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

Sedayu, Bakti B, Cran, Marlene and Bigger, Stephen W (2019) A Review of Property Enhancement Techniques for Carrageenan-based Films and Coatings. Carbohydrate Polymers, 216. pp. 287-302. ISSN 0144-8617

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

Bakti B. Sedayu[1,2], Marlene J. Cran[1*], Stephen W. Bigger[1]

[1]Institute for Sustainable Industries and Liveable Cities, Victoria University, PO Box 14428, Melbourne, 8001, Australia.

[2]Agency for Marine and Fisheries Research and Development, Republic of Indonesia. Jl. Pasir Putih II, Ancol Timur, Jakarta Utara 14430, Indonesia.

*Corresponding author: marlene.cran@vu.edu.au, Tel:,61 3 9919 7642

Abstract

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

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

1 Introduction

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

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

Extensive research has been conducted to produce bioplastics from many different sources including plants, microbes, and animals (Pathak, Sneha & Mathew, 2014). Some are now commercially available in the global market such as poly(lactic acid) (PLA), poly(hydroxyalkanoates) (PHAs) and starch-based polymers, with new materials frequently investigated for various uses (Accinelli, Sacca, Mencarelli & Vicari, 2012; Yates & Barlow, 2013). Even though these materials can be produced from many renewable sources, there are still challenges to be addressed due to their limited biomass-availability and also their cultivation or synthesis. Seaweed is one such material that can offer a source of raw materials from which packaging materials can be produced. Compared with terrestrial plant sources, seaweed offers some considerable advantages including its low cost and abundance in nature. Moreover, as a non-terrestrial plant material, it is unnecessary to clear valuable land to plant crops or compete with food production. Additionally, seaweeds are purported to lessen impacts on the food chain and are generally safe from exposure to chemicals or fertilizers (Rajendran, Puppala, Sneha, Ruth & Rajam, 2012).

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

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

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

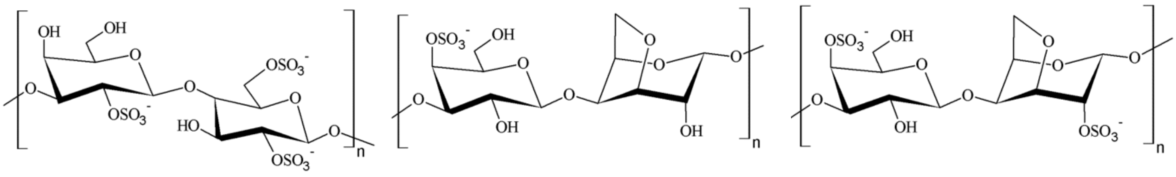
The development of carrageenan-based films for packaging purposes is a relatively new and emerging research area. Consequently, there are a limited number of articles in the literature that review the current status of this topic although some previous reviews have described the potential applications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

2 Carrageenan

2.1 Chemical Structures and Characteristics

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

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



λ-carrageenan κ-carrageenan ι-carrageenan

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

In addition to the specific types of carrageenan described above, there are also some hybrid types. In nature, seaweeds generally do not produce pure carrageenan but more likely mixtures of different sulfated polysaccharides in their structures including hybrid carrageenans (van de Velde, 2008). The composition of carrageenans in a given seaweed is determined by several factors, such as its biological stage (Gómez-Ordóñez & Rupérez, 2011), gender of the gametophyte, environmental condition (Hilliou, 2014), as well as the extraction method used in carrageenan recovery (Larotonda, Torres, Goncalves, Sereno & Hilliou, 2016; Souza, Hilliou, Bastos & Gonçalves, 2011). Hilliou (2014) reported that the vegetative phase of the *Gigartinales* seaweed order produces highly sulfated forms of μ-carrageenan, which is a non-gelling type, whereas in the reproductive life stage, κ- and ι- types of gelling carrageenan together with ν- and η-carrageenans are produced. Furthermore, in *Kappaphycus striatum* seaweed the young-age seaweed contains less-gelling carrageenan types than the matured seaweed (Hilliou, 2014).

2.2 Carrageenan Sources

The name carrageenan is derived from the Gaelic word, *carraigín* or “little rock” that has been used as early as 400 A.D. in Ireland. The first types of carrageenans were obtained from the “Irish moss” seaweed (*Chondus crispus*) which was used for animal feed and medicinal purposes (Loureiro, Cornish & Neish, 2017; Loureiro, Hurtado & Critchley, 2017). During World War II, the world’s demand for carrageenan noticeably increased particularly in relation to the food processing industries, with *Chondus crispus* and *Gigartina* seaweeds harvested from natural stock being the major sources. *Chondus crispus* grows naturally in Canada, Ireland, France, Spain and Portugal, and *Gigartina* beds are found in Southern Europe and South America (Valderrama, Cai, Hishamunda & Ridler, 2013). In the 1940’s, Canada with its abundant natural beds of *Chondus crispus* had become the world’s largest carrageenan-seaweed supplier which continued for almost three decades. However, the discovery of alternative carrageenan-seaweed species, *Eucheuma sp.* in the Philippines, followed by the success of its cultivation for large-scale farming production, has made this species a major source for carrageenan with the Philippines displacing Canada as the largest supplier of carrageenans. Indonesia soon followed and adopted successful seaweed farming from its neighboring country such that in the last few decades it has surpassed the Philippines' carrageenan-seaweed production to become the leading global supplier of carrageenan, predominantly derived from the *Kappaphycus* and *Eucheuma* seaweeds (Hurtado, Neish & Critchley, 2015; Valderrama et al., 2013). To date, around 90% of world's carrageenan is derived from these two species and their farming is now spreading worldwide including regions of South-east Asia, Pacific Islands, mainland of East Africa, South America, and the Central Americas (Hurtado et al., 2015). The success of carrageenan seaweed farming worldwide may also denote a sustainable resource of raw material stocks for future industrial production of carrageenan-based plastics.

Similar to land-based crops, however, carrageenan seaweed farming is also subjected to the challenges of nature *i.e.* herbivorous fish predation, stormy weather, parasite epiphyte, and outbreaks of the "ice-ice" disease. This disease, which presents as a white bleaching of the seaweed's thalli, is one of the biggest problems associated carrageenan seaweed farming. Outbreaks have been reported since the early years of *Kappaphycus* farming development in the Philippines and since then, the disease has been reported in almost all carrageenan seaweed farms worldwide (Hafting et al., 2015). This outbreak is recognized as the seaweed's physiological stress in responding to its surrounding environmental changes such as temperature and salinity fluctuations. However, it is commonly followed by pathogenic microbial infestations which cause complete necrosis and fragmentation of the infected thalli (Loureiro, Hurtado, et al., 2017). This, in turn, can cause a tremendous drop in seaweed production, as well as the quality of the carrageenan (Mendoza, Montaño, Ganzon-Fortes & Villanueva, 2002). To respond to this challenge, there is an urgent need to develop seaweed strains that are tolerant to fluctuations in marine environmental conditions, resistant to disease and produce greater carrageenan yields (Hayashi et al., 2017; Kim, Yarish, Hwang, Park & Kim, 2017).

2.3 Production of Carrageenan

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

Additional steps are performed for the *Eucheuma* and *Furcellaria* seaweed species, whereby precipitation using KCl solution is applied (Stanley, 1987). Following the hot water extraction step, the carrageenan slurry is extruded through spinnerets and collected in a container of cold KCl solution to form a gel before it is dehydrated, dried and powdered (Minghou, 1990). For the production of λ-carrageenan, *Gigartina* and *Chondrus* (Irish moss) seaweeds are commonly used (van de Velde & De Ruiter, 2002) and since λ-carrageenan does not characteristically form a gel, the dehydration process is usually performed using a drum dryer and/or alcohol precipitation with propanol or ethanol. However, thermal processing using a drum dryer may adversely impact the carrageenan quality, so alcohol precipitation is the more common industrial practice (Prajapati et al., 2014).

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

2.4 Semi-Refined Carrageenan

The aforementioned methods describe the production of refined carrageenan, but in addition to these materials, semi-processed/semi-refined carrageenans are also extensively produced for various industries including use as additives in pet foods and dairy products (Dewi, Darmanto & Ambariyanto, 2012). According to the US Food and Drug Administration (US Food and Drug Administration, 2017), semi-refined carrageenan (SRC) can be acceptably referred to as carrageenan and there is no legal distinction between these two materials. However, in the European Union (EU), these materials are recognized as different substances and are thus regulated separately. In this case, the SRC is regulated under the name "Processed Eucheuma Seaweed (PES)" with the trade "E" number of E407a, whereas pure carrageenan is registered with the number E407 (EUR Lex, 2004).

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

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

2.5 Economic Perspectives

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

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

In comparison with other sources of bio-based plastic materials such as those derived from corn, cassava, sugarcane, and other terrestrial crops, seaweed may be a less expensive material since it does not require the use of arable lands, fresh water, and fertilizer or chemicals (Konda, Singh, Simmons & Klein-Marcuschamer, 2015). However, the extraction process of carrageenan does requires a large amount of chemicals and energy (Abdul Khalil, Tye, et al., 2017) which is the key drawback that must be overcome to achieve economic feasibility for industrial implementation. Nonetheless, it has been previously observed that the price of bio-based plastics becomes more competitive with its synthetic counterparts whenever the economics of large-scale production, conversion into products, and logistics become more favorable (van den Oever et al., 2017). For example, various single use-plastic products such as bottles, food tray and lid containers, overwraps, cups, and some flexible films made from PLA are now widely available in the market with competitive prices to those made from conventional plastics. This is because PLA and its end-products are currently manufactured on a large industrial scale with similar product processing technologies that are utilized for synthetic plastics (Muller, Gonzalez-Martinez & Chiralt, 2017). Similarly, the price of bio-poly(butylene succinate) (bio-PBS) has dropped from 4.00 €/kg to *ca*. 2.50 €/kg due to the production of succinic acid from biomass becoming more efficient with larger production volumes (van den Oever et al., 2017).

To achieve successful commercial production of carrageenan films in a way similar to PLA, bio-PBS, and other commercial bio-based polymers, significant innovative breakthroughs are needed across the whole production chain, starting from seaweed cultivation and harvesting, transport, carrageenan extraction, through to the manufacture and marketing of products. Another important consideration that compensates in part for the higher production costs is that carrageenan-based plastics can offer consumers significant overall environmental benefits compared with some other materials and such perspectives have previously been associated with growing market demands (DeGruson, 2016). End-products derived from carrageenan may also be developed for niche markets where slightly higher production costs may be more acceptable. Moreover, utilization of less expensive semi-refined carrageenan may also reduce production costs of films for various uses (Sedayu, Cran & Bigger, 2018).

3 Carrageenan-Based Films

3.1 Gel Formation

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

To generate a helical structure in κ- or ι-carrageenan solutions, a minimum degree of polymerization of around one hundred is required (Hjerde, Smidsrød, Stokke

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

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

Hybrid carrageenan structures possess properties that are distinct from those of the single polymeric counterparts (Souza et al., 2011). However, because of the profound gelling ability among the hybrid groups, most studies have focused on the κ/ι-hybrid carrageenans (Larotonda et al., 2016; Sánchez-García, Hilliou & Lagarón, 2010; Souza et al., 2011; van de Velde, 2008). Kappa/iota-hybrid carrageenans are sulfated polysaccharide structures consisting of blocks of κ- or ι-carrageenan disaccharide units distributed in their molecular chain (van de Velde, 2008; van de Velde & De Ruiter, 2005), and are usually found together with small amounts of non-gelling disaccharide units, such as μ- and/or ν-carrageenans (Souza et al., 2011). The structure and composition of the disaccharide units determines the conformational transition from the random coil state to the helical state of the polymer during gel formation as well as the functional polymer properties (Larotonda et al., 2016; van de Velde, 2008). It has been reported that κ/ι-hybrid carrageenans extracted from *Martocarpus stellatus* seaweed exhibit a gelling property which is intermediate between those of single κ- and ι-carrageenans gels. In contrast, λ-carrageenan produces only viscous solutions, without gel formation (de Araújo et al., 2011; Gu, Decker & McClements, 2005).

3.2 Film Formation and Characteristics

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

Similarly, as in the case of ι-carrageenan, κ-carrageenan polymers exhibit a compact film structure (El-Fawal, 2014; Nanaki et al., 2010), and the high gelling ability of κ-carrageenan imparts excellent film-forming properties (Wu & Imai, 2012) with higher mechanical and water barrier properties, as well as greater transparency (Park, 1996; Paula et al., 2015). Table 1 lists various functional properties of carrageenan-based films in comparison with other bio-based and synthetic films used in food packaging applications. These basic properties are amongst the most important properties that are commonly considered when developing materials for industrial applications and include the physico-mechanical properties of tensile strength (TS) and elongation at break (EAB), along with the functional properties of water vapor permeability (WVP) and gas permeability. Clearly, the development of novel packaging films requires the optimization of these properties to ensure the material can adequately protect the product quality and safety during storage until it is delivered to consumers (Lagaron, 2011).

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

Film	TS **/MPa**	EAB **/%**	WVP **/10^{11} g m^{-1} Pa^{-1} s^{-1}**	OP **/10^{12} cm^{3} m^{-1} Pa^{-1} s^{-1}**	References
κ-carrageenan	42.5	3.9	7.5	5.2	Larotonda et al. (2016)
ι-carrageenan	2.5	1.04	36	-	Paula et al. (2015)
κ/ι-hybrid carrageenan	55.2	3.4	6.7	3.3	Larotonda et al. (2016)
SR κ-carrageenan	35.43^{a}	10.14^{a}	27.8^{a}	1.67^{b}	^{a}Sedayu et al. (2018) ^{b}Farhan & Hani (2017)
SR ι-carrageenan	8.9	12.05	-	-	Aji, Praseptiangga, Rochima, Joni & Panatarani (2018)
PLA	15.2^{a}	40.4^{a}	2.47^{a}	62^{b}	^{a}Li et al. (2017) ^{b}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^{a}	100-1330^{a}	0.091^{b}	21.6^{b}	^{a}MatWeb (2019) ^{b}Larotonda et al. (2016)
HDPE	11.6-228^{a}	160-1010^{a}	0.023^{b}	4.9^{b}	^{a}MatWeb (2019) ^{b}Larotonda et al. (2016)

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

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

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

4 Property Enhancement of Carrageenan-Based Films

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

Table 2. Property modifications of carrageenan-based films.

Carrageenan and other components	Property Enhancements	Disadvantages	Reference(s)
κ-carrageenan, alginate	Increased mechanical properties, thermal stability, optical properties		Ye et al. (2017)
κ-carrageenan, alginate	Improved water resistance, thermal stability		Xu et al. (2003)
κ-carrageenan, alginate	AM activity		Cha, Choi, Chinnan & Park (2002)
κ-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)
κ-carrageenan, rice starch	Improved barrier properties, increased T_g, mechanical properties		Larotonda, Hilliou, Sereno & Gonçalves (2005)
κ-carrageenan, agar	Increased EAB, water resistance, decreased WVP	Decreased TS	Rhim (2012)
κ-carrageenan, agar, konjac glucomanan	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 κ-carrageenan, carboxymethyl cellulose	Increased mechanical properties		Rudhziah, Rani, Ahmad, Mohamed & Kaddami (2015)
κ-carrageenan, pea starch	Increased EAB	Decreased TS, thermal stability	Lafargue, Lourdin & Doublier (2007)
κ-, ι-, λ-carrageenan blends			Nanaki et al. (2010)

Carrageenan and other components	Property Enhancements	Disadvantages	Reference(s)
κ-carrageenan, locust bean gum	Increased thermal stability, mechanical properties	Increased WVP	Martins, Cerqueira, et al. (2012)
κ-carrageenan, pectin, mica flakes	Increased hydrophobicity, mica flakes alone specifically increased WVP and gas barrier properties		Alves et al. (2010); Alves et al. (2011)
κ-carrageenan, chitosan	Increased EAB	Rougher surface, increased WVP, decreased TS, water resistance	Shahbazi, Rajabzadeh, Ettelaie & Rafe (2016)
κ-carrageenan, chitosan	Increased water resistance		
κ-carrageenan, plant essential oils (*Zataria multiflora* Boiss, *Mentha pulegium*, *Satureja hortensis*)	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)
κ-carrageenan, essential oils (oregano & thyme)	Decreased WVP, increased water resistance, EAB, AM activity	Decreased transparency, TS	Soni et al. (2016)
ι-carrageenan, fat, aroma compounds	Decreased permeability of aroma compounds, increased surface hydrophobicity	Rough microstructure, morphology	Hambleton, Fabra, Debeaufort, Dury-Brun & Voilley (2009)
ι-carrageenan, fat, emulsifier	Increased surface hydrophobicity	Rough microstructure, morphology	Karbowiak, Debeaufort, Champion & Voilley (2006)
κ-carrageenan, latex	Increased TS, energy absorption		Machmud, Fahmi, Abdullah & Kokarkin (2013)
κ-carrageenan, cinnamon oil	Decreased WVP	Decreased mechanical properties	Praseptiangga, Fatmala, Manuhara, Utami & Khasanah (2016)
κ-carrageenan, various plant oils (corn, soybean, olive, sunflower)	Decreased WVP, increased water resistance	Increased opacity, yellowish color, decreased TS	Rekemin & Abedin (2017)
κ-carrageenan, palmitic acid	Increased water resistance	Decreased mechanical properties	Wibowo, Listiyawati & Purnawan (2016)
κ/ι hybrid carrageenan, zein prolamine	Reduced WVP, improved TS, stretchability	Decreased water resistance, EAB	Sanchez-Garcia, Hilliou & Lagaron (2010)
κ-carrageenan, potassium sorbate	AM activity		Choi et al. (2005)
κ-carrageenan, citric acid	AM activity against *E. coli*, *P. mirabilis*, *D. chrysanthemi*, *S. aureus*, but not *P. aeruginosa*	Decreased mechanical properties, hydrophobicity	El-Fawal (2014)
κ-carrageenan, nano-silver	Fungicidal activity to *Fusarium*, *penicillium spp*. & *Aspergillus niger*, higher thermal stability, increased TS	Decreased transparency, hydrophobicity	Fouda et al. (2015)
κ-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)**
		hydrophobicity, mechanical properties	
κ-carrageenan/alginate, nisin, lysozyme, EDTA, grapefruit seed extract	AM activity	Decreased TS, EAB	Cha et al. (2002)
κ-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 *E. coli*, *L. monocytogenes*	Decreased TS	Oun & Rhim (2017)
Carrageenan, chitin nanofibrils	AM activity against *L. monocytogenes*, increased TS, EAB, thermal stability	Increased opacity, hydrophilicity	Shankar, Reddy, Rhim & Kim (2015)
κ-carrageenan, essential oils	AM activity, increased flexibility, improved water barrier properties	Decreased TS, optical properties	
κ-carrageenan, nanoclay, silver	Reduced WVP, increased TS, EAB, thermal stability, hydrophobicity and AM activity		Rhim & Wang (2014) Rhim & Wang (2013)
κ-carrageenan, nanocellulose fibers	Reduced WVP and gas barrier properties, increased TS		Savadekar, Karande, Vigneshwaran, Bharimalla & Mhaske (2012)
κ-carrageenan, chitin nanofibrils	Increased WVP, TS, AM activity, stiffness, hydrophobicity	Decreased EAB, transparency	Shankar et al. (2015)
κ-carrageenan, cellulose nano-crystals, nanoclay	Increased TS		Zakuwan, Ahmad & Ramli (2013)
κ-carrageenan, nanoclay	Increased TS, EAB, thermal stability, AM activity against *L. monocytogenes*	Rougher microstructure	Martins, Bourbon, et al. (2012)
κ-carrageenan, nanosilica	Increased mechanical properties, hydrophobicity, decreased WVP		Rane, Savadekar, Kadam & Mhaske (2014)
κ-carrageenan, nanoclay	Improved mechanical properties, barrier properties, hydrophobicity		Rhim (2012)
κ/ι 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)

411

4.1 Blending Carrageenans

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

4.1.1 Polysaccharides

Polysaccharides have been extensively explored for various film applications, and these are considered to be the most widely used biomaterials for both food and non-food purposes. A wide range of film properties can be obtained by combining different types of polysaccharides since these can demonstrate various intrinsic properties (Nisperos-Carriedo, 1994). Among the biopolymers, starch is the most popular resource used as a filler in polymer blending since it is less expensive than many other materials and is abundant in nature (Fakhouri et al., 2013). Starch consists of two main components: amylose and amylopectin, whereby the first structure is primarily linear and is crystalline with an average molecular weight around 500,000 Dalton, whereas the second is highly branched with very high molecular weight (Chandra & Rustgi, 1998; Hyang Aee, Nam Hie & Nishinari, 1998; Rosa, Lopes & Calil, 2005).

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

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

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

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

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

4.1.2 Lipids

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

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

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

4.1.3 Proteins

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

4.1.4 Other Materials

Some other materials have been investigated in mixtures with carrageenan including poly(vinyl pyrrolidone) (PVP) (Fouda et al., 2015), mica flakes (Alves et al., 2010), and latex (Machmud et al., 2013; Norhazariah, Azura, Sivakumar & Azahari, 2016). Blended carrageenan-PVP polymer film plasticized with polyethylene glycol (PEG) showed a high transparency with a homogenous polymer matrix and good flexibility (Fouda et al., 2015). It has been suggested that blending PVP into hydrocolloid polymer systems can increase the hydrophobicity of the hydrocolloid (Çaykara, Demirci, Eroğlu & Güven, 2006). It has also been suggested that blending a crude carrageenan with latex derived from *Calostropis gigantean* enhances the tensile properties with a demonstrated higher TS compared with those of starch-based plastics (Machmud et al., 2013). Furthermore, the inclusion of mica flakes in carrageenan has been shown to enhance its barrier properties including gas and WVP by creating a tortuous structure (Alves et al., 2011).

4.2 Incorporation of Plasticizers

Although carrageenan is well known for its film forming ability with excellent optical properties, its native film exhibits brittleness that restricts its functionality for food packaging applications. The addition of plasticizers is therefore an essential requirement in the formulation to improve film flexibility and workability. Plasticizers are generally additive substances with low molecular weights that intercalate and disperse within the polymer network, disrupting hydrogen bonding, and spreading the polymer chains apart, which then increases the flexibility of the film (McHugh & Krochta, 1994). Plasticizers incorporated into the matrix should be compatible with the polymer structure and have similar solubility in the solvent used to optimize the intermolecular reactions. Moreover, to maintain the physio-mechanical properties of the film it is also important that the plasticizer does not evaporate from the film matrix (Wittaya, 2012). Plasticizers derived from polyol groups including glycerol, sorbitol and poly(ethylene glycol) are the most commonly used in the production of hydrogel films. The strong molecular interaction between the polymer chains and plasticizer *via* hydrogen bonding is responsible for the mechanical strength improvement of the film (Khazaei, Esmaiili, Djomeh, Ghasemlou & Jouki, 2014; Sothornvit & Krochta, 2000). It has been reported that the addition of glycerol and sorbitol into carrageenan-based films enhances the flexibility, TS and EAB of the material (Farhan & Hani, 2017; Harumarani, Ma'ruf & Romadhon, 2016). However, other reports have suggested the opposite; that the incorporation of glycerol can result in a decrease of the TS of the final carrageenan film (Wibowo et al., 2016). This suggests that the type and amount of plasticizer critically influences the mechanical properties of the final product (Cao, Yang & Fu, 2009; Rahman & Brazel, 2004).

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

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

4.3 Incorporation of Antimicrobial Agents

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

Organic acids incorporated into carrageenan films have been shown to effectively inhibit microbial spoilage in packaged foods. The incorporation of citric, succinic or lactic acid in hydrocolloidal packaging film has demonstrated a bacteriocidal and bactiostatic action against *E. coli*, *P. mirablis*, *S. aureus* and some other pathogenic strains (El-Fawal, 2014; Rocha, Loiko, Tondo & Prentice, 2014; Schreiber, 2012). Due to the non-volatility of most organic acids under food-storage conditions, the transition of the active compound from the film packaging to the food product can only take place by direct contact between the film and the food surface (Hauser, Thielmann & Muranyi, 2016). In such cases, edible films or coatings may be the best concept for this type of AM packaging. However, the incorporation of organic acids such as citric acid into the carrageenan polymer structure appears to lessen its mechanical properties along with its water resistance (El-Fawal, 2014; Fouda et al., 2015). Hauser et al. (2016) suggested that to obtain desirable properties of the films that incorporate organic acids, the compatibility of the organic acids with the polymer and its constituents, the thickness of the film, and the storage conditions all have to be taken into consideration. Potassium sorbate is another commonly used AM agent in carrageenan film packaging formulations (Cha & Chinnan, 2004; Flores, Famá, Rojas, Goyanes & Gerschenson, 2007), and an investigation by Choi et al. (2005) found that such films exhibit a similar potential for inhibiting selective bacteria, yeast and mould to the use of potassium sorbate alone.

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

Various essential oils known to impart AM activity have also been incorporated into carrageenan-based films such as oregano, thyme, *Zataria multiflora Boiss, Mentha pulegium, Satureja hortensis*, and cinnamon oil (Praseptiangga et al., 2016; Shojaee-Aliabadi, Hosseini, et al., 2014; Shojaee-Aliabadi et al., 2013; Soni et al., 2016), with these oils resulting in similar effects as GSE incorporation. However, the hydrophobicity of these compounds profoundly enhances the water resistance and moisture transfer properties of the films. Some AM peptides such as nisin and lysozyme have also been used in carrageenan film formulations, but each of these compounds appears to effectively inhibit only specific bacterial growth, and imparts less antibacterial activity in comparison with other AM agents such as ethylenediaminetetraacetic acid (EDTA) and GSE (Cha et al., 2002). Furthermore, the AM activity of lysozyme is sensitive to high temperatures (Carrillo, GarcÍA-Ruiz, Recio & Moreno-Arribas, 2014) and this impacts its performance in film packaging applications.

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

4.4 Reinforcement with Nanoparticles

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

4.4.1 Nanoclays

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

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

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

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

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

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

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

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

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

4.4.2 Nanocellulose

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

Similar to the incorporation of nanoclays, a relatively small amount of nanocellulose can effectively improve the mechanical properties of carrageenan films. Zakuwan et al. (2013) found that the optimum TS and Young’s modulus were obtained by reinforcing carrageenan with a 4% (w/w) of CNCs, with values of 36.8 and 1340 MPa respectively. This result was also supported by Zarina & Ahmad (2015), however, Savadekar et al. (2012) reported that the addition of only 0.4 % (w/w) CNFs produced the maximum TS value of the carrageenan film and any additional CNFs decreased the TS. These contrasting results may suggest that different cellulose structures may have different effects on the mechanical properties of carrageenan films. It appears that CNCs exhibit optimum effects on the tensile properties of carrageenan films at higher loadings in comparison with CNFs. An excessive amount of nanocellulose added in the formulation can lead to particle agglomeration within the carrageenan polymer matrix, which consequently reduces the mechanical properties of the final films (Sánchez-García et al., 2010). In addition, increasing the amount of these materials also detrimentally affects the opacity of the film (Abdollahi, Alboofetileh, Behrooz, Rezaei & Miraki, 2013).

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

4.4.3 Chitin Nanofibers

Chitin is commonly extracted from the exoskeleton of marine crustaceans and insects, as well as the cell wall of fungi and yeast (Tharanathan & Kittur, 2003). Hence, its availability in nature is plentiful, and is the second most abundant biopolymer after cellulose (Azuma, Ifuku, Osaki, Okamoto & Minami, 2014). The chitin structure in the crustacean exoskeletons forms microfibrillar arrangements wrapped by protein, and the chitin nanofibers (ChNFs) obtained from further chemical processing are usually a few micrometers in length and 10-100 nm in diameter (Li et al., 2016). Reinforcing carrageenan polymers with ChNFs results in smooth and flexible films with good homogenous dispersion of the fibres (Shankar et al., 2015). The addition up to 5% (w/w) ChNF into a carrageenan matrix can increase its tensile strength and Young's modulus with a decrease in its WVP, however, this may cause a loss in flexural properties and transparency of the film. In addition to improving certain physico-mechanical properties, the inclusion of ChNF in carrageenan films can impart AM activity, particularly against the Gram-positive food-borne pathogens such as *Listeria monocytogenes* (Shankar et al., 2015).

4.5 Multilayer Carrageenan Films

Even though blending carrageenans with other biopolymers is considered to be the easiest and most effective method to improve the film properties, introducing synthetic hydrophobic polymers using this technique may not lead to desirable superior properties (Shojaee-Aliabadi et al., 2013). This is due to the high hydrophilicity of the carrageenan polymer which is immiscible with hydrophobic, synthetic polymers due to the low interfacial adhesion between the two phases in the matrix system (Avella et al., 2000). The hydrophilicity of carrageenan and other biopolymers is responsible for the inferior barrier properties and water sensitivity of these systems (Fabra et al., 2008) and this is of particular concern when these polymers are to be used for food packaging applications. The production of multilayer films may show potential for overcoming these limitations and as such films can be prepared without the problems of incompatibility that often exists when using blending methods (Rhim, Mohanty, Singh & Ng, 2006).

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

5 Applications of Carrageenan-Based Films

5.1 Edible Films and Coatings

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

In the case of fresh-cut fruit, carrageenan coatings form an effective barrier between the cut surface of the fruit and gas from the surroundings thereby reducing respiration and minimizing discoloration (Baeza, 2007). When used as an edible coating, carrageenan films can maintain fruit texture and provide antibacterial protection during storage (Bico et al., 2009; Plotto, Narciso, Rattanapanone & Baldwin, 2010). Although the use of hydrophobic substances such as waxes, resins, or water insoluble proteins imparts better moisture barrier properties to edible films or coatings, the application of water-soluble hydrocolloids usually results in better mechanical properties than those provided by the hydrophobic materials (Arvanitoyannis, 2010). In addition, water-soluble hydrocolloids also exhibit better gas barrier properties (Nussinovitch, 2009) due to their compact and tightly packed conformation that result from organized hydrogen bonded network structures (Atarés, Pérez-Masiá & Chiralt, 2011; Bonilla, Atarés, Vargas & Chiralt, 2012).

5.2 Pharmaceutical and Biomedical Applications

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

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

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

Another application of carrageenan films is wound healing aids (Boateng, Pawar & Tetteh, 2013; Fouda et al., 2015; Lloyd, Kennedy, Methacanon, Paterson & Knill, 1998; Pawar, Tetteh & Boateng, 2013; Wu, Bao, Yoshii & Makuuchi, 2001) with hydrocolloid films among the most widely applied due to their distinctive ability to adhere to both moist and dry surfaces (Heenan, 1998). These films have exhibited desirable properties in maintaining a moist environment, facilitating the drainage and evaporation of wound exudates, as well as allowing adequate gas exchange (Pawar et al., 2013; Sussman, 2010). Moreover, they have also been used for delivering pharmaceutical ingredients to wound surfaces and to oral cavities for medication purposes (Boateng et al., 2009; Cunha & Grenha, 2016; Zivanovic, Li, Davidson & Kit, 2007). In the preparation of these films, the polymer substances are usually cross-linked to enhance their water entrapping ability so that the films can highly absorb and retain the liquid upon contact with exuding wounds (Boateng, Matthews, Stevens & Eccleston, 2008).

5.3 Electrolytes/Electrically Conductive Materials

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

A study by Prasad & Kadokawa (2010) reported that the use of carrageenan-polymer film as the host polymer of two different ionic components, 1-(3-acryloyloxypropyl)-3-vinylimidazolium bromide and 1-vinyl-3-vinylbenzylimidazolium chloride, results in a material with good electrical conductivity and mechanical properties. It was further suggested that this composite has the potential to be applied for use in semiconductors or organic memory devices. Furthermore, the host polymer of the electrolyte composite which is prepared by blending carboxymethyl κ-carrageenan and carboxymethyl cellulose could also enhance the conductive properties of the material, and showed favourable characteristics for fabrication of dye-sensitized solar cells (Rudhziah, Ahmad, Ahmad & Mohamed, 2015). Another novel electrical conductive device involving carrageenan-based composites is the microbial fuel cell which offers economic benefits compared with the commonly used polymer material, poly(pyrrole) (Esmaeili et al., 2014).

6 Conclusions

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

References

Abdollahi, M., Alboofetileh, M., Behrooz, R., Rezaei, M., & Miraki, R. (2013). Reducing water sensitivity of alginate bio-nanocomposite film using cellulose nanoparticles. *International Journal of Biological Macromolecules, 54*(Supplement C), 166-173.

Abdou, E. S., & Sorour, M. A. (2014). Preparation and characterization of starch/carrageenan edible films. *International Food Research Journal, 21*(1), 189-193.

Abdul Khalil, H. P. S., Saurabh, C. K., Tye, Y. Y., Lai, T. K., Easa, A. M., Rosamah, E., Fazita, M. R. N., Syakir, M. I., Adnan, A. S., Fizree, H. M., Aprilia, N. A. S., & Banerjee, A. (2017). Seaweed based sustainable films and composites for food and pharmaceutical applications: A review. *Renewable and Sustainable Energy Reviews, 77*, 353-362.

Abdul Khalil, H. P. S., Tye, Y. Y., Saurabh, C. K., Leh, C. P., Lai, T. K., Chong, E. W. N., Nurul Fazita, M. R., Mohd Hafiidz, J., Banerjee, A., & Syakir, M. I. (2017). Biodegradable polymer films from seaweed polysaccharides: A review on cellulose as a reinforcement material. *Express Polymer Letters, 11*(4), 244-265.

Accinelli, C., Sacca, M. L., Mencarelli, M., & Vicari, A. (2012). Deterioration of bioplastic carrier bags in the environment and assessment of a new recycling alternative. *Chemosphere, 89*(2), 136-143.

Aji, A. I., Praseptiangga, D., Rochima, E., Joni, I. M., & Panatarani, C. (2018). Optical transparency and mechanical properties of semi-refined iota carrageenan film reinforced with SiO2 as food packaging material. *AIP Conference Proceedings, 1927*(1), 030039.

Al-Alawi, A. A., Al-Marhubi, I. M., Al-Belushi, M. S. M., & Soussi, B. (2011). Characterization of Carrageenan Extracted from Hypnea bryoides in Oman. *Marine Biotechnology, 13*(5), 893-899.

Aldalbahi, A. (2012). Nano-composite materials from carrageenan, conducting polymers and carbon nanotubes. PhD dissertation. School of Chemistry: University of Wollongong.

Alexandre, M., & Dubois, P. (2000). Polymer-layered silicate nanocomposites: preparation, properties and uses of a new class of materials. *Materials Science and Engineering: R: Reports, 28*(1–2), 1-63.

Ali Akbari Ghavimi, S., Ebrahimzadeh, M. H., Solati-Hashjin, M., & Abu Osman, N. A. (2015). Polycaprolactone/starch composite: Fabrication, structure, properties, and applications. *Journal of Biomedical Materials Research Part A, 103*(7), 2482-2498.

Almasi, H., Ghanbarzadeh, B., & Entezami, A. A. (2010). Physicochemical properties of starch–CMC–nanoclay biodegradable films. *International Journal of Biological Macromolecules, 46*(1), 1-5.

Alves, V. D., Castelló, R., Ferreira, A. R., Costa, N., Fonseca, I. M., & Coelhoso, I. M. (2011). Barrier properties of carrageenan/pectin biodegradable composite films. *Procedia Food Science, 1*, 240-245.

Alves, V. D., Costa, N., & Coelhoso, I. M. (2010). Barrier properties of biodegradable composite films based on kappa-carrageenan/pectin blends and mica flakes. *Carbohydrate Polymers, 79*(2), 269-276.

Alves, V. D., Costa, N., Hilliou, L., Larotonda, F., Gonçalves, M., Sereno, A., & Coelhoso, I. (2006). Design of biodegradable composite films for food packaging. *Desalination, 199*(1), 331-333.

Andrades, R., Martins, A. S., Fardim, L. M., Ferreira, J. S., & Santos, R. G. (2016). Origin of marine debris is related to disposable packs of ultra-processed food. *Marine Pollution Bulletin, 109*(1), 192-195.

Angles, M. N., & Dufresne, A. (2000). Plasticized starch/tunicin whiskers nanocomposites. 1. Structural analysis. *Macromolecules, 33*(22), 8344-8353.

Anisuzzaman, S. M., Bono, A., Samiran, S., Ariffin, B., & Farm, Y. Y. (2013). Influence of potassium hydroxide concentration on the carrageenan functional group composition. In R. Pogaku, A. Bono & C. Chu (Eds.). *Developments in Sustainable Chemical and Bioprocess Technology* (pp. 355-363). Boston, MA: Springer US.

Anitha, S., Brabu, B., Thiruvadigal, D. J., Gopalakrishnan, C., & Natarajan, T. S. (2012). Optical, bactericidal and water repellent properties of electrospun nano-composite membranes of cellulose acetate and ZnO. *Carbohydrate Polymers, 87*(2), 1065-1072.

Arof, A. K., Shuhaimi, N. E. A., Alias, N. A., Kufian, M. Z., & Majid, S. R. (2010). Application of chitosan/iota-carrageenan polymer electrolytes in electrical double layer capacitor (EDLC). *Journal of Solid State Electrochemistry, 14*(12), 2145-2152.

Arrieta, M. P., Samper, M. D., Aldas, M., & López, J. (2017). On the Use of PLA-PHB Blends for Sustainable Food Packaging Applications. *Materials, 10*(9), 1008.

Arvanitoyannis, I. S. (Ed.) (2010). *Irradiation of Food Commodities: Techniques, Applications, Detection, Legislation, Safety and Consumer Opinion*. London, UK: Academic Press.

Atarés, L., De Jesús, C., Talens, P., & Chiralt, A. (2010). Characterization of SPI-based edible films incorporated with cinnamon or ginger essential oils. *Journal of Food Engineering, 99*(3), 384-391.

Atarés, L., Pérez-Masiá, R., & Chiralt, A. (2011). The role of some antioxidants in the HPMC film properties and lipid protection in coated toasted almonds. *Journal of Food Engineering, 104*(4), 649-656.

Avella, M., Errico, M. E., Laurienzo, P., Martuscelli, E., Raimo, M., & Rimedio, R. (2000). Preparation and characterisation of compatibilised polycaprolactone/starch composites. *Polymer, 41*(10), 3875-3881.

Azuma, K., Ifuku, S., Osaki, T., Okamoto, Y., & Minami, S. (2014). Preparation and biomedical applications of chitin and chitosan nanofibers. *Journal of biomedical nanotechnology, 10*(10), 2891-2920.

Baeza, R. (2007). Comparison of technologies to control the physiological, biochemical and nutritional changes of fresh cut fruit. Masters dissertation. Food Science Institute: Kansas State University.

Baldwin, E. A., Hagenmaier, R., & Bai, J. (Eds.). (2011). *Edible Coatings and Films to Improve Food Quality*. Boca Rotan, FL: CRC Press.

Baldwin, E. A., & Wood, B. (2006). Use of edible coating to preserve pecans at room temperature. *HortScience, 41*(1), 188-192.

Barbeyron, T., Michel, G., Potin, P., Henrissat, B., & Kloareg, B. (2000). ι-Carrageenases constitute a novel family of glycoside hydrolases, unrelated to that of κ-carrageenases. *Journal of Biological Chemistry, 275*(45), 35499-35505.

Barbucci, R., Magnani, A., & Consumi, M. (2000). Swelling behavior of carboxymethylcellulose hydrogels in relation to cross-linking, pH, and charge density. *Macromolecules, 33*(20), 7475-7480.

Barreto, P. L. M., Pires, A. T. N., & Soldi, V. (2003). Thermal degradation of edible films based on milk proteins and gelatin in inert atmosphere. *Polymer Degradation and Stability, 79*(1), 147-152.

Bartkowiak, A., & Hunkeler, D. (2001). Carrageenan–oligochitosan microcapsules: optimization of the formation process. *Colloids and Surfaces B: Biointerfaces, 21*(4), 285-298.

Bico, S. L. S., Raposo, M. F. J., Morais, R. M. S. C., & Morais, A. M. M. B. (2009). Combined effects of chemical dip and/or carrageenan coating and/or controlled atmosphere on quality of fresh-cut banana. *Food Control, 20*(5), 508-514.

Blanco-Pascual, N., Montero, M. P., & Gómez-Guillén, M. C. (2014). Antioxidant film development from unrefined extracts of brown seaweeds *Laminaria digitata* and *Ascophyllum nodosum*. *Food Hydrocolloids, 37*, 100-110.

Blumstein, A. (1965). Polymerization of adsorbed monolayers. II. Thermal degradation of the inserted polymer. *Journal of Polymer Science Part A: Polymer Chemistry, 3*(7), 2665-2672.

Boateng, J. S., Matthews, K. H., Stevens, H. N. E., & Eccleston, G. M. (2008). Wound healing dressings and drug delivery systems: a review. *Journal of pharmaceutical sciences, 97*(8), 2892-2923.

Boateng, J. S., Pawar, H. V., & Tetteh, J. (2013). Polyox and carrageenan based composite film dressing containing anti-microbial and anti-inflammatory drugs for effective wound healing. *International journal of pharmaceutics, 441*(1), 181-191.

Boateng, J. S., Stevens, H. N., Eccleston, G. M., Auffret, A. D., Humphrey, M. J., & Matthews, K. H. (2009). Development and mechanical characterization of solvent-cast polymeric films as potential drug delivery systems to mucosal surfaces. *Drug development and industrial pharmacy, 35*(8), 986-996.

Bond, A. L., Provencher, J. F., Elliot, R. D., Ryan, P. C., Rowe, S., Jones, I. L., Robertson, G. J., & Wilhelm, S. I. (2013). Ingestion of plastic marine debris by Common and Thick-billed Murres in the northwestern Atlantic from 1985 to 2012. *Marine Pollution Bulletin, 77*(1–2), 192-195.

Bonilla, J., Atarés, L., Vargas, M., & Chiralt, A. (2012). Edible films and coatings to prevent the detrimental effect of oxygen on food quality: Possibilities and limitations. *Journal of Food Engineering, 110*(2), 208-213.

Campos, C. A., Gerschenson, L. N., & Flores, S. K. (2011). Development of edible films and coatings with antimicrobial activity. *Food and Bioprocess Technology, 4*(6), 849-875.

Cao, N., Yang, X., & Fu, Y. (2009). Effects of various plasticizers on mechanical and water vapor barrier properties of gelatin films. *Food Hydrocolloids, 23*(3), 729-735.

Carrillo, W., GarcÍA-Ruiz, A., Recio, I., & Moreno-Arribas, M. V. (2014). Antibacterial activity of hen egg white lysozyme modified by heat and enzymatic treatments against oenological lactic acid bacteria and acetic acid bacteria. *Journal of Food Protection, 77*(10), 1732-1739.

Çaykara, T., Demirci, S., Eroğlu, M. S., & Güven, O. (2006). Surface properties of binary blend films of poly(N-vinyl-2-pyrrolidone) and poly(vinyl alcohol) with sodium alginate. *Journal of Polymer Science Part B: Polymer Physics, 44*(2), 426-430.

Cha, D. S., & Chinnan, M. S. (2004). Biopolymer-based antimicrobial packaging: A review. *Critical Reviews in Food Science and Nutrition, 44*(4), 223-237.

Cha, D. S., Choi, J. H., Chinnan, M. S., & Park, H. J. (2002). Antimicrobial films based on Na-alginate and κ-carrageenan. *LWT - Food Science and Technology, 35*(8), 715-719.

Chandra, R., & Rustgi, R. (1998). Biodegradable polymers. *Progress in Polymer Science, 23*(7), 1273-1335.

Changwichan, K., Silalertruksa, T., & Gheewala, S. H. (2018). Eco-Efficiency Assessment of Bioplastics Production Systems and End-of-Life Options. *Sustainability, 10*(4), 952.

Chen, Y., Liu, C., Chang, P. R., Cao, X., & Anderson, D. P. (2009). Bionanocomposites based on pea starch and cellulose nanowhiskers hydrolyzed from pea hull fibre: Effect of hydrolysis time. *Carbohydrate Polymers, 76*(4), 607-615.

Cheng, L. H., Karim, A. A., & Seow, C. C. (2006). Effects of water-glycerol and water-sorbitol interactions on the physical properties of konjac glucomannan films. *Journal of Food Science, 71*(2), E62-E67.

Choi, J. H., Choi, W. Y., Cha, D. S., Chinnan, M. J., Park, H. J., Lee, D. S., & Park, J. M. (2005). Diffusivity of potassium sorbate in κ-carrageenan based antimicrobial film. *LWT - Food Science and Technology, 38*(4), 417-423.

Cian, R. E., Salgado, P. R., Drago, S. R., & Mauri, A. N. (2014). Effect of glycerol and Ca^{+2} addition on physicochemical properties of edible carrageenan/porphyran-based films obtained from the red alga, *Pyropia columbina*. *Journal of Applied Phycology, 27*(4), 1699-1708.

Cunha, L., & Grenha, A. (2016). Sulfated seaweed polysaccharides as multifunctional materials in drug delivery applications. *Marine Drugs, 14*(3), 42.

de Araújo, I. W. F., Vanderlei, E. d. S. O., Rodrigues, J. A. G., Coura, C. O., Quinderé, A. L. G., Fontes, B. P., de Queiroz, I. N. L., Jorge, R. J. B., Bezerra, M. M., e Silva, A. A. R., Chaves, H. V., Monteiro, H. S. A., de Paula, R. C. M., & Benevides, N. M. B. (2011). Effects of a sulfated polysaccharide isolated from the red seaweed *Solieria filiformis* on models of nociception and inflammation. *Carbohydrate Polymers, 86*(3), 1207-1215.

DeGruson, M. L. (2016). Biobased Polymer Packaging. *Reference Module in Food Science*: Elsevier.

Desai, K. G. H., & Jin Park, H. (2005). Recent developments in microencapsulation of food ingredients. *Drying technology, 23*(7), 1361-1394.

Dewi, E. N., Darmanto, Y. S., & Ambariyanto. (2012). Characterization and quality of semi refined carrageenan (SRC) products from different coastal waters based on fourier transform infrared technique. *Journal of Coastal Develpopment, 16*(1), 25-31.

Distantina, S., Rochmadi, R., Fahrurrozi, M., & Wiratni, W. (2013). Synthesis of hydrogel film based on carrageenan extracted from *Kappaphycus alvarezii*. *Modern Applied Science, 7*(8), 22.

Efferth, T., & Paul, N. W. (2017). Threats to human health by great ocean garbage patches. *The Lancet Planetary Health, 1*(8), e301-e303.

El-Fawal, G. (2014). Preparation, characterization and antibacterial activity of biodegradable films prepared from carrageenan. *Journal of Food Science and Technology, 51*(9), 2234-2239.

Enders, K., Lenz, R., Stedmon, C. A., & Nielsen, T. G. (2015). Abundance, size and polymer composition of marine microplastics ≥ 10 μm in the Atlantic Ocean and their modelled vertical distribution. *Marine Pollution Bulletin, 100*(1), 70-81.

Esmaeili, C., Ghasemi, M., Heng, L. Y., Hassan, S. H. A., Abdi, M. M., Daud, W. R. W., Ilbeygi, H., & Ismail, A. F. (2014). Synthesis and application of polypyrrole/carrageenan nano-bio composite as a cathode catalyst in microbial fuel cells. *Carbohydrate Polymers, 114*, 253-259.

EUR Lex (2004). Commision Directive 2004/45/EC. Amending Directive 96/77/EC laying down specific purity criteria on food additives other than colours and sweeteners. Accessed: 27 March, 2018. Available at: https://eur-lex.europa.eu/legal-content/EN/TXT/?uri=CELEX:32004L0045.

Fabra, M. J., Talens, P., & Chiralt, A. (2008). Effect of alginate and λ-carrageenan on tensile properties and water vapour permeability of sodium caseinate–lipid based films. *Carbohydrate Polymers, 74*(3), 419-426.

Fakhouri, F. M., Costa, D., Yamashita, F., Martelli, S. M., Jesus, R. C., Alganer, K., Collares-Queiroz, F. P., & Innocentini-Mei, L. H. (2013). Comparative study of processing methods for starch/gelatin films. *Carbohydrate Polymers, 95*(2), 681-689.

Farhan, A., & Hani, N. M. (2017). Characterization of edible packaging films based on semi-refined kappa-carrageenan plasticized with glycerol and sorbitol. *Food Hydrocolloids, 64*, 48-58.

Finkenstadt, V. L. (2005). Natural polysaccharides as electroactive polymers. *Applied microbiology and biotechnology, 67*(6), 735-745.

Flores, S., Famá, L., Rojas, A. M., Goyanes, S., & Gerschenson, L. (2007). Physical properties of tapioca-starch edible films: Influence of filmmaking and potassium sorbate. *Food Research International, 40*(2), 257-265.

Fouda, M. M. G., El-Aassar, M. R., El Fawal, G. F., Hafez, E. E., Masry, S. H. D., & Abdel-Megeed, A. (2015). k-Carrageenan/poly vinyl pyrollidone/polyethylene glycol/silver nanoparticles film for biomedical application. *International Journal of Biological Macromolecules, 74*, 179-184.

Fu, J., & Naguib, H. E. (2006). Effect of nanoclay on the mechanical properties of PMMA/clay nanocomposite foams. *Journal of cellular plastics, 42*(4), 325-342.

García-González, C. A., Alnaief, M., & Smirnova, I. (2011). Polysaccharide-based aerogels—Promising biodegradable carriers for drug delivery systems. *Carbohydrate Polymers, 86*(4), 1425-1438.

Garcia, J., & Ghaly, E. (2001). Evaluation of bioadhesive glipizide spheres and compacts from spheres prepared by extruder/marumerizer technique. *Pharmaceutical development and technology, 6*(3), 407-417.

Ghadiri, M., Chrzanowski, W., & Rohanizadeh, R. (2015). Biomedical applications of cationic clay minerals. *RSC Advances, 5*(37), 29467-29481.

Ghosh, P. K., Siddhanta, A. K., Prasad, K., Meena, R., & Bhattacharya, A. (2006). Process of preparation of biodegradable films from semi refined kappa carrageenan. In W. I. P. Organization (Ed.). *Patent* (Vol. WO 2006/059180 A2, p. 22).

Gómez-Ordóñez, E., & Rupérez, P. (2011). FTIR-ATR spectroscopy as a tool for polysaccharide identification in edible brown and red seaweeds. *Food Hydrocolloids, 25*(6), 1514-1520.

Gu, Y. S., Decker, E. A., & McClements, D. J. (2005). Influence of pH and carrageenan type on properties of β-lactoglobulin stabilized oil-in-water emulsions. *Food Hydrocolloids, 19*(1), 83-91.

Gunning, A. P., Cairns, P., Kirby, A. R., Round, A. N., Bixler, H. J., & Morris, V. J. (1998). Characterising semi-refined iota-carrageenan networks by atomic force microscopy. *Carbohydrate Polymers, 36*(1), 67-72.

Hafting, J. T., Craigie, J. S., Stengel, D. B., Loureiro, R. R., Buschmann, A. H., Yarish, C., Edwards, M. D., & Critchley, A. T. (2015). Prospects and challenges for industrial production of seaweed bioactives. *Journal of Phycology, 51*(5), 821-837.

Hambleton, A., Fabra, M.-J., Debeaufort, F., Dury-Brun, C., & Voilley, A. (2009). Interface and aroma barrier properties of iota-carrageenan emulsion–based films used for encapsulation of active food compounds. *Journal of Food Engineering, 93*(1), 80-88.

Hambleton, A., Perpiñan-Saiz, N., Fabra, M. J., Voilley, A., & Debeaufort, F. (2012). The Schroeder paradox or how the state of water affects the moisture transfer through edible films. *Food Chemistry, 132*(4), 1671-1678.

Hamzah, H. M., Osman, A., Tan, C. P., & Mohamad Ghazali, F. (2013). Carrageenan as an alternative coating for papaya (*Carica papaya* L. cv. Eksotika). *Postharvest Biology and Technology, 75*(Supplement C), 142-146.

Harumarani, S., Ma'ruf, W. F., & Romadhon. (2016). The effect of different glycerol concentration on characteristic of composite *Eucheuma cottonii* semi refined carrageenan edible film and beeswax. *Jurnal Pengolahan dan Bioteknologi Hasil Perikanan, 5*(1), 101-105.

Haug, A. (1967). The effect of alkali treatment on the chemical heterogeneity and physical properties of some carrageenans. *Acta Chemica Scandinavica, 21*(10), 2585-2598.

Hauser, C., Thielmann, J., & Muranyi, P. (2016). Organic acids: Usage and potential in antimicrobial packaging. In J. Barros-Velázquez (Ed.). *Antimicrobial Food Packaging* (Vol. 26, pp. 563-580). San Diego: Academic Press.

Hayashi, L., Reis, R. P., dos Santos, A. A., Castelar, B., Robledo, D., de Vega, G. B., Msuya, F. E., Eswaran, K., Yasir, S. M., Ali, M. K. M., & Hurtado, A. Q. (2017). The Cultivation of Kappaphycus and Eucheuma in Tropical and Sub-Tropical Waters. In A. Q. Hurtado, A. T. Critchley & I. C. Neish (Eds.). *Tropical Seaweed Farming Trends, Problems and Opportunities: Focus on Kappaphycus and Eucheuma of Commerce* (pp. 55-90). Cham: Springer International Publishing.

Heenan, A. (1998). Hydrocolloids: Frequently asked questions. *World Wide Wounds, 1,* 1-17.

Hilliou, L. (2014). Chapter Two - Hybrid Carrageenans: Isolation, Chemical Structure, and Gel Properties. In S.-K. Kim (Ed.). *Advances in Food and Nutrition Research* (Vol. 72, pp. 17-43): Academic Press.

Hjerde, T., Smidsrød, O., Stokke, B. T., & Christensen, B. E. (1998). Acid hydrolysis of κ-and ι-carrageenan in the disordered and ordered conformations: characterization of partially hydrolyzed samples and single-stranded oligomers released from the ordered structures. *Macromolecules, 31*(6), 1842-1851.

Hoffman, A. S. (2002). Hydrogels for biomedical applications. *Advanced Drug Delivery Reviews, 54*(1), 3-12.

Hotchkiss, J. H. (1997). Food-packaging interactions influencing quality and safety. *Food Additives and Contaminants, 14*(6-7), 601-607.

Hurtado, A. Q., Neish, I. C., & Critchley, A. T. (2015). Developments in production technology of Kappaphycus in the Philippines: more than four decades of farming. *Journal of Applied Phycology, 27*(5), 1945-1961.

Hyang Aee, L., Nam Hie, K., & Nishinari, K. (1998). DSC and rheological studies of the effects of sucrose on the gelatinization and retrogradation of acorn starch. *Thermochimica Acta, 322*(1), 39-46.

Jafarzadeh, S., Alias, A. K., Ariffin, F., Mahmud, S., & Najafi, A. (2016). Preparation and characterization of bionanocomposite films reinforced with nano kaolin. *Journal of Food Science and Technology, 53*(2), 1111-1119.

Jongjareonrak, A., Benjakul, S., Visessanguan, W., & Tanaka, M. (2005). Effects of plasticizers on the properties of edible films from skin gelatin of bigeye snapper and brownstripe red snapper. *European Food Research and Technology, 222*(3-4), 229-235.

Jonoobi, M., Oladi, R., Davoudpour, Y., Oksman, K., Dufresne, A., Hamzeh, Y., & Davoodi, R. (2015). Different preparation methods and properties of nanostructured cellulose from various natural resources and residues: a review. *Cellulose, 22*(2), 935-969.

Jouanneau, D., Guibet, M., Boulenguer, P., Mazoyer, J., Smietana, M., & Helbert, W. (2010). New insights into the structure of hybrid κ-/μ-carrageenan and its alkaline conversion. *Food Hydrocolloids, 24*(4), 452-461.

Jurasek, P., & Phillips, G. O. (1998). The classification of natural gums. Part IX. A method to distinguish between two types of commercial carrageenan. *Food Hydrocolloids, 12*(4), 389-392.

Kampf, N., & Nussinovitch, A. (2000). Hydrocolloid coating of cheeses. *Food Hydrocolloids, 14*(6), 531-537.

Kanmani, P., & Rhim, J.-W. (2014a). Development and characterization of carrageenan/grapefruit seed extract composite films for active packaging. *International Journal of Biological Macromolecules, 68*, 258-266.

Kanmani, P., & Rhim, J.-W. (2014b). Properties and characterization of bionanocomposite films prepared with various biopolymers and ZnO nanoparticles. *Carbohydrate Polymers, 106*, 190-199.

Karbowiak, T., Debeaufort, F., Champion, D., & Voilley, A. (2006). Wetting properties at the surface of iota-carrageenan-based edible films. *Journal of Colloid and Interface Science, 294*(2), 400-410.

Karbowiak, T., Ferret, E., Debeaufort, F., Voilley, A., & Cayot, P. (2011). Investigation of water transfer across thin layer biopolymer films by infrared spectroscopy. *Journal of Membrane Science, 370*, 82-90.

Karel, M., & Lund, B. D. (2003). Protective packaging. In O. R. Fennema, Y. H. Hui, M. Karel, P. Walstra & J. R. Whitaker (Eds.). *Physical Principles of Food Preservation* (pp. 514-592). New York: Marcel Dekker, Inc.

Khazaei, N., Esmaiili, M., Djomeh, Z. E., Ghasemlou, M., & Jouki, M. (2014). Characterization of new biodegradable edible film made from basil seed (*Ocimum basilicum* L.) gum. *Carbohydrate Polymers, 102*, 199-206.

Kim, J. K., Yarish, C., Hwang, E. K., Park, M., & Kim, Y. (2017). Seaweed aquaculture: cultivation technologies, challenges and its ecosystem services. *ALGAE, 32*(1), 1-13.

Kim, K. M., Son, J. H., Kim, S. K., Weller, C. L., & Hanna, M. A. (2006). Properties of chitosan films as a function of pH and solvent type. *Journal of Food Science, 71*(3), E119-E124.

Konda, N. V. S. N. M., Singh, S., Simmons, B. A., & Klein-Marcuschamer, D. (2015). An Investigation on the Economic Feasibility of Macroalgae as a Potential Feedstock for Biorefineries. *BioEnergy Research, 8*(3), 1046-1056.

Kumar, P., Sandeep, K. P., Alavi, S., Truong, V. D., & Gorga, R. E. (2010). Preparation and characterization of bio-nanocomposite films based on soy protein isolate and montmorillonite using melt extrusion. *Journal of Food Engineering, 100*(3), 480-489.

Kuorwel, K. K., Cran, M. J., Sonneveld, K., Miltz, J., & Bigger, S. W. (2011). Essential oils and their principal constituents as antimicrobial agents for synthetic packaging films. *Journal of Food Science, 76*(9), R164-R177.

Kvien, I., Tanem, B. S., & Oksman, K. (2005). Characterization of cellulose whiskers and their nanocomposites by atomic force and electron microscopy. *Biomacromolecules, 6*(6), 3160-3165.

Lafargue, D., Lourdin, D., & Doublier, J.-L. (2007). Film-forming properties of a modified starch/κ-carrageenan mixture in relation to its rheological behaviour. *Carbohydrate Polymers, 70*(1), 101-111.

Lagaron, J. M. (2011). *Multifunctional and Nanoreinforced Polymers for Food Packaging*. Cambridge: Woodhead Publishing.

Lahaye, M. (2001). Developments on gelling algal galactans, their structure and physico-chemistry. *Journal of Applied Phycology, 13*(2), 173-184.

Larotonda, F., Hilliou, L., Sereno, A., & Gonçalves, M. (2005). Green edible films obtained from starch-domestic carrageenan mixtures. 2nd Mercosur Congress on Chemical Engineering and 4th Mercosur Congress on Process Systems Engineering. ENPROMER: Rio de Janeiro, Brazil.

Larotonda, F. D. S. (2007). Biodegradable films and coatings obtained from carrageenan from *Mastocarpus stellatus* and starch from *Quercus suber*. PhD dissertation. Department of Chemical Engineering: University of Porto.

Larotonda, F. D. S., Torres, M. D., Goncalves, M. P., Sereno, A. M., & Hilliou, L. (2016). Hybrid carrageenan-based formulations for edible film preparation: Benchmarking with kappa carrageenan. *Journal of Applied Polymer Science, 133*(2), 1-10.

Lee, J.-E., & Kim, K. M. (2010). Characteristics of soy protein isolate-montmorillonite composite films. *Journal of Applied Polymer Science, 118*(4), 2257-2263.

Li, L., Ni, R., Shao, Y., & Mao, S. (2014). Carrageenan and its applications in drug delivery. *Carbohydrate Polymers, 103*(Supplement C), 1-11.

Li, M. C., Wu, Q., Song, K., Cheng, H. N., Suzuki, S., & Lei, T. (2016). Chitin nanofibers as reinforcing and antimicrobial Agents in carboxymethyl cellulose films: Influence of partial deacetylation. *ACS Sustainable Chemistry and Engineering, 4*(8), 4385-4395.

Li, W., Zhang, C., Chi, H., Li, L., Lan, T., Han, P., Chen, H., & Qin, Y. (2017). Development of Antimicrobial Packaging Film Made from Poly(Lactic Acid) Incorporating Titanium Dioxide and Silver Nanoparticles. *Molecules, 22*(7).

Ljungberg, N., Bonini, C., Bortolussi, F., Boisson, C., Heux, L., & Cavaillé. (2005). New nanocomposite materials reinforced with cellulose whiskers in atactic polypropylene: Effect of surface and dispersion characteristics. *Biomacromolecules, 6*(5), 2732-2739.

Lloyd, L. L., Kennedy, J. F., Methacanon, P., Paterson, M., & Knill, C. J. (1998). Carbohydrate polymers as wound management aids. *Carbohydrate Polymers, 37*(3), 315-322.

Loureiro, R. R., Cornish, M. L., & Neish, I. C. (2017). Applications of Carrageenan: With Special Reference to Iota and Kappa Forms as Derived from the Eucheumatoid Seaweeds. In A. Q. Hurtado, A. T. Critchley & I. C. Neish (Eds.). *Tropical Seaweed Farming Trends, Problems and Opportunities: Focus on Kappaphycus and Eucheuma of Commerce* (pp. 165-171). Cham: Springer International Publishing.

Loureiro, R. R., Hurtado, A. Q., & Critchley, A. T. (2017). Impacts of AMPEP on Epiphytes and Diseases in Kappaphycus and Eucheuma Cultivation. In A. Q. Hurtado, A. T. Critchley & I. C. Neish (Eds.). *Tropical Seaweed Farming Trends, Problems and Opportunities: Focus on Kappaphycus and Eucheuma of Commerce* (pp. 111-119). Cham: Springer International Publishing.

Luiz de Paula, E., Mano, V., & Pereira, F. V. (2011). Influence of cellulose nanowhiskers on the hydrolytic degradation behavior of poly(d,l-lactide). *Polymer Degradation and Stability, 96*(9), 1631-1638.

Machmud, M. N., Fahmi, R., Abdullah, R., & Kokarkin, C. (2013). Characteristics of red algae bioplastics/latex blends under tension. *International Journal of Science and Engineering, 5*(2), 81-88.

Makhijani, K., Kumar, R., & Sharma, S. K. (2015). Biodegradability of blended polymers: A comparison of various properties. *Critical Reviews in Environmental Science and Technology, 45*(16), 1801-1825.

Makino, K., Idenuma, R., Murakami, T., & Ohshima, H. (2001). Design of a rate-and time-programming drug release device using a hydrogel: pulsatile drug release from κ-carrageenan hydrogel device by surface erosion of the hydrogel. *Colloids and Surfaces B: Biointerfaces, 20*(4), 355-359.

Martins, J. T., Bourbon, A. I., Pinheiro, A. C., Souza, B. W. S., Cerqueira, M. A., & Vicente, A. A. (2012). Biocomposite films based on κ-carrageenan/locust bean gum blends and clays: Physical and antimicrobial properties. *Food and Bioprocess Technology, 6*(8), 2081-2092.

Martins, J. T., Cerqueira, M. A., Bourbon, A. I., Pinheiro, A. C., Souza, B. W. S., & Vicente, A. A. (2012). Synergistic effects between κ-carrageenan and locust bean gum on physicochemical properties of edible films made thereof. *Food Hydrocolloids*, *29*(2), 280-289.

MatWeb (2019). MatWeb. Material Property Data. Accessed: March 19, 2019. Available at: http://www.matweb.com/index.aspx.

McHugh, D. J. (2003). *A guide to the seaweed industry*. Rome, Italy: Food and Agriculture Organization of the United Nations.

McHugh, T. H., & Krochta, J. M. (1994). Sorbitol- vs glycerol-plasticized whey protein edible films: Integrated oxygen permeability and tensile property evaluation. *Journal of Agricultural and Food Chemistry, 42*(4), 841-845.

Mekonnen, T., Mussone, P., Khalil, H., & Bressler, D. (2013). Progress in bio-based plastics and plasticizing modifications. *Journal of Materials Chemistry A, 1*(43), 13379-13398.

Mendoza, W. G., Montaño, N. E., Ganzon-Fortes, E. T., & Villanueva, R. D. (2002). Chemical and gelling profile of ice-ice infected carrageenan from Kappaphycus striatum (Schmitz) Doty "sacol" strain (Solieriaceae, Gigartinales, Rhodophyta). *Journal of Applied Phycology, 14*(5), 409-418.

Minghou, J. (1990). Processing and extraction of phycocolloids. Regional Workshop on the Culture and Utilization of Seaweeds: Cebu City, Philippines.

Mirzataheri, M., Atai, M., & Mahdavian, A. R. (2010). Physical and mechanical properties of nanocomposite barrier film containing encapsulated nanoclay. *Journal of Applied Polymer Science, 118*(6), 3284-3291.

Morris, E. R., Rees, D. A., & Robinson, G. (1980). Cation-specific aggregation of carrageenan helices: domain model of polymer gel structure. *Journal of molecular biology, 138*(2), 349-362.

Muller, J., Gonzalez-Martinez, C., & Chiralt, A. (2017). Combination of Poly(lactic) Acid and Starch for Biodegradable Food Packaging. *Materials, 10*(8).

Mustapha, S., Chandar, H., Abidin, Z. Z., Saghravani, R., & Harun, M. Y. (2011). Production of semi-refined carrageenan from *Eucheuma cotonii*. *Journal of Scientific and Industrial Research*, *70*, 865-870.

Nagai, T. (1985). Adhesive topical drug delivery system. *Journal of Controlled release, 2*, 121-134.

Nanaki, S., Karavas, E., Kalantzi, L., & Bikiaris, D. (2010). Miscibility study of carrageenan blends and evaluation of their effectiveness as sustained release carriers. *Carbohydrate Polymers*, *79*(4), 1157-1167.

Nazir, M. S., Kassim, M. H. M., Mohapatra, L., Gilani, M. A., Raza, M. R., & Majeed, K. (2016). Characteristic properties of nanoclays and characterization of nanoparticulates and nanocomposites. In M. Jawaid, A. E. K. Qaiss & R. Bouhfid (Eds.). *Nanoclay Reinforced Polymer Composites* (pp. 35-55). Singapore: Springer Science + Business Media.

Necas, J., & Bartosikova, L. (2013). Carrageenan: a review. *Veterinarni Medicina, 58*(4), 187-205.

Neves, D., Sobral, P., Ferreira, J. L., & Pereira, T. (2015). Ingestion of microplastics by commercial fish off the Portuguese coast. *Marine Pollution Bulletin, 101*(1), 119-126.

Nisperos-Carriedo, M. O. (1994). Edible coatings and films based on polysaccharides. In J. M. Krochta, E. A. Baldwin & M. O. Nisperos-Carriedo (Eds.). *Edible Coatings and Films to Improve Food Quality* (pp. 305-335). Lancaster, PA: Technomic.

Norhazariah, S., Azura, A. R., Sivakumar, R., & Azahari, B. (2016). Effect of different preparation methods on crosslink density and mechanical properties of carrageenan filled natural rubber (NR) latex films. *Procedia Chemistry, 19,* 986-992.

Nussinovitch, A. (2009). Biopolymer films and composite coatings. In I. T. Norton & J. B. Ubbink (Eds.). *Modern Biopolymer Science* (Vol. 10, pp. 295-326). San Diego: Academic Press.

Osorio, F. A., Molina, P., Matiacevich, S., Enrione, J., & Skurtys, O. (2011). Characteristics of hydroxy propyl methyl cellulose (HPMC) based edible film developed for blueberry coatings. *Procedia Food Science, 1*(Supplement C), 287-293.

Oun, A. A., & Rhim, J.-W. (2017). Carrageenan-based hydrogels and films: Effect of ZnO and CuO nanoparticles on the physical, mechanical, and antimicrobial properties. *Food Hydrocolloids, 67*, 45-53.

Park, H. J. (1996). Gas and mechanical barrier properties of carrageenan-based biopolymer films. *Food Science and Industry, 29*(2), 47-53.

Park, S. Y., Lee, B. I., Jung, S. T., & Park, H. J. (2001). Biopolymer composite films based on k-carrageenan and chitosan. *Materials Research Bulletin, 36,* 511-519.

Pathak, S., Sneha, C. L. R., & Mathew, B. B. (2014). Bioplastics: Its timeline based scenario and challenges. *Journal of Polymer and Biopolymer Physics Chemistry, 2*(4), 84-90.

Paula, G. A., Benevides, N. M. B., Cunha, A. P., de Oliveira, A. V., Pinto, A. M. B., Morais, J. P. S., & Azeredo, H. M. C. (2015). Development and characterization of edible films from mixtures of κ-carrageenan, ι-carrageenan, and alginate. *Food Hydrocolloids, 47*, 140-145.

Pavlidou, S., & Papaspyrides, C. D. (2008). A review on polymer–layered silicate nanocomposites. *Progress in Polymer Science, 33*(12), 1119-1198.

Pawar, H. V., Tetteh, J., & Boateng, J. S. (2013). Preparation, optimisation and characterisation of novel wound healing film dressings loaded with streptomycin and diclofenac. *Colloids and Surfaces B: Biointerfaces, 102*, 102-110.

Phillips, G. O. (1996). The chemical identification of PNG-carrageenan. In G. O. Phillips, P. A. Williams & D. J. Wetlock (Eds.). *Gums and Stabilisers for the Food Industry* (p. 472). Oxford, UK: Oxford University Press.

Picker, K. M. (1999). Matrix tablets of carrageenans. I. A compaction study. *Drug development and industrial pharmacy, 25*(3), 329-337.

Piculell, L. (1995). Gelling carrageenans. In A. M. Stephen (Ed.). *Food Polysaccharides and Their Applications* (Vol. 8, pp. 205-244). New York: Marcel Dekker.

Piculell, L., Borgström, J., Chronakis, I., Quist, P.-O., & Viebke, C. (1997). Organisation and association of κ-carrageenan helices under different salt conditions. *International Journal of Biological Macromolecules, 21*(1-2), 141-153.

Pinheiro, A. C., Bourbon, A. I., Quintas, M. A. C., Coimbra, M. A., & Vicente, A. A. (2012). K-carrageenan/chitosan nanolayered coating for controlled release of a model bioactive compound. *Innovative Food Science and Emerging Technologies, 16*, 227-232.

Plastic Europe. (2014). Plastics – the Facts 2015: An analysis of European plastics production, demand and waste data.

Plotto, A., Narciso, J. A., Rattanapanone, N., & Baldwin, E. A. (2010). Surface treatments and coatings to maintain fresh ‐ cut mango quality in storage. *Journal of the Science of Food and Agriculture, 90*(13), 2333-2341.

Prachayawarakorn, J., & Pomdage, W. (2014). Effect of carrageenan on properties of biodegradable thermoplastic cassava starch/low-density polyethylene composites reinforced by cotton fibers. *Materials & Design, 61*, 264-269.

Prajapati, V. D., Maheriya, P. M., Jani, G. K., & Solanki, H. K. (2014). Carrageenan: A natural seaweed polysaccharide and its applications. *Carbohydrate Polymers, 105*, 97-112.

Prasad, K., & Kadokawa, J.-i. (2010). Preparation of composite materials composed of ι-carrageenan and polymeric ionic liquids. *Polymer Composites, 31*(5), 799-806.

Praseptiangga, D., Fatmala, N., Manuhara, G. J., Utami, R., & Khasanah, L. U. (2016). Preparation and preliminary characterization of semi refined kappa carrageenan-based edible film incorporated with cinnamon essential oil. *AIP Conference Proceedings, 1746*, 020036.

Prata, J. C. (2018). Airborne microplastics: Consequences to human health? *Environmental Pollution, 234*, 115-126.

Quinn, J. F., & Caruso, F. (2004). Facile tailoring of film morphology and release properties using layer-by-layer assembly of thermoresponsive materials. *Langmuir, 20*(1), 20-22.

Rahman, M., & Brazel, C. S. (2004). The plasticizer market: an assessment of traditional plasticizers and research trends to meet new challenges. *Progress in Polymer Science, 29*(12), 1223-1248.

Rajendran, N., Puppala, S., Sneha, R. M., Ruth, A. B., & Rajam, C. (2012). Seaweeds can be a new source for bioplastics. *Journal of Pharmacy Research, 5*(3), 1476-1479.

Rane, L. R., Savadekar, N. R., Kadam, P. G., & Mhaske, S. T. (2014). Preparation and characterization of κ-carrageenan/nanosilica biocomposite Film. *Journal of Materials, 2014,* 1-8.

Rees, D., Scott, W., & Williamson, F. (1970). Correlation of optical activity with polysaccharide conformation. *Nature, 227*(5256), 390-392.

Rekemin, N. F. N., & Abedin, N. H. Z. (2017). Physicochemical characterization of kappa-carrageenan (*Euchema cottoni*) based films incorporated with various plant oils. *Carbohydrate Polymers, 157*, 1479-1487.

Rhim, J.-W. (2011). Effect of clay contents on mechanical and water vapor barrier properties of agar-based nanocomposite films. *Carbohydrate Polymers, 86*(2), 691-699.

Rhim, J.-W. (2012). Physical-mechanical properties of agar/κ-carrageenan blend film and derived clay nanocomposite film. *Journal of Food Science, 77*(12), N66-N73.

Rhim, J.-W. (2013). Effect of PLA lamination on performance characteristics of agar/κ-carrageenan/clay bio-nanocomposite film. *Food Research International, 51*(2), 714-722.

Rhim, J.-W., & Hong, S. (2007). Wetting properties of biopolyester films prepared by thermo-compression method. *Food Science and Biotechnology, 16*(2), 234-237.

Rhim, J.-W., Mohanty, K. A., Singh, S. P., & Ng, P. K. W. (2006). Preparation and properties of biodegradable multilayer films based on soy protein isolate and poly(lactide). *Industrial and Engineering Chemistry Research, 45*(9), 3059-3066.

Rhim, J.-W., & Wang, L. F. (2013). Mechanical and water barrier properties of agar/κ-carrageenan/konjac glucomannan ternary blend biohydrogel films. *Carbohydrate Polymers, 96*(1), 71-81.

Rhim, J.-W., & Wang, L. F. (2014). Preparation and characterization of carrageenan-based nanocomposite films reinforced with clay mineral and silver nanoparticles. *Applied Clay Science, 97-98*, 174-181.

Ribeiro, C., Vicente, A. A., Teixeira, J. A., & Miranda, C. (2007). Optimization of edible coating composition to retard strawberry fruit senescence. *Postharvest Biology and Technology, 44*(1), 63-70.

Rocha, M. d., Loiko, M. R., Tondo, E. C., & Prentice, C. (2014). Physical, mechanical and antimicrobial properties of Argentine anchovy (*Engraulis anchoita*) protein films incorporated with organic acids. *Food Hydrocolloids, 37*(Supplement C), 213-220.

Roh, Y. H., & Shin, C. S. (2006). Preparation and characterization of alginate–carrageenan complex films. *Journal of Applied Polymer Science, 99*(6), 3483-3490.

Rosa, D. S., Lopes, D. R., & Calil, M. R. (2005). Thermal properties and enzymatic degradation of blends of poly(ε-caprolactone) with starches. *Polymer Testing, 24*(6), 756-761.

Rozali, M., Samsudin, A., & Isa, M. (2012). Ion conducting mechanism of carboxy methylcellulose doped with ionic dopant salicylic acid based solid polymer electrolytes. *International Journal of Applied, 2*(4), 113-121.

Rudhziah, S., Ahmad, A., Ahmad, I., & Mohamed, N. S. (2015). Biopolymer electrolytes based on blend of kappa-carrageenan and cellulose derivatives for potential application in dye sensitized solar cell. *Electrochimica Acta, 175*, 162-168.

Rudhziah, S., Rani, M. S. A., Ahmad, A., Mohamed, N. S., & Kaddami, H. (2015). Potential of blend of kappa-carrageenan and cellulose derivatives for green polymer electrolyte application. *Industrial Crops and Products, 72*, 133-141.

Rummel, C. D., Löder, M. G. J., Fricke, N. F., Lang, T., Griebeler, E.-M., Janke, M., & Gerdts, G. (2016). Plastic ingestion by pelagic and demersal fish from the North Sea and Baltic Sea. *Marine Pollution Bulletin, 102*(1), 134-141.

Sanchez-Garcia, M. D., Hilliou, L., & Lagaron, J. M. (2010). Nanobiocomposites of carrageenan, zein, and mica of interest in food packaging and coating applications. *Journal of Agricultural and Food Chemistry, 58*(11), 6884-6894.

Sánchez-García, M. D., Hilliou, L., & Lagarón, J. M. (2010). Morphology and water barrier properties of nanobiocomposites of κ/ι-hybrid carrageenan and cellulose nanowhiskers. *Journal of Agricultural and Food Chemistry, 58*(24), 12847-12857.

Sánchez-González, L., Vargas, M., González-Martínez, C., Chiralt, A., & Cháfer, M. (2009). Characterization of edible films based on hydroxypropylmethylcellulose and tea tree essential oil. *Food Hydrocolloids, 23*(8), 2102-2109.

Sankalia, M. G., Mashru, R. C., Sankalia, J. M., & Sutariya, V. B. (2006). Physicochemical characterization of papain entrapped in ionotropically cross ‐ linked kappa ‐ carrageenan gel beads for stability improvement using Doehlert shell design. *Journal of pharmaceutical sciences, 95*(9), 1994-2013.

Savadekar, N. R., Karande, V. S., Vigneshwaran, N., Bharimalla, A. K., & Mhaske, S. T. (2012). Preparation of nano cellulose fibers and its application in kappa-carrageenan based film. *International Journal of Biological Macromolecules, 51*(5), 1008-1013.

Schreiber, S. B. (2012). Chitosan-gallic acid films as multifunctional food packaging. Masters dissertation. Graduate School at Trace: The University of Tennessee.

Sedayu, B. B., Cran, M. J., & Bigger, S. W. (2018). Characterization of Semi-refined Carrageenan-Based Film for Primary Food Packaging Purposes. *Journal of Polymers and the Environment, 26*(9), 3754-3761.

Seol, K.-H., Lim, D.-G., Jang, A., Jo, C., & Lee, M. (2009). Antimicrobial effect of κ-carrageenan-based edible film containing ovotransferrin in fresh chicken breast stored at 5°C. *Meat Science, 83*(3), 479-483.

Serizawa, T., Yamaguchi, M., & Akashi, M. (2002). Enzymatic hydrolysis of a layer-by-layer assembly prepared from chitosan and dextran sulfate. *Macromolecules, 35*(23), 8656-8658.

Setha, B., Mailoa, M. N., & Gaspersz, F. F. (2016). Analysis of quality sheet carrageenan of *Eucheuma Cottonii*. *International Journal of ChemTech Research, 9*(1), 92-94.

Shahbazi, M., Rajabzadeh, G., Ettelaie, R., & Rafe, A. (2016). Kinetic study of kappa-carrageenan degradation and its impact on mechanical and structural properties of chitosan/kappa-carrageenan film. *Carbohydrate Polymers, 142*, 167-176.

Shahbazi, M., Rajabzadeh, G., Rafe, A., Ettelaie, R., & Ahmadi, S. J. (2017). Physico-mechanical and structural characteristics of blend film of poly (vinyl alcohol) with biodegradable polymers as affected by disorder-to-order conformational transition. *Food Hydrocolloids, 71*(Supplement C), 259-269.

Shankar, S., Reddy, J. P., Rhim, J.-W., & Kim, H. Y. (2015). Preparation, characterization, and antimicrobial activity of chitin nanofibrils reinforced carrageenan nanocomposite films. *Carbohydrate Polymers, 117*, 468-475.

Shojaee-Aliabadi, S., Hosseini, H., Mohammadifar, M. A., Mohammadi, A., Ghasemlou, M., Hosseini, S. M., & Khaksar, R. (2014). Characterization of κ-carrageenan films incorporated plant essential oils with improved antimicrobial activity. *Carbohydrate Polymers, 101*, 582-591.

Shojaee-Aliabadi, S., Hosseini, H., Mohammadifar, M. A., Mohammadi, A., Ghasemlou, M., Ojagh, S. M., Hosseini, S. M., & Khaksar, R. (2013). Characterization of antioxidant-antimicrobial kappa-carrageenan films containing *Satureja hortensis* essential oil. *International Journal of Biological Macromolecules, 52*, 116-124.

Shojaee-Aliabadi, S., Mohammadifar, M. A., Hosseini, H., Mohammadi, A., Ghasemlou, M., Hosseini, S. M., Haghshenas, M., & Khaksar, R. (2014). Characterization of nanobiocomposite kappa-carrageenan film with *Zataria multiflora* essential oil and nanoclay. *International Journal of Biological Macromolecules, 69*, 282-289.

Siah, W. M., Aminah, A., & Ishak, A. (2015). Edible films from seaweed *Kappaphycus alvarezii*. *International Food Research Journal, 22*(6), 2230-2236.

Siracusa, V., Rocculi, P., Romani, S., & Dalla Rosa, M. (2008). Biodegradable polymers for food packaging: a review. *Trends in Food Science and Technology, 19*(12), 634-643.

Song, J. H., Murphy, R. J., Narayan, R., & Davies, G. B. (2009). Biodegradable and compostable alternatives to conventional plastics. *Philos Trans R Soc Lond B Biol Sci, 364*(1526), 2127-2139.

Soni, A., Kandeepan, G., Mendiratta, S. K., Shukla, V., & Kumar, A. (2016). Development and characterization of essential oils incorporated carrageenan based edible film for packaging of chicken patties. *Nutrition and Food Science, 46*(1), 82-95.

Sorrentino, A., Gorrasi, G., & Vittoria, V. (2007). Potential perspectives of bio-nanocomposites for food packaging applications. *Trends in Food Science and Technology, 18*(2), 84-95.

Sothornvit, R., & Krochta, J. M. (2000). Plasticizer effect on oxygen permeability of β-lactoglobulin films. *Journal of Agricultural and Food Chemistry, 48*(12), 6298-6302.

Souza, H. K. S., Hilliou, L., Bastos, M., & Gonçalves, M. P. (2011). Effect of molecular weight and chemical structure on thermal and rheological properties of gelling κ/ι-hybrid carrageenan solutions. *Carbohydrate Polymers, 85*(2), 429-438.

Stanley, N. (1987). Production, properties and uses of carrageenan. *Production and utilization of products from commercial seaweeds. FAO Fisheries Technical Paper 288* (pp. 116-146). Rockland, USA: FAO.

Stuchell, Y. M., & krochta, J. M. (1995). Edible coatings on frozen king salmon: effect of whey protein isolate and acetylated monoglycerides on moisture loss and lipid oxidation. *Journal of Food Science, 60*(1), 28-31.

Šturcová, A., Davies, G. R., & Eichhorn, S. J. (2005). Elastic modulus and stress-transfer properties of tunicate cellulose whiskers. *Biomacromolecules, 6*(2), 1055-1061.

Suppakul, P., Miltz, J., Sonneveld, K., & Bigger, S. W. (2003). Active packaging technologies with an emphasis on antimicrobial packaging and its applications. *Journal of Food Science, 68*(2), 408-420.

Sussman, G. (2010). Technology update: Understanding foam dressings. *Wounds International, 1*(2), 1-4.

Tavassoli-Kafrani, E., Shekarchizadeh, H., & Masoudpour-Behabadi, M. (2016). Development of edible films and coatings from alginates and carrageenans. *Carbohydrate Polymers, 137*, 360-374.

Tee, Y. B., Talib, R. A., Abdan, K., Chin, N. L., Kadir Basha, R., & Md Yunos, K. F. (2015). *Comparative Study of Chemical, Mechanical, Thermal, and Barrier Properties of Poly(Lactic Acid) Plasticized with Epoxidized Soybean Oil and Epoxidized Palm Oil*.

Tharanathan, R. N., & Kittur, F. S. (2003). Chitin — The undisputed biomolecule of great potential. *Critical Reviews in Food Science and Nutrition, 43*(1), 61-87.

The Lancet Planetary Health. (2017). Microplastics and human health—an urgent problem. *The Lancet Planetary Health, 1*(7), e254.

Thompson, R. C., Moore, C. J., vom Saal, F. S., & Swan, S. H. (2009). Plastics, the environment and human health: current consensus and future trends. *Philosophical Transactions of the Royal Society B: Biological Sciences, 364*(1526), 2153-2166.

Torrieri, E., Cavella, S., & Masi, P. (2015). Effect of rosemary oil and an emulsion of essential oils on structure and physical properties of chitosan film. *Chemical Engineering Transactions, 43*, 25-30.

US Food and Drug Administration. (2017). Food and Drugs. Part 172. Food Additives Permited for Direct Addition for Human Consumption. Section 172.620 Carrageenan. (p. 21). Silver Spring, MD, USA.

Valderrama, D., Cai, J., Hishamunda, N., & Ridler, N. (2013). Social and economic dimensions of carrageenan seaweed farming. *Fisheries and Aquaculture Technical Paper No. 580* (p. 204). Rome: FAO.

Valero, D., Díaz-Mula, H. M., Zapata, P. J., Guillén, F., Martínez-Romero, D., Castillo, S., & Serrano, M. (2013). Effects of alginate edible coating on preserving fruit quality in four plum cultivars during postharvest storage. *Postharvest Biology and Technology, 77*(Supplement C), 1-6.

van de Velde, F. (2008). Structure and function of hybrid carrageenans. *Food Hydrocolloids, 22*(5), 727-734.

van de Velde, F., & De Ruiter, G. A. (2002). Carrageenan. In A. Steinbüchel, S. De Baets & E. J. van Damme (Eds.). *Biopolymers, Biology, Chemistry, Biotechnology, Applications, Volume 6, Polysaccharides II: Polysaccharides from Eukaryotes* (pp. 245-274). Weinheim, Germany: Wiley-VCH.

van de Velde, F., & De Ruiter, G. A. (2005). Carrageenan. In A. Steinbüchel (Ed.). *Biopolymers online*.

van den Oever, M., Molenveld, K., van der Zee, M., & Bos, H. (2017). *Bio-based and biodegradable plastics - Facts and Figures. Wageningen Food & Biobased Research No. 1722*. Wageningen, The Netherlands: Wageningen Food & Biobased Research.

Wang, X., Hu, X., Daley, A., Rabotyagova, O., Cebe, P., & Kaplan, D. L. (2007). Nanolayer biomaterial coatings of silk fibroin for controlled release. *Journal of Controlled release, 121*(3), 190-199.

Wibowo, A. H., Listiyawati, O., & Purnawan, C. (2016). The effects of plasticizers and palmitic acid toward the properties of the carrageenan film. *IOP Conference Series: Materials Science and Engineering, 107*, 012043.

Wittaya, T. (2012). Rice starch-based biodegradable films: Properties enhancement. In A. A. Eissa (Ed.). *Structure and Function of Food Engineering*: IntechOpen.

Wood, K. C., Boedicker, J. Q., Lynn, D. M., & Hammond, P. T. (2005). Tunable drug release from hydrolytically degradable layer-by-layer thin films. *Langmuir, 21*(4), 1603-1609.

Woodall, L. C., Sanchez-Vidal, A., Canals, M., Paterson, G. L. J., Coppock, R., Sleight, V., Calafat, A., Rogers, A. D., Narayanaswamy, B. E., & Thompson, R. C. (2014). The deep sea is a major sink for microplastic debris. *Royal Society Open Science, 1*(4), 140317.

Wu, M., Bao, B., Yoshii, F., & Makuuchi, K. (2001). Irradiation of crosslinked, poly (vinyl alcohol) blended hydrogel for wound dressing. *Journal of Radioanalytical and Nuclear Chemistry, 250*(2), 391-395.

Wu, P., & Imai, M. (2012). Outstanding molecular size recognition and regulation of water permeability on κ-carrageenan-pullulan membrane involved in synergistic design of composite polysaccharides–structure. *Procedia Engineering, 42,* 1313-1325.

Wu, Y., Rhim, J., Weller, C., Hamouz, F., Cuppett, S., & Schnepf, M. (2000). Moisture loss and lipid oxidation for precooked beef patties stored in edible coatings and films. *Journal of Food Science, 65*(2), 300-304.

Xu, J. B., Bartley, J. P., & Johnson, R. A. (2003). Preparation and characterization of alginate–carrageenan hydrogel films crosslinked using a water-soluble carbodiimide (WSC). *Journal of Membrane Science, 218*(1–2), 131-146.

Xu, X., Liu, F., Jiang, L., Zhu, J. Y., Haagenson, D., & Wiesenborn, D. P. (2013). Cellulose nanocrystals vs. cellulose nanofibrils: A comparative study on their microstructures and effects as polymer reinforcing agents. *ACS Applied Materials and Interfaces, 5*(8), 2999-3009.

Yamada, K., Kamada, N., Odomi, M., Okada, N., Nabe, T., Fujita, T., Kohno, S., & Yamamoto, A. (2005). Carrageenans can regulate the pulmonary absorption of antiasthmatic drugs and their retention in the rat lung tissues without any membrane damage. *International journal of pharmaceutics, 293*(1), 63-72.

Yang, Y., Hu, H., Zhou, C.-H., Xu, S., Sebo, B., & Zhao, X.-Z. (2011). Novel agarose polymer electrolyte for quasi-solid state dye-sensitized solar cell. *Journal of Power Sources, 196*(4), 2410-2415.

Yates, M. R., & Barlow, C. Y. (2013). Life cycle assessments of biodegradable, commercial biopolymers—A critical review. *Resources, Conservation and Recycling, 78,* 54-66.

Ye, Z., Ma, P., Tang, M., Li, X., Zhang, W., Hong, X., Chen, X., & Chen, D. (2017). Interactions between calcium alginate and carrageenan enhanced mechanical property of a natural composite film for general packaging application. *Polymer Bulletin, 74*(8), 3421-3429.

Yuguchi, Y., Thu Thuy, T. T., Urakawa, H., & Kajiwara, K. (2002). Structural characteristics of carrageenan gels: temperature and concentration dependence. *Food Hydrocolloids, 16*(6), 515-522.

Zakuwan, S. Z., Ahmad, I., & Ramli, N. (2013). Preparation of hybrid nano biocomposite κ-carrageenan/cellulose nanocrystal/nanoclay. *AIP Conference Proceedings, 1571*, 738-743.

Zarina, S., & Ahmad, I. (2015). Biodegradable composite films based on κ-carrageenan reinforced by cellulose nanocrystal from kenaf fibers. *BioResources, 10*(1), 256-271.

Zhang, W., Piculell, L., & Nilsson, S. (1991). Salt dependence and ion specificity of the coil–helix transition of furcellaran. *Biopolymers, 31*(14), 1727-1736.

Zhang, W., Piculell, L., Nilsson, S., & Knutsen, S. H. (1994). Cation specificity and cation binding to low sulfated carrageenans. *Carbohydrate Polymers, 23*(2), 105-110.

Zivanovic, S., Li, J., Davidson, P. M., & Kit, K. (2007). Physical, mechanical, and antibacterial properties of chitosan/PEO blend films. *Biomacromolecules, 8*(5), 1505-1510.

Zulfiqar, S., Ahmad, Z., & Sarwar, M. I. (2008). Preparation and properties of aramid/layered silicate nanocomposites by solution intercalation technique. *Polymers for Advanced Technologies*, *19*(12), 1720-1728.