5

Carrageenan

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5.1   Introduction

For many centuries, red seaweeds have been used for foods in the Far East and Europe. Different species of *Rhodophycae* contain naturally occurring polysaccharides which fill the voids within the cellulose structure of the plant. This family of polysaccharides include carrageenan, furcellaran and agar. These polymers have a backbone of galactose but differ in the proportion and location of ester sulfate groups and the proportion of 3,6-anhydrogalactose. The differences in composition and conformation produce a wide range of rheological properties which are utilised in a large number of foods.

Different carrageenans cover a wide spectrum of rheological behaviour going from a viscous thickener to thermally reversible gels which range in texture from soft and elastic to firm and brittle. Kappa carrageenan is able to interact synergistically with other gums, such as locust bean gum and konjac mannan, to modify further the gel texture. A specific interaction between kappa carrageenan and kappa casein is widely used to stabilise dairy products.
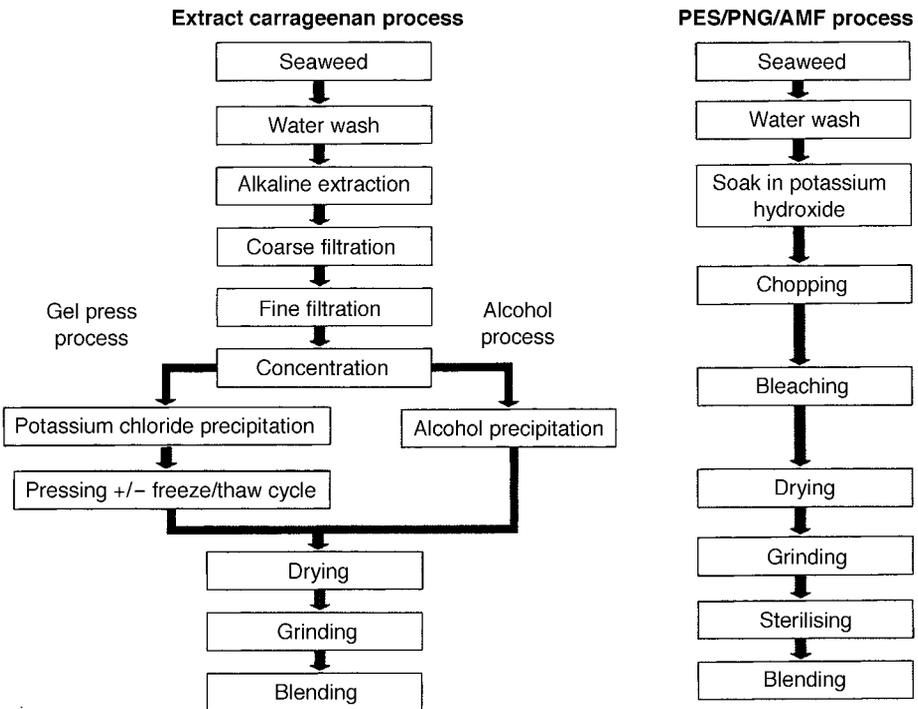
5.2   Manufacture

5.2.1   Raw materials

The main species of *Rhodophycae* used in the commercial production of carrageenan include *Euchema cottonii* and *E. spinosum*. These are spiny bushy plants, about 50cm high, which grow on reefs and in shallow lagoons around the Philippines and Indonesia and other island coasts in the Far East. *E. cottonii* yields kappa carrageenan and *E. spinosum* contains iota carrageenan. *Chondrus crispus* is the most familiar of the red seaweeds and is found as a small bushy plant, only about 10cm in height, widely distributed around the coasts of the North Atlantic. Carrageenan extracted from this species comprises both kappa and lambda types although it has been shown that these do not occur within the same plant but in individual plants which grow together (McCandless *et al.*, 1973). *Gigartina* species are large plants up to 5m in length which

are collected from the cold deep coastal waters off Chile and Peru to give kappa and lambda carrageenans. *Furcellaria* species are found in the cold waters around Northern Europe and Asia and yield kappa and lambda carrageenans.

5.2.2   Manufacturing process

The manufacturing processes for extracting carrageenan are shown in Fig. 5.1. The processes commence with the selection of seaweed to ensure it is harvested at the right time. After the seaweed is collected it is washed to remove sand and stones and then dried quickly to prevent microbial degradation and thus preserve the quality of carrageenan. The weed is then baled and shipped to the processing plants and warehoused before use. Manufacturing plants located near the harvesting site may utilise wet seaweed to avoid the costly drying and subsequent rehydration stages. At the manufacturing site, the baled seaweed is tested and various lots are selected to produce the desired extract. Proper selection of the raw materials and an understanding of the influence of the process on the properties of the final carrageenan are vital to the production of a high quality and consistent end-product.

After the seaweeds are identified and chosen to make a particular extract, they are washed to remove sand and stones before treating with appropriate amounts of various alkalis to swell the seaweed and extract the carrageenan. The alkali may be selected to determine the particular salt type of carrageenan produced by the process which, as discussed later, has important consequences for the properties of the resultant extract, including dispersion, hydration, thickening and gel formation. Prolonged treatment with

Fig. 5.1   Manufacturing processes for carrageenan and processed *Euchema* seaweed.

alkali promotes an internal rearrangement which modifies the polysaccharide backbone. With kappa carrageenan the anhydride bridge formed by this rearrangement allows adjacent chains to form helical structures which, after neutralisation of the exposed sulfate groups by appropriate cations, aggregate to form junction zones. Hence, the alkali modification produces carrageenans that form firm, brittle gels. Iota carrageenans are modified by alkali so that they form weak, elastic gels. After extraction and modification, the dilute carrageenan solutions are filtered and clarified by high-speed centrifugation and concentrated by a range of methods. The solutions are then precipitated with isopropyl alcohol to give a fibrous mass which is pressed to remove impurities and then dried.

An alternative recovery process utilises the specific selectivity of kappa carrageenan for potassium salts to form a gel. As kappa carrageenan solution is extruded into a concentrated solution of potassium chloride a fibrous mass is formed. The precipitated mass synerises or exudes free water and is dewatered under pressure to make 'gel press' carrageenan. The precipitated carrageenan may be frozen and thawed to assist this dewatering step. The pressed fibres are then dried and ground to the appropriate particle size.

Each manufacturer carefully controls the raw materials and process parameters to produce a large number of extracts with well-defined properties. Individual extracts are characterised by their thickening and gelling properties and finished products are made by blending various extracts in order to maintain consistent quality from lot to lot and to provide the specific properties needed to meet particular customer requirements and to suit particular applications.

Processed *Euchema* seaweed (PES), Philippines Natural Grade (PNG), semi-refined carrageenan (SRC), alternatively refined carrageenan (ARC) and alkali-modified flour (AMF) are the various terms used to describe *Euchema* seaweeds which are harvested around the Philippines and Indonesia and directly treated with alkali to modify the carrageenan within the seaweed. This is a more economic process as it avoids extracting carrageenan into dilute solutions which require expensive concentration and drying steps to make the finished carrageenan powder.

The process by which processed *Euchema* seaweed is converted into commercial gelling grade products is compared to the traditional extraction process in Fig. 5.1. The process commences with selection and washing. Thereafter the process diverges from the manufacture of extract carrageenans. The *Euchema* seaweed is soaked in potassium hydroxide solution *in situ* before chopping and bleaching to reduce the colour of the finished powder. After washing, drying and grinding, the powder is sterilised to control the microbiological levels of the finished product, which are now tightly controlled by legislation.

5.3   Structure

Carrageenan is a high molecular weight linear polysaccharide comprising repeating galactose units and 3,6-anhydrogalactose (3,6 AG), both sulfated and non-sulfated, joined by alternating α-(1,3) and β-(1,4) glycosidic links. An almost continuous spectrum of carrageenans exist but the work of Rees and co-workers (Rees, 1963; Anderson, Dolan and Rees, 1965) was able to distinguish and attribute definite chemical structures to a small number of idealised polysaccharides. The main carrageenan types, lambda, kappa and iota, can be prepared in pure form by selective extraction techniques. Mu and nu
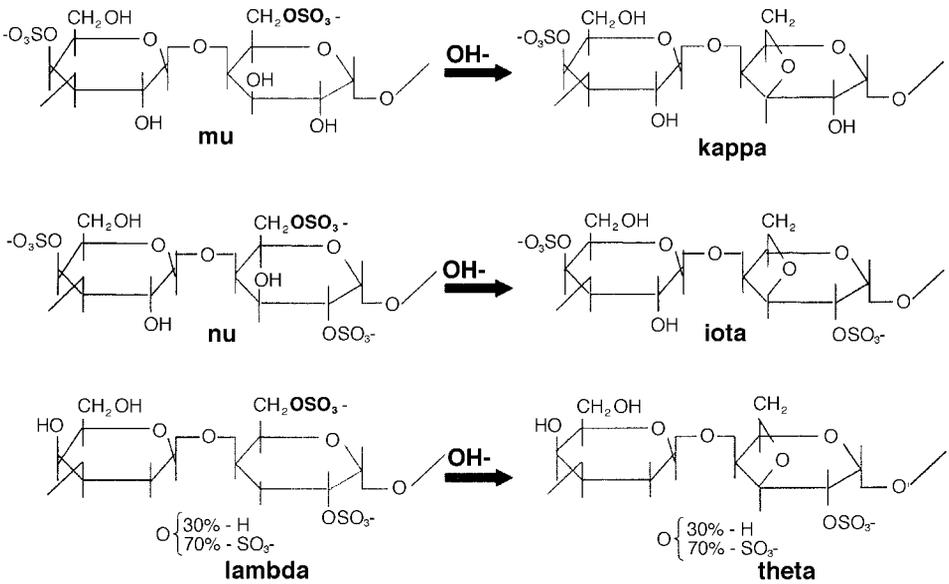
Fig. 5.2   Carrageenan structures (alkali conversion of mu > kappa, nu > iota and lambda > theta).

carrageenans are postulated as the precursor structures which, as a result of the internal rearrangement by alkali treatment, form kappa and iota carrageenans. The basic disaccharide units that make up the various carrageenans are shown in Fig. 5.2.

The distinct carrageenan structures differ in 3,6-anhydrogalactose and ester sulfate content. Variations in these components influence hydration, gel strength and texture, melting and setting temperatures, syneresis and synergism. These differences are controlled and created by seaweed selection, processing and blending of different extracts. The ester sulfate and 3,6-anhydrogalactose content of carrageenans is approximately 25% and 34% respectively for kappa carrageenan and 32% and 30% respectively for iota carrageenan. Lambda carrageenan contains 35% ester sulfate with little or no 3,6-anhydrogalactose content. Even furcellaran, which in the past has been rather misleadingly called 'Danish agar', contains 16–20% sulfate content. These high sulfate levels contrast with agar-agar which has a very low sulfate content, always below 4.5% and typically it is from 1.5–2.5%. For food applications, carrageenan is best described as 'extracts from *Rhodophyceae* which contain an ester sulfate content of 20% and above and are alternately α-(1,3) and β-(1,4) glycosidically linked' (Anon., 1988).

Processed *Euchema* seaweed differs from the traditional carrageenan extracts in that it contains 8–15% acid insoluble matter compared to 2% maximum for an extract (Anon., 1998). The acid insoluble matter mainly consists of a network of cellulose which modifies the hydration, appearance and gel characteristics of the gels which are described in more detail later. The heavy metal content of processed *Euchema* seaweed is higher than extract carrageenan but still well below limits set for food additives (Phillips, 1996).

Carrageenan is a high molecular weight, polydisperse material. Commercial kappa carrageenan extracts are between 400–560kDa and processed *Euchema* seaweed has a slightly higher molecular weight of 615kDa (Hoffmann, Russell and Gidley, 1996). All carrageenans contain a fraction ($< 5\%$) of material below 100kDa and this low molecular weight material is believed to be inherent in native algal weed.

5.4   Physical properties

The thickening and gelling properties of the different types of carrageenan are quite different. For example, kappa carrageenan forms a firm gel with potassium ions while iota and lambda are only slightly affected. Iota carrageenan interacts with calcium ions to give soft elastic gels but salts have no effect on the properties of lambda carrageenan. Application of these combinations requires experience and understanding of carrageenans but this expertise is available from the major suppliers of this material.

5.4.1   Solution properties

All carrageenans are soluble in hot water. However, only lambda and the sodium salts of kappa and iota are soluble in cold water. Lambda carrageenan gives viscous solutions which show pseudoplasticity or shear-thinning when pumped or stirred. These solutions are used for thickening, particularly in dairy products, to give a full body with a non-gummy, creamy texture.

The influence of temperature is an important factor in deciding which carrageenan should be used in a food system. All carrageenans hydrate at high temperatures and kappa and iota carrageenans in particular exhibit a low fluid viscosity. On cooling, these carrageenans set between 40–60ºC, depending on the cations present, to form a range of gel textures.

5.4.2   Acid stability

Carrageenan solutions will lose viscosity and gel strength in systems below pH values of about 4.3. This effect is due to autohydrolysis which occurs at low pH values as carrageenan in the acid form cleaves the molecule at the 3,6-anhydrogalactose linkage (Hoffmann, Russell and Gidley, 1996). The rate of autohydrolysis increases at elevated temperatures and at low cation levels. However, once it has been cooled below the gelling temperature, carrageenan retains the sulfate-bound potassium ions and this prevents autohydrolysis proceeding. Consequently, in acidic products, the carrageenan should be added at the last moment to avoid excessive acid degradation and, if possible, acid should be added to the food immediately before depositing and filling to minimise polymer breakdown.

Table 5.1 shows approximate processing times at various pH values for a gel produced with 0.5% kappa carrageenan and 0.2% potassium chloride, such that no more than 20–

Table 5.1   Gel processing times

Temperature	Final pH						
(ºC)	3	3.5	4	4.5	5	5.5	6
120	2s	6s	20s	1min	3min	10min	30min
110	6s	20s	1min	3min	10min	30min	1.5h
100	20s	1min	3min	10min	30min	1.5h	5.0h
90	1min	3min	10min	30min	1.5h	5.0h	15.0h
80	3min	10min	30min	1.5h	5.0h	15.0h	2.0 days
70	10min	30min	1.5h	5.0h	15.0h	2.0 days	6.0 days
60	30min	1.5h	5.0h	15.0h	2.0 days	6.0 days	20.0 days
50	1.5h	5.0h	15.0h	2.0 days	6.0 days	20.0 days	60.0 days
40	5.0h	15.0h	2.0 days	6.0 days	20.0 days	60.0 days	200.0 days

*Gel process times are the times at various pH and temperatures to reduce the gel strength by about 25%.

25% of the original gel strength is lost when the solution is cooled. In general, each 0.5 pH unit reduction will decrease the potential processing time by a factor of three. Times will vary somewhat depending on carrageenan concentrations or system ingredients such as salts and sugars. In a continuous process the processing time should be kept to a minimum. In systems above about pH 4.5 the process conditions become irrelevant as the carrageenan solution is stable to most food processing times.

5.4.3   Gel properties

Hot solutions of kappa and iota carrageenans set to form a range of gel textures when cooled to between 40 and 60ºC depending on the cations present. Carrageenan gels are thermally reversible and exhibit hysteresis or a difference between setting and melting temperatures. These gels are stable at room temperature but can be remelted by heating to 5–20ºC above the gelling temperature. On cooling the system will re-gel.

The ionic composition of a food system is important for effective utilisation of the carrageenan. For example, kappa carrageenan selects for potassium ions to stabilise the junction zones within the characteristically firm, brittle gel as shown in Fig. 5.3(a). Iota carrageenan selects for calcium ions to bridge between adjacent chains to give typically soft elastic gels in Fig. 5.3(b).

The presence of these ions also has a dramatic effect on the hydration temperature of the carrageenan and on its subsequent setting and remelting temperatures. For example, iota carrageenan will hydrate at ambient temperature in water but the addition of salt raises the gel point so that the solution is converted into a gel with distinct yield point which is used for cold-prepared salad dressings. Sodium salts of kappa carrageenan will hydrate at 40ºC but the same carrageenan in a meat brine will only show full hydration at 55ºC or above. These effects are shown in Fig. 5.4.

(a) firm, brittle kappa-carrageenan gel   (b) elastic iota-carrageenan gel
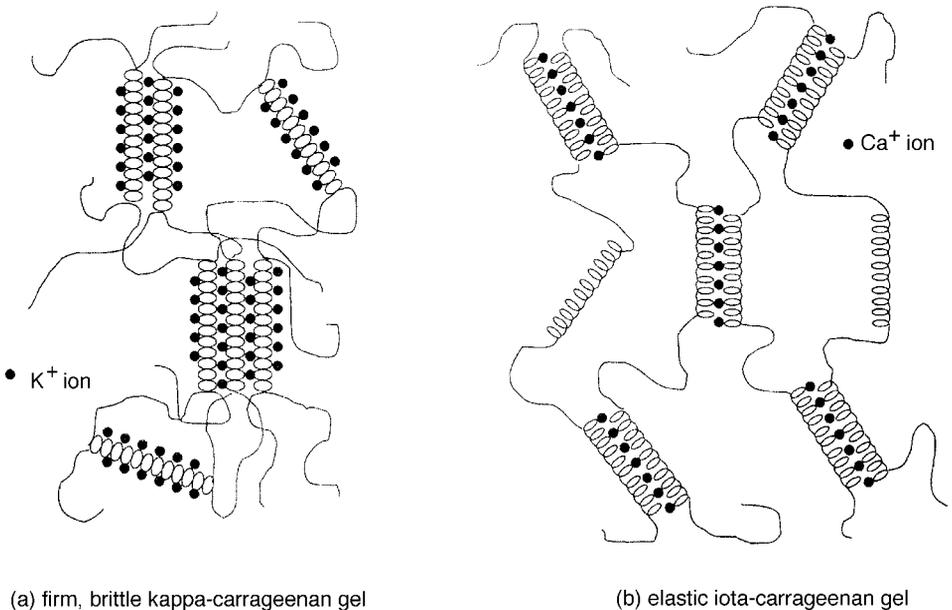
Fig. 5.3   Gelation of kappa and iota carrageenans with cations.
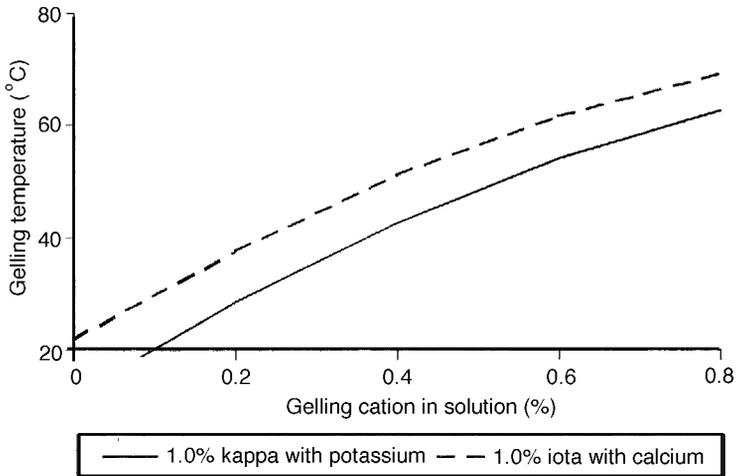
Fig. 5.4   Hydration and setting temperatures for dispersions of kappa and iota carrageenan in different salt solutions.

As a carrageenan dispersion is heated there is no significant particle swelling or hydration until the temperature exceeds about 40–60°C (Fig. 5.4). As the particles hydrate the viscosity rises as the swollen particles offer more resistance to flow. Further heating to 75–80°C produces a drop in viscosity. On cooling, the solution shows a marked increase in viscosity followed by gelation below temperatures of 40–50°C. The hydration and gelation temperatures are strongly dependent on the salts associated with the carrageenan or added separately to the solution. For example, levels above about 4% sodium chloride can prevent full hydration of carrageenan in meat products. In contrast, the very dilute levels of around 200ppm of carrageenan used to stabilise chocolate milks and other dairy beverages may not form a stabilising gel network until the temperature drops below 20°C. The presence of high solids, such as in confectionery, effectively concentrates the carrageenan and cations on the aqueous phase so the gelation may occur at 80–85°C or higher placing limitations on the levels and types of carrageenan suitable to such food applications.

As mentioned above, kappa carrageenan makes a firm brittle gel which has very poor freeze-thaw stability whereas iota carrageenan forms a thixotropic solution or very elastic gel which has good freeze-thaw stability. Kappa and iota systems may be blended to obtain a range of gel textures with intermediate properties of freeze-thaw stability and moisture binding as illustrated in Fig. 5.5.

Processed *Euchema* seaweeds yield a limited range of products suited to medium gel strength applications such as cooked meats and some dairy products. The solution and gel properties of processed *Euchema* seaweed and kappa carrageenan obtained by traditional extraction processes are similar with some specific differences. The cellulose network in processed *Euchema* seaweed reduces the rate of hydration so that solutions develop viscosity after longer heating periods or after heating to higher temperatures. The presence of cellulose in the finished gel gives a lower rupture strength with a more brittle and fragile gel. The cellulose particles make the product cloudy and therefore unsuited to clear gel applications such as water dessert gels and cake glazes. The less refined material may also have slight odour and colour differences compared to carrageenan extracts.
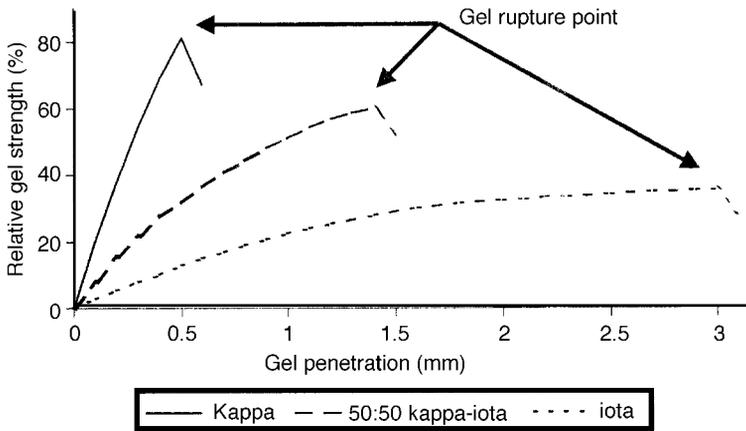
Fig. 5.5   Gel properties of mixtures of kappa and iota carrageenans.

5.4.4   Synergism with other gums

Hot solutions of kappa carrageenan-locust bean gum form strong elastic gels with low syneresis when cooled below 50–60°C. Locust bean gum is a galactomannan with a level of substitution of one part mannose to four units of galactose. However, this substitution is not regular and regions of the locust bean gum are unsubstituted. The mannose-free regions of the locust bean gum are able to associate with the repeating helical structure of carrageenan dimers to form gels. The maximum interaction, and hence peak rupture gel strength, occurs at a ratios between 60:40 and 40:60 kappa carrageenan to locust bean gum as shown in Fig. 5.6. These polymer combinations are used in very large quantities in cooked meats and in gelled petfoods.

Kappa carrageenan and clarified locust bean gum mixtures can be used for cake glaze and flan gels or formulated to give clear water dessert gels with an elastic cohesive gel texture like gelatin. Recent improvements in formulations of kappa and iota carrageenan blends are also able to give elastic cohesive gels similar to gelatin in texture. Konjac flour
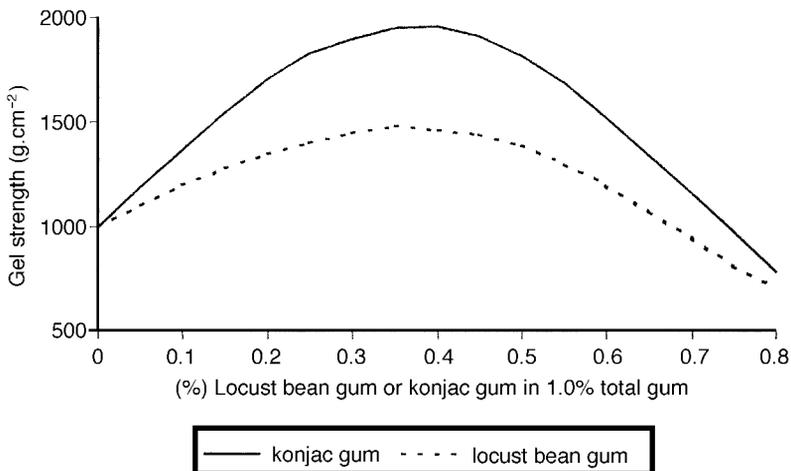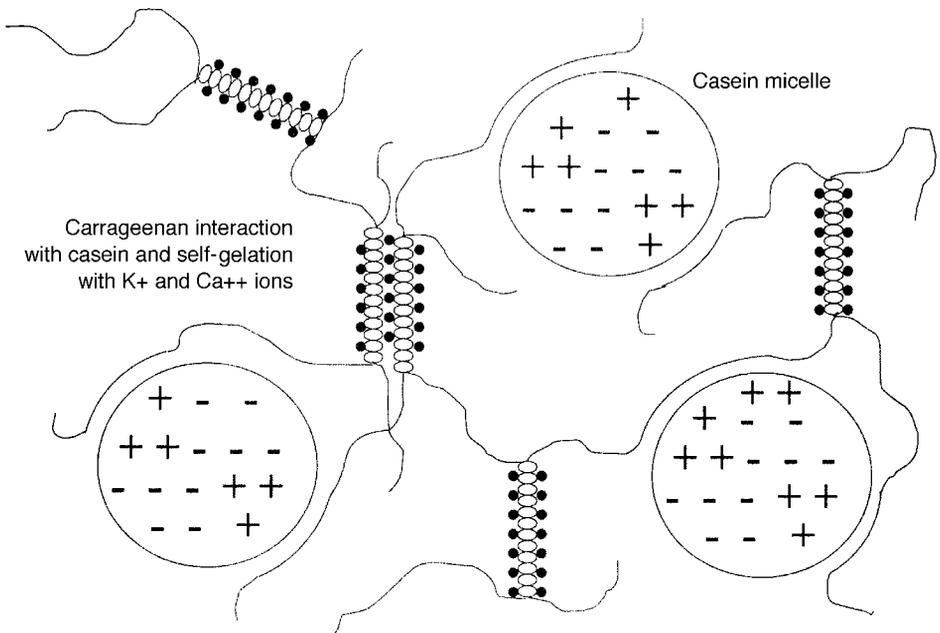

Fig. 5.6   Gel strength of blends of kappa carrageenan with locust bean gum or konjac mannan.

Fig. 5.7   Kappa carrageenan-kappa casein milk protein interaction.

(E425i) interacts even more strongly than locust bean gum to form strong elastic gels with kappa carrageenan which are at least four times the rupture strength of kappa carrageenan alone.

Probably the best known synergistic carrageenan interaction is that involving milk proteins. Some of the first uses of carrageenan were in milk gels and flans, and in the stabilisation of evaporated milk and ice cream mixes. In these applications the kappa carrageenan forms a weak gel in the aqueous phase and it also interacts with positively charged amino acids in the proteins in the surface of the casein micelles.

The specific kappa carrageenan-kappa casein interaction is shown diagramatically in Fig. 5.7. Very low levels of 150–250ppm of carrageenan are sufficient to prevent whey separation from a range of dairy products during manufacture and storage. These include ice cream and milk shake mixes, cream cheese and dairy desserts. In chocolate milks, this low level of carrageenan is able to prevent separation and also generate a stabilising network which maintains the cocoa particles in suspension.

Iota carrageenan, in combination with starch, gives dessert products with a body that is equivalent to four times that of starch alone.

A summary of the solution and gelation properties of carrageenan and its synergy with other materials is given in Table 5.2.

5.5   Food applications

Carrageenans which are able to hydrate at low temperatures present problems for their efficient use. Any lumps which are produced when the carrageenan is dispersed in water or milk greatly reduce the rate of hydration and may limit the development of full viscosity or gel strength. Various methods may be used to ensure that the carrageenan particles are fully dispersed before hydration commences. Mixing the carrageenan with

Table 5.2   Summary of carrageenan properties

	Lambda	Iota	Kappa
Solubility			
Hot (80ºC) water	Soluble	Soluble	Soluble
Cold (20ºC) water	All water soluble	Na^+ salt soluble Ca^{++} salt gives thixotropic sols	Na^+ salt soluble Limited swelling of K^+, Ca^{++} salts
Hot (80ºC) milk	Soluble	Soluble	Soluble
Cold (20ºC) milk	Thickens	Insoluble	Insoluble
Cold milk (TSPP added)	Increased thickening or gelling	Thickens or gels	Thickens or gels
50% sugar solutions	Soluble	Insoluble	Soluble hot
10% salt solutions	Soluble hot	Soluble hot	Insoluble
Gelation			
Effect of cations	Non-gelling	Strongest gels with Ca^{++}	Strongest gels with K^+
Gel texture	–	Elastic	Brittle
Shear reversible gel	–	Yes	No
Syneresis	–	No	Yes
Hysteresis	–	5–10ºC	10–20ºC
Freeze-thaw stable	Yes	Yes	No
Synergy with locust bean gum	No	No	Yes
Synergy with konjac flour	No	No	Yes
Synergy with starch	No	Yes	No
Salt tolerance	Good	Good	Poor
Stability in acid	Hydrolysis	Hydrolysis of solution, accelerated by heat Gels are stable	
Protein reactivity	Strong interaction increasing at acid pH		Specific reaction with kappa-casein

5–10 times its weight of an inert filler such as sugar, maltodextrin or salt physically separates the carrageenan particles. Slurrying the powder in oil gives a hydrophobic barrier around the particles so that the powder may be dispersed throughout the liquid before the particles start to hydrate. The powder may be dispersed into a salt solution, or in a sugar syrup or alcohol or similar medium which impedes the hydration of the particles or raises the temperature at which the carrageenan particles hydrate.

Kappa-carrageenan may be processed with potassium chloride to assist gelation. The potassium ions prevent the hydrocolloid hydrating at ambient temperatures and these products may be readily dispersed in cold water or milk without lumping. High shear mixing may be used to break up the lumps produced during dispersion and vigorous agitation by high-speed or high-shear mixing will quickly hydrate the dispersed particles. The broad spectrum of thickening and gelling properties of carrageenan result in its use in a wide range of water- and milk-based food products described below.

5.5.1   Water gels

Water dessert gels and cake glazes are one of the most traditional uses for carrageenan. These products are based on the firm, brittle gels properties of kappa carrageenan with

Formulation 5.1   Fruit-flavoured water dessert jelly

Ingredients	%
Sugar	15.00–20.00
Carrageenan (kappa-iota blend)	0.60–0.90
Potassium citrate	0.20–0.35
Citric acid	0.30–0.45
Colour	as required
Flavour	as required
Water	to 100.00
Total	100.00

Formulation 5.2   Cooked ham with 30% added brine

Ingredients	%
Meat, lean ham muscles	62.50
Carrageenan (firm gelling kappa)	0.60
Sodium tripolyphosphate	0.50
Nitrate salt*	1.67
Sodium chloride	0.53
Dextrose	1.20
Water	32.95
Total	100.00

*Sodium chloride containing 0.6% sodium nitrite, giving a 100ppm sodium nitrite in the finished product. The total brine concentration of sodium chloride is 2.2%.

the texture modified as appropriate for elasticity, cohesiveness and syneresis control using iota carrageenan. Recent improvements in the combinations used for these applications has produced vegetarian products which have a similar appearance and texture to traditional gelatin products whilst giving additional benefits of fast setting and stability at ambient temperatures. An example recipe is given in Formulation 5.1.

Similar gels are also used for aspics and gels in canned meats and petfoods and in cooked sliced meats. In these latter products the carrageenan is incorporated to improve moisture retention, cooking yields, slicing properties and mouthfeel and succulence. A typical formulation for a 30% added-water sandwich ham is given in Formulation 5.2.

In this product the carrageenan disperses readily in the meat brine when it is added after phosphate and salt addition. The brine has a very low viscosity and is easily injected and distributed within the meat. During cooking the carrageenan hydrates above about 50–55ºC to bind moisture as the ham is cooked to 72–74ºC. When the product is cooled a cohesive gel forms which maintains product integrity during high-speed slicing operations and reduces moisture loss throughout the product shelf life. Other water gel applications for carrageenan include gelled petfoods and meat and fish aspics.

Processed *Euchema* seaweed is principally used in cooked sliced meats. This material is very cost effective and it disperses readily without lumping in meat brines. During processing some differences are apparent between this and traditional carrageenan extracts. The small particles do not swell in the brine and may cause less damage when injected into the meat (Philp *et al.*, 1998). The cellulose network in processed *Euchema* seaweed reduces the rate of hydration during heating so that solutions develop viscosity

after longer heating periods or after heating to higher temperatures. The presence of cellulose in the finished gel gives a lower rupture strength with a less cohesive and more fragile structure. The dispersed cellulose particles make the product cloudy and any gel spots in the injected meat will be masked against the background of the meat. As a consequence, meat brines may include both carrageenan and processed *Euchema* seaweed to optimise properties and costs. In markets such as the EU, where carrageenan and processed *Euchema* seaweed have distinct E numbers and must be labelled separately, companies may prefer to use carrageenan alone. In the US and other markets where no distinction is made between carrageenan and processed *Euchema* seaweed, meat brines often contain both materials.

The synergy of kappa carrageenan and locust bean gum is also used in water dessert gels and glazes, cooked, sliced hams and poultry products, canned meats and petfoods, air fragrance gels and similar very firmly gelled products. The gel produced by this gum combination exhibits benefits of high gel strength, a cohesive, elastic texture, excellent syneresis control and cost-effectiveness. The gums also have an increased hot viscosity to retain juices better in cooked meats and to reduce emulsion separation and splashing during filling and cooling in fragrance gels. Petfood is the largest single use for processed *Euchema* seaweed. It is used in combination with locust bean gum for gelled products or with guar gum for gravies.

The interaction between kappa carrageenan and konjac gum is used to a lesser extent at present as a result of the relatively short time this latter material has been available in a purified form. However, the greater synergy of this gum combination will be utilised in new food developments and initial products have been commercialised in petfoods, surimi and air freshener gels.

The reversible gel properties of dilute iota carrageenan are used to stabilise suspended herbs and vegetables in vinaigrette dressings. Firstly the carrageenan is dispersed into water at ambient temperature to give a viscous solution. Salt (sodium chloride) is then added to produce a reversible gel which is very effective for suspending particulates over the long shelf life of such products. A recipe is given in Formulation 5.3.

Other applications which utilise the stabilising properties of this reversible gel network include soy milks and sterilised milk drinks. Higher concentrations of this carrageenan give soft elastic gels suited to gravies for canned meats and petfoods and for various toothpastes.

Beer and wine fining are applications which rely on the protein reactivity of carrageenan. Coarse particles of kappa carrageenan or processed *Euchema* seaweed are used to interact

Formulation 5.3   Vinaigrette-style salad dressing

Ingredients	%
7% spirit vinegar	12.50
Sugar	9.50
Salt	3.20
Carrageenan (iota)	0.30
Xanthan gum	0.15
Chopped spice pieces	1.00
Colour and preservative	as required
Water	to 100
Total	100.00

Table 5.3 Typical applications for carrageenan in water

Use	Function	Carrageenan type	Use level (%)
Dessert gels	Gelation	kappa + iota	0.5–1.0
		kappa + iota + locust bean gum	
Low calorie gels	Gelation	kappa + iota	0.5–1.0
Non-dairy puddings	Emulsion stabilisation	kappa	0.1–0.3
Syrups	Suspension, bodying	kappa, lambda	0.3–0.5
BBQ and pizza sauces	Bodying	kappa	0.2–0.5
Whipped toppings	Emulsion stabilisation	kappa, iota	0.1–0.3
Imitation coffee creams	Emulsion stabilisation	lambda	0.1–0.2
Petfoods	Thickening, suspending,	iota + guar gum	0.5–1.0
	Gelation, fat stabilisation	kappa + locust bean gum	0.5–1.0

with proteinaceous materials and small protein fragments produced during pasteurisation to form aggregates which can be readily filtered to clarify the beer and reduce chill haze. Applications for carrageenan in water-based products are shown in Table 5.3.

5.5.2 Dairy applications

Milk-based puddings were one of the original uses for carrageenan from *Chondrus crispus* harvested off Ireland. The seaweed was boiled in milk and the extracted carrageenan formed a gel on cooling. These properties are now widely adopted world-wide for a large number of instant and ready-to-eat flans, crème dessert and mousse. These products utilise the complete range of carrageenan types for thickening and gelling products. In many cases lambda carrageenan is used with kappa in milk systems to obtain a suspension or creamy gel. Iota carrageenans are often used in combination with reduced levels of starch to lower process viscosity and improved body with a soft spoonable texture to desserts. Textures may range from firm gels in crème caramel to soft gels in ready-to-eat spoonable desserts to thickened custards, vla and cream desserts.

Extremely low levels of carrageenan, around 100–200ppm, are used to stabilise and prevent whey separation in a number of dairy products. These include milk shake and ice cream mixes, chocolate milks, and pasteurised and sterilised creams. In these applications

Formulation 5.4 Typical ice cream mix

Ingredients	%
Butterfat	8.00–10.00
Milk solids non-fat	11.10–10.80
Sugar	10.00
Corn syrup solids	3.50
Carrageenan (kappa)	0.015–0.025
Other hydrocolloids (guar gum, locust bean gum, xanthan gum, sodium alginate)	0.10–0.20
Emulsifier (glyceryl monostearate)	0.20–0.50
Vanilla flavour	as required
Water	to 100.00
Total	100.00
(Total solids)	33.3–35.0

Table 5.4 Typical applications for carrageenan in dairy products

Use	Function	Carrageenan type	Use level (%)
Milk gels			
Cooked flans	Gelation, mouthfeel	kappa, kappa + iota	0.2–0.3
Cold-prepared custards	Thickening, gelation	kappa, iota, lambda	0.2–0.3
Pudding and pie fillings	Reduced starch, lower burn-on	kappa	0.1–0.2
Ready-to-eat desserts	Syneresis control, mouthfeel	iota	0.1–0.2
Whipped products			
Whipped cream	Stabilise overrun	lambda	0.05–0.15
Aerosol cream	Stabilise overrun, emulsion stabilisation	kappa	0.02–0.05
Cold-prepared milks			
Shakes	Suspension, mouthfeel, stabilise overrun	lambda	0.1–0.2
Frozen desserts			
Ice cream, ice milk	Whey prevention, control meltdown	kappa	0.01–0.02
Pasteurised milks			
Chocolate milks	Suspension and mouthfeel	kappa	0.015–0.03
	Suspension and mouthfeel	kappa + lambda	0.03–0.10
Soy milks	Suspension and mouthfeel	kappa + iota	0.02–0.04
Sterilised milks			
Chocolate milks	Suspension and mouthfeel	kappa, lambda	0.01–0.03
Evaporated milks	Emulsion stabilisation	kappa	0.005–0.015
Processed cheese			
Cheese slices and blocks	Improve slicing and grating Control melting	kappa	0.5–3.0
Cream cheese and spreads	Gelation, moisture binding	kappa + locust bean gum	0.3–0.6

the carrageenan interacts with the dairy proteins to form a stabilising network which is able to suspend particulates such as cocoa in chocolate milks. The network prevents protein-protein interaction and aggregation during storage. This avoids whey separation in fluid products and reduces shrinkage in ice cream.

Processed cheese is another application where the protein reactivity and gelling properties of carrageenan are used. Processed cheese is made by incorporating 'melting' or 'emulsifying' salts into the cheese mix to control the melting temperature whilst maintaining firmness and mouthfeel, ensuring slice integrity and producing a strong block suitable for grating. It is possible to reduce the cheese content in such products and substitute a gel containing 0.5–3% carrageenan to give a product with excellent mouthfeel properties and good melting, grating and slicing properties.

Acidic dairy products, such as soft cheese and yoghurt, are generally unsuitable for carrageenan; the low pH increases the electrostatic interactions between protein and carrageenan producing unstable aggregates which flocculate and separate. However, careful selection of appropriate carrageenan-galactomannan blends is able to control this aggregation. These blends are effective stabilisers which prevent moisture separation whilst conferring a smooth, creamy mouthfeel to the finished product. The many dairy products which utilise the properties of carrageenan are shown in Table 5.4.

5.6   Regulatory status

Material extracted from *Furcellaria* species, furcellaran, also known as Danish agar, was given a separate classification of E408 under EC food legislation. However, a later reassessment of carrageenan and furcellaran recognised the structural and functional similarity of the two materials and reclassified them together as E407.

In the EU, carrageenan and processed *Euchema* seaweed are listed in Annex 1 of the European Parliament and Council Directive 95/2/EC on Food Additives other than Colours and Sweeteners (Anon., 1995). Carrageenan and processed *Euchema* seaweed are approved as E407 and E407A respectively in the list of permitted emulsifiers, stabilisers, thickening and gelling agents for use 'quantum satis', the level required to achieve a given technological benefit. Purity standards for food-grade carrageenan and processed *Euchema* seaweed have been amended recently under Council Directive 98/86/EC which revises the heavy metal limits and defines the limits for acid insoluble matter in food-grade carrageenan and processed *Euchema* seaweed (Anon., 1998).

Toxicological reviews have considered the implications of the low molecular weight material found in all carageenans, including native carrageenan, and the possible degradation of carrageenan during food processing and digestion. On this latter point, the presence of associated cations prevents carrageenan hydrolysis in the gastric environment (Marrs, 1998) and recent EU purity standards do not specify any limit for material below 100kDa (Anon., 1998).

A study on the fate of carrageenan subjected to a range of conditions revealed that normal food processes do not substantially increase the proportion of low molecular weight material (Marrs, 1998). The level of this material only increases significantly when processing combines the effects of high temperatures, low pH and and long process times. For instance, heating kappa carrageenan solutions at pH4 at 120ºC for 15 seconds does not significantly increase the low molecular weight fraction but a gel strength reduction of over 25% is seen when heating this solution at 135–140ºC for 10 seconds. In fact, as material with a molecular weight below 100kDa has little or no thickening or gelling properties it is not valued for food applications and processes are designed to minimise degradation.

In the US, no distinction is made between carrageenan and processed *Euchema* seaweed; both are described as carrageenan and are generally recognised as safe (GRAS) in accordance with experts of the Food and Drug Administration.

5.7   References and further reading

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