with agar has been reported  
458 to exhibit an improvement in its moisture barrier properties and water resistance, but it  
459 lowered the optical and tensile properties (Rhim, 2012; Rhim & Wang, 2013). In  
460 another study, blending carrageenan with alginate resulted in an increase in its flexural  
461 properties and transparency, and also increased its thermal stability (Ye et al., 2017).

462 The level of hydrophilicity from each of these polymer groups appears to impact the  
463 moisture transfer rate, water resistance as well as the mechanical properties of the  
464 products, and it is associated with the amount of polar sulfate groups in their molecular  
465 structures (Roh & Shin, 2006; Xu et al., 2003).

466 The blending of carrageenan with other polysaccharide-based polymers  
467 including carboxymethyl cellulose (CMC), konjac glucomanan, pectin, locust bean  
468 gum (LBG), and chitosan, has also been investigated in the production of various films  
469 (see Table 2). It is reported that the addition of LBG or CMC can significantly increase  
470 the mechanical strength of carrageenan films (Martins, Bourbon, et al., 2012; Rudhziah,  
471 Rani, et al., 2015), whereas pectin and konjac glucomanan can be added in the  
472 formulation to improve the water sensitivity and elongation properties of the films  
473 (Alves et al., 2006; Rhim & Wang, 2013).

474 In blends of carrageenan with chitosan, organic acids are usually involved in  
475 film preparation since chitosan can only be dissolved in organic or acidified solutions  
476 (Kim, Son, Kim, Weller & Hanna, 2006). As the interaction of carrageenan-chitosan in  
477 the polymer matrix is driven by electrostatic attraction forces between negatively  
478 charged carrageenan and the positively charged chitosan molecules, the final properties  
479 of carrageenan-chitosan films is affected by the types and concentrations of the organic  
480 solvents that are used (Park, Lee, Jung & Park, 2001). The level of acidity of the  
481 solvents influences the electrostatic bonds since the protons from the acidic solvent  
482 protonate the sulfonate anionic groups of carrageenan, which can subsequently reduce  
483 the electrostatic interactions between the carrageenan and chitosan (Park et al., 2001).

#### 484 **4.1.2 Lipids**

485 Hydrophobic polymers such as lipids have been frequently used in hydrogel  
486 films to typically improve barrier properties and water resistance (Hambleton et al.,

487 2009). In food packaging applications, barrier properties play an important role as the  
488 mass transfer of various components such as water vapor, gas and flavor compounds  
489 can permeate through a membrane between the food and its surrounding environment,  
490 which leads to physico-chemical changes and ultimately to food deterioration (Karel &  
491 Lund, 2003). In the case of lipid-blended carrageenan films, the properties are strongly  
492 affected by their structure (bilayer formation) and the distribution of fat molecules  
493 within the matrix (Fabra et al., 2008). Among the groups of lipids used in carrageenan  
494 film production, plant oils appear to be the most popular compounds that are  
495 incorporated into the polymer matrix.

496         Microstructure morphological studies using scanning electron microscopy  
497 (SEM) have shown that pure carrageenan films form a smooth and compact surface  
498 area (Shojaee-Aliabadi et al., 2013), and that the moisture diffusion through a  
499 carrageenan film is mainly governed by the hydrophilic layer of the matrix. When lipids  
500 are added to the carrageenan matrix, lipid layers form within the polymer structure that  
501 can significantly decrease the water transfer (Karbowski, Ferret, Debeaufort, Voilley  
502 & Cayot, 2011). Furthermore, Shojaee-Aliabadi et al. (2013) suggest that the  
503 hydrophobic dispersed phase in hydrocolloid matrices form a tortuous conformation  
504 and this obstructs the water vapor transmission through the film. A similar phenomenon  
505 was also found in the transfer rates of flavour compounds, whereby carrageenan films  
506 incorporated with fats exhibited a less uniform matrix, which appeared as a solid  
507 emulsion in which the hydrocolloid polymer matrix surrounded the lipid phase  
508 dispersion of fat globules in various dimensions (Karbowski et al., 2011). The globule  
509 particles result in fewer open spaces in the matrix that would facilitate the diffusion of  
510 flavour compounds and this subsequently limits the permeability of the latter  
511 (Hambleton et al., 2009).



512 An increase in water resistance has also been reported after blending  
513 carrageenan with lipids (Karbowski et al., 2006) and this may be due to a decrease in  
514 the hydrophilicity of the carrageenan matrix. The hydroxyl groups within the  
515 carrageenan may interact with the oil component of the lipid through non-covalent  
516 bonds, thus reducing the availability of the hydroxyl groups to interact with water  
517 molecules resulting in a more water-resistant film (Shojaee-Aliabadi et al., 2013;  
518 Torrieri, Cavella & Masi, 2015). Conversely, incorporating lipids into the carrageenan  
519 matrix can also impair the mechanical properties of the carrageenan whereby the lipid  
520 structure may partially substitute the stronger hydrocolloid polymer network with  
521 weaker hydrocolloid-lipid interactions within the matrix. This may lead to a weakening  
522 of the mechanical properties of the film such as the TS (Rekemin & Abedin, 2017),  
523 although this is often accompanied by an increase in the EAB. This is possibly caused  
524 by the lipid generating a plasticizing effect in the polymer matrix by altering the strong  
525 interaction forces of the hydrocolloid polymer network with a lessening of polymer  
526 cohesion, which then enables chain mobility during film stretching (Atarés, De Jesús,  
527 Talens & Chiralt, 2010). In addition, the carrageenan-lipid polymer structure also  
528 influences the optical properties of the film which will generally increase with the  
529 addition of lipids in the formulation as a result of the lipid droplets in the polymer  
530 matrix contributing to a greater extent of light scattering. The extent of scattering also  
531 depends on the size of the droplets and the components in the dispersed phase of the  
532 polymer matrix (Sánchez-González, Vargas, González-Martínez, Chiralt & Cháfer,  
533 2009; Shojaee-Aliabadi, Hosseini, et al., 2014)

#### 534 **4.1.3 Proteins**

535 Although carrageenan blends with protein-based polymers are less common in  
536 the scientific literature, most investigations are aimed at improving the mechanical

537 properties of the films. This ultimately results in poor water barrier and water resistance  
538 properties, since both components are highly hydrophilic (Fabra et al., 2008).  
539 Interestingly, the addition of zein into carrageenan film formulations studied by  
540 Sanchez-Garcia et al. (2010) not only exhibited improved mechanical properties but  
541 also profoundly decreased the WVP. Zein is a biopolymer from the prolamine-group  
542 that can be found in corn endosperm and it has a special feature of an unusually high  
543 resistance to water. A carrageenan-zein film plasticized with glycerol was found to  
544 exhibit strong adhesion between the two components however a phase separation  
545 within its polymer matrix was still identified suggesting that both components although  
546 not entirely miscible, are relatively compatible (Sanchez-Garcia et al., 2010). It was  
547 reported that the TS of the carrageenan-zein film was up to 72% greater than that of a  
548 pure carrageenan film, with 17% lower WVP, and the film was notably more water  
549 resistant than the plasticized pure carrageenan (Sanchez-Garcia et al., 2010).

#### 550 **4.1.4 Other Materials**

551 Some other materials have been investigated in mixtures with carrageenan  
552 including poly(vinyl pyrrolidone) (PVP) (Fouda et al., 2015), mica flakes (Alves et al.,  
553 2010), and latex (Machmud et al., 2013; Norhazariah, Azura, Sivakumar & Azahari,  
554 2016). Blended carrageenan-PVP polymer film plasticized with polyethylene glycol  
555 (PEG) showed a high transparency with a homogenous polymer matrix and good  
556 flexibility (Fouda et al., 2015). It has been suggested that blending PVP into  
557 hydrocolloid polymer systems can increase the hydrophobicity of the hydrocolloid  
558 (Çaykara, Demirci, Eroğlu & Güven, 2006). It has also been suggested that blending a  
559 crude carrageenan with latex derived from *Calostropis gigantean* enhances the tensile  
560 properties with a demonstrated higher TS compared with those of starch-based plastics  
561 (Machmud et al., 2013). Furthermore, the inclusion of mica flakes in carrageenan has

562 been shown to enhance its barrier properties including gas and WVP by creating a  
563 tortuous structure (Alves et al., 2011).

#### 564 **4.2 Incorporation of Plasticizers**

565 Although carrageenan is well known for its film forming ability with excellent  
566 optical properties, its native film exhibits brittleness that restricts its functionality for  
567 food packaging applications. The addition of plasticizers is therefore an essential  
568 requirement in the formulation to improve film flexibility and workability. Plasticizers  
569 are generally additive substances with low molecular weights that intercalate and  
570 disperse within the polymer network, disrupting hydrogen bonding, and spreading the  
571 polymer chains apart, which then increases the flexibility of the film (McHugh &  
572 Krochta, 1994). Plasticizers incorporated into the matrix should be compatible with the  
573 polymer structure and have similar solubility in the solvent used to optimize the  
574 intermolecular reactions. Moreover, to maintain the physio-mechanical properties of  
575 the film it is also important that the plasticizer does not evaporate from the film matrix  
576 (Wittaya, 2012). Plasticizers derived from polyol groups including glycerol, sorbitol  
577 and poly(ethylene glycol) are the most commonly used in the production of hydrogel  
578 films. The strong molecular interaction between the polymer chains and plasticizer *via*  
579 hydrogen bonding is responsible for the mechanical strength improvement of the film  
580 (Khazaei, Esmaili, Djomeh, Ghasemlou & Jouki, 2014; Sothornvit & Krochta, 2000).  
581 It has been reported that the addition of glycerol and sorbitol into carrageenan-based  
582 films enhances the flexibility, TS and EAB of the material (Farhan & Hani, 2017;  
583 Harumarani, Ma'ruf & Romadhon, 2016). However, other reports have suggested the  
584 opposite; that the incorporation of glycerol can result in a decrease of the TS of the final  
585 carrageenan film (Wibowo et al., 2016). This suggests that the type and amount of

586 plasticizer critically influences the mechanical properties of the final product (Cao,  
587 Yang & Fu, 2009; Rahman & Brazel, 2004).

588         The selection of a plasticizer to modify the properties of a specific polymer  
589 system is usually based on its compatibility with the polymer system, the amount of it  
590 required in the formulation, the processing method used, the desired physical, thermal,  
591 and electrical properties of the final film products, and also cost considerations (Cao et  
592 al., 2009; Cheng, Karim & Seow, 2006). In addition to increasing the mechanical  
593 properties, incorporating plasticizer in the carrageenan film matrix may also enhance  
594 the optical properties. This is ascribed to the intermolecular spacing of the plasticizer  
595 within the polymer conformation, which enables more light to pass through the film  
596 (Jongjareonrak, Benjakul, Visessanguan & Tanaka, 2005). This is also supported by  
597 several investigations reporting that higher amounts of plasticizer incorporated in a  
598 hydrocolloid polymer result in a smoother surface texture of the film, which  
599 subsequently benefits the optical properties (Farhan & Hani, 2017).

600         Conversely, the addition of plasticizers to a carrageenan polymer matrix may  
601 also increase its moisture sensitivity and WVP. This is due to the reorganization that  
602 occurs in the hydrocolloid polymer structure that increases the free volume and  
603 segmental motions of the polymer network, hence facilitating water molecules to  
604 permeate more easily through the membrane (Khazaei et al., 2014). In addition, the  
605 moisture transfer is also affected by the hydrophilic character of the added plasticizer  
606 whereby the more hydrophilic the plasticizer, the higher the rate of moisture transfer  
607 through the film (Wittaya, 2012).

### 608 4.3 Incorporation of Antimicrobial Agents

609 The incorporation of AM compounds into polymeric packaging materials has  
610 become one of the most popular concepts in developing active packaging. The purpose  
611 of this approach is to protect food products from microbial growth, particularly from  
612 surface spoilage, thus prolonging the shelf-life, and maintaining the safety and quality  
613 of the foodstuff contained in the package (Choi et al., 2005; Hotchkiss, 1997). Such is  
614 the case with the development of carrageenan-based films where several AM agents  
615 have been incorporated into the matrix including organic acids (El-Fawal, 2014;  
616 Wibowo et al., 2016), essential oils (Shojaee-Aliabadi et al., 2013), natural extract AM  
617 compounds (Kanmani & Rhim, 2014a), and metallic oxides (Oun & Rhim, 2017).

618 Organic acids incorporated into carrageenan films have been shown to  
619 effectively inhibit microbial spoilage in packaged foods. The incorporation of citric,  
620 succinic or lactic acid in hydrocolloidal packaging film has demonstrated a  
621 bacteriocidal and bactiostatic action against *E. coli*, *P. mirabilis*, *S. aureus* and some  
622 other pathogenic strains (El-Fawal, 2014; Rocha, Loiko, Tondo & Prentice, 2014;  
623 Schreiber, 2012). Due to the non-volatility of most organic acids under food-storage  
624 conditions, the transition of the active compound from the film packaging to the food  
625 product can only take place by direct contact between the film and the food surface  
626 (Hauser, Thielmann & Muranyi, 2016). In such cases, edible films or coatings may be  
627 the best concept for this type of AM packaging. However, the incorporation of organic  
628 acids such as citric acid into the carrageenan polymer structure appears to lessen its  
629 mechanical properties along with its water resistance (El-Fawal, 2014; Fouda et al.,  
630 2015). Hauser et al. (2016) suggested that to obtain desirable properties of the films that  
631 incorporate organic acids, the compatibility of the organic acids with the polymer and  
632 its constituents, the thickness of the film, and the storage conditions all have to be taken

633 into consideration. Potassium sorbate is another commonly used AM agent in  
634 carrageenan film packaging formulations (Cha & Chinnan, 2004; Flores, Famá, Rojas,  
635 Goyanes & Gerschenson, 2007), and an investigation by Choi et al. (2005) found that  
636 such films exhibit a similar potential for inhibiting selective bacteria, yeast and mould  
637 to the use of potassium sorbate alone.

638         Recent studies have reported an increasing interest in the use of natural AM  
639 compounds for use in active packaging such as plant extracts and essential oils  
640 (Kuorwel, Cran, Sonneveld, Miltz & Bigger, 2011; Suppakul, Miltz, Sonneveld &  
641 Bigger, 2003). Kanmani & Rhim (2014a) and Cha et al. (2002) investigated the addition  
642 of grapefruit seed extract (GSE) that has a high content of polyphenolic compounds  
643 into a  $\kappa$ -carrageenan film matrix and found the film to have an effective antibacterial  
644 effect against food-borne pathogens. The phenolic compounds in the GSE, however,  
645 impacted the optical properties of the film in that it imparted a yellowish colour to it.  
646 Nonetheless, it was reported that the colour change did not significantly impact the film  
647 transparency, and to the contrary, it notably increased the ultraviolet barrier property of  
648 the film. Other disadvantages were also found in relation to the mechanical properties  
649 and sensitivity of the film to moisture.

650         Various essential oils known to impart AM activity have also been incorporated  
651 into carrageenan-based films such as oregano, thyme, *Zataria multiflora* Boiss, *Mentha*  
652 *pulegium*, *Satureja hortensis*, and cinnamon oil (Praseptianga et al., 2016; Shojaee-  
653 Aliabadi, Hosseini, et al., 2014; Shojaee-Aliabadi et al., 2013; Soni et al., 2016), with  
654 these oils resulting in similar effects as GSE incorporation. However, the  
655 hydrophobicity of these compounds profoundly enhances the water resistance and  
656 moisture transfer properties of the films. Some AM peptides such as nisin and lysozyme  
657 have also been used in carrageenan film formulations, but each of these compounds

658 appears to effectively inhibit only specific bacterial growth, and imparts less  
659 antibacterial activity in comparison with other AM agents such as  
660 ethylenediaminetetraacetic acid (EDTA) and GSE (Cha et al., 2002). Furthermore, the  
661 AM activity of lysozyme is sensitive to high temperatures (Carrillo, García-Ruiz,  
662 Recio & Moreno-Arribas, 2014) and this impacts its performance in film packaging  
663 applications.

664 In addition to the wide range of organic AM compounds, the incorporation of  
665 inorganic materials in carrageenan films has been investigated due to their high  
666 performance in inhibiting food deterioration as well as their stability during high  
667 temperature treatment. Zinc oxide (ZnO), copper oxide (CuO), and silver nanoparticles  
668 (AgNPs) are among the inorganic compounds that have been used in AM carrageenan  
669 films. The incorporation of ZnO and CuO in carrageenan films has demonstrated a  
670 strong antibacterial activity against *E. coli* and *L. monocytogenes* and these have been  
671 notably observed to perform more effectively against the former Gram-negative  
672 bacterium (Oun & Rhim, 2017). Moreover, AgNPs were also shown to be effective in  
673 inhibiting pathogenic fungi growth including the growth of *Aspergillus* sp., *Penicillin*  
674 sp., and *Fusarium oxysporum* (Fouda et al., 2015). This antifungal activity may be  
675 attributed to the interaction between the positively-charged metallic ions with the  
676 negatively-charged species of the membrane and other biomolecules (protein and DNA)  
677 of the microorganisms, which consequently alters the membrane and internal structures,  
678 and finally leads to bacterial death (Anitha, Brabu, Thiruvadigal, Gopalakrishnan &  
679 Natarajan, 2012). Similar to the incorporation of organic AM agents, these metallic  
680 compounds also diminish the mechanical and optical properties, but they can improve  
681 the thermal stability of the final carrageenan films (Fouda et al., 2015; Kanmani &  
682 Rhim, 2014b).

## 683 **4.4 Reinforcement with Nanoparticles**

684 The development of nanotechnologies in the field of biodegradable films has  
685 been a significant recent breakthrough. Reinforcing a biopolymer matrix with small  
686 amounts of nanomaterials can significantly enhance the physico-mechanical, thermal,  
687 and barrier properties, which can enable the development and extend the use of these  
688 materials in various applications including food packaging. Different types of nano-  
689 sized materials are frequently used in film packaging applications to improve the final  
690 properties of the packaging material. Considered below are the nanomaterials that have  
691 been used in carrageenan-based film production.

### 692 **4.4.1 Nanoclays**

693 Clay minerals are the major components of clay raw materials and these have a  
694 dominant platelet microstructure. The shape of individual layers depends on the type of  
695 clay which may be composed of two, three, or four tetrahedral silicates and octahedral  
696 hydroxide sheets (Ghadiri, Chrzanowski & Rohanizadeh, 2015; Nazir et al., 2016). In  
697 carrageenan films, the main types of clays that have been investigated include mica  
698 (Sanchez-Garcia et al., 2010), and montmorillonite (Rhim, 2012; Shojaee-Aliabadi,  
699 Mohammadifar, et al., 2014) with the purpose of enhancing the functional properties of  
700 the resulting composites. Nanoclays have been widely used as nano-fillers as they are  
701 abundant, readily available, low cost, and are environmentally friendly materials  
702 (Jafarzadeh, Alias, Ariffin, Mahmud & Najafi, 2016).

703 Nanoclay minerals are rigid fillers used to reinforce soft polymeric matrices and  
704 these generally increase the stiffness (Nazir et al., 2016), with agglomerated nanoclays  
705 typically decreasing the film's flexural properties (Fu & Naguib, 2006). Carrageenan  
706 composites reinforced with nanoclays exhibit a remarkable improvement particularly  
707 in their mechanical and barrier properties compared with the base material alone



708 (Shojaee-Aliabadi, Mohammadifar, et al., 2014). For example, the WVP of pure  $\kappa$ -  
709 carrageenan film decreased by around 26% after reinforcement with 5% (w/w) of  
710 nanoclay, and similar results have also been reported for the film prepared from  
711 carrageenan blended with other polysaccharides (Rhim & Wang, 2013; Shojaee-  
712 Aliabadi, Mohammadifar, et al., 2014). The enhancement of moisture barrier properties  
713 may have resulted from the dispersed clay layer subsequently increasing the tortuosity  
714 imposed by the matrix and the obstruction of the micro-paths within the polymer  
715 network (Rhim, 2011; Sorrentino, Gorrasi & Vittoria, 2007). In addition, reinforcing  
716 clay nanoparticles can also increase the gas barrier properties as well as the water  
717 resistance of carrageenan composites and this has been observed by contact angle and  
718 swelling analyses (Alves et al., 2010; Rane et al., 2014; Rhim, 2013). However, the  
719 latter properties are found to be highly influenced by the hydrophilicity of the materials  
720 that are used (Rane et al., 2014). If excessive amounts of nanoclays are incorporated  
721 within a polymer matrix, particle agglomeration can occur resulting in reduced barrier  
722 properties which can consequently impact the blocking mechanism (Sanchez-Garcia et  
723 al., 2010).

724         The inclusion of nanoclays within a carrageenan polymer matrix can  
725 significantly improve the mechanical strength of the sample films. This may be due to  
726 the strong interaction between the intercalated silicates and the polymer matrix through  
727 hydrogen or ionic bonds (Almasi, Ghanbarzadeh & Entezami, 2010; Lee & Kim, 2010).  
728 The distribution of intercalated clay particles with a high elastic modulus profile creates  
729 strong interfacial contact with the polymer network and enables effective stress transfer,  
730 finally resulting in a higher TS and Young's modulus (Alexandre & Dubois, 2000;  
731 Pavlidou & Papaspyrides, 2008; Sanchez-Garcia et al., 2010). Shojaee-Aliabadi,  
732 Mohammadifar, et al. (2014) reported that the incorporation of nanoclays up to a 10%

733 (w/w) loading significantly increased the TS of carrageenan films and other  
734 investigations have also reported similar findings (Martins, Bourbon, et al., 2012;  
735 Zakuwan et al., 2013).

736 Due to its superior biodegradability, biocompatibility, as well as its economic  
737 advantages, carrageenan has been widely studied for use in a broad range of  
738 applications. Its hydrophilic characteristics along with high content of ester sulfate  
739 groups in its structure render carrageenan film suitable for edible food packaging, as  
740 well as for pharmacological, biomedical, and electrical applications. However, the  
741 hydrophilicity is also a major disadvantage, particularly in food containment  
742 applications where high moisture transfer and low water resistance of the film is of  
743 concern. Numerous physical and chemical techniques have been studied for the purpose  
744 of obtaining desirable film properties. Blending carrageenans with hydrophobic  
745 compounds, reinforcement with nanomaterials, or layering with other polymer films  
746 have resulted in significant enhancements to carrageenan film properties. These  
747 developments show that carrageenan possesses great potential for further development  
748 in the quest to produce eco-friendly, cost-effective food packaging materials.

749 Differences in the flexural properties of carrageenan films incorporated with  
750 nanoclay minerals have also been reported (Rhim & Wang, 2014) and instead of  
751 increasing the EAB some nanoclays have been shown to decrease the flexibility of the  
752 resultant film (Shojaee-Aliabadi, Mohammadifar, et al., 2014). This may be caused by  
753 different inherent characteristics of the various types of nanoclays with organically  
754 modified clays such as Cloisite®30B imparting higher hydrophobicity than the  
755 unmodified materials. The addition of such clays may result in stronger interfacial  
756 affinity and interactions between the clay and polymer matrix resulting in cross-linked  
757 networks that subsequently increase the flexural properties (Mirzataheri, Atai &

758 Mahdavian, 2010). In addition to the type of clay that is incorporated in the formulation,  
759 the degree of exfoliation/intercalation of the clay in the polymer matrix also  
760 substantially influences the mechanical properties of carrageenan films (Martins,  
761 Bourbon, et al., 2012).

762 Higher thermal stability of carrageenan films has also been obtained by the  
763 inclusion of nanoclays. The conformation of the carrageenan-nanoclay composite  
764 structure causes a more restricted thermal transmission through the silicate interlayers  
765 (Blumstein, 1965). The nanoclay structure may also act as an insulator and barrier to  
766 the transmission of volatile compounds that are produced during the decomposition of  
767 the composites (Kumar, Sandeep, Alavi, Truong & Gorga, 2010; Zulfiqar, Ahmad &  
768 Sarwar, 2008).

#### 769 **4.4.2 Nanocellulose**

770 In comparison with the inorganic nano-materials that are used in carrageenan  
771 composites, cellulose nanoparticles facilitate some additional advantages including  
772 their sustainability and biodegradability in nature, lower density, and the ability to be  
773 incorporated into biopolymers using solvent casting methods (Angles & Dufresne,  
774 2000; Kvien, Tanem & Oksman, 2005; Šturcová, Davies & Eichhorn, 2005). Two  
775 major types of nanocellulose morphological structures have been applied in biopolymer  
776 matrices, namely cellulose-nanofibrils (CNFs) and cellulose-nanocrystals or  
777 nanowhiskers (CNCs). The CNCs have particle shapes like needle crystals that are 100-  
778 1000 nm in length and 4-25 nm in diameter and are obtained by removing most of the  
779 amorphous cellulose phase (Jonoobi et al., 2015; Xu et al., 2013).

780 Similar to the incorporation of nanoclays, a relatively small amount of  
781 nanocellulose can effectively improve the mechanical properties of carrageenan films.  
782 Zakuwan et al. (2013) found that the optimum TS and Young's modulus were obtained

783 by reinforcing carrageenan with a 4% (w/w) of CNCs, with values of 36.8 and 1340  
784 MPa respectively. This result was also supported by Zarina & Ahmad (2015), however,  
785 Savadekar et al. (2012) reported that the addition of only 0.4 % (w/w) CNFs produced  
786 the maximum TS value of the carrageenan film and any additional CNFs decreased the  
787 TS. These contrasting results may suggest that different cellulose structures may have  
788 different effects on the mechanical properties of carrageenan films. It appears that  
789 CNCs exhibit optimum effects on the tensile properties of carrageenan films at higher  
790 loadings in comparison with CNFs. An excessive amount of nanocellulose added in the  
791 formulation can lead to particle agglomeration within the carrageenan polymer matrix,  
792 which consequently reduces the mechanical properties of the final films (Sánchez-  
793 García et al., 2010). In addition, increasing the amount of these materials also  
794 detrimentally affects the opacity of the film (Abdollahi, Alboofetileh, Behrooz, Rezaei  
795 & Miraki, 2013).

796 In general, nanocellulose reinforcement has been shown to produce typically  
797 similar effects on the physico-mechanical properties of carrageenan-based film as is  
798 produced by the nanoclays, with a demonstrated increase in water resistance,  
799 enhancement of the moisture and gas barrier properties, as well as an enhancement of  
800 the thermal stability of the film (Savadekar et al., 2012; Zarina & Ahmad, 2015). These  
801 properties are also affected by the degree of particle dispersion in the polymer matrix,  
802 as well as degree of crystallinity of the nanocellulose materials (Chen, Liu, Chang, Cao  
803 & Anderson, 2009; Ljungberg et al., 2005; Luiz de Paula, Mano & Pereira, 2011).

#### 804 **4.4.3 Chitin Nanofibers**

805 Chitin is commonly extracted from the exoskeleton of marine crustaceans and  
806 insects, as well as the cell wall of fungi and yeast (Tharanathan & Kittur, 2003). Hence,  
807 its availability in nature is plentiful, and is the second most abundant biopolymer after

808 cellulose (Azuma, Ifuku, Osaki, Okamoto & Minami, 2014). The chitin structure in the  
809 crustacean exoskeletons forms microfibrillar arrangements wrapped by protein, and the  
810 chitin nanofibers (ChNFs) obtained from further chemical processing are usually a few  
811 micrometers in length and 10-100 nm in diameter (Li et al., 2016). Reinforcing  
812 carrageenan polymers with ChNFs results in smooth and flexible films with good  
813 homogenous dispersion of the fibres (Shankar et al., 2015). The addition up to 5% (w/w)  
814 ChNF into a carrageenan matrix can increase its tensile strength and Young's modulus  
815 with a decrease in its WVP, however, this may cause a loss in flexural properties and  
816 transparency of the film. In addition to improving certain physico-mechanical  
817 properties, the inclusion of ChNF in carrageenan films can impart AM activity,  
818 particularly against the Gram-positive food-borne pathogens such as *Listeria*  
819 *monocytogenes* (Shankar et al., 2015).

#### 820 **4.5 Multilayer Carrageenan Films**

821 Even though blending carrageenans with other biopolymers is considered to be  
822 the easiest and most effective method to improve the film properties, introducing  
823 synthetic hydrophobic polymers using this technique may not lead to desirable superior  
824 properties (Shojaee-Aliabadi et al., 2013). This is due to the high hydrophilicity of the  
825 carrageenan polymer which is immiscible with hydrophobic, synthetic polymers due to  
826 the low interfacial adhesion between the two phases in the matrix system (Avella et al.,  
827 2000). The hydrophilicity of carrageenan and other biopolymers is responsible for the  
828 inferior barrier properties and water sensitivity of these systems (Fabra et al., 2008) and  
829 this is of particular concern when these polymers are to be used for food packaging  
830 applications. The production of multilayer films may show potential for overcoming  
831 these limitations and as such films can be prepared without the problems of

832 incompatibility that often exists when using blending methods (Rhim, Mohanty, Singh  
833 & Ng, 2006).

834 Research reported by Rhim (2013) demonstrated the effectiveness of multilayer  
835 carrageenan/agar film reinforced by nanoclays, which was laminated with PLA. The  
836 PLA layer appeared to firmly adhere to the carrageenan-based layer *via* hydrogen-bond  
837 interactions, and it increased the transparency of the film due to the high transparency  
838 of the PLA layer. Double-layer films (carrageenan/agar-PLA) and triple-layer (PLA-  
839 carrageenan/agar-PLA) of similar overall thickness exhibited an increase in the TS from  
840  $48.2 \pm 4.5$  MPa (carrageenan/agar alone) to  $59.9 \pm 0.5$  and  $50.7 \pm 8.4$  MPa respectively.  
841 However, the PLA significantly decreased the elongation properties from  $26.3 \pm 5.1\%$   
842 to  $9.4 \pm 2.6\%$  and  $17.9 \pm 1.9\%$  for the double-layer and triple-layer films respectively.  
843 Moreover, the PLA layer dramatically reduced the WVP of the carrageenan-based film  
844 more than 24-fold. Higher hydrophobicity was also shown by the increase in the contact  
845 angle values from  $50^\circ$  to  $60^\circ$  with the latter value comparable with those of synthetic  
846 plastic films such as low-density polyethylene (LDPE), Ecoflex™ and poly(3-  
847 hydroxybutyrate-co-3-hydroxyvalerate) (Rhim & Hong, 2007). Moreover, the PLA  
848 layer also significantly increased the water resistance and thermal stability of the  
849 carrageenan-based film (Rhim, 2013). Overall, these results demonstrate the  
850 effectiveness of using a multilayer approach to improve the barrier properties of  
851 carrageenan films, thereby rendering these systems suitable candidates for food  
852 packaging applications.

## 853 **5 Applications of Carrageenan-Based Films**

### 854 **5.1 Edible Films and Coatings**

855 Utilizing carrageenan for edible films and coatings covers a broad range of food  
856 industry applications such as fresh and frozen fish, meat, and poultry (Baldwin,  
857 Hagenmaier & Bai, 2011; Cha et al., 2002; Seol, Lim, Jang, Jo & Lee, 2009; Stuchell  
858 & Krochta, 1995; Wu et al., 2000), various dried food products (Kampf & Nussinovitch,  
859 2000), fruit coatings (Bico, Raposo, Morais & Morais, 2009; Hamzah, Osman, Tan &  
860 Mohamad Ghazali, 2013; Ribeiro, Vicente, Teixeira & Miranda, 2007), and  
861 microencapsulation (Bartkowiak & Hunkeler, 2001; Desai & Jin Park, 2005). The  
862 principal goal in these applications is the prevention of dehydration, undesired chemical  
863 reactions (Baldwin & Wood, 2006; Osorio, Molina, Matiacevich, Enrione & Skurtys,  
864 2011; Valero et al., 2013), as well as the inhibition of spoilage and deterioration by  
865 microbial contamination (Arvanitoyannis, 2010; Soni et al., 2016). Moreover,  
866 carrageenans can also be functionalized to improve the delivery and dispersion of food  
867 additives or to control the release of active agents, particularly in active packaging  
868 applications (Barreto, Pires & Soldi, 2003; Campos, Gerschenson & Flores, 2011; Soni  
869 et al., 2016).

870 In the case of fresh-cut fruit, carrageenan coatings form an effective barrier  
871 between the cut surface of the fruit and gas from the surroundings thereby reducing  
872 respiration and minimizing discoloration (Baeza, 2007). When used as an edible coating,  
873 carrageenan films can maintain fruit texture and provide antibacterial protection during  
874 storage (Bico et al., 2009; Plotto, Narciso, Rattanapanone & Baldwin, 2010). Although  
875 the use of hydrophobic substances such as waxes, resins, or water insoluble proteins  
876 imparts better moisture barrier properties to edible films or coatings, the application of

877 water-soluble hydrocolloids usually results in better mechanical properties than those  
878 provided by the hydrophobic materials (Arvanitoyannis, 2010). In addition, water-  
879 soluble hydrocolloids also exhibit better gas barrier properties (Nussinovitch, 2009) due  
880 to their compact and tightly packed conformation that result from organized hydrogen  
881 bonded network structures (Atarés, Pérez-Masiá & Chiralt, 2011; Bonilla, Atarés,  
882 Vargas & Chiralt, 2012).

## 883 **5.2 Pharmaceutical and Biomedical Applications**

884 Carrageenan utilization in pharmaceutical and biomedical applications has been  
885 extensively investigated (Garcia & Ghaly, 2001; Hoffman, 2002; Park et al., 2001;  
886 Picker, 1999; Sankalia, Mashru, Sankalia & Sutariya, 2006; Yamada et al., 2005), and  
887 it has been regulated recently in Europe, the United States and the United Kingdom  
888 (García-González, Alnaief & Smirnova, 2011; Li, Ni, Shao & Mao, 2014). The  
889 application of carrageenan-based films in these areas are primarily related to drug  
890 delivery systems and wound dressings.

891 In the area of drug delivery systems, a multilayered polymeric film is usually  
892 applied due to its ability to manipulate the release of active compounds. Incorporating  
893 pharmaceutical agents into a polymer film followed by organizing the layers of the film  
894 in a particular way may prevent the loss of the drug substances (Wang et al., 2007).  
895 Various multilayered films have been investigated to obtain the controlled release of  
896 active compounds which can be triggered by certain conditions such as temperature,  
897 pH, enzymes, or ionic strength (Pinheiro, Bourbon, Quintas, Coimbra & Vicente, 2012;  
898 Quinn & Caruso, 2004; Serizawa, Yamaguchi & Akashi, 2002; Wood, Boedicker, Lynn  
899 & Hammond, 2005).



900 An early report by Nagai (1985) described that a multilayered drug-delivery  
901 films are typically comprised of two main components: carrier film(s) and barrier  
902 film(s). The carrier film contains the pharmaceutical or active compounds that are  
903 usually dissolved or dispersed homogenously in the polymer matrix. It was also  
904 reported that configuring the concentration of the active compounds to increase from  
905 the outer wall to the inner part of the film results in better control of the release of the  
906 compounds. The barrier film is joined to one surface of the carrier film to essentially  
907 "lock in" the active compounds and maintain stability until the release is triggered by  
908 certain conditions. Examples of this mode of delivery include film strips containing  
909 active ingredients such as mouth freshener, nutrients or herbs, caffeine, and  
910 pharmaceutical ingredients (Siah et al., 2015). Medicinal strips made from edible films  
911 containing drug substances can be administered without water, which is helpful for  
912 persons who have difficulty in swallowing tablets or capsules such as children and the  
913 elderly (Siah et al., 2015). In addition, the use of edible films for drug delivery may be  
914 convenient for administering prescribed drugs where different doses can be obtained  
915 by using different lengths of edible film (Nagai, 1985).

916 Another application of carrageenan films is wound healing aids (Boateng,  
917 Pawar & Tetteh, 2013; Fouda et al., 2015; Lloyd, Kennedy, Methacanon, Paterson &  
918 Knill, 1998; Pawar, Tetteh & Boateng, 2013; Wu, Bao, Yoshii & Makuuchi, 2001) with  
919 hydrocolloid films among the most widely applied due to their distinctive ability to  
920 adhere to both moist and dry surfaces (Heenan, 1998). These films have exhibited  
921 desirable properties in maintaining a moist environment, facilitating the drainage and  
922 evaporation of wound exudates, as well as allowing adequate gas exchange (Pawar et  
923 al., 2013; Sussman, 2010). Moreover, they have also been used for delivering  
924 pharmaceutical ingredients to wound surfaces and to oral cavities for medication

925 purposes (Boateng et al., 2009; Cunha & Grenha, 2016; Zivanovic, Li, Davidson & Kit,  
926 2007). In the preparation of these films, the polymer substances are usually cross-linked  
927 to enhance their water entrapping ability so that the films can highly absorb and retain  
928 the liquid upon contact with exuding wounds (Boateng, Matthews, Stevens & Eccleston,  
929 2008).

### 930 **5.3 Electrolytes/Electrically Conductive Materials**

931 In addition to their environmental benefits, the high degree of compatibility with  
932 salts makes some biopolymers including carrageenan attractive in the development of  
933 electrically conductive materials (Barbucci, Magnani & Consumi, 2000; Rozali,  
934 Samsudin & Isa, 2012). The large number of hydroxyl groups in its molecular structure  
935 allows carrageenan to form cross-linking networks with other constituents, and  
936 substituents with other functional groups in polymer electrolytes (Yang et al., 2011).  
937 Finkenstadt (2005) reported that these polymers, with their extensive hydrogen bonding,  
938 usually exhibit a higher conductivity than those with a lesser extent of such bonding.  
939 Even though liquid electrolytes show better conductivity and the ability to transmit  
940 larger currents, flexible carrageenan-based films can be suitable for use in electrically  
941 conductive devices (Arof, Shuhaimi, Alias, Kufian & Majid, 2010).

942 A study by Prasad & Kadokawa (2010) reported that the use of carrageenan-  
943 polymer film as the host polymer of two different ionic components, 1-(3-  
944 acryloyloxypropyl)-3-vinylimidazolium bromide and 1-vinyl-3-  
945 vinylbenzylimidazolium chloride, results in a material with good electrical conductivity  
946 and mechanical properties. It was further suggested that this composite has the potential  
947 to be applied for use in semiconductors or organic memory devices. Furthermore, the  
948 host polymer of the electrolyte composite which is prepared by blending carboxymethyl

949  $\kappa$ -carrageenan and carboxymethyl cellulose could also enhance the conductive  
950 properties of the material, and showed favourable characteristics for fabrication of dye-  
951 sensitized solar cells (Rudhziah, Ahmad, Ahmad & Mohamed, 2015). Another novel  
952 electrical conductive device involving carrageenan-based composites is the microbial  
953 fuel cell which offers economic benefits compared with the commonly used polymer  
954 material, poly(pyrrole) (Esmaeili et al., 2014).

## 955 **6 Conclusions**

956 Due to its superior biodegradability, biocompatibility, as well as its economic  
957 advantages, carrageenan has been widely studied for use in a broad range of  
958 applications. Its hydrophilic characteristics along with high content of ester sulfate  
959 groups in its structure render carrageenan film suitable for edible food packaging, as  
960 well as for pharmacological, biomedical, and electrical applications. However, the  
961 hydrophilicity is also a major disadvantage, particularly in food containment  
962 applications where high moisture transfer and low water resistance of the film is of  
963 concern. Numerous physical and chemical techniques have been studied for the purpose  
964 of obtaining desirable film properties. Blending carrageenans with hydrophobic  
965 compounds, reinforcement with nanomaterials, or layering with other polymer films  
966 have resulted in significant enhancements to carrageenan film properties. These  
967 developments show that carrageenan possesses great potential for further development  
968 in the quest to produce eco-friendly, cost-effective food packaging materials.

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