36

Seaweed Polysaccharides – Food Applications

Vazhiyil Venugopal Menon
Seafood Technology Section, Food Technology Division, Bhaba Atomic Research Center, Mumbai, India

36.1 Introduction

Development of food products to satisfy consumer interests depends on appropriate uses of various ingredients at required levels to impart proper texture and flavor as well as storage stability to the processed products. Polysaccharides immensely contribute to food technology through their interesting functional properties, which can be exploited to impart attractive properties to foods. Besides, polysaccharides also enhance fiber contents and have potential to function as edible coatings to foods retaining their shelf lives. The wide sources of polysaccharides include those from terrestrial plants, seaweeds, crustacean shellfish, and microorganisms. This article will discuss food applications of major polysaccharides from seaweed. At the onset some basic aspects of polysaccharides as food additives will be briefly pointed out.

36.2 Major functions of polysaccharides in a food system

36.2.1 Water-binding capacity

Polysaccharides are able to bind large amounts of water, because of the presence of various functional groups in their molecules (Mitchell, 1998). For example, alginates contain carboxylic groups; carrageenans, sulfonic groups; and chitosan, amino groups, which help these polysaccharides bind water several times their weights, making them referred to as ‘hydrocolloids’. Through this property these compounds are able to modify texture, control of syneresis (a phenomenon of separation of water during freeze–thawing of foods), and to stabilize the food matrix. Furthermore, the ability to bind water also helps polysaccharides function as a cellular scaffold, biodegradable packaging material, and carriers of drugs and nutraceuticals (Tharanathan, 2002; Kavanagh and Ross-Murphy, 1998)

36.2.2 Gelation

The ability to undergo gelation is probably the most important functional property of polysaccharides. A gel is composed of at least two components, where a polymer forms a three-dimensional network in a liquid medium such as water. A minimum amount of water is required for ensuring flexible and elastic properties of the gel. The process is reversible; melting of the gel is therefore possible by heating. Such gels may be covalently cross-linked networks or physical gels that involve non-covalent interactions, such as hydrogen bonding, hydrophobic, and ionic interactions among the constituents. Food gels are mostly physical gels resulting from cooling of heated solutions of polymers; their minimum concentration required for gelation varies from 0.1 to 15% (w/w). The gels can be rigid, flowing,

---

Handbook of Marine Macroalgae: Biotechnology and Applied Phycology, First Edition. Edited by Se-Kwon Kim.

brittle, sparingly, firm, soft, spreadable, sliceable, rubbery, or grainy, depending upon the degree of interactions of polymers. (Nishinari and Zhang, 2004; Barbucci *et al.*, 2002; Morris, 1998).

36.2.3 Emulsions and foams

Emulsions and foams represent fine dispersions of oil, water, or air (droplets and air bubbles) in an immiscible liquid. Food emulsions can be mainly of three types:

1. *Oil-in-water* or *water-in-oil* emulsions. A system that consists of oil droplets dispersed in an aqueous phase is called an oil-in-water (O/W) emulsion, whereas a system that consists of water droplets dispersed in an oil phase is called water-in-oil (W/O) emulsion).
2. *Foam*, in which air (gas) bubbles are dispersed in an aqueous medium.
3. *Sol*, which is small solid particles dispersed in liquid medium.

Multilayer emulsions of oil and water such as W/O/W and O/W/W are also possible. Most food emulsions are O/W emulsions, which include milk, cream, mayonnaise, sauces, salad dressing; custard, cake batter, mayonnaise, and sauces; butter; margarine, and spreads are examples of W/O emulsions. Since emulsion results in a large interfacial area between two immiscible phases (usually oil and water), they are thermodynamically unstable; tending to undergo phase separation over time due to gravitational separation, flocculation, coalescence and other reasons, gravitational separation being most common in food emulsions. Emulsifiers are molecules that facilitate the formation and stabilization of emulsions. Polysaccharides are able to function as emulsifiers. During emulsification, large deformable drops must be broken down, which can be accomplished using homogenizers such as high shear mixers, high-pressure homogenizers, colloid mills, ultrasonic homogenizers, and membrane homogenizers. The science and technology of emulsions have been described (Friberg *et al.*, 2007; McClements, 2006; Norton and Foster, 2002)

36.3 Interactions of polysaccharides with food components

Interactions of polysaccharides with food components have profound influence on the quality and stability of processed foods. Apart from their structural features, physicochemical factors such as pH, ionic strength, temperature, pressure, shearing rate, mixing time, ratio of polysaccharide to other food components such as proteins, their charges and molecular weights dictate these interactions. Food polysccharides may also interact among themselves to give mixed polymer gels that impart novel texture to food products. The minimum concentration of polysaccharide for gelation usually decreases when another incompatible biopolymer is added, presumably due to an exclusion effect. Careful selection of hydrocolloid types and their concentrations can lead to the formation of a broad range of gel textures. Methodologies to understand polysaccharide–polysaccharide and polysaccharide–protein interactions include differential scanning calorimetry (DSC), rheometry, UV absorption and circular dichroism (CD) measurements (de Kruif and Tuinier, 2001; Narchi and Djelvehl, 2009; Dickinson, 2008).

36.4 Major food applications of polysaccharides

Gelation and other functional properties of polysaccharides, briefly discussed above, make them valuable additives as thickening and texture modifiers, stabilizers, water retention compounds, emulsifiers, foam stabilizers, binders of ingredients, and modifiers of viscosity. They also control syneresis and starch retrogradation, enhance flavor, retard crystal growth, replace fat and improve satiety and fiber contents of foods. Hydration (solubility, viscosity), structure (aggregation, gelation) and surface (foaming, emulsifying) properties of polysaccharides and their complexes can be exploited to optimize the sensory properties of foods. Food texture is perceived when the food materials are stirred, poured, pumped, stretched and finally, eaten. Mixed dispersions of polysaccharides may evoke entirely new oral sensations as compared with those containing individual biopolymers (Williams and Phillips, 2003). These changes may be evaluated by sensory analysis, which use trained panelists to evaluate specific textural attributes such as 'hardness' and 'stickiness' and/or by 'texture profile analysis' using texturometers, which gives a force–displacement curve obtained from a double compression test providing interpretation to a number of texture features such as hardness, cohesiveness, viscosity, elasticity, adhesiveness, brittleness, chewiness and gumminess (Walkenstrom, 2003). Polysaccharides, at concentrations varying from 0.1 to 1.0% contribute significantly to development of food emulsions and foams to aid in keeping solids dispersed in medium such as chocolate in milk, air in whipping creams and carbonated soft drinks, fat in salad dressings, canned meats or fish, marshmallows and jelled candies, ice cream, sauces and dressings. In bakery products, they are used to enhance dough strength and stability, preserve freshness, viscoelastic properties and other quality criteria such as increased water absorption, specific and loaf volume. They can also replace the wheat protein, gluten, without adversely affecting the texture and also control retrogradation of starch. Polysaccharides retain volatile flavor compounds in many food systems, ranging from wine to salad dressing and dessert gels (Koliandris, 2008). Besides, polysaccharides can also function as dietary fiber and have potential for use as biodegradable edible films and encapsulation materials possessing excellent barrier properties against moisture and gases. Many of them also exhibit antimicrobial and/or antioxidant properties (Venugopal, 2011; Walkenstrom, 2003). Being of natural origin, they are quite safe, unlike many synthetic food additives.

36.4.1 Seaweed polysaccharides

Seaweeds are widespread throughout the world's oceans. They have traditionally been used as food in several parts of the world, especially in East and South-east Asia. They enjoy wide popularity as food due to their low calorie contents, high amounts of fiber and minerals such as potassium, magnesium, iron, and also iodine. Some of the popular edible seaweed species include nori (laver) (*Porphyra* spp.), Irish moss (*Chondrus* spp.), kombu *(Laminaria* spp.), wakame (*Undaria* spp.), and dulse (*Euchema* spp). Nori (laver and also called purple laver, or sea tangle) is commonly eaten, especially by the Japanese. Blanched and salted seaweed prepared from wakame (*U. pinnatifida*) is another popular product that has high dietary fiber content and has health benefits, including protection against diabetes and fat-burning properties The brown seaweed, *Sargassum* (also called gulfweed and sea holly) is used in soups. Because of their commercial importance, some seaweed species such as nori (*Porphyra* spp), kombu (*Laminaria* spp.) and wakame (*Undaria* spp.) are also grown by aquaculture. Processed *Euchema* seaweed (PES) also known as Philippines Natural Grade (PNG), semirefined carrageenan (SRC), alternatively refined carrageenan (ARC) or alkali modified flour (AMF) prepared from *E. cottonii* and *E. spinosum* contains polysaccharides, particularly, carrageenan, imparting significant water- and fat-holding capacities and hence making it an interesting food additive. Other products include 'Modifilan', a patented commercial extract of *Laminaria* spp. (contains significant amounts of organic iodine, fucoxanthine, alginate, fucoidan and laminarin). Microparticles of red seaweed *Gracilaria rhodophyta*, developed by high speed shearing techniques, have potentials as low-cost fat replacers for food and texturizers for beverages. The composition of seaweed and their nutritional values have been discussed recently in detail (Braune and Guiry, 2011; Venugopal, 2009a; Kumar *et al.*, 2008; McHugh, 2003; Rudolph, 2000; Ito and Hori, 1989). Seaweed species are rich sources of polysaccharides, which include agar, alginate and carrageenans, which are being isolated for their food and other applications (Kohajdová *et al.*, 2007; Sen, 2005; Roller and Dea, 2002). Incorporation of these polysaccharides have shown numerous functional benefits, as indicated in Table 36.1.

The major seaweed polysaccharides and their food applications are described below:

Agar

The term 'agar' (synonymous with agar-agar, the Japanese gelatin, Japanese isinglass, vegetable gelatin and angel's hair) accumulates in the cell walls of agarophyte red seaweed; its content varying with seasons. Agar is mostly extracted from seaweed such as *Gracilaria* spp. and *Gelidium* spp. belonging to the Rhodophyceae. For extraction, the algae are boiled (4–10 h) in acidified water (pH 5–6) containing bleaching agents. After extraction, the sediments are allowed to settle and the crude extract is filtered out usually under pressure. The extract is dried outdoors and the crude agar is subjected to repeat freezing and thawing, draining out the liquid formed that contain salts and other impurities followed by further drying in the sun for 15 to 30 days. The dried agar is packed as strips, threads or shredded or powdered form and graded according to color, luster, gel strength, etc. Agar from the crude extract may also be precipitated by alcohol. The yield varies with species and ranges between 30–35% (Venugopal, 2009b, 2011; Li *et al*, 2008; Chattopadhyay, 2007; Naidu, 2000; Wheaton and Lawson, 1985).Commercial agar is shiny, semitransparent, tasteless and odorless, having less than 20% moisture and about 7% ash. It is a hydrophilic colloid, composed of two polysaccharides, agarose and agaropectin. Agarose consists of alternating 1,4-linked 3,6 anhydro-α-L-galactopyranose and 1,3-linked β-D-galactopyranose. Agaropectin is more complicated in structure and contains sulfonic, pyruvic, and uronic acids. Agar contains 3–5% sulfate groups. Agar forms a strong gel, due to coil–helix transition followed by aggregation of helices, holding water molecules within the interstices, when a hot aqueous solution of agar is cooled. Difference in gelling (32–40 °C) and melting (85 °C) temperatures of agar, known as "hysteresis", makes it useful in food, microbiological and pharmaceutical applications (Rodriguez *et al.*, 2009; Prasad *et al.*, 2007; Lahaye and Rochas, 1991).

Table 36.1 Functional claims made by seaweed polysaccharides in diverse food products

Product categories	Functional claims by major seaweed polysaccharides	
Baked goods Beverages Confectionery Dairy Desserts Dressings and dips Fried foods Frozen foods Meat analogs Meat products Pasta Restructured products Sauces and gravies Snack foods Soups	Alginate	Forms gel Emulsifier Fat replacer Water binding agents Controls syneresis Provides smooth texture Creates creamy mouth feel Enhances fiber content Antioxidant activity Antimicrobial activity Increase yield Reduce production costs
	Carrageenan	Forms heat stable gel Controls syneresis Emulsifier Adds to mouth feel Adds viscosity Antioxidant activity Antimicrobial activity Anti-browning activity Moisture retention Enhances texture Forms creamy and smooth gel Enhances fiber content Increase yield Reduce production costs
	Agar	Forms gel Syneresis control Emulsifier Adds texture Reduces sugar bloom Enhances fiber content Increase yield Reduce production costs

Food uses

Agar is a popular thickener, gelling agent, stabilizer, lubricant, emulsifier, and absorbent. Unlike starch, agar is not readily digested and therefore has little calorific value. Although agar costs more than some synthetic and natural gelling agents, it is usually superior to such products because of its greater transparency, strength and stability over a range of acidities and alkalinities. Food grade agar is used as a stabilizer in canned meat, confectionery, and glazing and as icing in the baking industry. It is also used to make jellies, puddings, and custards. Interaction of agar with sugar increases the strength of the gel, by a phenomenon called "sugar reactivity". Because of its bland taste, agar does not interfere with the flavors of foodstuffs. The popular Japanese sweet dish, *mitsumame* consists of cubes of agar gel containing fruit and added colors. It can be canned and sterilized without the cubes melting. In Indian cuisine, agar is known as "China grass" and is used for making desserts. It has been used to clarify wines, especially plum wine, which is difficult to clarify by traditional methods. It improves the texture of dairy products like cream cheese and yoghurt (Meena *et al.*, 2006; Armisen, 1999).

In bakery products, agar modifies starch properties resulting in reduction in starch pasting temperatures (which could be measured by the amylograph parameters). This property is important since it indicates an early start of starch gelatinization and, in turn, an increase in the susceptibility of starch to the enzyme amylase. Due to its high water-binding properties agar also helps improves crust characteristics such as texture, color and moisture, and viscoelastic characteristics of baked products. In addition, it improves dough stability during fermentation and hence causes increase in the specific volume. The effects of the hydrocolloid in this respect, however, were highly dependent on flour types (white and whole flours) and the bread making process. Agar is usually added at 0.8% (w/w) level in baked goods and baking mixes; 2.0% in confections and frostings; and 1.2% in soft candies. As an emulsifier, it exhibits both synergistic and antagonistic interactions among antistaling additives. It is well known that the characteristic textures of bread and other baked products are due to the interactions between the gluten protein of wheat and its polysaccharides (starch, pentosans). However, certain population is intolerant to gluten, reflected as celiac disease. Agar can replace gluten to develop gluten-free breads for these individuals. Besides, it can also function as fat replacers in such breads (Kohajdova and Karovcova, 2009; Guarda *et al.*, 2004).

With the incidences of bovine spongiform encephalopathy (BSE, or mad cow disease) and foot-and-mouth disease, agar, is finding a role as substitutes for bovine gelatin in jelly candies, marshmallows, puddings, fruit batters, and jams (Karim and Rajiv, 2009). Because of its higher melting temperature and gel strength, the polysaccharide is added to frozen desserts of fruit juice, soy, water or milk, and ice cream at about 0.1% (w/v), often in combination with gum tragacanth and locust bean gum (LBG). An amount of 0.1–1% (w/v) agar stabilizes yoghurt, some cheeses, and candy and pastry fillings. It is also added to desserts and pretreated instant cereal products. In confectionery, jelly-type candies are made with agar, at concentrations ranging from 0.3 to 1.8% by weight. An agar-containing diet has been developed for obesity and for patients with impaired glucose tolerance and type 2 diabetes. The diet resulted in marked weight loss due to the maintenance of reduced calorie intake (Maeda *et al*., 2005). The various food uses of agar have been discussed recently (Venugopal, 2011). There is recent interest to modify the gelling properties and solubility of agar for novel food uses. Microparticles of agar have been prepared by high-speed shearing of gels dispersed in cold water. The product can confer a range of textures to fluid gels including beverages (Ellis and Jacquier, 2009). Table 36.2 shows the major applications of agar in food processing.

Alginic acid and alginates

The term 'algin' or 'alginate' is used as a generic name for the salts of the alginic acid such as sodium, potassium, ammonium, calcium, and propylene glycol alginates. The important algal sources of alginate are the brown seaweed species, *Macrocystis pyrifera*, *Ascophyllum nodosum* and *Laminaria* spp., *Ecklonia maxima*, *E. cava*, *E. bicyclis*, *Lessonia nigrecans*, and *Sargassum* spp (Draget *et al*., 2005) The two popular methods for production of alginate are the Green and Le Gloahec-Herter processes (Sen, 2005; Owusu-Apenten, 2004) In the Green's process, fresh alga is demineralized with 0.3% aqueous HCl, pulverized and treated with an aqueous 8% soda ash (pH 10–11). The treated material is ground well, diluted with water and allowed to settle. The supernatant is heated to 50 °C, passed through a filter press and then mixed with 10–12% aqueous $CaCl_{2,}$ when the insoluble calcium alginate floats to the surface. It is separated, bleached with 10% aqueous sodium hypochlorite, drained and mixed with 5% HCl. The precipitated alginic acid is thoroughly washed and is converted to desired salt by treatment with appropriate carbonate, oxide or hydroxide, which is dried, grounded and packed. (McHugh, 2003; Zvyagintseva, 1999; Wheaton and Lawson, 1985)

Table 36.2 Applications of agar in food products

Food products	Applications
Bakery items	Texture improvement, stabilization of dough, reduction of pasting temperatures of starch, replacement of gluten, prevention of adhering of product to packages. Micro-particles of agar are particularly useful for texture modification
Dairy and related products	Stabilizes yoghurt, cheeses, and candy and pastry fillings. In confectionery, jelly type candies are made with agar
Vegetable products	Improves texture Replacement of gelatin. Reduction of torque in extrusion cooked products
Miscellaneous	Hydrogels of agar (and also alginates and carrageenans) can enhance texture. Enhances satiety and hence useful as dietetic foods

Alginates are linear unbranched polymers containing β-(1→4)-linked D-mannuronic acid (M) and α-(1→4)-linked L-guluronic acid (G) residues. The ratio of D-mannuronic to L-glucoronic acids in alginic acids vary with type of seaweed, its age, portions of the seaweed used, and its location. Alginic acid is essentially insoluble in water; monovalent ions such as sodium and ammonium interact with the carboxyl groups of alginic acid to form water-soluble salts. G blocks are believed to be important since they determine binding capacity of alginate with Ca^{2+}. Molecular weights of alginic acid range between 32 and 200 kDa. Biochemical and biophysical properties of alginate are dependent on the molecular weights and G:M ratios, which are usually in the range of 1.45 to 1.85 (Draget *et al*., 2005; Clementi, 1999). Addition of divalent alkali metal ions (Ba^{2+}, Ca^{2+}, Mg^{2+}, Sr^{2+}, etc.) induces gelation of alginate, which occurs without any heating or cooling. During gelation junction zones are formed due to formation of metal ions cross-links with guluronic acid residues from adjacent poly-G chains. The structure of the alginate gels has been described by the so-called "egg-box model", in which each divalent cation (e.g., Ca^{2+}) is coordinated to the carboxyl and hydroxyl groups of four guluronate monomers from two adjacent chains of the polymer (Rastall, 2001).

Food uses

Alginic acid and alginates are used as thickening and stabilizing agents in a variety of food products, which include salad dressings, sauces, syrups, milk shakes, ice cream toppings, pie fillings, cake mixes, canned meat, and vegetables. Alginate is used in a variety of other gel products such as cold instant puddings, fruit gels, dessert gels, onion rings, among others. The polysaccharide prevents formation of large crystals in ice cream during storage and improves stability of salad dressings, milk chocolates, and fresh fruit juice, among others. Sodium alginate had better stabilizing effect improving textural quality and acceptance of ice creams during prolonged storage. Furthermore, alginate provides uniform viscosity during aging, lighter color, smoother and cleaner melt down and better flavor. One of the major uses of alginate is as suspending agent for cocoa in chocolate milk. It is used as a foam stabilizer in beer and cider and emulsifier in high oil salad dressings. The whipping ability of mixes containing alginate is significantly more than that of similar mixes containing gelatin. It is also used in making soft cheese spreads at 0.1–0.2%. The colloid should be dissolved in hot water and added to the cream before pasteurization. The hydrocolloid is also used in several bakery products such as icing, filling, marshmallow toppings, jellies, glazes, syrup, and bread. It is also added to puddings, cheese spreads, and confectioneries. In most of these products it helps to retain moisture, while in some others it thickens the batter, besides aiding moisture retention. The disadvantage of alginate, namely its insolubility when added to cold mixes, could be overcome by warming the mixture to 68–70 °C before its addition. The remarkable gelling properties of alginic acid have also found unique application in restructured foods due to its interactions with proteins. Wherever alginate is required at high levels for specific functionality, such as stabilization of emulsion, less expensive hydrocolloids such as xanthan could be used to partially replace alginate to reduce the costs. Ppropylene glycol alginate (PGA) is the only commercial chemically modified alginate (Onsoyen, 1997; Lee *et al.*, 2009).

Alginate and also other hydrocolloids (xanthan and κ-carrageenan) at concentrations as low as 0.1% (w/w, flour basis) improve properties of bread in terms of specific volume index, width/height ratio, crumb hardness, sensory characteristics (visual appearance, aroma, flavor, crunchiness) and overall acceptability. The hydrocolloids also prevent staling in bread stored for 24 h, retain moisture content and reduce the dehydration of crumb during storage. Further, the syneresis of the wheat flour gel was significantly reduced during freeze-thaw treatments when alginate was incorporated. (Kohajdova and Karovcova, 2009). The alginate-containing wheat noodles exhibit an increase in the cooked weight and a decrease in the cooking loss, besides significant increase in the cutting and tensile forces (Lee *et al.*, 2009). Coating with alginate prevents loss of quality of onion rings during storage enabling providing extended shelf-life (Hershko and Nussinovitch, 1998).

Restructured meat products are made by binding meat pieces together and shaping them to resemble usual cuts of meat, such as nuggets, roasts, meat loaves, and even steaks. A mixture of sodium alginate along with calcium carbonate, lactic acid and calcium lactate can bind the meat pieces together (Chidanandaiah *et al.*, 2009) Alginate, along with carrageenan (see below), could be used to develop low-fat, precooked, beef patties. These products are comparable with respect to yields and textural properties to regular beef patties having 20% fat (Weilin and Keeton, 1998). If beef cuts are coated with calcium alginate films before freezing, the meat juices released during thawing are reabsorbed into the meat. The coating also prevents bacterial contamination of the product (McHugh, 2003). Similarly, alginate can also be used to modify the texture of restructured shrimp, crab or fish meat products, which contain proteins such as soy protein concentrate and seafood flavors. The ingredient mixture is extruded into a calcium chloride bath to form edible fibers which are chopped, coated with sodium alginate and shaped in a mold. Alginate at 0.5 % (w/w) helped retain water-holding capacity of raw whiting muscle and also prevented increase in toughness of the minced fillets stored at –18 °C for 2 months. Calcium alginate, besides modifying texture also functioned as a cryoprotectant in frozen fish products to control denaturation of proteins (Perez-Mateos *et al.*, 2002; Lian *et al.*, 2000). Freezing fatty fish such as herring and mackerel in calcium alginate jelly controls rancidity development during storage (McHugh, 2003)

Alginate gels in the form of sponges can be useful as a carrier of vitamin A. Administration of the sponges to children having endemic vitamin A deficiency enhanced their vitamin A level (Reifen *et al.*, 1998). A low viscosity soybean beverage was prepared through a lactic acid fermentation of soy milk with *Lactobacillus casei*. Incorporation of PGA along with calcium lactate suppressed fermentation-related undesirable powdery-gritty sensation and provided emulsion stability to the product (Sugimoto *et al.*, 1982) Alginate in foods also functions as dietary fiber, since it is non-digestible. It reduces intestinal absorption, increases satiety, reduces glycemic index value, modulates colonic microflora, elevates colonal barrier function, and stimulates the immune system. Consumption of alginate at a rate of 10 g once a day for two weeks has beneficial effect on the levels of bifidobacteria, which increase significantly, while the levels of Enterobacteriaceae decrease. Because of these benefits, alginates are components of slimming diet foods, particularly biscuits (Brownlee *et al.*, 2005). Table 36.3 depicts common uses of alginates in food products.

Carrageenan

The anionic polysaccharide carrageenan is classified into three industrially relevant types, kappa (κ), iota (ι) and lambda (λ). A hybrid form consisting of κ- and ι-carrageenans is also found. Main sources of carrageenans are red seaweed such as *Gigartina*, *Chondrus*, *Euchema*, and *Furcellaria* spp. belonging to the Rhodophyceae, the principal species being *E. cottoni*, *E. spinosum*, *C. crispus* (known as Irish moss), and *G. stellata. Chondrus* spp. are abundant

Table 36.3 Common uses of alginates in food products

Applications	Remark
Foam stabilizer in beer	Propylene glycol alginate (PGA) provides better head retention and prevents foam-negative contaminants
Texturized foods	Endows food products with thermostability and desired consistency
Other uses	PGA is acid stable and resists loss of viscosity. Has unique suspension and foaming properties. Hence used in soft drinks, milk drinks, sorbet, ice cream, noodles, pasta, etc.
Bakery products	Provides freeze–thaw stability and reduced syneresis to some products
Fruit preserves	Commonly used as thickening, gelling, stabilizing agents in jams, marmalades and fruit sauces. Alginate-pectin gels are heat reversible and gives better gel strength than individual components
Ice cream	Gives ideal viscosity, prevents crystallization and shrinkage, help homogenous melting without whey separation. Used in combination with other gums
Others	Desserts, emulsions (e.g., low fat mayonnaise) and sauces, extruded foods (noodles and pasta)

in the Atlantic coast of North America, particularly Canada, while. *Eucheuma* spp. occurs in the Philippines, Indonesia and East Africa (McHugh, 2003). The relative content of caarrageenan in seaweed depends on the algal source, season of its harvest as well as on the extraction procedure used. For isolation of the polysaccharide, the thoroughly washed seaweed is subjected to extraction with dilute hot calcium or sodium hydroxide. Carrageenan is precipitated from the supernatant using isopropyl alcohol, dried under vacuum, ground and packed (Hilou *et al*., 2006; McHugh, 2003; Sen, 2005) Alkali treatment, however, could influence the sulfate and 3,6-anhydro-D-galactose contents of the sample (McHugh, 2003).

Commercial carrageenans, which are usually mixtures of κ-, ι- and λ-carrageenans, have molecular weights in the range of 10^5 to 10^6 Da. The three carrageenans differ prominently in their sulfate group contents. κ-Carrageenan has only one sulfate ester group, making it less hydrophilic and less soluble in water. The polysaccharide is composed of D-galactose, 3,6-anhydro-D-galactose and ester bound sulfate in a molar ratio of 6:5:7. λ-Carrageenan has no 3,6-anhydrogalactose, but has three sulfate groups, and hence readily soluble in water due to good hydrophilic character. ι-Carrageenan is intermediate with a 3,6-anhydrogalactose and two sulfate ester groups. The structure of ⇓-carrageenan consists of an alternating disaccharide repeating unit of (1–3)-linked β-D-galactopyranosyl 1–4-sulfate and (1–4)-linked-3,6-anhydro-α-D-galactopyranosyl 1,2-sulfate residues. κ- and ι-carrageenans exist as right-handed, threefold helices that form double helices reversibly. The double helical segments can then interact to form a three-dimensional network. (McHugh, 2003; Belitz *et al*., 2004; MacArtain *et al*., 2003; Angelin *et al*., 2004) Upon heating and subsequent cooling, ι- and κ-carrageenan form thermoreversible gels in the presence of gel-promoting cations. Salts enhance the interaction effect in the following order: Na_2SO_4, NaCl, KCl, and NH_4Cl. K^+ salts must be added to the system before cooling below the gelling temperature (García-García and Totosaus, 2008). Carrageenans are strongly negatively charged over the entire pH range usually encountered in food. As pH value decreases below 6.0, carragenan solutions become increasingly unstable when heated, resulting in loss of viscosity due to irreversible cleavage of polymer chains (MacArtain *et al*., 2003; Angelin *et al*., 2004).These aspects need to be considered in developing foods using the polysaccharide as food additive Measurement of carrageenans in food: challenges, progress, and trends in analysis have been discussed (Roberts, and Quemener, 1999).

Food uses

Carrageenans are ideal food additives. They have a range of gelling and emulsifying properties. The important applications of the hydrocolloid as additives in foods include modification of texture, reduction of fat and salt, enhancement of storage stability and flavor, fiber contents, antioxidant and antimicrobial activities, among others. The concentrations of the additive required for these applications range from 0.005–3% (w/w) (Venugopal, 2011). They have a high reactivity with a range of materials including, most importantly, milk proteins, being widely used at low concentrations in dairy products to prevent fractionation of milk constituents. Formation of a stable complex between carrageenan and protein is through the sulfate groups of carrageenan with anions groups in proteins (Verbeken *et al*., 2004). Carrageenans allow textural modification of diverse food products through changes in water binding, emulsifying and foaming properties. Gelation properties and interactions of the polysaccharide with other food components including cations significantly influence these

Table 36.4 Comparison of properties of carrageenans

Medium	κ-carrageenan	ι-carrageenan	λ-carrageenan
Hot water	Soluble at > 60 °C	Soluble at > 60 °C	Soluble
Cold water	Sodium salt soluble K and Ca salts insoluble	Sodium salt soluble K and Ca salts give thixotropic dispersion	Sodium salt soluble
Hot (80 °C) milk	Soluble	Soluble	Soluble
Cold (20 °C) milk	Na, Ca, Ki salts insoluble, but swells	Insoluble	Soluble, thickens
Gelation	Gels, strongest with K^+	Gels strongest with Ca^{2+}	No gelation
Concentrated sugar solution	Soluble, when hot	Soluble with difficulty	Soluble, when hot
Concentrated salt solution	Insoluble	Soluble, when hot	Soluble, when hot
Stability			
Freeze–thaw	No	Yes	Yes
pH > 5	Stable	Stable	Stable
Syneresis	Yes	No	No
Salt tolerance	Poor	Good	Good

Source: Adapted from Rudolph (2000).

modifications. The net effects could be additive or sometimes, synergistic. Addition of limited amounts of carrageenan has been found to be useful to reduce fat-free palatable, healthier, and convenient third-generation foods. Functional properties of carrageenans in food products, however, depend on types of carrageenan. These properties are also influenced by process variables such as temperature, pH, ionic strength, cations, etc. The ι-carrageenan is particularly thixotrophic, that is, a gel that has been broken will reform if left for sometimes without disturbance. ι-Carrageenan is often used in cold-filled, ready to consume desserts. The carrageenan is also freeze–thaw stable. To avoid agglomeration, the carrageenans are often premixed with high concentrations of other ingredients such as sugar, usually in a ratio of 1:10. If premixing is not possible stirring with a high-speed mixer together with slow addition of carrageenan can prevent agglomeration. In instant preparations, carrageenan must be used as a powder to be mixed with cold water, when a thickening effect is caused by the swelling of the hydrocolloid. In solution, with a high content of soluble solids (>50%), the temperature is increased to a level favoring gelation of the polysaccharide Mixed gels of LBG and carrageenan are brittle, slightly elastic gels, whereas xanthan gum and κ-carrageenan form soft cohesive gels. Combinations of carrageenan with LBG and starch could be used in sausages for improved texture (Soumya and Ryan, 2003). Carrageenan at 0.25 to 0.75% helped develop low-fat ground pork patties that had better cooking yield and higher moisture contents. The polysaccharide can also significantly reduce NaCl without affecting texture and sensory properties of the products. (Garcí-García and Totosaus, 2008; Manish Kumar and Sharma, 2004) Table 36.4 compares properties of carrageenans with respect to their food uses.

Carrageenan can also function as a fat substitute in food products including emulsified cheese spreads, meat balls and beef frankfurters, among others (Mahungu *et al.*, 2002). Lambda carrageenan at 0.1 to 0.5% (w/w) levels suppressed release of aroma compounds including aldehydes, esters, ketones and alcohols in thickened viscous solutions containing 10% of sucrose (Bylaite *et al.*, 2004). Similarly, κ-carrageenan enhanced flavor in a formulation containing a mixture of spices, hydrolyzed vegetable protein, and salt (Mahungu *et al.*, 2002). Carrageenan at a concentration of 0.5 to 0.7% can be used to increase fiber content of low-fiber foods such as fishery products (e.g., salmon burger), besides improving their texture (Borderýáas *et al.*, 2006). κ-Carrageenan and its oligosaccharides can also provide significant antioxidant activities to foods (Yuaw *et al*, 2005; Venugopal, 2011).Carrageenans (ι-, κ-, or λ) at 0.1% level with 0.5% citric acid synergistically prevent browning in apple juice and dried apples containing 0.1% sodium benzoate for up to 3 months at 3 °C (Tong and Hicks, 1991). Carrageenans, particularly ι-carrageenan, can possess antimicrobial (bacteriostatic) activities against food-borne pathogens such as *Salmonella enteritidis*, *S. typhimurium*, *Vibrio mimicus*, *Aeromonas hydrophila*, enterotoxigenic *Escherichia coli* O157:H7 and *Staphylococcus aureus*. The anionic properties of carrageenan, due to its sulfate content, play an essential role in this effect. This property can be

Table 36.5 Typical dairy applications of carrageenans

Product	Function	Product	Use level (%)
Milk gels			
Cooked flans or custards	Gelation	K, K + I	0.20–0.30
Cooked prepared custards (with TSPP)	Thickening Gelation	K, I, L	0.20–0.30
Pudding and pie fillings			
Dry mix cooked with milk	Level starch gelatinization	K	0.10–0.20
Ready-to-eat	Syneresis control, bodying	I	0.10–0.20
Whipped products	Stabilize overrun	L	0.05–0.15
Aerosol whipped cream	Stabilize overrun and emulsification	K	0.02–0.05
cold prepared milks			
Instant breakfast	Suspension, bodying agent	L	0.10–0.20
Shakes	Suspension, bodying, overrun	L	0.10–0.20

‘K’, k-carrageenan; ‘I’, i-carrageenan; and, ‘L, λ-carrageenan.
Adapted from Rudolph (2000).

used to control pathogens in poultry and meat products (Yamashita *et al*., 2001).

In dairy products carrageenan is preferred over other gums to impart texture for functional and economic reasons. The polysaccharide stabilizes cocoa particles and fat suspensions, preventing separation of fat in chocolate milks. It also prevents separation of whey in ice cream while thawing. Such stabilizing interactions are also useful in producing condensed milk, infant formula and whipped creams. Carrageenan of the λ type, which is insensitive to cations, gives evaporated skim milk consistency like that of cream. Carrageenans can be used to improve sensory properties of dairy products such as water dessert gels, whipped toppings, instant whipped desserts, and egg-less custards and flavors; they also function as emulsifiers and stabilizers. At a concentration as low as 0.025% a weak thixotropic gel is formed in milk via interaction of κ-carrageenan with casein micelles, by a phenomenon, known as “milk reactivity”. Because of this, the thickening effect of κ-carragenan in milk is 5 to 10 times greater than it is in water λ-Carrageenan has the ability to disperse in milk at 5–10 °C and thicken it without any salts (Verbeken *et al*., 2004). Carrageenans offer smoothness and a sensation of richness to cheese, ice creams and egg-less milk puddings, preventing separation of fat and syneresis. Carrageenan gels do not require refrigeration because they do not melt at room temperature. ι-Carrageenan at concentrations of 0.15–0.25% (w/w) was effective in preventing syneresis and increasing the rigidity of processed cheeses in comparison with κ-carrageenan. The effect of carrageenan was also influenced by the fat content of the cheese (Cernikova *et al*., 2008). Multilayer emulsions containing carragenan or other biopolymer provide better stability against droplet aggregation than single-layer emulsions under same environmental conditions of pH, ionic concentrations, temperature, etc., providing enhanced stability to dairy products (Hansen, 1994). Table 36.5 indicates the typical dairy applications of carrageenans.

In bakery products, carrageenan improves batter quality and properties of dough and pastes associated with higher water absorption and loaf volume (Techawipharat *et al*., 2008). Coated, deep fat fried and frozen products constitute an important sector in the ready-meals market and include chicken nuggets, “fish fingers” (prepared from fish such as cod, haddock, pollock, perch, catfish, etc.) and crustacean products (shrimp, crab cakes, and crawfish). For coating, the raw materials are exposed to a batter that contains starch, proteins, fat/hydrogenated oils and seasonings suspended in water. Incorporation of carrageenan in the batter improves viscosity, suspension-characteristics, emulsifying capacity to the raw material, in addition to giving enhanced refrigerated shelf life for the coated products. (Other ingredients useful in this respect are methylcellulose and alginates, among others). Besides, presence of carrageenan is also beneficial to reduce oil uptake during deep fat frying of the products, prior to freezing (Annapure *et al*., 1999).

In muscle products, injection of carrageenan improves firmness and color and decreased cooking loss. The hydrocolloid also finds application as binder in making restructured products such as turkey rolls, beef rolls, chicken

Table 36.6 Some applications of carrageenan in food product development

Products	Polysaccharide and action	References
Bakery products	Carrageenan enhanced loaf volume, water absorption and improved crumb grain score	Kohajdova and Karovcova (2009); Guarda *et al* (2004)
Fishery products such as surmi and other gel and novel fish products, e.g., fish burgers, sausages	Carrageenan and alginate enhance cooking yield, hardness and bind strength, text're and fiber content	García-García, and Totosaus (2008); Lian *et al.* (2000)
Red meat products such as turkey, restructured beef products, low-fat meat balls, beef burgers, etc.	Carrageemam increases yield, improved visual appearance, sliceability and rigidity and decreased expressible juice. Enhances storage stability	Trius. and Sebranek (1996); García-García, and Totosaus (2008). Cierach *et al.* (2009)
Vegetable products	Reduces or replaces pectin in jams and jellies and helps low sugar products, improves texture, controls browning	Hamza-Chaftai (1990); Mahungu *et al.* (2002); Tong and Hicks (1991)
Flavored soy milk	ι-carrageenan increases viscosity and sensory values	Wang *et al.* (2001)
Fruit juices	ι-, κ-, or λ-carrageenan, alone or with citric acid inhibit browing	Hamza-Chaftai (1990)
Clarification of wine, Colloidal stabilization of beer	Carrageenan, alginic acid	Cabello-Pasini *et al.* (2005)
Goat milk	Improves viscosity to goat milk	Hansen (1994) See also Table 36.5 for other dairy products

rolls, sausages and cutlets from meat trimmings (Cierach *et al.*, 2009; Trius and Sebranek, 1996). All the three types (κ, ι and λ) improved water-holding ability of cooked surimi (concentrate of washed fish myofibrillar proteins) prepared from fish such as Atlantic pollock and blue whiting (Perez-Mateos *et al.*, 2002). Carrageenan and also alginic acid have good wine stabilization capacity. Protein flocculation and precipitation capacities of carrageenan and alginic acid were two times greater than that of agar (Cabello-Pasini *et al.*, 2005) In general, agar, alginate and carrageenan have wide applications in the food processing sector, showing wide potential for further enhancement. It has been concluded that in general, the three polysaccharides modify food texture from firm, brittle to soft in the order agar > κ-carrageenan > high 'G' alginate > high 'M' alginate > ι-carrageenan (Rudolph, 2000). Table 36.6 gives some applications of carrageenan in food product development.

Other seaweed polysaccharides

Some of the other seaweed polysaccharides that have shown food applications are furcellaran, fucoidans, ulvan, and floridean starch. Furcellaran forms thermally reversible aqueous gels, similar to κ-carrageenan; gelation being influenced by the cations such a K^+, $NH_4{}^+$ and $Cs^{+,}$, while Na^+ prevents gel formation. Presence of sugar influences the gel texture changing it from brittle to elastic. The gel is stable at low pH. Furcelleran gel is used in puddings, cake fillings and icings and in marmalades has the advantage over pectin since it allows stable gel at sugar concentrations below 50–60%.

Furcelleran is also used in processed meat products, such as meat spreads, pastes and pastry fillings (Belitz, 2004). It man be mentioned that fucoidans and laminarins are more important for their health applications, rather than food applications. The anti-inflammatory, antiangiogenic, anticoagulant and antiadhesive properties of fucoidans have been well recognized. Furthermore, they can have antitumor, antimutagenic, anticomplementary, immunomodulating, hypoglycemic, antiviral, hypolipidemic, and anti-inflammatory activities (Venugopal, 2011). Ulvan is a polysaccharide from *Ulva* spp., commonly referred to as sea lettuce, one of the commonly consumed seaweeds. It is not fermented by colonic bacteria, because of its particular chemical structure. Dietary fibers from sea lettuce

Table 36.7 Seaweed polysaccharides in the Food Additives Status List of the US FDA

Polysaccharide	Description	Applications
Agar-agar	MISC, GRAS/FS, GRAS	In baked goods and baking mixes 2%); in confectionery/ frosting, 1–2%, soft candies (0.25%)
Ammonium alginate	MISC, REG	Boiler water additive
Potassium-alginate	GRAS	Stabilizer & thickener, <0.1% in confections & frostings, <0.7% in gelatins & puddings, <0.25% in processed fruits & fruit juices, <0.01% in all other food categories
Alginic acid/algin	GRAS/FS	Cheeses, frozen desserts, jellies, preserves
Sodium alginate	STAB, GRAS/FS	Cheeses, frozen desserts <0.5%, finished products
Calcium or potassium alginate	GRAS	Confectioneries, gelatin, pudding, processed foods
Carrageenan and its NH_4/K/Na/Ca salts/*Gigartina* extracts	STAB, REG, GMP, REG/FS	<0.8% in finished cheese. Also added with polysorbate80 at a maximum of 500 ppm level
Furcelleran and its K/Na/Ca salts	MISC, EMUL, STAB, REG/FS, GMP	Ice cream

EMUL, emulsifier; STAB, stabilizer; FS, substances permitted as optional ingredient in a standardized food, GRAS, Generally Recognized As Safe; GRAS/FS, Substances generally recognized as safe in foods but limited in standardized foods where the standard provides for its use, REG, Food additives for which a petition has been filed and a regulation issued, REG/MS, Food additives regulated and included in a specific food standard, MISC, Miscellaneous. Source: US FDA (2009).

can function as bulking agents with little effect on nutrient metabolism. Floridean starch, isolated from red seaweed exhibits low gelatinization temperature, lowviscosity, high clarity and little or no retrogradation upon repetitive freeze-thaw cycles. These properties make floridean starch suitable for applications such as in instant noodles and deep-frozen food (Venugopal, 2011; Yu, *et al.*, 2002).

36.5 Regulatory and commercial aspects

Agar, alginate and carrageenan have received regulatory approvals from the United States Food and Drug Administration (US FDA), the European Council (EC) and the Codex Alimentarius Commission (CAC) of the Food and Drug Administration (FAO), Rome. Agar enjoys Generally Regarded As Safe (GRAS) status of the US FDA. Alginic acid, its sodium, potassium, ammonium and calcium salts and PGA and agar have been approved by the EC with approval numbers from E400 to E406 (International Numbering System numbers: INS 400 to INS 406). In North America, since 1990, the PES has been approved and labeled as carrageenan Whereas carrageenan *per se* is safe, its degradation products (poligeenans) having molecular weights of 20 to 30 kDa could exhibit toxicological properties. The US FDA considers natural carrageenans (E407) to be safe as food additive but advises molecular weight determination to be made on samples prior to their use in foods, to ensure degraded products are not used (FDA, 2006). Table 36.7 shows marine polysaccharides in the Food Additives Status List of the US FDA and Table 36.8 gives seaweed polysaccharides permitted by the European Council.

Seaweed species as sources of commercial hydrocolloids approved by the Codex Food Standards of the FAO, Rome and the World Health Organization (WHO), Geneva, include Danish agar (*Furcellaria fastigiata*), Eucheuman (*Eucheuma* spp.), Furcellaran agar (*Furcellaria fastigiata*), Hypnean (*Hypnea* spp.), Iridophycan (*Iridaea* spp.) and Irish moss (*Chondrus* spp.). Alginate, carrageenan and agar have shown significant growth in the last decade the value which has increased from US $644 million in 1999 to US $1020 million in 2009. Reported production and value of these polysaccharides during the year 2009 were as follows: alginate, 26 500 t valued at US $318 million; agar, 9600 t, US $173 million; and carraageenan, 50 000 t, US $527 million (Bixler, 2010). Agar is currently facing increasing competition from other gelling agents. **A**bout 30% of the total production of alginate is used by the food industry, chiefly as sodium and calcium alginates, the only commercially important derivative being PGA. Almost all the carrageenan produced is used by the food industry, (often labeled as "Natural Food Stabilizer" by some food companies). However, pure carrageenan is facing competion from Processed

Table 36.8 Selected seaweed polysaccharides permitted by the European Council

Name of polysaccharide and E Number	Source	Functions, food products and permitted levels
Alginic acid (E400), Sodium alginate (E401), Potassium alginate (E402) Ammonium alginate (E403) Calcium alginate (E404) Propylene glycol alginate(E405)	Large brown seaweeds such as *Laminaria hyperborea*, *Ascophyllum nodosum* and *Macrocystis* species	*Functions* Emulsifier, suspending, stabilizer, gelling agent, thickener *Products* Jam, jellies and marmalades Sterilized, pasteurized and UHT cream, low calorie cream, pasteurized low fat cream, weaning foods for infants and young children in good health *Permitted levels* 10 g/kg (individual or in combination) 0.5 g/kg in weaning foods (individual or in combination)
Agar (E406)	Mainly species of *Gelidium*, *Pterocladia*, and *Gracilaria*	*Functions:* Emulsifier, stabilizer, gelling agent, thickener. *Products*: Ice-creams, tinned goods, glaze for meats, etc Ice-creams, milk shakes, instant desserts, custard tarts. Suspending agent in soft drinks. Spreads and many others.
Carrageenan (E407)	Mainly *Eucheuma*, *Betaphycus*, *Kappaphycus*, amd *Chondrus crispus*	Partially dehydrated and dehydrated milk Permitted level *Quantum satis*
Carrageenan (E407)		*Functions* Emulsifier, stabilizer, gelling agent, thickener *Products* Ice-creams, milk shakes, instant desserts, custard tarts. Suspending agent in soft drinks. Spreads and many others *Permitted level* 0.3g per l in infant formulae

Source: Directive 95.2 EC 20 February 1995 European Parliament and Council Directive No 95/2/EC of 20 February 1995 on food additives other than colors and sweeteners.

Euchema seaweed (PES). (Seisun, 2009). A recent survey has shown world wide availability of about 200 carrageenan-containing food products (Shah and Huffman, 2003). In summary. seaweed polysaccharides have established themselves as food additives having interesting functional properties.

References

Angelin, T.S. *et al.* (2004) Physicochemical properties of carrageenans extracted from *Sarconema filiforme* and *Hypnea valentiae*. *Seaweed Research and Utilization*, **26**, 197.

Annapure, U.S., Singhal, R.S., Kulkarni, P.R. (1999) Screening of hydrocolloids for reduction in oil uptake of a model deep fat fried product, *Lipids*, **101**, 217.

Armisen, R (1999) Agar. In: *Thickening and Gelling agents for food*, 2nd edn. (ed. A. Imesen). Blackie Academic & Professional, London, p. 1.

Barbucci, R., *et al.* (2003) Polysaccharides based hydrogels for biological applications, *Macromolecular Symposia*, **204**, 37–58.

Belitz, H.D., Grosch, W. and Schieberle, P. (2004) Carbohydrates. In: *Food Chemistry*, 3rd edn. Springer-Verlag, Berlin, Heidelberg, p. 245.

Bixler, H. (2010) http://www.seaweed.ie/uses_general/industrialgums.html (accessed January, 2011).

Borderýáas, A.J., Sánchez-Alonso, L. and Pérez-Mateos, M., (2006) New applications of fibers in foods: Addition to fishery products, *Trends Food Sci. Technol.*, **16**, 458–462

Braune, W and Guiry, M. (2011) *Seaweeds: A Colorful Identification Guide to Seaweeds of the World*. Koeltz Scientific Books, Koenigstein, Germany.

Brownlee, A., Allen, J.P., Datamar, P.W. *et al.* (2005) Alginates as a source of dietary fiber. *Crit. Rev. Food Sci. Nutr.*, **45**, 497–510.

Bylaite, E., lgūnaitė, Z., Anne, S., Meyer, A.S. and Adler-Nissen, J. (2004) Influence of λ-carrageenan on the release of systematic series of volatile flavor compounds from viscous food model systems. *J. Agric. Food Chem.*, **52**, 3542–3546.

Cabello-Pacini, A., Victoria-Cota, N., Macias-Carranza, V., Hernandez-Garibay, E. and Muñiz-Salazar, R. (2005) Clarification of wines using polysaccharides extracted from seaweed. *Am. J. Enol. Viticuli.*, **56**, 52–56.

Cernikova, M. *et al.* (2008) Effect of carrageenan type on viscoelastic properties of processed cheese. *Food Hydrocolloids*, **22**, 1054–1061.

Chattopadhyay, K. (2007) Sulphated polysaccharides from Indian samples of *E. compressa* (Ulvales, Chlorophyta): Isolation and structural features. *Food Chem.*, **104**, 928–935.

Chidanandaiah, K., Leshri, R.C. and Sanyal, M.K. (2009), Effect of sodium alginate coating with preservatives on the quality of meat patties during refrigerated storage. *J. Muscle Foods*, **20**, 275–292.

Cierach, C., Modzelewska-Kapituła, M. and Szaciło, K. (2009) The influence of carrageenan on the properties of low-fat frankfurters, *Meat Sci.*, **82**, 295–299.

Clementi, F., Crudele, M.A. and Parente, E., *et al.* (1999) Production and characterisation of alginate from *Azotobacter vinelandii. J. Sci. Food Agric.*, **79**, 602–610.

de Kruif and Tuinier, R. (2001) Protein-polysaccharide interactions. *Food Hydrocolloids*, **15**, 555–563.

Dickinson, E. (2008) Interfacial structure and stability of food emulsions as affected by protein–polysaccharide interactions. *Soft Matter*, **4**, 932–941.

Draget, K. I., Smidsrod, O. and Skjak-Broek, G. (2005) Alginates from algae. In: *Polysaccharides and Polyamides in the Food Industry.* (eds A. Steinbucke and S.K. Rhee). Wiley-VCH, Weinheim, p. 1.

Ellis, A. and Jacquier, J. C. (2009) Manufacture and characterisation of agarose microparticles. *J. Food Eng.*, **90**, 141–147.

Friberg, S. Larsson; K. and Sjoblom, J. (eds) (2007) *Food Emulsions*, Vol. 1. Taylor & Francis, Boca Raton, FL, p. 86.

García-García, E. and Totosaus, A. (2008) Low-fat sodium-reduced sausages: Effect of the interaction between locust bean gum, potato starch and κ-carrageenan by a mixture design approach. *Meat Sci.*, **78**, 406–411.

Guarda, A., Rosell, C.M., Benedito, C. and Galotto, M.J. (2004), Different hydrocolloids as bread improvers and anti-staling agents. *Food Hydrocolloids*, **18**, 241–249.

Hamza-Chaftai, A. (1990) Effect of manufacturing conditions on rheology of banana gelified milk: optimization of the technology. *J. Food Sci.*, **55**, 1630–1635.

Hansen, P.M.T. (1994) Food hydrocolloids in the dairy industry. In: *Food Hydrocolloids.* (eds. E. Nishinari, and K. Doi) Plenum Press, New York, p. 211.

Hershko, V. and Nussinovitch, A. (1998) Physical properties of alginate-coated onion (*Allium cepa*) skin. *Food Hydrocolloids*, **12**, 115–119.

Hilou, L. *et al.* (2006) Effect of extraction parameters on the chemical structure and gel properties of k/i-hybrid carrageenans obtained from *Mastocarpus stellatus*. *Biomolec. Eng.*, **23**, 201–208.

Ito, K, and Hori, K. (1989) Seaweed, chemical composition and potential food uses. *Food Rev. Int.*, **5**, 101–107

Karim, A.A. and Rajiv, B. (2009) Gelatin alternatives for the food industry: recent developments, challenges and prospects. *Trends Food Sci. Technol.*, **19**, 644–639.

Kavanagh, G.M. and Ross-Murphy, S.B. (1998) Rheological characterization of polymer gels. *Progr. Polym. Sci.*, **23**, 533–562.

Kohajdova, Z. and Karovcova, J., (2009) Application of hydrocolloids as baking improvers. *Chemical Papers*, **63**, 26–38.

Kohajdová, Z. *et al.* (2007), Marine biotechnology for production of food ingredients. *Adv. Food Nutr. Res.*, **52**, 237–251.

Koliandris, A. Lee, A., Ferry, A.-L., Hill, S., and Mitchell, J, (2008) Relationship between structure of hydrocolloid gels and solutions and flavor release, *Food Hydrocolloids*, **22**, 623–630.

Kumar, C.S., Ganesan, P., Suresh P.V., and Bhaskar, N. (2008) Seaweed as a source of nutritionally beneficial compounds – A review. *J. Food Sci. Technol.*, **45**, 1–9.

Lahaye, M. and Rochas, C. (1991) Chemical structure and physicochemical properties of agar. *Hydrobiologia*, **221**, 137–142.

Lee, S. *et al.* (2009) Physicochemical, textural and noodle-making properties of wheat dough containing alginate. *J. Text. Stud.*, **39**, 393–404.

Li, H., Yu, X., Jim, Y., Zhan, W., and Liu, Y. (2008) Development of an eco-friendly agar extraction technique from the red seaweed *Gracilaria lemaneiformis*. *Bioresour. Technol.*, **99**, 3301–3305.

Lian, P.Z., Lee, C.M. and Hufnagel -L. (2000) Physicochemical properties of frozen red hake (*Urophycis chuss*) mince as affected by cryoprotective ingredients. *J. Food Sci.*, **65**, 1117–1121

MacArtain, P. Jacquier, J.-C. and Dawson, K-A (2003) Physical characteristics of calcium induced *κ*-carrageenan networks. *Carbohydr. Polym.*, **53**, 395

Maeda J. *et al.* (2005) Effects of agar (kanten) diet on obese patients with impaired glucose tolerance and type 2 diabetes. *Diabet. Obesity Metab.*, **7**, 40–45.

Mahungu, S.M., Hansen, S.L. and Artz, W.E. (2002) Fat substitutes. In: *Food Additives* (eds A.L. Brown, P.M. Davidson, S. Salminen and J.H. Thorngate III). Marcel Dekker, New York, p. 311.

Manish Kumar and Sharma, B. D. (2004) The storage stability and textural, physico-chemical and sensory quality of low-fat ground pork patties with carrageenan as fat replacer. *Int. J. Food Sci. Technol.*, **39**, 31–39.

McClements, D.J. (2006) Formation, stability and properties of multilayer emulsions for application in the food industry. *Adv. Colloid Interf. Sci.*, **128**, 227–248.

McHugh, D.J. (2003) A guide to the seaweed industry. *FAO Fisheries Technical Paper* No. 441, Food and Agriculture Organization of the United Nations, Rome, p. 105.

Meena, R., Prasad, K. and Siddhanta, A. K (2006) Studies on "sugar-reactivity" of agars extracted from some Indian agarophytes. *Food Hydrocolloids*, **20**, 1206–1211.

Mitchell, J. R (1998) Water and food macromolecules. In: *Functional Properties of Food Macromolecules* (eds S.E. Hill, D.A. Ledward and J.R. Mitchell). Aspen Publ., New York, p. 50.

Morris, V.J (1998) Gelation of polysaccharides. In: *Functional Properties of Food Macromolecules* (eds S.E. Hill, D.A. Ledward and J.R. Mitchell). Aspen Publ., New York, p. 143.

Naidu, A.S. (2000) Agar. In: *Natural Food Antimicrobial Systems* (ed. A.S. Naidu). CRC Press, Boca Raton, FL, p. 417.

Narchi, Ch. and DjelvehI, V. G. (2009) Effect of protein–polysaccharide mixtures on the continuous manufacturing of foamed food products. *Food Hydrocolloids*, **23**, 188–201.

Nishinari, K. and Zhang, H. (2004) Recent advances in the understanding of heat set gelling polysaccharides. *Trends Food Sci. Technol.*, **15**, 305–312.

Norton, I. T. and Foster, T. J. (2002) Hydrocolloids in real food systems. In: *Gums and Stabilizers for the Food Industry*, Vol. 11 (eds P.A. Williams and G.O. Philips). The Royal Society of Chemistry, Cambridge, p. 187.

Onsoyen, E. (1997) Alginates. In: *Thickening and Gelling Agents for Food* (ed. A. Imeson). Blackie Academic and Professional, London, p. 22.

Owusu-Apenten, R.K. (2004) *Introduction to Food Chemistry*. CRC Press, Boca Raton, FL, p. 55.

Perez-Mateos, M., Solas, M. and Montero, P. (2002) Carrageenans and alginate effects on properties of combined pressure and temperature in fish mince gels. *Foods Hydrocolloids*, **16**, 225–233.

Prasad, K., Sidhartha, M., Ganesan, B.K., Ranewal, B.K., Jha, B., and Ghosh, P.K. (2007) Agars of *Gelidiella acerosa* of west and southeast coasts of India. *Biores. Technol.*, **98**, 1907–1915.

Rastall, R. (2001) Tailor-made food ingredients: enzymatic modulation of nutritional and functional properties. IFIS Publ. http://www.foodsciencecentral.com/fsc/ixid3729 (accessed 20 April 2011).

Reifen, R., Edris, M and Nussinovitch A. (1998) A novel, vitamin A-fortified, edible hydrocolloid sponge for children. *Food Hydrocolloids*, **12**, 111–114.

Roberts, M.A. and Quemener, B. (1999) Measurement of carrageenans in food: challenges, progress, and trends in analysis. *Trends Food Sci. Technol.*, **10**, 169

Rodriguez, M.C., Matulewicz, M.C., Noseda, M.D., Ducatti, D.R.B. and Leonardi, P.I. (2009) Agar from *Gracilaria gracilis* of the Patagonic coast of Argentina – content, structure and physical properties. *Biores. Technol.*, **100**, 1435–1441.

Roller, S. and Dea, I.C.M. (2002) Biotechnology in the production and modification of biopolymers for foods. *Crit. Rev. Biotechnol.*, **12**, 261–275.

Rudolph, B. (2000) Seaweed products: Red algae of economic importance. In: *Marine & Freshwater Products Handbook*. VCH Publ., Lancaster, p. 315.

Seisun, D. (2009) *Hydrocolloid News*. IMR International, San Diego, CA, 92127, USA.

Sen, D.P., (2005) Selected byproducts from the sea. In: *Advances in Fish Processing*, Allied Publishers, New Delhi, p. 616.

Shah, Z.C. and Huffman, F. G. (2003) Current availability and consumption of carrageenan-containing foods. *Ecol. Food Nutr.*, **42**, 357–362.

Soumya, R. and Ryan, A.L (2003) Method of preparing food products with carrageenan, US Patent 6663910B2.

Sugimoto, S. *et al.* (1982). Improvement of organoleptic quality of fermented soybean beverage by additions of propylene glycol alginate and calcium lactate. *J. Food Process. Preserv.*, **5**, 83–88.

Techawipharat, J., Suphantharika, M. and BeMiller, J.N. (2008) Effects of food gums on viscosities of starch suspensions during pasting. *Carbohydr. Polym.*, **73**, 417–426.

Tharanathan, R. N. (2002). Food-derived carbohydrates – structural complexity and functional diversity. *Crit. Rev. Biotechnol.*, **22**, 65–84.

Tong, C.B.S. and Hicks, K.B. (1991) Sulfated polysaccharides inhibit browning of apple juice and diced apples. *J. Agric. Food Chem.*, **39**, 1719–1722.

Trius, A. and Sebranek, J. G. (1966) Carrageenans and their use in meat product. *Crit. Rev. Food Sci. Nutr.*, **36**, 69.

US FDA, US Food and Drug Administration (2006) Food additives permitted for direct addition to food for human consumption 21CFR172, subpart C. US FDA, Silver Spring, MD.

US FDA (2009) Listing of Food Additive Status Part I. http://www.fda.gov/Food/FoodIngredientsPackaging/FoodAdditives/FoodAdditiveListings/ucm091048.htm (accessed 20 April 2011).

Venugopal, V (2011) Seaweed, microalgae, and their polysaccharides: food applications. In: *Marine Polysaccharides: Food Applications*. CRC Press, Boca Raton, Florida, Ch. 7.

Venugopal, V. (2009a) Seaweed: nutritional value, bioactive properties and uses. In: *Marine Products for Healthcare.* CRC Press, Boca Raton, FL, Ch.9

Venugopal, V. (2009b) Seaweed hydrocolloids. In: *Marine Products for Healthcare*. CRC Press, Boca Raton, FL, Ch. 10.

Verbeken, D. Thas, O. and Dewittinck, K. (2004) Textural properties of gelled dairy desserts containing κ-carrageenan and starch. *Food Hydrocolloids*, **18**, 817–823.

Walkenstrom, P. (2003) The creation of new food structures and textures by processing. In: *Texture in Food*, Vol.1 (ed. B.M. McKenna). Woodhead Publishers, Cambridge, UK, p. 201.

Wang, B., Xiong, Y.L. and Wang, C. (2001) Physico-chemical and sensory characteristics of flavored soymilk during refrigeration storage. *J. Food Quality*, **24**, 513–519.

Weilin, K. and Keeton, J.T. (1998) Textural and physico-chemical properties of low-fat, precooked ground beef patties containing carrageenan and sodium alginate. *J. Food Sci.*, **63**, 571–574.

Wheaton, F.W. and Lawson, T. B. (1985) *Processing of Aquatic Food Products*. John Wiley & Sons, New York, p. 42.

Williams, P. A. and Phillips, G.O. (2003) The use of hydrocolloids to improve food texture. In: *Texture in Food*, Vol. 1 (ed. B.M. McKenna). Woodhead Publishers, Cambridge, UK, p 251.

Yamashita, S., Sugita, K.Y and Shimizu, -M. (2001) In vitro bacteriostatic effects of dietary polysaccharides. *Food Sci. Technol. Res.*, **7**, 262

Yu, S., Blennhow, A., Bojko, M., Madisen, M., Cisen, C.F., and Engeisen, S.B. (2002) Physico-chemical characterization of Floridean starch of red algae. *Starch/Stärke*, **54**, 66–69.

Yuan, H., Zhang, W., Lu, X., Li, H., Geo, X. and Song, J. (2005) Preparation and in vitro antioxidant activity of κ-carrageenan oligosaccharides and their oversulfated, acetylated, and phosphorylated derivatives. *Carbohydr. Res.*, **340**, 685.

Zvyagintsova, T.N. Shevehenko, N.M., Popivnieb, I.B., Iskov, V.V., Sundukova, V. and Elyakova, L.A. (2004) A new procedure for the separation of water-soluble polysaccharides from brown seaweed. *Carbohydr. Res.*, **322**, 32–38.

Zvyagintseva, T.N., Shevchenkoa, N.M., Popivnicha, I.B., *et al.* (1999) A new procedure for the separation of water-soluble polysaccharides from brown seaweeds. **322**, 32–39.