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The Americas:

1735 Market Street
Philadelphia, PA 19103
Phone: 1-800-526-3649 Fax: 1-215-299-5809
1-215-299-6234

Galeria Plaza
Av. Dr. Jose Bonifácio
Coutinho Nogueira 150-1° A
13091-611 Campinas
Sao Paulo, Brazil
Phone: 55-19-3735-4465 Fax: 55-19-3735-4480

Av. De las Granjas No. 300
Colonia Electricistas
Del. Azcapotzalco
C.P. 02060, Mexico, D.F.
Phone: 52-55-352-3589 Fax: 52-55-352-3273

Europe:

Avenue E. Mounier 83
1200 Brussels, Belgium
Phone: 32-2 775-8311 Fax: 32-2 775-8300

Toll-free Phone Numbers:

Belgium: 0800-73663
France: 0800-908120
Germany: 0800-1818841
Netherlands: 0800-0229205
Spain: 0900-973251
United Kingdom: 0808-2341126

Asia Pacific:

FMC (Shanghai) Commercial Enterprise
Room 105, Innovation Building
1009 Yi Shan Lu
Shanghai 200233
Peoples Republic of China
Phone: 86-21 5427-1177 Fax: 86-21 5427-0193

FMC BioPolymer

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FMC Marine Colloids™ Carrageenan

General Technology

- DANAGEL™
- GELCARIN®
- ISAGEL™
- LACTARIN®
- LACTOGEL™
- SEAGEL®
- SEAKEM®
- SEASPEN®
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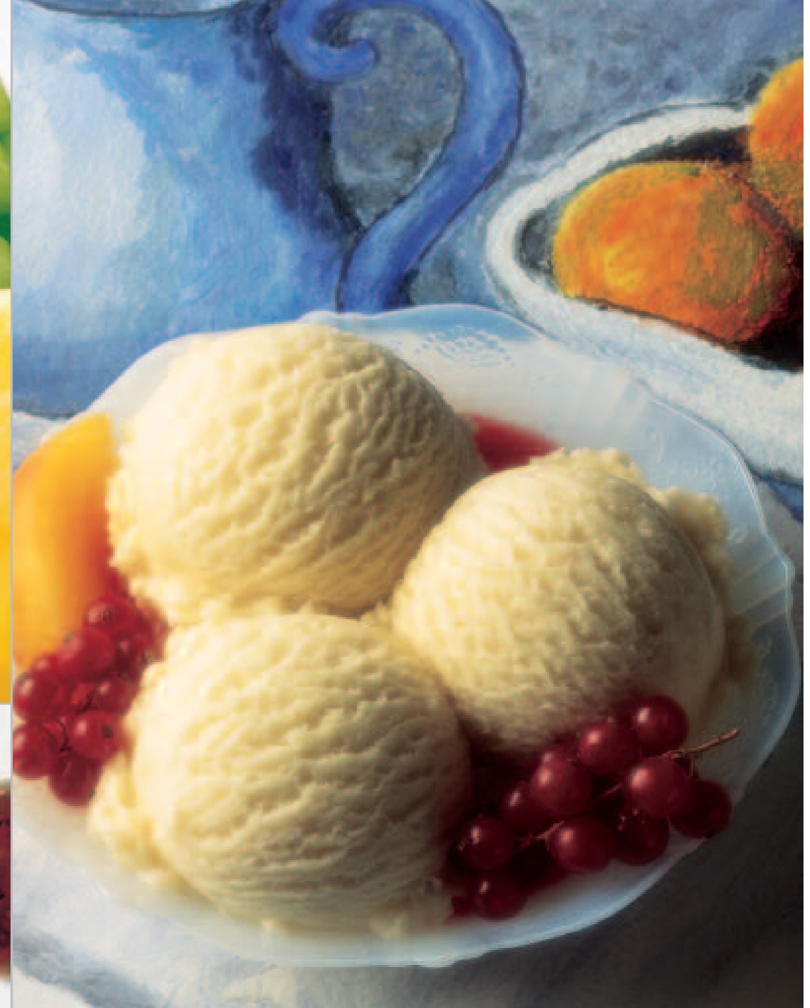


Know how. It works.[SM]

With over 60 years of experience in the development and production of carrageenan products, FMC BioPolymer is well prepared to serve you as a resourceful and reliable partner.

Working with a broad palette of carrageenans and an even broader range of problem-solving skills, our know-how can help you add structure, texture and stability to achieve optimum results.

Our high quality carrageenans are manufactured under the stringent requirements of ISO certification. And the customer service we provide, both before and after the sale, adds great value to our products. You can rely on us for the sound advice and formulation and processing problem-solving that can help you reach new levels of efficiency in your operation. You can also count on FMC BioPolymer to help turn your innovative thinking into practical, profitable reality.

FMC BioPolymer. Adding structure, texture and stability– naturally.

Danagel *Gelcarin* *Isagel* *Lactarin*

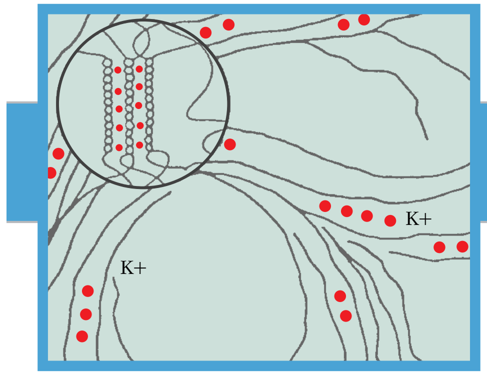
An Introduction to Marine Colloids™ Carrageenan

Carrageenan is a naturally-occurring family of carbohydrates extracted from red seaweed. From this natural source, FMC BioPolymer develops and customizes blends of carrageenans for specific gelling, thickening, and stabilizing properties.

FMC BioPolymer is the largest and most experienced producer of carrageenan extracts worldwide. During the past 60 years, FMC BioPolymer has established a tradition for providing high quality carrageenans, technical expertise, and service.

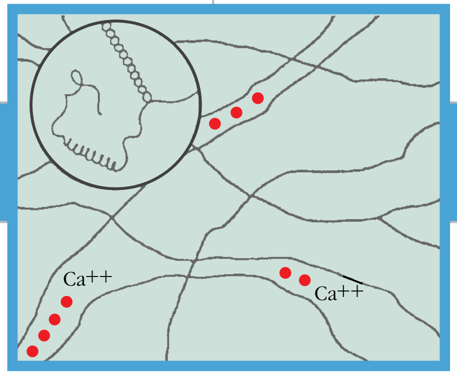
FMC BioPolymer builds quality and performance into its carrageenan products at three levels—seaweed sourcing, extract manufacturing, and understanding and tailoring the functional properties of each product.

The Three Basic Types of Carrageenan



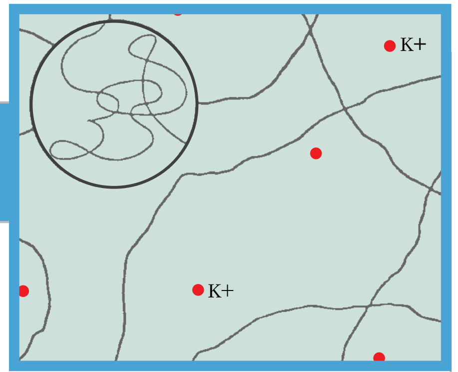
Kappa carrageenan (Figure 1)

- Soluble in hot water
- The addition of potassium ions induces the formation of a durable, brittle gel; it also increases the gelling and melting temperatures.
- Strong, rigid gel, some syneresis, forms helix with K+ ions. Ca++ causes helices to aggregate and the gel to contract and become brittle.
- Slightly opaque gel. Becomes clear with sugar.
- Approximately 25% ester sulfate and 34% 3,6-AG
- Compatible with water miscible solvents
- Insoluble in most organic solvents
- Typical use levels — 0.02 to 2.0%



Iota carrageenan (Figure 2)

- Dilute solutions exhibit thixotropic characteristics
- Soluble in hot water; sodium iota carrageenan is soluble in cold and hot water
- The addition of calcium ions will induce the formation of a durable, elastic gel, and increase gelling and melting temperatures.
- Elastic gels, forms helix with Ca++. Limited aggregation contributes to elasticity, no syneresis.
- Clear gel
- Freeze/thaw stable
- Insoluble in most organic solvents
- Approximately 32% ester sulfate and 30% 3,6-AG
- Typical use levels — 0.2 to 2.0%



Lambda carrageenan (Figure 3)

- Free flowing, non-gelling pseudo-plastic solutions in water
- Partially soluble in cold water, fully soluble in hot water
- No gel, random distribution of polymer chains
- Range from low to high viscosity
- Addition of cations has little effect on viscosity
- Compatible with water miscible solvents
- Insoluble in most organic solvents
- Stable over a wide range of temperatures, including freeze/thaw cycles
- Soluble in 5% salt solution, hot or cold
- Approximately 35% ester sulfate and little or no 3,6-AG
- Typical use levels — 0.1 to 1.0%

Manufacturing

Quality control of carrageenan extract begins at the harvest. FMC BioPolymer sources its raw materials from independent seaweed harvesters worldwide and FMC BioPolymer-operated cultivation sites. The seaweed is systematically gathered, quickly dried and then baled to maintain its quality.

At the manufacturing site the dried seaweed is mechanically ground and sieved to eliminate impurities such as sand and salt.

Following extensive washing to ensure additional quality, the seaweed undergoes a hot extraction process to separate the carrageenan from the extraneous plant fiber.

Removal of the cellulosic material requires a two-step clarification process. First, we centrifuge the dissolved carrageenan mixture to eliminate the dense cellulosic particles. Then, filtration is used to remove the smaller particles.

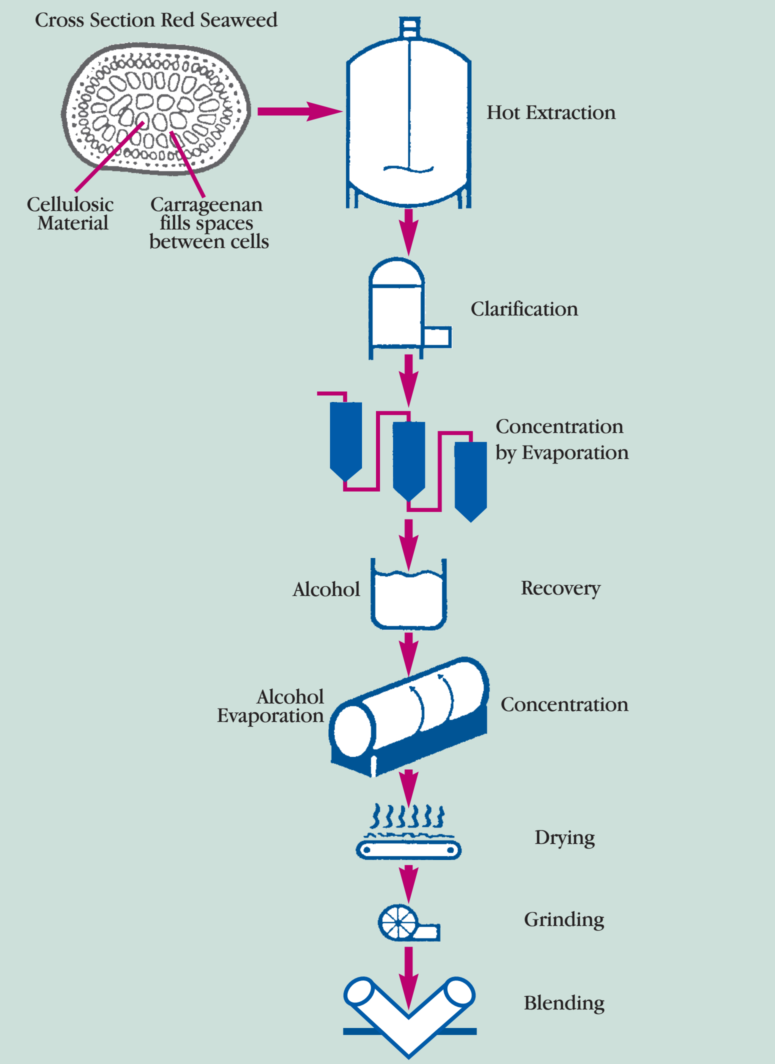
The solution is then concentrated by evaporation to accommodate the removal of water.

The concentrated carrageenan solution is precipitated in isopropyl alcohol. As carrageenan is insoluble in alcohol, the filtrate turns into a coagulum of carrageenan, alcohol and water. The coagulum is compressed to remove the liquids and vacuum dried to completely remove the alcohol.

Drying is completed on a belt drier and the dried coagulum is then ground to specification.

Finally, the carrageenan is blended to meet the finished product's exact specifications.

Figure 4– Manufacturing process

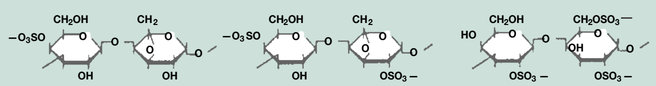


Chemistry, Functions & Properties

Carrageenan is a high molecular weight polysaccharide made up of repeating galactose units and 3,6 anhydrogalactose (3,6-AG), both sulfated and nonsulfated. The units are joined by alternating alpha 1-3 and beta 1-4 glycosidic linkages.

The primary differences which influence the properties of kappa, iota and lambda carrageenan are the number and position of the ester sulfate groups on the repeating galactose units. Higher levels of ester sulfate lower the solubility temperature of the carrageenan and produce lower strength gels, or contribute to gel inhibition (lambda carrageenan).

Figure 5– Properties of carrageenan



	Kappa	Iota	Lambda
Solubility			
80°C (176°F) Water	yes	yes	yes
20°C (68°F) Water	Na+ salt soluble	Na+ salt soluble	yes
	K+, Ca++ and NH_4+ salt swells	Ca++ salt swells to form thixotropic dispersion	
80°C (176°F) Milk	yes	yes	yes
20°C (68°F) Milk	no	no	thickens
50% Sugar Solution	hot	no	yes
5% Salt Solution -Hot	swell	swell	soluble
5% Salt Solution -Cold	no	no	soluble
Gelation— Heat to 80°C (176°F)/Cool to <49°C (120°F)			
Strongest Gels	with K+ ion	with Ca++ ion	no gel
Gel Texture	brittle	elastic	no gel
Regelation after Shear	no	yes	no
Syneresis	yes	no	no
Freeze/Thaw Stability	no	yes	yes
Synergism with Locust Bean Gum	yes	no	no
Interaction with Milk Proteins	brittle gel	elastic gel	weak gel
Acid Stability*			
Hot Solutions	no	no	no
Gels	stable above pH 3.8	stable above pH 3.8	not applicable

*Hydrolysis in low pH systems accelerated by heat

Functions

Binds Moisture– Carrageenan has excellent moisture binding capabilities. This allows formulators to manage water and other aqueous fluids in their systems.

Stabilizes Emulsions– Although carrageenan is not a surfactant, it will stabilize existing emulsions. Its thickening and thixotropic properties give integrity to the system and inhibit the oil from coalescing and separating into an oil phase and water phase.

Suspends Particles– The 3-dimensional network which helps stabilize emulsions also functions to suspend particulates. Insolubles will remain uniformly distributed in the bottle for extended periods without remixing or shaking.

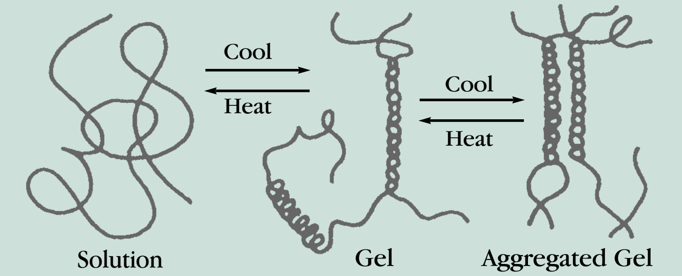
Controls Flow Properties– Controlling flow properties of food systems is essential from processing to the final product consistency. Carrageenan is thermally-reversible, so at high temperatures it will impart minimal viscosity, allowing for easier processing conditions and improved heat transfer. Upon cooling the carrageenan will thicken. With most gelling carrageenans, solutions will begin to solidify and form gels when cooled below 49°C (120°F).

Produces Stable Gels at Room Temperature– Most kappa and iota carrageenan solutions will set into a gel structure at ambient temperatures. The gels require heat to melt into a fluid state for reprocessing.

Generally, carrageenan should be dispersed in cold water and then heated above the solubility temperature of the carrageenan to obtain maximum functionality. There are several other methods of incorporating carrageenan into complex systems or processes that allows it to offer optimum functionality.

Upon cooling and in the presence of appropriate cations, kappa and iota carrageenan polymers align themselves to form individual helices. These helices can further associate with divalent cations that are present, e.g. calcium, to form a gel matrix. **Figure 6** is a schematic representation of the gelling mechanism for carrageenan.

Figure 6– Gelation mechanism



Water Systems

Kappa carrageenan binds water to form strong, rigid gels. Potassium salts are essential in order to form this firm gel structure. As the level of potassium is increased, the resulting gel structure becomes tightly aggregated and may cause syneresis (moisture on the gel surface).

Iota carrageenan also binds water, but forms a dry, elastic gel, especially in the presence of calcium salts. The divalent calcium ions help form bonds between the carrageenan molecules to form helices. The 2-sulfate group on the outside of the iota carrageenan molecule does not allow the helices to aggregate to the same extent as kappa carrageenan, but form additional bonds through calcium interactions. The gels are more elastic, dry and provide excellent freeze/thaw stability.

Lambda carrageenan is highly sulfated and therefore less likely to form a gel structure. The ester sulfate distribution of lambda carrageenan is randomly distributed on the molecule. This prevents gelation and promotes viscous solutions. Lambda carrageenan is primarily used to thicken liquids and modify the texture of foods.

Gel Texture

The gel texture of the basic carrageenans can be modified by blending carrageenans to meet specified gel texture parameters. **Figure 7** (at right) illustrates the penetration or elasticity of carrageenan gels before the gels are fractured. The gels can be made more elastic or less elastic by combining kappa and iota carrageenans until the desired texture is achieved.

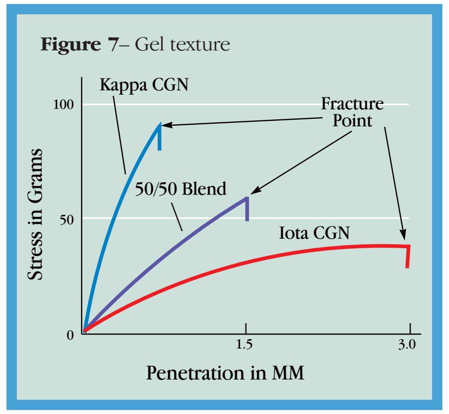


Figure 7– Gel texture

Gels prepared with carrageenan are thermally-reversible. The gels will become fluid when heated above the gels' melting point and will reset into a gel when cooled, with minimal loss of the original gel strength.

Factors Affecting Water Gels

Cations– As the absolute concentration of cations increases:

- dispersion improves
- temperature at which carrageenan goes into solution increases
- gelling temperature increases
- remelt temperature increases

Potassium and calcium ions are essential for effective carrageenan gelation. Increasing the level of potassium ions increases the strength of the resulting gel. **Figure 8** illustrates the relative increase in gel strength when the level of potassium (% KCl) is increased.

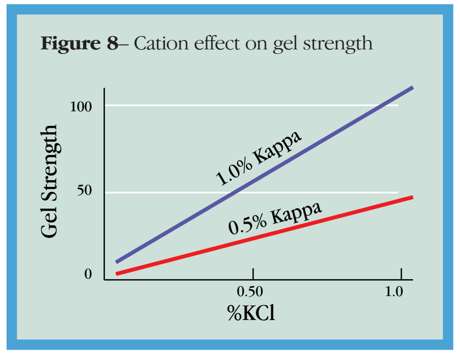


Figure 8– Cation effect on gel strength

Temperature– As discussed earlier, carrageenan water gels are thermally reversible. The gels can be subjected to repeated heat/cool cycles with very little effect on the resulting gel structure (at neutral pH).

The set and melt temperatures of carrageenan gels are dependent on cation concentration. Increasing the level of calcium or potassium in an aqueous solution will result in increased gelling temperatures as illustrated in **Figure 9**.

This allows formulators to regulate gelling and melting temperatures to accommodate their processing parameters. Most other hydrocolloids do not offer this flexibility.

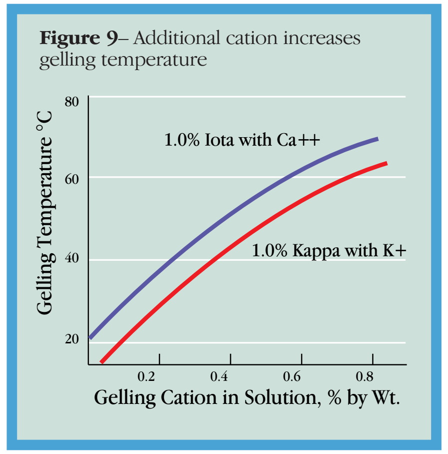


Figure 9– Additional cation increases gelling temperature

Sugars– High levels of sugars, a common component in many food gels, reduce the solubility of carrageenan. Carrageenan should be dissolved in available water if the sugar concentration of the food system is higher than 50% of the finished product.

Synergism with Other Gums– Kappa carrageenan is synergistic with locust bean gum and konjac flour. The interaction significantly increases gel strength, improves moisture binding capabilities and modifies gel texture to be more elastic and resilient, as shown in **Figure 10**.

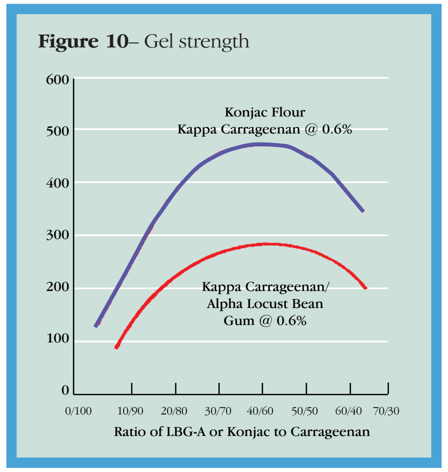


Figure 10– Gel strength

Synergism with Starch– Iota carrageenan increases the viscosity of starch systems by as much as 10 times the viscosity of the starch alone. When kappa carrageenan is added to starch systems no increase is noted.

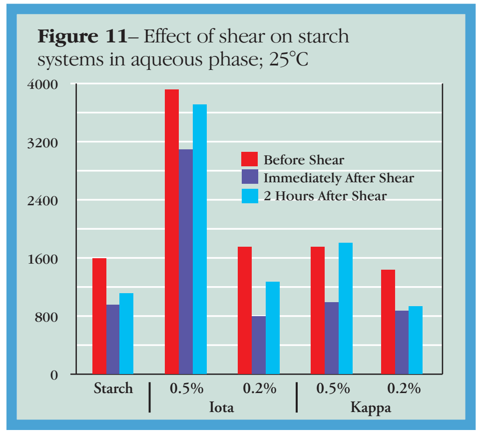


Figure 11– Effect of shear on starch systems in aqueous phase; 25°C

Figure 11 compares the effects of shear on a starch-only system with starch/iota carrageenan and starch/kappa carrageenan systems. The starch system exhibits a loss in its viscosity when subjected to shear. The presence of 0.5% kappa or iota carrageenan allows a starch system to recover its pre-shear viscosity.

Carrageenan may be useful in altering the textural, mouthfeel and processing properties of a starch system. The increased viscosity will allow processors to reduce the overall starch content, often by as much as 35-40%, and improve the texture and flavor release of the finished product.

Acidulants or pH– Solutions and gels that are formed with carrageenan are stable at room and refrigerated temperatures. At high temperatures, carrageenan solutions that contain acidulants exhibit some loss in viscosity and potential gel strength. See **Figure 12**.

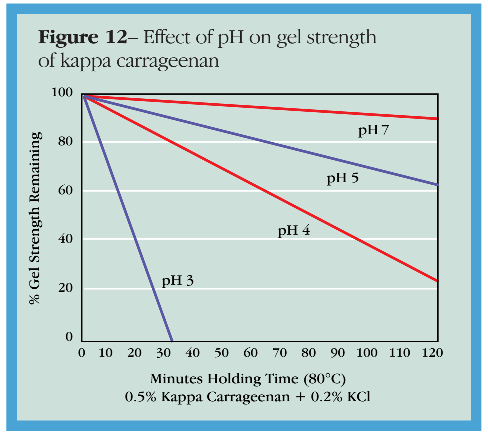


Figure 12– Effect of pH on gel strength of kappa carrageenan

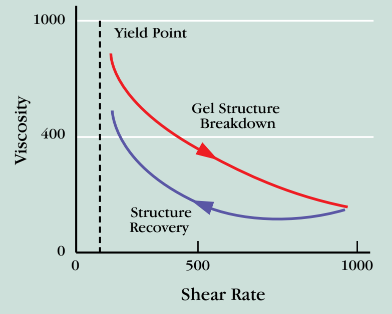
In low pH systems, it is recommended that the acidulant be added at the last step of processing, or just prior to filling into containers.

Thixotropy

At low concentrations iota water gels have thixotropic rheological properties. They can be fluidized by agitation or shear and will form elastic gels when allowed to stand quiescently. **Figure 13** illustrates the gel structure breakdown of dilute iota carrageenan as shear is increased. The gel structure is recovered when shear is removed. This thixotropic property is especially useful for suspending insoluble particulates.

Water gels formed with kappa carrageenan are not thixotropic; once the gel is broken it will not reset unless the gel is heated and then cooled again.

Figure 13– Thixotropic properties of dilute iota carrageenan gels

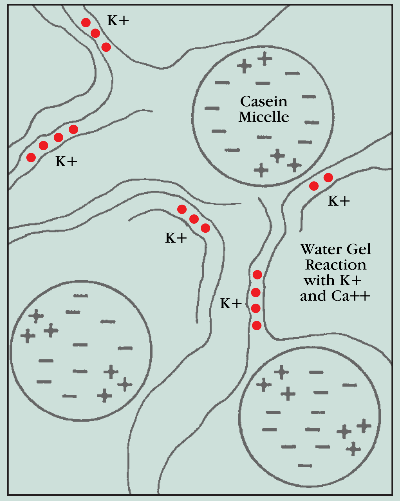


Milk Protein Interaction

In food systems, one of the most important properties that truly differentiates carrageenan from other hydrocolloids is its ability to complex or interact with proteins. In milk protein systems, at peripheral locations on the casein micelle there is a concentration of positive charges. This positive electrostatic charge attracts the negatively-charged sulfate groups of the carrageenan molecule to form linkages among the dispersed casein micelles as illustrated in **Figure 14**. This reaction, in combination with the normal water gelling capabilities of carrageenan can increase the gel strength about 10-fold.

Carrageenan's ability to complex with milk proteins, combined with its water gelling properties enhances carrageenan's functionality, e.g. increased gel potential. For this reason carrageenan will form a weak thixotropic gel structure which will suspend cocoa in chocolate milk at 0.02% and form milk gels, such as flans, at 0.20%.

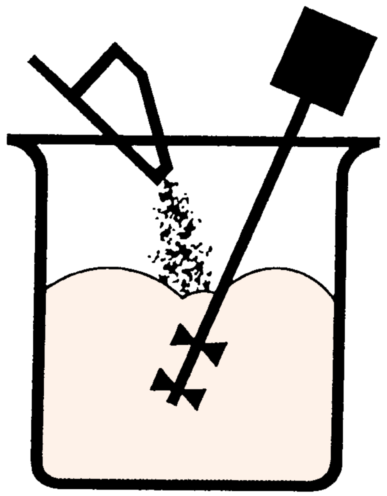
Figure 14– Interaction of milk protein with carrageenan



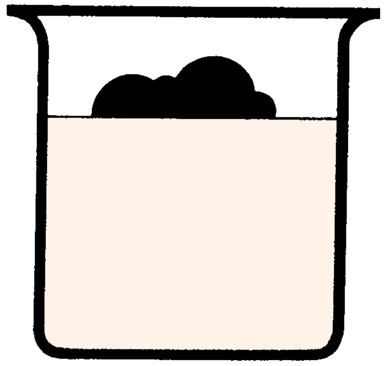
How to Disperse and Solubilize

Generally, carrageenan should be dispersed in cold water, and then heated above its solubility temperature to obtain optimum functionality. The solubility temperature will depend on the level of potassium and calcium ions associated with the carrageenan or the amount of salt present in the water. Both kappa and iota carrageenans typically require heating to 77°-79°C (170-175°F) for complete solubility. Higher activation temperatures may be necessary should solids or cations be present in high concentrations.

How to Mix Carrageenan



DO add the stabilizer slowly to rapidly agitated water.



DON'T allow to lump by trying to dissolve the stabilizer too fast.

For easy dispersion and to avoid lumping, use any of the following recommendations:

- Premix the carrageenan with a dispersant, such as sugar. Use a minimum of 5 parts by weight of the sugar before dispersing into cold water or milk. The carrageenan can also be blended with the dry ingredients in the formulation to avoid lumping,

OR

- Disperse carrageenan in liquid sugar, salt or glycerin (if present in the formulation). These ingredients retard the hydration of carrageenan which make it easier to disperse and dissolve.
- Add the carrageenan powder slowly to the vortex of rapidly agitating fluid.
- Agitate vigorously with a high speed mixer.
- Heat carrageenan to 82°C (180°F) to solubilize, unless the carrageenan is designated to be cold soluble or swelling.

Cold soluble carrageenans may be dispersed into cold water by adding the carrageenan powder slowly with agitation. Premixing with sugar is recommended.