
Introduction to Carrageenan

Introduction

The practical utility of carrageenan stems from two key properties. Its ability to form strong gels with certain salts or other gums and its ability to interact with certain dairy proteins. Carrageenan is mainly used in the food industry with some applications in the toiletries industry. Industrial applications of carrageenan are rare.



Chondrus crispus Seaweed

Carrageenan is a misleading term as it covers a large diversity of products which can vary in the functionality depending on the original weed source, how the material has been processed and the environment the product is exposed to.

Carrageenan is traditionally split into three basic forms:

Lambda Carrageenan

Lambda carrageenan is a highly sulphated type of carrageenan mainly used for its ability to impart mouth feel and a creamy sensation to dairy products. Lambda carrageenan does not gel. Commercially it is supplied as it is extracted from the seaweed which is as a kappa / lambda mixture.

Iota Carrageenan

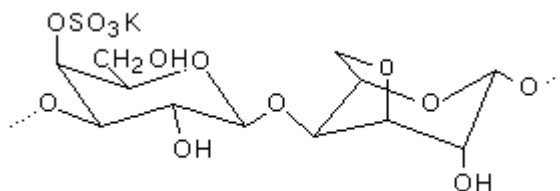
Iota carrageenan is a type of carrageenan with a sulphate content intermediate between kappa and lambda carrageenan. Iota carrageenan forms an elastic gel with good freeze thaw and reheating properties.

Kappa Carrageenan

Kappa carrageenan is the most commonly used type of carrageenan. Its most important properties are its high gel strength and strong interaction with milk proteins. About 70% of the world's carrageenan production is based on kappa carrageenan.

Primary structure

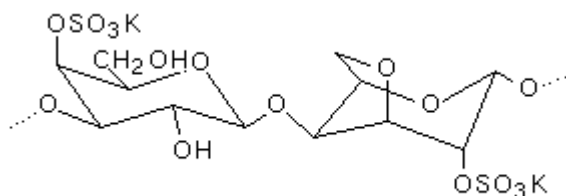
The basic structure of carrageenan is a linear polysaccharide made up of a repeating disaccharide sequence of α -D-galactopyranose linked 1,3 called the A residue and β -D-galactopyranose residues linked through positions 1,4 (B residues). Carrageenans are distinguished from agars in that the B units in carrageenan are in the D form whereas they are in the L form in agar's.



Kappa Carrageenan

The regular backbone structure of The basic structure of carrageenan is disrupted by a more or less ordered distribution of sulphate hemi ester groups. Carrageenan can also contain some methoxy and pyruvate groups.

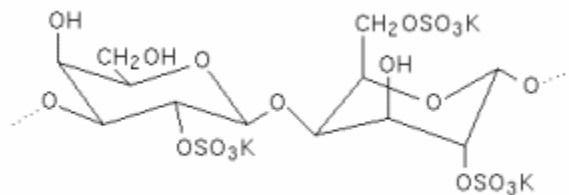
The original classification of carrageenan was determined by the fractionation of the polysaccharide with potassium chloride. The fraction that was soluble in 0.25M KCl was called lambda carrageenan and the fraction that was insoluble was called kappa carrageenan. Rees and his co-workers later altered this so that kappa and lambda carrageenan referred to idealised specific disaccharides.



Iota Carrageenan

Gelling in carrageenan is caused by helix formation and this can only occur in repeat structures where the B residue is in a 1-C-4 conformation. Lambda carrageenan has both its sugar residues in a 4-C-1 conformation and does not form gels. All the gelling types of carrageenan which include κ and ι all contain a 3,6 anhydro bridge on the B unit which forces the sugar to flip from a 4-C-1 conformation to a 1-C-4 conformation and can then form cross-link networks and gels.

Some types of seaweed species contains relatively pure carrageenan fractions *Kappaphycus alvarezii* & *K. striatum* contain largely κ carrageenan and μ carrageenan which may be converted to kappa carrageenan by alkali treatment. *Eucheuma denticulatum* contains a similarly high level of ι carrageenan with some ν carrageenan precursor. *Furcellaria* contains a strong gelling type carrageenan, known as furcellaran, which is very much like kappa carrageenan. Other seaweed types, such as *Chondrus crispus* and *Gigartina* types contain not only a mix of κ and λ type carrageenans but also a type of carrageenan polymer that is essentially a block copolymer of different carrageenan types. This gives the carrageenan made from *Gigartina* or *Chondrus* weed species quite different properties from those made from the *Kappaphycus* & *Eucheuma* type species from South east Asia. you will also see later that the differences in structure also enable quite different processing conditions to be utilised for the different weed types.



Lambda Carrageenan

Sources

The 'original' carrageenan was extracted from *Chondrus crispus*, a red seaweed found in the north Atlantic. Another name for this seaweed is 'Irish moss'; a name still used in the brewing industry. *Chondrus crispus* actually contains a mix of carrageenan types, the predominant ones being kappa and lambda. Today, *Chondrus crispus* is not a major source of carrageenan in world terms. *Chondrus crispus* is wild harvested and some is farmed for use in the culinary market.

Today, most carrageenan is extracted from the tropical red species of *Kappaphycus* and *Eucheuma*. *Kappaphycus* is commercially known as "cottonii". It is primarily grown in Southeast Asia but also elsewhere around the tropics. *Eucheuma*, commercially known as "spinosum" is mostly cultivated in Africa but also in SE Asia. These species are relatively pure in the carrageenan type they contain. *Cottonii* is predominantly kappa carrageenan and *Spinosum* is largely iota carrageenan. This allows greater flexibility in formulation because you are not restricted to the ratios of kappa and iota that happen to occur in the native weedstock.

Gigartina skottsbergii and *Sarcothalia crispata* are also key species used in the extraction of carrageenan, both are harvested off the coast of Chile and other South American countries. Similar species, *Mazzaella*, *Chondracanthus* are harvested in smaller amounts. Unlike the seaweeds previously mentioned, the Gigartinaceae type weeds have the various carrageenan types actually mixed up along the same polymer chain in a 'hybrid' type of polymer. They are often referred to as "Hybrid" types and contain mixtures of kappa, iota and lambda carrageenan. These carrageenans are often preferred in some dairy applications.

Hypnea and *Furcellaria* are other types of carrageenan bearing seaweeds that are occasionally used. *Furcellaria* is a North Atlantic species and there is a small industry in Estonia. *Furcellaria* yields a kappa type carrageenan that was historically referred to as Danish agar. It can be used in much the same way as kappa carrageenan.

Production

Carrageenan production goes back many decades and only recently, with the introduction of new weed sources, as there been any major developments in the processes involved. There are four basic processes used for the production of carrageenan. For the sake of convenience we will refer to these as:

- Alcohol Precipitation
- KCl Precipitation or gel press
- Danisco process
- Semi refined

The traditional process for the production of carrageenan is the alcohol precipitation process. It has the major advantage of being able to handle any type of seaweed source and hence can produce any type of carrageenan. The major drawback of this type of processing is the cost. The extra capital cost involved in the installation of flameproof equipment and the added equipment needed to re distill the large volumes of alcohol required make it a very expensive process. However it is the only commercial

method of manufacturing lambda carrageenan, which is very soluble. Another advantage is the ability to use south American weed stocks such as *Gigartina* which can be very cost effective due to their high yield.

In recent years Alcohol precipitation has been declining and one of the processes that has taken its place is the gel press or KCl precipitation process. This technology comes from agar processing and is essentially identical to the manner in which agar is made from *Gracillaria* type weed stocks.

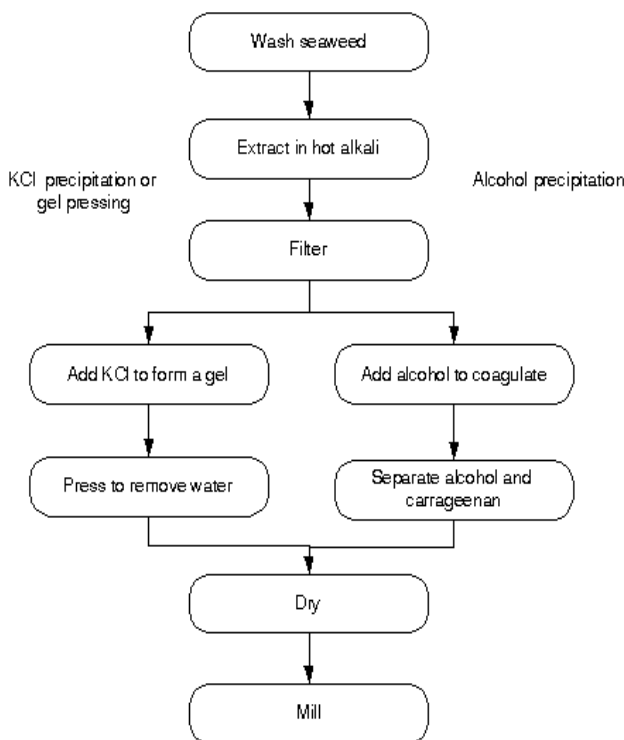
Kappaphycus species have a very high kappa carrageenan content and when purified by filtration it is then possible to precipitate the carrageenan using potassium chloride, generally this forms a large jelly like mass that can be pressed to remove water. The pressed cake can then be dried and milled as usual. The great advantage of this process is that you have produced a refined product without incurring the extra costs of the alcohol recovery. On the downside the process only works with *Kappaphycus* species and can only make kappa type carrageenan gels. This process has had great success the large Asian dessert jellies market.

There are two processes that aim to cheapen the production of carrageenan by not going to a highly dilute solution and then precipitating but applying a slurry process. The most important of these is the semi refined process which became possible with the farming of *Kappaphycus* species. The second is a compromise process developed by Danisco especially for treating south American species but would work on most weed types.

The semi refined process developed originally to produce a high gel strength, cheap carrageenan for use in the petfood industry. It has since developed into the fastest growing carrageenan technology and in conjunction with gel pressing has been the major cause of the decline and closure of many alcohol precipitation plants. In a semi refined process seaweed, either *Kappaphycus* or *Eucheuma* species, is first washed. The washed weed is then treated in a hot alkali mix with a very high potassium level. Many people use 5-8% potassium hydroxide. If the cooking temperature is kept below 80°C (for *Kappaphycus*) then the seaweed does not dissolve and the mu to kappa conversion is completed with the carrageenan still within the seaweed. The hot alkali and subsequent washing removes residual minerals, proteins and fats leaving behind the converted carrageenan and some residual cellulose from the cell walls. Hence semi refined carrageenan always contains residual cellulose and will never be clear. Semi refined carrageenan has experienced strong growth in the meats industry and in the dairy industry where clarity is not an issue. the main advantage of semi refined carrageenan is the low cost although it has been claimed that semi refined products are actually superior to refined in meat processing (Philp et al 1998. Vol 9 of Gums and Stabilisers for the Food Industry).

Danisco have a propriety process that is very similar to the semi refining process. In this process the seaweed is alkali treated in an alcohol slurry. Although this is not as cheap as the semi refining process it does allow the treatment of a wide variety of weed types.

The legal position was fought over by the large western companies trying to stop its use and the Asian manufacturers trying to get it accepted on a par with traditional products. According to FDA regulations semi refined carrageenan is now accepted as carrageenan and there is no legal distinction. EU regulations are different and semi refined carrageenan is allowed as its own e number (E407a) under the name Processed Eucheuma Seaweed (PES). The distinction is drawn on the level



of residual cellulose in the product. Ironically the Danisco process is often used to process *Gigartina* type seaweeds but due to the natural low level of cellulose in the seaweed it is legally classified as refined in the EU despite being processed in a process almost identical to semi refining.

Synergistic Interactions

Mixtures of hydrocolloids are commonly used to impart novel and improved rheological characteristics to food products and an added incentive is a reduction in costs. The nature of the synergy can be due to association of the different hydrocolloid molecules or to non-association. If the two hydrocolloids associate then precipitation or gelation can occur. Oppositely charged hydrocolloids (e.g., a protein below its isoelectric point and an anionic polysaccharide) are likely to associate and form a precipitate while there is evidence to show that for some stiff polysaccharide molecules (e.g., locust bean gum and kappa carrageenan) association results in gel formation.

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 dimmers 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.

These polymer combinations are used in very large quantities in cooked meats and in gelled pet foods. 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 (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. Iota carrageenan, in combination with starch, gives dessert products with a body that is equivalent to four times that of starch alone.

Milk protein Interactions

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 interacts with positively charged amino acids in the proteins at the surface of the casein micelles. The specific kappa carrageenan-kappa casein interaction is shown diagrammatically.

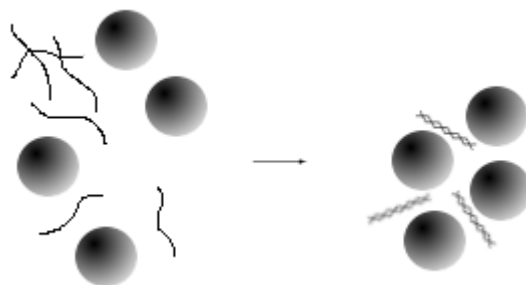


Figure 1. Carrageenan and milk proteins

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 generate a stabilising network, which maintains the cocoa particles in suspension.

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