CP Kelco
Combining STRENGTHS
Creating SOLUTIONS
GENU® Carrageenan
GENU® Carrageenan Book
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GENU® CARRAGEENAN
GENERAL DESCRIPTION

CP Kelco ApS
Ved Banen 16 • 4623 Lille Skensved
Denmark
Telephone: +45 56 16 56 16
TeleFax: +45 56 16 94 46
Index

General Description of Carrageenan

Definition ..................................................................................................................... 3
Raw Material .................................................................................................................. 3
Manufacture ................................................................................................................... 4
Structure ...................................................................................................................... 5

General Properties of Carrageenan

Solubility ..................................................................................................................... 8
Counter Ions ................................................................................................................... 8
Other Solutes ................................................................................................................ 8
Dispersion .................................................................................................................... 9
Reactions ..................................................................................................................... 10
Stability in solution ..................................................................................................... 10
Reaction with other Electrically charged Hydlocolloids ........................................... 11
Gelling Mechanism ................................................................................................... 12

Commercial Carrageenans

Powder Characteristics and Storage Stability .......................................................... 22
Stability ..................................................................................................................... 22
Standardization ........................................................................................................ 22
Quality Control ....................................................................................................... 22

Applications

Food Applications .................................................................................................... 24
Gel Formation ........................................................................................................... 24
Stabilization ............................................................................................................. 24
Milk Based Foods ................................................................................................... 25
Non-Food Applications ........................................................................................... 25

GENU Carrageenans

GENU Carrageenans ............................................................................................... 26
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General Description of Carrageenan

DEFINITION
Carrageenan is obtained by extraction with water or alkaline water of certain species of the class Rhodophyceae (red seaweeds). It is a hydrocolloid consisting mainly of the potassium, sodium, magnesium, and calcium sulphate esters of galactose and 3.6-anhydro-galactose copolymers. The relative proportion of cations existing in carrageenan may be changed during processing to the extent that one may become predominant.

Carrageenan is recovered by alcohol precipitation, by drum drying, or by freezing. The alcohols used during recovery and purification are restricted to methanol, ethanol, and isopropanol.

The commercial products classified as carrageenan are frequently diluted with sugars for standardization purposes and mixed with food grade salts required for obtaining gelling or thickening characteristics.

RAW MATERIAL
The most well-known and still most important red seaweed used for manufacturing carrageenan is Chondrus crispus, which grows along the coast of the Northern part of the Atlantic, the main harvesting areas being maritime provinces of Canada, Maine, Brittany in France, and the Iberian peninsula.

Chondrus crispus is a dark red parsley-like plant which grows attached to the rocks at a depth of up to approx. 3 meters.

Most of the „moss“ is harvested by rakes from small boats. The rakes may be operated by hand only or drawn after a boat.

The wet moss is brought to drying plants operated by the carrageenan manufacturers and dried to less than 20% humidity to preserve the quality of the seaweed and facilitate transportation to the extraction plant.

Other red seaweeds are growing in importance as carrageenan raw materials, improving stability of supply and broadening the range of properties which can be achieved. Important species are Eucheuma cottonii, which yields kappa-carrageenan, and Eucheuma spinosum which yields iota-carrageenan. These Eucheuma species are harvested along the coasts of the Philippines and Indonesia.
Long term stability of supply and price of carrageenan raw material will be ensured by seaweed farming. Seaweed farms are already operated on the Philippines, yielding sufficient Eucheuma cottonii of good and consistent quality to cover the present demand. Eucheuma spinosum, the raw material for iota-carrageenan has recently been farmed successfully.

The advantages of seaweed farming are obvious:

- Independence of fluctuating climatic conditions.
- Independence of the labour intensive seaweed collecting.
- A more pure raw material.
- The possibility of selecting seaweed strains with high carrageenan content and yielding carrageenans of desired compositions and properties.

MANUFACTURE
Carrageenan is extracted from the raw material with water at high temperatures. The liquid extract is purified by centrifugation and/or filtration. The liquid extract may be converted into a powder by simple evaporation of water to yield the so called drum dried carrageenan. Proper release of the dried material from the dryer roll requires addition of a small amount of roll-stripping agents (mono- and diglycerides).

The content of mono- and diglycerides is responsible for the drum dried carrageenans being turbid in watery solutions, and drum dried carrageenan consequently finds little use in water gel applications. Also, drum dried carrageenans contain all soluble salts present in the extract, which may influence the properties - for instance solubility of the carrageenan. Most of the carrageenan used in foods is isolated from the liquid extract by selective precipitation of the carrageenan with isopropanol. This process gives a more pure and concentrated product.

The flow sheet below describes in general the process used by CP Kelco ApS.
**STRUCTURE**

Carrageenan is a linear polysaccharide, more specifically a galactan with the galactose residues linked with alternating

- \((1\rightarrow 3)\) linkages and
- \((1\rightarrow 4)\) linkages

In addition, the galactose units linked \((1\rightarrow 3)\) in this general structure often occur as 3.6-anhydro-D-galactose and sulphate ester groups may be present on some or all galactose units.
It is evident that since carrageenan is a large molecule being made up of some 1000 residues, the possibility for structural variations are enormous. In order to simplify matters it is convenient to define three main types, kappa, iota, and lambda carrageenans, which are idealized molecules assigned definitive structures. Hardly any seaweed yields these ideal carrageenans. The normal situation is probably a range of intermediate structures.

Idealized Structures

Galactose residues in carrageenan
Kappa carrageenan is made up of

- $(1 \rightarrow 4)$ D-galactose-4-sulphate and
- $(1 \rightarrow 3) 3.6$-anhydro-D-galactose.

In a kappa-type seaweed extract some of the D-galactose contains 6-sulphate ester groups and some of the 3.6-anhydro-D-galactose contains 2-sulphate ester groups. 6-sulphate ester groups reduce the gelling power considerably, but by alkali treatment it is possible to transelminate 6-sulphate groups, which results in the formation of 3.6-anhydro-
D-galactose imparting a higher degree of regularity to the molecule and thus the gelling power is increased.

Kappa-type extracts are made from Eucheuma cottonii and some Chondrus and Gigartina species. Iota carrageenan is characterized by having 4-sulphate ester groups on all D-galactose residues and 2-sulphate ester groups on all 3.6-anhydro-D-galactose residues. 2-sulphate ester groups are not removed by alkali treatment.

As in the case of kappa carrageenan, iota carrageenan also shows irregularities in the form of 6-sulphate ester groups on some D-galactose residues and through alkali treatment the iota carrageenan becomes more regular.

It follows that a lack of 2-sulphate ester groups on some 3.6-anhydro-D-galactose residues makes iota carrageenan more irregular. Lambda carrageenan differs from kappa and iota carrageenan by having a disulphated $\alpha(1\rightarrow 4)$-D-galactose residue and no 4-sulphate in the $\alpha(1\rightarrow 3)$-D-galactose residue. Instead of 4-sulphate ester groups lambda carrageenan contains variable amounts of 2-sulphate ester groups. The position of sulphate ester groups in determined with an infrared spectrophotometer.

Typical infrared spectra are shown below:

![Infrared spectra](image)

<table>
<thead>
<tr>
<th>Wave number cm$^{-1}$</th>
<th>Functional group</th>
<th>Kappa Absorbance</th>
<th>Iota Absorbance</th>
<th>Lambda Absorbance</th>
</tr>
</thead>
<tbody>
<tr>
<td>1210 - 1260</td>
<td>Ester sulphate</td>
<td>vs</td>
<td>vs</td>
<td>vs</td>
</tr>
<tr>
<td>1010 - 1080</td>
<td>Glycosidic linkage</td>
<td>vs</td>
<td>vs</td>
<td>vs</td>
</tr>
<tr>
<td>928 - 933</td>
<td>3.6-anhydro-D-galactose</td>
<td>s</td>
<td>s</td>
<td>a - l</td>
</tr>
<tr>
<td>840 - 850</td>
<td>D-galactose-4-sulphate</td>
<td>m</td>
<td>m</td>
<td>a</td>
</tr>
<tr>
<td>820 - 830</td>
<td>D-galactose-2-sulphate</td>
<td>a</td>
<td>a</td>
<td>m</td>
</tr>
<tr>
<td>810 - 820</td>
<td>D-galactose-6-sulphate</td>
<td>a</td>
<td>a</td>
<td>m</td>
</tr>
<tr>
<td>800 - 805</td>
<td>3.6-anhydro-D-galactose-2-sulphate</td>
<td>a - l</td>
<td>m</td>
<td>a</td>
</tr>
</tbody>
</table>

vs = very strong  s = strong  m = medium  l = low  a = absent
General Properties of Carrageenan

SOLUBILITY
Carrageenan exhibits the solubility characteristics normally shown by hydrophilic colloids. It is water soluble and insoluble in most organic solvents. Water miscible alcohols and ketones, while themselves non-solvents for carrageenan, are tolerated in admixture with carrageenan solutions at levels up to 40%. More highly polar solvents, such as formamide and N,N-dimethylformamide, are tolerated in still higher proportion and alone cause a marked swelling of the polymer.
The solubility characteristics of carrageenan in water are influenced by a number of factors most important of which are

a. the type of carrageenan
b. counter ions present
c. other solutes
d. temperature
e. pH

Type of Carrageenan
The many forms of carrageenan possible through variation in structural detail, provide much variability in regard to solubility properties. For practical purposes, however, it is convenient to speak in terms of several general structural types and to equate solubility with the overall balance of hydrophilicity as provided by the hydrophilic sulphate and hydroxyl groups on one hand and the more hydrophobic 3.6-anhydro-D-galactose residues on the other.

Thus, lambda carrageenan, by definition void of 3.6-anhydro-D-galactose units and being highly sulphated is easily soluble under most conditions. Kappa carrageenan containing 3.6-anhydro-D-galactose as part of the repeating unit and fewer sulphate groups is less hydrophilic and less soluble. Intermediate is iota carrageenan, more hydrophilic by virtue of its 2-sulphate which in addition to its position counteracts the less hydrophilic character of the 3.6-anhydro-D-galactose residue.

Counter Ions
Solubility characteristics are also affected by the salt form of the sulphated ester groups, particularly in the case of less soluble kappa carrageenan. The sodium forms are generally more easily soluble, while forms in which the cation is potassium dissolve with more difficulty.

Thus, kappa carrageenan in the potassium form may for practical purposes be considered insoluble in cold water, heat being required to bring it into solution, whereas in the sodium form it dissolves readily. The potassium salt of iota carrageenan is also insoluble in cold water although it swells markedly. Lambda carrageenan is soluble in all its salt forms.

Other Solutes
Both the dissolving rate and solubility of carrageenan are affected by the presence of other solutes, the effect mainly being to compete for available water and thus to alter the state of hydration of the polysaccharide. Sensitivity to other solutes parallels solubility with kappa carrageenan being the most sensitive to the presence of solutes.
Inorganic salts are most effective in altering the hydration of carrageenan, particularly when the cation is potassium. 1.5 to 2% potassium chloride is sufficient to prevent the dissolution of kappa carrageenan at normal temperatures while sodium chloride solutions of 4 to 4.6% and above are also non-dissolving. Considerably higher concentrations of nonionics are required before similar effects are noted.

Sucrose shows little effect on hydration of kappa carrageenan until present in concentrations of 50% and above while glycerol must be present in very high amounts before appreciable effects are seen. In cases where more than one solute is present, their combined effect on hydration is generally additive and may be predicted from a knowledge of individual effects. For example, in the presence of high amounts of glycerol, solubility is markedly influenced by traces of potassium ions.

Of practical importance is the fact that iota carrageenan will dissolve with heating in solutions containing relatively high concentrations of salts and thus is able to provide gelation in certain applications where an excessive amount of salts would preclude the use of kappa carrageenan.

**Dispersion**

Being a water soluble polysaccharide, carrageenan is difficult to disperse in water due to the formation of a film layer around each carrageenan particle. This leads to the formation of large agglomerates (lumps) which, due to the protective film layer, are very difficult for the water molecules to penetrate.

The less soluble the carrageenan the easier the dispersion, for example, a potassium kappa carrageenan being insoluble in cold water is much easier to disperse in cold water than a sodium kappa carrageenan. Both, however, are soluble in hot water and therefore equally difficult to disperse in hot water. Other factors which decrease the solubility of carrageenan will improve the dispersibility.

In most applications carrageenan may be preblended with other ingredients such as sugar, and in order to achieve complete dispersion 1 part of carrageenan should be blended with 10 parts of sugar.

In applications where carrageenan cannot be preblended with other ingredients, a high speed mixer is necessary in order to break up the lumps formed by adding the carrageenan to the water.

Although potassium or calcium carrageenans are not or only slightly soluble, they swell in cold water producing viscous dispersion. Thus, dispersing carrageenan in cold water using a high speed mixer limits the strength of the dispersion to approx. 3% depending on the type of mixer.

In hot (60 - 75EC) water carrageenan can be dissolved to make 7 - 8% solution. This leads immediately to the formation of lumps, but high speed mixers are available which easily break these lumps. In hot water the carrageenan goes into true solution, and in this state the viscosity is much lower than in the state of hydration.
<table>
<thead>
<tr>
<th>Medium</th>
<th>Kappa</th>
<th>Iota</th>
<th>Lambda</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hot water.</td>
<td>Soluble above 60°C (140°F).</td>
<td>Soluble above 60°C (140°F).</td>
<td>Soluble.</td>
</tr>
<tr>
<td>Cold water.</td>
<td>Sodium salt soluble.</td>
<td>Sodium salt soluble.</td>
<td>Soluble.</td>
</tr>
<tr>
<td></td>
<td>Potassium and calcium salt,</td>
<td>Calcium salts gives</td>
<td></td>
</tr>
<tr>
<td></td>
<td>insoluble.</td>
<td>thixotropic dispersions.</td>
<td></td>
</tr>
<tr>
<td>Cold milk.</td>
<td>Sodium salt, calcium salt and</td>
<td>Insoluble.</td>
<td>Soluble.</td>
</tr>
<tr>
<td></td>
<td>potassium salt insoluble, but</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>swells markedly.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Concentrated</td>
<td>Soluble hot.</td>
<td>Not easily soluble.</td>
<td>Soluble hot.</td>
</tr>
<tr>
<td>sugar solutions.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Concentrated</td>
<td>Insoluble.</td>
<td>Soluble hot.</td>
<td>Soluble hot.</td>
</tr>
<tr>
<td>salt solutions.</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**REACTIONS**

**Stability in Solution:**
Acid and oxidizing agents may hydrolize carrageenan in solution leading to loss of physical properties through cleavage of glycosidic bonds. Acid hydrolysis depends on pH, temperature and time.

For minimum degradation during processing, high temperature short time processes are preferred. Carrageenan in solution has maximum stability at pH = 9 and should not be heat processed at pH-values below 3.5. At pH = 6 or above, carrageenan solutions withstand processing conditions normally encountered by sterilizing fish and meat products in cans as in the case of pet foods.

**Effect of Acid on Gel Strength of Carrageenan at 58°C**
- 1.2% Kappa - iota carrageenan
- 8.0% Sugar
- 0.2% Potassium citrate
- Citric acid

![Graph showing gel strength over time at different pH values](attachment:gel_strength_graph.png)
Effect of Acid on Gel Strength of Carrageenan at 115°C
1.0% Kappa Carrageenan - locust bean gum
1.0% Sodium chloride
0.5% Potassium chloride
0.7% Sodium citrate
Citric acid buffer

Effect of heat treatment on Gel Strength of Carrageenan at pH = 3.6
1.2% Kappa - iota Carrageenan
8.0% Sugar
0.2% Potassium citrate
Citric acid

The acid hydrolysis takes place only when the carrageenan is dissolved, and the hydrolysis is accelerated as the processing temperature and/or the processing time is increased. However, when the carrageenan is in its gelled state the acid hydrolysis no longer takes place.

<table>
<thead>
<tr>
<th>Stability</th>
<th>Kappa</th>
<th>Iota</th>
<th>Lambda</th>
</tr>
</thead>
<tbody>
<tr>
<td>At the neutral and alkaline pH.</td>
<td>Stable.</td>
<td>Stable.</td>
<td>Stable.</td>
</tr>
<tr>
<td>At acid pH.</td>
<td>Hydrolized in solution</td>
<td>Hydrolized in solution</td>
<td>Stable in gelled form.</td>
</tr>
<tr>
<td></td>
<td>when heated.</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Stable in gelled form.</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Reaction with other Electrically Charged Hydrocolloids
Carrageenan is a sulphated galactan being strongly negatively charged over the entire pH-range encountered in food.

Carrageenan may interact with other charged macromolecules, e.g. proteins, to give various effects such as viscosity increase, gel formation, stabilization or precipitation. The result of the carrageenan-protein interaction is highly dependent on pH of the system and the isoelectric pH of the protein. When carrageenan and gelatine are used together in a system in which the pH is higher than the isoelectric pH of gelatine, carrageenan increases the melting temperature of the gel without influencing the texture of the gel significantly.
GELLING MECHANISM

<table>
<thead>
<tr>
<th></th>
<th>Kappa</th>
<th>Iota</th>
<th>Lambda</th>
</tr>
</thead>
<tbody>
<tr>
<td>Effect of cations.</td>
<td>Gels most strongly with potassium ions.</td>
<td>Gels most strongly with calcium ions.</td>
<td>Non-gelling.</td>
</tr>
<tr>
<td>Type of gel.</td>
<td>Strong and brittle with syneresis.</td>
<td>Elastic and cohesive without syneresis.</td>
<td>Non-gelling.</td>
</tr>
<tr>
<td>Synergistic effect</td>
<td>High.</td>
<td>High.</td>
<td>None.</td>
</tr>
<tr>
<td>with locust bean</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>gum.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Freeze/thaw</td>
<td>None.</td>
<td>Stable.</td>
<td>None.</td>
</tr>
<tr>
<td>stability.</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The structure of kappa and iota carrageenan allows segments of the two molecules to form so called double helices which bind the chain molecules in the three dimensional network, a gel. Lambda carrageenan has a structure that does not allow such double helix formation.

Gel Formation of Kappa and Iota Carrageenans
When dissolved by heating, followed by cooling below certain temperatures, kappa and iota carrageenans form thermoreversible water gels in a concentration as low as 0.5%, provided gelling cations are present. A gel has some properties of a solid and some of a liquid. Thus, it keeps its shape when tipped out of a container and yet retains the vapour pressure and conductivity of the liquid from which it is made.

Kappa carrageenan gels in the presence of potassium ions, the rigidity of the gel increasing with increasing potassium ion concentration.
Effect of Potassium Chloride on Gel Strength of Kappa Carrageenan Gel 1.50% Kappa Carrageenan

Potassium ions also have the effect of increasing the melting and gelling temperature.

<table>
<thead>
<tr>
<th>Ionic radius, A</th>
<th>Na⁺</th>
<th>K⁺</th>
<th>Rb⁺</th>
<th>Cs⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ionic radius, A</td>
<td>0.60</td>
<td>0.95</td>
<td>1.33</td>
<td>1.48</td>
</tr>
<tr>
<td>Hydrated radius, A</td>
<td>3.40</td>
<td>2.76</td>
<td>2.32</td>
<td>2.28</td>
</tr>
<tr>
<td>Helix radius, A</td>
<td>1.9 - 1.4</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Calcium ions and barium ions increase the rigidity of a carrageenan gel, the effect being most pronounced when potassium ions are added as well.
Effect of Calcium Chloride on Gel Strength of Kappa Carrageenan Gel 1.50% Kappa Carrageenan

Effect of Barium Chloride on Gel Strength of Kappa Carrageenan Gel 1.50% Kappa Carrageenan

It is believed that calcium and barium ions form bridges between adjacent double helices through an electrostatic binding to two adjacent sulphate groups, thus stabilizing and strengthening the network.

When removing cations which cause gelation of carrageenan from the medium as well as from the carrageenan, a solution of carrageenan is obtained which does not form a gel irrespective of the temperature. As soon as gelling cations are present the carrageenan solution will gel at a specific temperature, the gelling temperature. Thus, the gelling temperature of a carrageenan solution is a function of the concentration of gelling cations present in the system.

\[ T_g = f \left( C_{\text{gelling cations}} \right) \]

The use in practice of the effect of potassium chloride on the gel strength and gelling temperature is limited by organoleptic considerations, due to the bitter taste of potassium chloride. The upper limit for delicately flavoured foods is 0.1-0.2% chloride. However, in salty foods such as meat products up to 0.5% of sodium chloride may be replaced by potassium chloride without detection.
Potassium chloride has the highest effect on gel strength per potassium unit but other potassium salts may be used for taste considerations. Potassium phosphates are neutral in taste whereas potassium citrate yields a more acidulous taste in acid systems at pH-values below 4.

A secondary function of the phosphates and citrates is to buffer the system to a relatively high pH, where the carrageenan is more stable.

The strongest kappa carrageenan gel is produced in the presence of potassium and calcium ions. However, the presence of calcium ions makes the kappa carrageenan gel brittle, whereas a pure potassium carrageenan gel is elastic, cohesive and transparent. Addition of sodium ions to a carrageenan gel makes the gel short and brittle. Large amounts of sodium ions disturb the gelation of carrageenan and reduce the gel strength. This is of special interest in gelled meat products in which sodium chloride is added as a spice.

Strength, texture and gelling temperature are influenced by other solutes than salts. Sucrose increases the gelling and melting temperature. High solids means that a higher temperature is needed in order to dissolve kappa carrageenan, and low pH increases the hydrolytic degradation of kappa carrageenan. Therefore, working with high solids one should add the acid as late in the process as possible.

In practice it is not possible to use kappa carrageenan in foods with a sugar content higher than 60%.

### Effect of Sucrose on Gelling and Melting Temperature of a Kappa Carrageenan Gel

- **0.65% Kappa Carrageenan**
- **0.13% Potassium Chloride**

Contrary to kappa carrageenan, iota carrageenan gels most strongly with calcium ions to form a very elastic and very coherent gel which is completely syneresis-free. Iota-carrageenan is an excellent water binder in concentrations as low as 0.2%. In combinations with kappa carrageenan it adds elasticity and prevents syneresis.

Iota carrageenan is the only carrageenan type which is freeze/thaw stable. Thus, a frozen iota carrageenan gel will be completely syneresis-free when thawed, unlike a kappa carrageenan gel.

### Interaction with Other Gums

Kappa carrageenan forms strong and brittle gels which exude water (syneresis) and in many applications such textural properties are disadvantageous.
Where gelatine has traditionally been the preferred gelling agent - particularly in dessert gels - combinations of kappa carrageenan and other gums have been used in an attempt to duplicate the texture produced by gelatine.

When locust bean gum is added to kappa carrageenan, the gel breaking strength increases reaching a maximum at a 1 : 1 ratio of the two hydrocolloids. Rigidity also increases, reaching a maximum at approx. 0.25% locust bean gum, while cohesiveness increases steadily with increasing locust bean gum concentration. From a sensory standpoint, locust bean gum makes the kappa carrageenan gel less brittle and more elastic, thus approaching the texture of a gelatine gel. At high locust bean gum levels, the gel becomes gummy and very difficult to break in the mouth.

Gels containing a 1 : 1 ratio of the two hydrocolloids are considered the most palatable. However, the breaking strength is too high. The breaking strength is decreased by reducing the concentration of hydrocolloids but this has an adverse effect on gel syneresis.

Contrary to locust bean gum, iota carrageenan significantly decreases the breaking strength and rigidity of kappa carrageenan gels, the effect being related to the proportion of iota carrageenan in the system. Cohesiveness stays constant, and this combined with lower breaking strength indicate that iota carrageenan makes the gel less brittle.

Iota carrageenan also increases water holding and sensory elasticity of the gels, thus making the gels more “gelatine-like“ than locust bean gum does.

Contrary to locust bean gum and iota carrageenan, amidated low methoxyl pectin does not contribute significantly to kappa carrageenan gel formation, the textural parameters of cohesiveness and elasticity being essentially the same as for pure kappa carrageenan. However, due to its excellent water holding properties, amidated low methoxyl pectin allows a decrease in the concentration of kappa carrageenan and produces softer, more palatable gels. The low cohesiveness of such gels may be increased by incorporating locust bean gum.

Another advantage of using amidated low methoxyl pectin is its excellent flavour release. On the negative side, pectin gels are always somewhat cloudy and dessert gels made with amidated low methoxyl pectin are not as transparent as those made from pure carrageenan.

Addition of xanthan gum makes a kappa carrageenan gel softer, more cohesive, and more elastic. In addition, xanthan gum reduces syneresis as much as iota carrageenan does. A disadvantage of using xanthan gum in combination with kappa carrageenan is that such gels contain air bubbles which detract from their appearance. This is apparently due to the high „working yield value“ of xanthan gum, which makes the air bubbles difficult to remove even at higher temperatures.

Contrary to locust bean gum, guar gum does not exhibit synergistic effect with kappa carrageenan. Like locust bean gum guar gum is a galactomannan, but two factors make these gums different. Firstly, guar gum contains approximately twice the amount of galactose. Secondly, the length of unsubstituted regions in guar gum is significantly shorter than those in locust bean gum.
This difference in arrangement of galactose explains why guar gum is cold soluble whereas lucust bean gum must be heated to temperatures above 80 - 90°C in order to dissolve.

Furthermore it explains why carrageenan may interact with locust bean gum and not with guar gum.

**Schematic representation of the structure of locust bean gum and guar gum.**

G = • (1 → 6)-D-galactose. The arrows indicate possible interaction sites of kappa and iota carrageenan.

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**Milk Reactivity**

Carrageenan reacts with the fraction of milk protein called kappa casein, resulting in the formation of a three dimensional network (a gel) within which water, salts, and particles are trapped.

Being a protein, kappa casein possesses a positively and a negatively charged terminal, and the overall charge is dependent upon the pH of the medium. At the isoelectric pH, the overall charge of the protein is zero.

For kappa casein the isoelectric pH is 4.4, and below pH = 4.4 the protein is positively charged while the overall charge is negative at pH-values above 4.4.

Being a sulphated galactan, carrageenan is negatively charged independent of the pH of the medium. At pH-values below 4.4 kappa casein and carrageenan are oppositely charged, and a carrageenan-kappa casein complex will precipitate. At pH-values above 4.4 carrageenan and kappa casein bear the same overall charge, but the two molecules do not repel one another.

Milk contains large amounts of calcium ions, and one way of explaining the reaction between carrageenan and kappa casein is the formation of a calcium bridge between the two molecules.
This theory, however, is not able to explain the interaction between carrageenan and kappa casein completely, as carrageenan and kappa casein react without calcium ions present.

Kappa casein is composed of a large number of aminoacids (approx. 170), some of which are more electropositive than others. In fact, an extensive positively charged region exists between the residues 20 and 115 of kappa casein.

Such a distribution of negative and positive aminoacids is not found in beta casein nor in alpha S1 casein. The positively charged region in kappa casein is large enough to make the electrostatic interaction with carrageenan possible.
The interaction between kappa casein and carrageenan is, however, not responsible for the gelation of milk products.

On cooling below the gelling temperature of carrageenan, sectors of carrageenan molecules form double helices as in water systems, but the kappa casein-carrageenan interaction reinforces the network, and as a result the necessary amount of carrageenan to gel a milk system is much less (approx. 1/5) of the amount necessary to gel a water system. Similarly lambda carrageenan produces viscosity in milk in concentrations of 0.05-0.1% where a similar effect in a water system would require a concentration of 0.5-1.0%.

Rheology
Carrageenan solutions show pseudoplastic flow behaviour as do most hydrocolloids: With increasing shear rate the viscosity decreases whereas the viscosity instantly increases as the shear rate is decreased.

Flow Curve of Kappa Carrageenan
Water Solution
1.50% Kappa Carrageenan
Solutions of carrageenan have low viscosity and are thus easy to handle. A kappa carrageenan water gel is irreversibly destroyed when subjected to shear. Kappa carrageenan water gels are thus not thixotropic.

When used in low concentrations in milk, kappa carrageenan shows rheological properties similar to those of iota carrageenan in water. Hence, the weak gel produced by the kappa carrageenan-milk protein complex breaks when shear is applied and the flow becomes pseudoplastic. When shear is decreased the gel reforms thus showing a thixotropic nature.
The weak gel - the small yield value ($\bar{\tau}_0$) - is sufficient to prevent solid particles, for instance cocoa particles, from settling.
Commercial Carrageenans

POWDER CHARACTERISTICS AND STORAGE STABILITY
Carrageenan is sold as a powder. The colour ranges from white to brownish depending on raw material and process used. A typical mesh specification is

99% through a 60 mesh (0.25 mm) sieve.

A typical powder density of an alcohol precipitated carrageenan is 0.7.
A typical equilibrium water content of an alcohol precipitated carrageenan is

15% at 50% r.h. 25% at 70% r.h.

Carrageenan is insoluble in organic solvents such as alcohol, ether, and oil.

Solubility in water depends on the structure of the particular carrageenan, the medium, and the temperature. Generally the gelling carrageenans must be heated to dissolve whereas non-gelling carrageenans may be dissolved in cold water.

Stability
Carrageenan will depolymerize slowly when stored. As the two most important properties of carrageenan, gel strength and protein reactivity, are hardly dependent on degree of polymerization, the loss in strength over a period of one year at room temperature is undetectable.

It is generally undesirable to blend a carrageenan powder with other powdered or crystalline ingredients of an acidic nature. However, when specific precautions are taken, it is possible to make stable blends of carrageenan and citric acid for example.

STANDARDIZATION
Carrageenan is used in concentrations from as low as 0.005% to as high as 3.0% in a broad variety of products. Many types of carrageenan are made, some being standardized for general use as a gelling agent in water or milk systems and some being controlled by application tests, designed in coorporation between the user and the manufacturer.

Standardization is done by blending different batches of carrageenan and/or by blending with an inert material such as sucrose or dextrose.

Standardization of carrageenan with sugar is recognized in the EU stabilizer directive and the FAO/WHO-specification.

QUALITY CONTROL
Carrageenan has a high (natural) ash content, originating from the sulphate half ester groups and the cations. On ashing, some of the sulphate evaporates as SO$_3$, and the ash content is accordingly found to be lower than expected from SO$_4$ and cation content.

Reference is made to our Product specification for carrageenan, PS 002.
Applications

FOOD APPLICATIONS
Water Based Foods

Gel Formation
Carrageenan is a thermoreversible gelling agent. Gel formation is obtained only in the presence of potassium ions (kappa and iota carrageenan) or calcium ions (iota carrageenan).

When potassium ions are present, and the system is cooled below the gelling temperature, the carrageenan gels instantaneously.

As no methods of releasing potassium slowly from slightly soluble salts or complexes are known today, potassium must be present in the system or added to the system before cooling below the gelling temperature in order to avoid pregelation. However, in certain applications for instance in the making up of solid bacteriological media, gelation by diffusion of potassium ions may be used. Carrageenan may be used in instant preparations (powders to be dissolved in cold water). However, only a thickening effect is obtained, caused by swelling of the carrageenan.

When the soluble solids content increases much above 50%, the gelling temperature of carrageenan is increased to a level that limits its use. High temperature, in combination with acid-pH normally applied in products with more than 50% soluble solids, causes rapid depolymerization of carrageenan. In spite of the fact that carrageenan is a weaker gelling agent than agar, carrageenan finds extensive use as a gelling agent and stabilizing agent in the water phase of foods. This is mainly due to carrageenan’s ability to produce gels with a wide variety of textures. This is understandable when it is considered that carrageenan is not just a single polymer-type but rather family of gelling and non-gelling sulphated galactans.

Combination with locust bean gum further expands the texture range available. Iota carrageenan gels exhibit the unique property of freeze/thaw stability and thixotropy.

The thixotropic nature of an iota carrageenan gel is essential when ready-to-eat water gels are filled at temperatures below the gelling temperature. Cold filling makes it possible to produce dessert gels topped with whipped cream or multilayer desserts and only an iota carrageenan gel will reform after mechanical destruction.

STABILIZATION
Permanent stabilization of a suspension requires the continuous liquid phase of the food to shows a yield value (a gel).

Sedimentation rate decreases with decreasing difference in specific gravity and increasing viscosity (Stokes law). Increased viscosity will slow down the sedimentation but (unless the continuous phase possesses a yield value, i.e. is a weak gel, which traps the solid particles) the sedimentation rate will never be zero.
Carrageenan is used in low concentrations to stabilize suspensions and emulsions. When used in the proper low concentrations the gel structure of the carrageenan is not detectable when the suspension is poured and consumed.

When the milk protein reactivity of carrageenan cannot be used (for instance in salad dressing and in soy protein based drinks) iota carrageenan is the preferred carrageenan as iota carrageenan produces thixotropic water gels.

Apart from the stabilizing property, carrageenan may be used to increase viscosity and add mouthfeel to a liquid food product.

**Milk Based Foods**

In milk products where gelation or structural viscosity is required, carrageenan is normally preferred of function and economic reasons.

In gelled milk desserts kappa carrageenan is the most economical gelling agent to obtain a certain firmness, and is widely used in powder preparations for making flans.

In ready-to-eat flan desserts the kappa carrageenan has insufficient water binding over the required shelf life of several weeks and „weaker“ kappa types, sometimes combined with iota types or LM-pectin, are used.

When ready-to-eat milk dessert must be topped with whipped cream, cold (10°C) filling must be used. Only iota carrageenan can be used as it gives a thixotropic gel - a gel which reforms after mechanical destruction.

Stabilization of cocoa particles and fat suspension in chocolate milk is obtained with as little as 0.02-0.03% kappa carrageenan. Viscosity control and foam stability of instant breakfast preparations are obtained by incorporation of lambda carrageenan. Ice cream stabilizers based on guar gum, locust bean gum and/or cellulose gum cause separation (whey off) of the ice cream mix. Low concentrations (0.01-0.02%) of kappa carrageenan forms a weak gel in the ice cream mix which prevents the separation.

**Non-Food Applications**

Gel formation, thickening effect, film forming ability, and diffusion rate in carrageenan gels are some of the properties which make carrageenan suited in many non-food applications.

The ability of binding water effectively and forming weak water gels which are very stable against enzymatic degradation makes carrageenan unique as a thickener in toothpaste, the gel imparting excellent stand up of the paste and excellent flavour release and rinsability.

The film forming ability of carrageenan makes carrageenan an excellent conditioner in shampoo, as well as a suitable tablet coating agent.

In photographic films carrageenan may be used to increase the melting temperature of the gelatine gel.

The ability to form strong water gels in which solutes diffuse rapidly makes carrageenan a possible gelling agent for immobilization of enzymes and living cells.
Special carrageenans, which are chemically gelled without applying heat may find use as gelling agents for solid bacteriological media.

**GENU Carrageenans**

GENU carrageenans are purified, natural hydrocolloids extracted from selected species of red seaweed and marketed as highly active, standardized powdered carrageenans:

- GENULACTA types find application in milk systems
- GENUGEL types find application in water systems
- GENUVISCO types are used as thickening agents/stabilizing agents.

GENU carrageenans have established their position within the food industry as uniform gelling and texturizing agents of high quality.

GENU is the trademark for pectins and carrageenans marketed by CP Kelco ApS who is the largest and most modern plant for manufacturing natural hydrocolloids. GENU pectins and carrageenans are marketed in more than sixty countries.

In the research and application laboratories of CP Kelco formulas and processing methods for new and traditional food products are continuously developed and perfected. In close contact with the industry new carrageenan types and production processes are further developed to meet specific demands within the market.

Customer service is considered a very important part of the activities of CP Kelco ApS.

**Additional literature is available - such as: Application Guides and Application Notes**

Application guides providing an overview of a particular application area (e.g. milk products, meat products, etc.). Application Notes offering specific recipe suggestions.

Individual technical advice freely available throughout the world either by contacting our local sales representatives or directly from:

**CP Kelco ApS**  
**DK-4623 Lille Skensved, Denmark**

Phone:  +45-56 16 56 16  
Telefax:  +45 56 16 94 46