

ABSTRACT

Title of Thesis:

**RHEOLOGICAL AND TEXTURAL
CHARACTERISTICS OF
COPOLYMERIZED HYDROCOLLOIDAL
SOLUTIONS CONTAINING CURDLAN
GUM**

Lisa Noel Sadar, Master of Science, 2004

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Curdlan, a microbial hydrocolloid, has the ability to form strong, irreversible gels when heated above 80°C, which distinguishes curdlan from other hydrocolloids. To date, however, very limited information is available on copolymerized solutions containing curdlan gum and other hydrocolloids.

The objective was to characterize the rheological and textural behavior of copolymerized hydrocolloidal solutions containing curdlan gum.

Hydrocolloidal mixtures containing curdlan were prepared respectively with carrageenan, xanthan, guar, and locust bean gum. Rheological properties under shear and dynamic shear at various concentration ratios were measured using an AR 2000 rheometer. The textural properties were measured using a TA.XT2i Texture Analyzer by Texture Technologies Corp.

Synergistic increases in apparent viscosity were observed when curdlan was combined with guar and locust bean gum, which is attributed to the chemical structure.

An additive effect was observed in gel strength for all copolymers. Curdlan added to the heat stability of locust bean and guar gum.

RHEOLOGICAL AND TEXTURAL CHARACTERISTICS OF
COPOLYMERIZED HYDROCOLLOIDAL SOLUTIONS CONTAINING
CURDLAN GUM

By

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Chapter 1

INTRODUCTION

Many ingredients are added to various food systems in order to provide a wide selection of products for the consumer to choose from. Food hydrocolloids or food gums are added to food systems for numerous reasons, mainly to modify the texture, increase the stability, or reduce the fat or calories of a product. Specifically, food hydrocolloids are used to thicken, gel, control syneresis, stabilize an emulsion or suspension, function as a coating, and bind water. Use of food hydrocolloids continues to increase with recent development of low-fat and reduced-fat products as well as in the formulation of products in need of thermal or freeze-thawing stability. There are a variety of hydrocolloids on the market, including those derived from plants or seaweed, and those produced by microorganisms. Increasing numbers of products in the form of a blend of hydrocolloids are now available commercially for specific areas of applications such as reduced gelling points or increased viscosity. However, only limited information exists in the literature that fully characterized their applicability in mixture.

It has been demonstrated that the structure of the hydrocolloid, including the type and number of monosaccharide backbone as well as the type, number, and distribution of side units, determines its characteristics and behavior in solutions. Moreover, the net charges on the polymeric side chains also play an important role in their functionality as well. In general, hydrocolloids have a

sugar backbone that contains protruding substituents such as esters, sulfates, or additional sugars. Hydrocolloids available for food applications are either neutral or negatively charged. Guar gum and locust bean gum, both classified as galactomannans with the same mannose backbone, are used in products such as cheeses, frozen desserts, processed meats, and bakery products. However, these two galactomannans differ in cold water solubility as well as in their gelling capability due to their difference in the degree of substitution and the distribution of side units. Carrageenan, a negatively charged hydrocolloid derived from red seaweed plants, has been widely used in ice cream, chocolate milk, jellies, sauces and dessert gels. The three basic types of carrageenan (kappa, iota, and lambda) exhibit their own unique properties when incorporated into food products, due mainly to the sulfate side groups and anhydro bridges, which are responsible for influencing cold water solubility and degree of rheological behavior (Moirano 1977; Hoefler 2001) . Xanthan gum, also negatively charged with trisaccharide side chains, is the most industrially important microbial exopolysaccharide known for its thickening ability and shear thinning behavior. The functionality of xanthan gum is highly dependent on the ionic strength of the solution (Sworn 2000), suggesting electrostatic interactions between the polymer and its surrounding electrolytes.

Curdlan gum, a neutral linear homopolymer produced by the microorganism *Alcaligenes faecalis* var. *myxogenes*, is known for its ability to form both thermal reversible and irreversible gels without the addition of cations or salts (Kanzawa 1987; Nakao 1991) and possesses special diffusion properties

because of its characteristic viscoelastic behavior (Lo 2003). With a backbone similar to cellulose, curdlan gum does not have protruding side units. Instead, it is a linear homopolymer chain. However, it is capable of forming complex tertiary structures believed to be caused by intramolecular and intermolecular hydrogen bonding (Nishinari 2000). Recently, researchers in the Food Bioprocess Engineering Laboratory at the University of Maryland discovered that, unlike other hydrocolloids, curdlan gel forms smooth layers of sheets when frozen and dried, indicating an intriguing two-dimensional network of the gel (Lo 2004). This two-dimension configuration indicates a different pattern of stretch during the polymerization process and suggests potential notable effects on the textural and flow behavior of other hydrocolloidal polymers

The ultimate goal of this study was to elucidate and characterize the interactions of curdlan with carrageenan, xanthan, guar, and locust bean gum. To achieve the goal, there were two specific objectives to accomplish. First, the rheological and textural properties such as steady state flow, dynamic oscillatory tests, and gel strength of the copolymers containing curdlan gum were investigated. The optimum combinations of curdlan gum with the other four hydrocolloids in terms of rheological and textural properties were identified using response surface methodology (RSM) (Wheeler 2003). Secondly, the stability of the copolymers over a wide range of temperature and freeze-thaw cycles were evaluated. It was anticipated that this work would provide useful information (e.g. synergistic or diminishing effects, if any) on the relationship and interactions among these food hydrocolloids.

Chapter 2

LITERATURE REVIEW

2.1 HYDROCOLLOIDS

Hydrocolloids are defined as “a macromolecular substance such as a protein or polysaccharide which swells by absorption of water, in some cases forming a stiff gel” (Ockerman 1978). Food hydrocolloids, or food gums, have high molecular weights when compared to carbohydrate ingredients, such as sugar or corn syrup (Hegenbart 1993). Food gums are usually added to food systems/products for specific purposes, such as thickening agents, stabilizers, emulsifiers, gelling, etc (Kuntz 1999; Hoefler 2001). Hydrocolloids ultimately alter the rheological properties in a desired fashion for food systems (Pedersen 1979).

2.1.1 Basic Structure

The typical structure of a food hydrocolloid includes a sugar backbone with protruding substituents (Kuntz 2002). The backbone can vary in length from several hundred to several thousand sugar units long (Kuntz 1999). These sugar units are most commonly linear in form, but branched backbones have been seen. The backbone provides pertinent information such as the acid stability of the particular hydrocolloid. The type, number, and distribution of substituents

protruding from the backbone determine whether a gum is a thickening agent or a gelling agent (Hegenbart 1993).

2.1.2 Factors Influencing Behavior

The four major factors influencing food gum properties include molecular weight, the monosaccharide backbone, type of side chains, and distribution of side chains (Kuntz 1999; Hoefler 2001). The molecular weight of the food gum is basically the chain length. An example presented by Hoefler (2001) includes a linear gum that occupies a certain volume as it randomly tumbles through a solution. If the chain length is doubled, the chain will now occupy eight times the volume it did before, thus it is eight times more likely to collide with an adjacent chain. These collisions and restrictions are referred to as resistance to flow, which is measured as viscosity. The composition of the backbone also indicates gum properties. The monosaccharide composition influences properties such as pH stability, ability to thicken or gel in food systems. Therefore the molecular weight and monosaccharide composition affects the final behavior of the food hydrocolloid (Hegenbart 1993).

In addition to those two factors, the type of side chains or substituents also plays a part in determining gum behavior (Klahorst 2002). The main influence of side units is whether the gum will become a thickening or a gelling agent. Side chains can vary drastically in size. In the case of pectin and carrageenan, the side units are small in size and are simply a carboxyl or a sulfate group respectively. Side units can be an additional sugar protruding off the backbone as is the case

with both guar gum and locust bean gum. In the case of xanthan gum, the side unit is a whole group of sugars. Depending on the type of side chain, different properties can be seen.

The final factor that influences food gum properties is the distribution or uniformity of these side chains (Kuntz 1999). The distribution of side chains can determine cold water solubility and synergistic effects with other gums (Hegenbart 1993; Hoefler 2001). Substituents are distributed either evenly or unevenly on the sugar backbone. Uneven substitution results in smooth and hairy regions. Smooth areas are defined by areas on the backbone that do not contain any side units. In contrast, hairy regions contain a cluster of side units projecting from the backbone. An example of distribution of side units is seen by locust bean gum and guar gum. Both hydrocolloids have the same galactomannan backbone, but locust bean gum is unevenly distributed and guar gum is evenly distributed. Due to the substitution difference, they both possess different cold water solubility properties as well as synergistic relationships with other gums.

The next question to address is why side units are needed on these backbones. They weaken the intermolecular association between layers and may provide space for water to “slip” between layers, thus making the hydrocolloid water soluble (Hoefler 2001). The substituents prevent hydrogen bonding to occur between the backbone chains. A common example is cellulose and cellulose gum. Cellulose is composed of layers of linear glucose molecules with hydroxyl groups protruding from each glucose molecule. Hydrogen bonding occurs at these hydroxyl groups with neighboring cellulose chains. The hydrogen

bonds are tight which prevents water from separating the chains, thus making the cellulose water insoluble. However, in the case of cellulose gum, carboxymethyl groups substitute some of the hydroxyl groups, which allow separation of adjacent cellulose chains. The substitution prevents hydrogen bonding from occurring which leads to water able to get between the chains and hydrate, thus making cellulose gum water soluble (Hoefer 2001).

Another example regarding the importance of substituents is with carrageenan. Carrageenan comes in three forms: kappa, iota, and lambda. All three have the same galactose sugar backbone, however, each varies with the number of sulfate groups and anhydro bridges. The sulfate groups (OSO^{-3}) increases water solubility whereas anhydro bridges have hydrophobic properties. The number of sulfate groups, anhydro bridges, and final texture is presented below in the table.

Table 1: Differences Between Carrageenan Types

	Kappa	Iota	Lambda
Sulfate Group	1	2	3
Anhydro Bridge	1	1	0
Texture	firm, brittle syneresis	elastic, cohesive no syneresis	no gelling, thickening provides "body"

Some other general concepts that need to be addressed are the degree of polymerization and degree of substitution (Kuntz 1999). Degree of polymerization (DP) is basically the chain length of the hydrocolloid. The higher the DP, the higher the viscosity of the hydrocolloid in solution. In addition to this, the bigger the chain length, or DP, the longer it will take to hydrate the

hydrocolloid. Degree of substitution (DS) is the number of side units for every sugar molecule. The more substitution the hydrocolloid has, the more water soluble it will be (Hoefler 2001). Therefore, this leads to quicker hydration of the gum. In addition to this, the higher the degree of substitution the more uniform the side units will be distributed.

Hydration of hydrocolloids is an important concept to mention as they behave very differently from common food ingredients (Imeson 2000; Klahorst 2002). In the case of ordinary food ingredients, such as sucrose, when they are introduced to water they begin to dissolve starting with the outside layer. As time passes, their general size decreases and soon they are fully dissolved in water. However, when hydrocolloids are introduced to water, they absorb water and swell, similar to that of a sponge (Deis 2001; Hoefler 2001). It will reach a maximum point where the molecules will start to unravel starting with the outside surface. In time, the molecules will float away resulting in a completely hydrated hydrocolloid. The figure below shows the difference between the hydration of sugars versus gums.

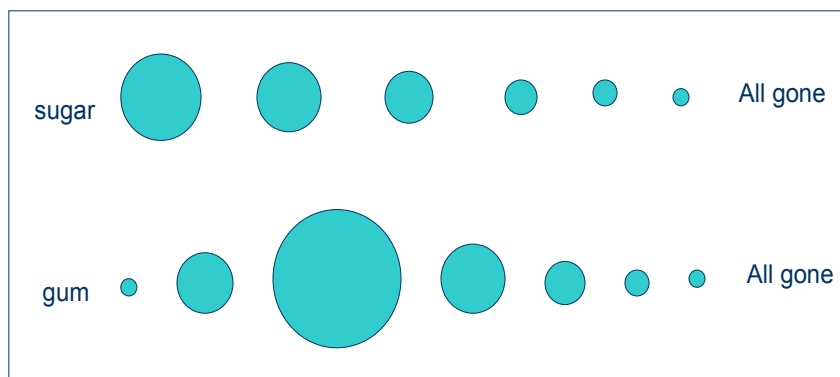


Figure 1: Hydration of hydrocolloids compared to Sugar

Due to the fact that food gums swell when they are first introduced to water, the particles need to be separated just before contacting the water surface (Imeson 2000; Hoefler 2001). If the gum particles would not be separated, each particle would absorb water, leading to swelling and would stick together to form a large lump. Lumping is not desirable, since it will take much time to fully hydrate each gum particle. Therefore, to insure lumping does not occur, the gum particles need to be slightly separated (Hegenbart 1993). Separation will allow each molecule to go through the initial swelling without colliding with any other swelling molecules. Particles can be separated one of four ways: eductor funnel, 5/1 sugar, non solvents, and high shear (Imeson 2000). An eductor funnel separates particles with a stream of air right before they contact the water. Another way of separating these particles is by the use of sugar. Five parts of sugar are dry blended with one part of food hydrocolloid. The sugar will separate the hydrocolloid molecules enough so they will not contact each other upon swelling. The third way to separate particles is through the use of non solvents, such as vegetable oil, glycerine, or corn syrup (Hoefler 2001). These substances coat the hydrocolloid particles, but when they are introduced into water, they cannot swell. Lastly, high shear can be used, which uses fast moving water to separate particles as they are added.

2.1.3 Functions

As stated previously, hydrocolloids are added to various food systems for a variety of reasons. Listed below in Table 2 are some of the functions of

hydrocolloids along with the types of foods they are used in. However, there is usually one of three reasons why they are added to any food product. Those reasons are to influence the texture, to increase the stability, or to reduce fat or calories in a food product.

Table 2: Functions and products hydrocolloids are used in

Function	Type Of Products Used In
Thickening	canned goods, gravies, sauces, soups, dressings, low calorie foods and beverages
Suspending	salad dressings, fruit juice drinks, chocolate milk
Instant Viscosity	dry mix beverages
Gelling	jams, jellies, preserves, dessert gels, canned pet foods
Emulsion Stabilization	salad dressings, cream sauces
Protein Stabilization	yogurt drinks, low pH milk beverages, chocolate milk
Crystallization Inhibition	ice cream, confectionary
Water Binding	baked goods, icings, and candy
Film Forming/Fat Holdout	french fries, batter and breaded foods
Syneresis Control	sauces, low calorie preserves, pie filling, desserts

2.1.4 Types of Hydrocolloids

Not only can hydrocolloids perform numerous functions, but there is a wide selection of hydrocolloids available for manufacturers. The function of each gum varies and certain ones are chosen for particular reasons. Decisions may be based on solution clarity, solubility at various temperatures, suspension ability, natural versus not natural, ability to stabilize proteins at a low pH, acid stability, or relative cost per pound. All hydrocolloids either carry a negative charge or a neutral charge. At the present time, there are no food hydrocolloids that possess a positive charge. Table 3 lists the food hydrocolloids available for use.

Table 3: Various types of hydrocolloids

Types of Hydrocolloids	
Agar	Gum Arabic
Alginates	Gum Karaya
Carrageenan	Gum Ghatti
Cellulose Gums	Gum Tragacanth
(MCC, CMC, MC)	Locust Bean Gum
Curdlan	Konjac
Furcellaran	Pectin
Gelatin	Pollulan
Gellan Gum	Tara Gum
Guar Gum	Xanthan

The hydrocolloids highlighted in yellow will be studied for this research project.

2.2 CARRAGEENAN

Red and brown seaweed provides many different types of hydrocolloids for the food industry. Brown seaweed species provide alginate food gums, where the red seaweed family, *Rhodophyceae*, provides the polysaccharides agar, carrageenan, and furcellaran. The main species of the *Rhodophyceae* family include *Euchema cottonii* and *Euchema spinosum* which carrageenan gum is extracted from. *E. cottonii* produces kappa carrageenan, *E. spinosum* yields iota carrageenan, and *Chondrus crispus* yields both kappa and lambda carrageenan, although the same plant does not produce both types. Individual plants that grow together will produce both types of carrageenan (McCandless 1973).

2.2.1 Structure

Carrageenan gum has a linear backbone of repeating galactose units with different proportions and locations of ester sulfate groups and 3,6-anhydrogalactose (anhydro bridges). Carrageenan is one of the two food gums that is naturally sulfated, furcellan being the other. Varying compositions and conformations provide different rheological behavior, ranging from viscous thickeners to thermally reversible gels, which range in texture from soft and elastic to firm and brittle. The main types of carrageenan are kappa, lambda, and iota. Rees (1963) and coworkers were able to distinguish these different types and assign different chemical properties to identify each of them. Three other forms were also found called mu, nu, and theta, which are precursors to kappa and iota forms and a successor to lambda respectively (Rees 1963).

The number of ester sulfate groups and anhydro bridges present on the backbone distinguishes kappa, lambda, and iota carrageenan from one another. These variations allow different rheological properties to be attained as well as influencing hydration, gel strength, texture, syneresis, synergism, melting and setting temperatures. The differences among these carrageenan types are due to the type of seaweed, as well as the processing and blending processes. The sulfate groups make the carrageenan molecule more water soluble, whereas the anhydro bridges inhibit water solubility because of its natural hydrophobic properties (Hoefler 2001). Kappa carrageenan has approximately 25% ester sulfate and 34% anhydro bridges with iota having approximately 32% ester sulfate and 30% anhydro bridges (Moirano 1977). Lambda has the highest

amount of ester sulfate at 35% with little or no anhydro bridges. Kappa carrageenan has one sulfate group and one anhydro bridge for every two galactose molecules. Iota carrageenan has a similar structure; however it possesses an additional sulfate group, making iota carrageenan more water soluble than kappa. Lambda, which is the most water soluble of the three, consists of three sulfate groups and no anhydro bridges for every two galactose molecules. For simplicity of categorizing carrageenan gum it is described as 'extracts from Rhodophyceae which contain an ester sulfate content of 20% or above and are alternatively alpha-(1,3) and beta-(1,4) glycosidically linked' (Anon 1988).

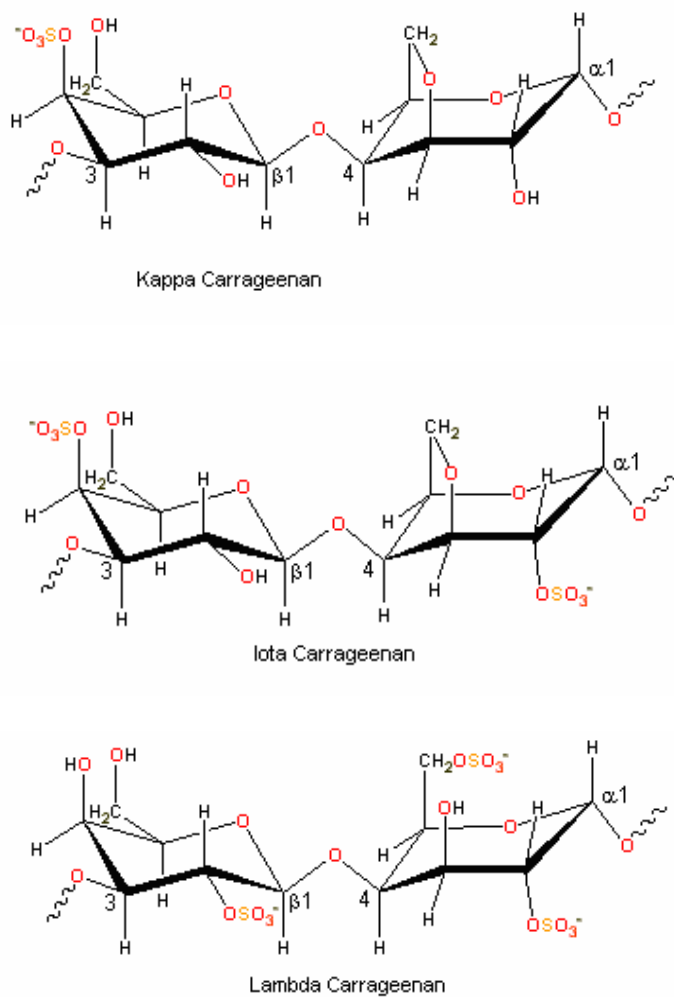


Figure 2: Structures of Kappa, Iota, and Lambda Carrageenan

2.2.2 Properties of Carrageenan

Each type of carrageenan gum has its own physical properties, which will be discussed in this section. All carrageenan types are hot water soluble. However, not all of them are soluble in cold water. Only lambda is fully soluble in cold water in addition to Na^+ salts of kappa and iota. Lambda carrageenan

produces a viscous solution, which exhibits pseudoplastic characteristics when it is pumped or stirred. Usually it is used for thickening in order to provide body to a product. When heating a carrageenan solution, the required temperature of hydration depends on factors such as concentration of carrageenan, the cations associated with it, as well as the cations present in the food system. In most food products, full hydration of kappa and iota is achieved at temperatures above 70°C. (Moirano 1977).

Carrageenan is most stable at neutral and alkaline pH, even at increased temperature. However, if a pH drops below 4.5, carrageenan solutions will lose viscosity and gel strength. This occurs because of autohydrolysis, which is due to the acid form of carrageenan cleaving the glycosidic linkages (Moirano 1977; Hoffmann 1996). At elevated temperatures and low cation concentrations, this process occurs even quicker. An exception to this is when kappa and iota carrageenan are used in low pH food systems when gelling is induced prior to a decrease in pH. Once the carrageenan is in a gelled state, the secondary and tertiary structures protect the glycosidic linkages from cleavage as well as the cations being unavailable (Moirano 1977; Imeson 2000).

Kappa and iota carrageenan is capable of forming a range of gel textures upon cooling of a hot solution. The gel textures depend on the cations used to induce gelling. The gels are thermally reversible, as they remelt 5-20°C above the gelling temperature and re-gel upon cooling. It is believed the ability of gelling is due to double helix formation (Anderson 1969; Rees 1969; Glicksman 1979; Hoefler 2001).

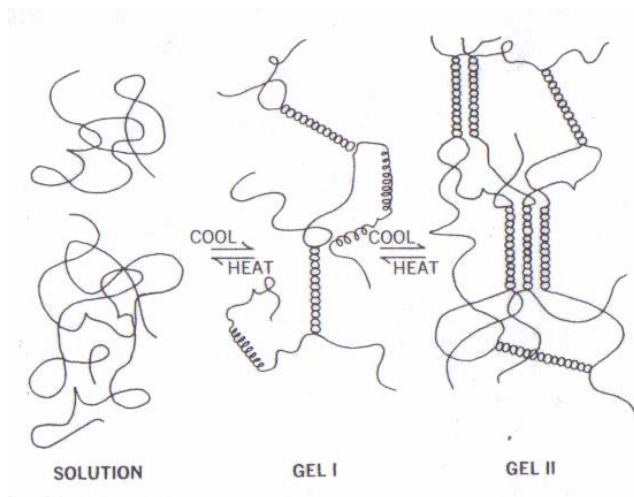


Figure 3: Double helix formation of carrageenan upon cooling

When the temperature is above the melting point of the gel, random coils are present because thermal agitation overcomes the ability to form helices. Upon cooling, double helices form junction zones which produces a three dimensional network. Further cooling induces aggregation of these junction zones by hydrogen bonding of adjacent double helices (Rees 1969; Moirano 1977; Hoefler 2001). Sulfation of carrageenan can explain some of the gelling properties. The sulfate group in lambda carrageenan acts as a "wedging group" which prevents the double helix from forming. However the sulfate on the anhydro bridge of iota projects outward and does not interfere with double helix formation. This is also true for kappa though the sulfate group is located on the 1,3-linked galactoside (Moirano 1977). The higher degree of anhydro bridges the better the gelling properties (Moirano 1977) as it increased the capability of forming double helices.

The type of cations used to induce gelling is extremely important in the gelling properties of carrageenan. The most common cations used in food applications are K^+ , Ca^{++} , and NH_4^+ . These cations influence the hydration

temperature as well as the setting and melting temperatures. Carrageenan exhibits hysteresis, which means there is a difference between the gelling and remelting temperature of a carrageenan gum. The melting temperatures are always higher than the gelling temperatures due to the need of extra energy to disrupt the existing gel network. Kappa carrageenan when used with potassium cations forms a firm and brittle gel seen in the figure below (Imeson 2000). This gel is subject to syneresis, which causes gel shrinkage due to the loss of fluid. Because of this, kappa carrageenan exhibits very poor potential for good freeze-thaw stability. Also seen below is the structure of an elastic iota carrageenan gel, which is induced by calcium cations. Iota carrageenan can also gel using potassium and NH_4^+ , but the strongest gel results when calcium is used. Iota gels are not subject to syneresis, which results in good freeze-thaw stability. Different combinations of kappa and iota carrageenan can be made in order to have a range of gelling textures, which in turn can exhibit good freeze-thaw stability as well as moisture binding (Imeson 2000).

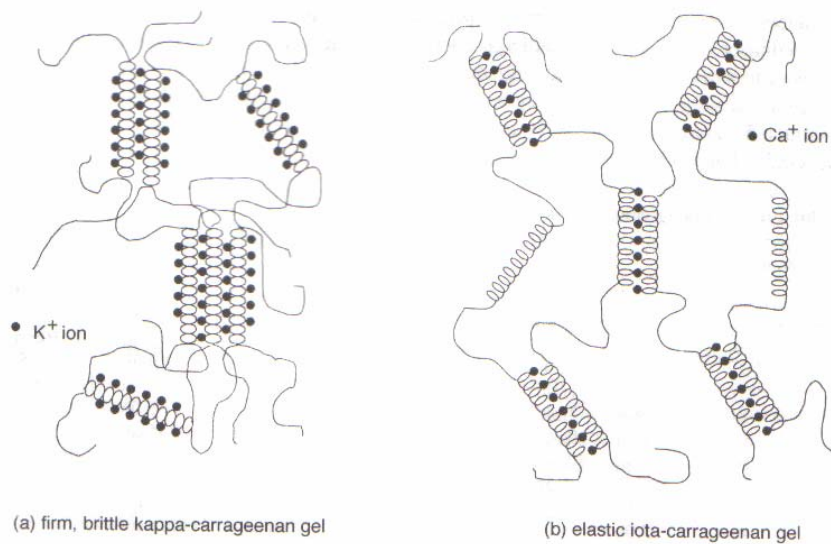


Figure 4: Structures of kappa-carrageenan and iota-carrageenan

Synergistic interactions have been researched with carrageenan gum. The most famous combination is kappa carrageenan and locust bean gum. This combination can lead to elastic gels with low syneresis when cooled below 50-60°C. Locust bean gum is a galactomannan with one galactose side unit for every four mannose units. The substitution, however, is unevenly and randomly distributed, which creates smooth areas on the locust bean backbone. This area is capable of associating with helical structure of the kappa carrageenan to form gels. Not only does locust bean gum influence the type of gel formed but the gel strength is increased also. The gel strength is maximized within the ratio range of 40:60 and 60:40 of kappa carrageenan and locust bean gum (Imeson 2000). This combination is frequently used in cooked meats, gelled pet food, as well as cake glaze. Another synergistic relationship exists between konjac flour and kappa carrageenan. A strong elastic gel is created with a gel rupture strength four times greater than kappa carrageenan by itself.

Carrageenan has a synergistic relationship with the casein molecules in milk. It is just about 5 times more effective in milk than it is in water, which means less carrageenan can be used to achieve the same effect. Kappa carrageenan has the ability to interact with positively charged amino acids present in the casein molecules thus incorporating the casein micelles directly into its gel structure. Enhanced gelling properties have been discovered in milk when appropriate cations are present and when the concentration of carrageenan is relatively high.

2.2.3 Applications

Carrageenan has various uses in the food industry. The basic carrageenan types may be used individually or mixed together to form blends. For simplicity, the food applications of carrageenan gum have been divided into dairy based and water based topics.

2.2.3.1 Dairy Based Applications

Since carrageenan can interact synergistically with the casein molecules in milk, it is easier to divide the applications into categories. The original use of carrageenan was in milk gels, such as flans and custards. The carrageenan imparts a creamy mouthfeel and reduces syneresis. It is also added to products such as puddings and pie fillings. It is responsible for reducing the amount of starch, minimizing syneresis development, in addition to modifying the texture of the final product. The most common use for carrageenan gum in dairy products is in ice cream or ice milk. It is added to control ice crystallization as well as whey

separation. Carrageenan is also used in chocolate, eggnog, and fruit flavored pasteurized milks. The carrageenan can suspend particles, such as cocoa, as well as providing a rich mouthfeel by adding thickness to the product. Rich mouthfeel is also achieved when carrageenan is added to reconstituted nonfat dry milk, as well as stabilizing the emulsion. Another product carrageenan is added to is creamed cottage cheese. The creamy mixture that surrounds the curds needs to be stable and have the ability to cling on to the cottage cheese curd. Carrageenan is added to controlled calorie milk drinks in order to prevent fat particles from settling out as well as adding a rich mouthfeel. Carrageenan gum may be used in processed cheese to give the final product good mouthfeel characteristics and good grating, melting, and slicing properties. It is also added to evaporated milk and infant formulations as well. In evaporated milk it is added to prevent fat separation and in infant formulas it is added to stabilize proteins and fats. Lastly, carrageenan is added to whipped cream and yogurt. It is added to these two products to stabilize and suspend.

Table 4 :Typical Milk (Dairy) Applications of Carrageenan (adapted from Moirano 1977)

Use	Function	Product	Use Level (%)
Frozen Desserts	whey prevention	Kappa	0.010-0.030
Ice cream, ice milk	control meltdown		
Pasteurized Milk Products			
Chocolate, egg-nog, fruit-flavored	suspension, bodying	Kappa	0.025-0.035
fluid skim milk	bodying	kappa, iota	0.025-0.035
filled milk	emulsion stabilization	kappa, iota	0.025-0.035
	bodying		
creamy mixture for cottage cheese	cling	kappa	0.020-0.035
Sterilized Milk Products			
chocolate, etc	suspension, bodying	kappa	0.010-0.035
controlled calorie	suspension, bodying	kappa	0.010-0.035
evaporated	emulsion stabilization	kappa	0.005-0.015
infant formulations	fat and protein stabilization	kappa	0.020-0.040
Milk Gels			
cooked flans or custards	gelation	kappa, kappa + iota	0.20-0.30
cold prepared custards	thickening, gleation	kappa, iota, lambda	0.20-0.50
pudding and pie fillings	level starch gelatinization	kappa	0.10-0.20
	syneresis control, bodying	iota	0.10-0.20
Whipped Products			
whipped cream	stabilize overrun, stabilize	lambda	0.05-0.15
aerosol whipped cream	stabilize overrun, stabilize	kappa	0.02-0.05
	emulsion		
Cold Prepared Milks			
instant breakfast	suspension, bodying	lambda	0.10-0.20
shakes	suspension, bodying, stabilize	lambda	0.10-0.20
	overrun		
Acidified milks			
yogurt	bodying, fruit suspension	kappa + locust bean	0.20-0.50

2.2.3.2 Water Based Applications

Carrageenan is added to products such as dessert gels, cake glazes, and low calorie jellies for the main purpose of controlling syneresis, yet providing elastic and cohesive texture. It is also added to replace gelatin in order to meet religious and vegetarian beliefs. Carrageenan improves water retention, cooking yields, slicing properties, mouthfeel, and succulence in canned meat products, luncheon meats, fish aspics, and pet foods. Syrups, particularly chocolate syrup, and salad dressings are other products that use carrageenan. It is used in order to suspend particles, such as cocoa in chocolate syrup and herbs and spices in salad

dressings. Surprisingly, carrageenan is used in some low pH foods such as relishes, pizza, and barbecue sauces. The carrageenan provides body to these food products. In addition to the above mentioned products, carrageenan is added to imitation milk and imitation coffee creams. For each of these products, carrageenan adds body and stabilizes the emulsion.

Table 5: Typical Water Application of Carrageenan

Use	Function	Product	Use Level (%)
Dessert gels	gelation	kappa + iota kappa + iota + locust bean gum	0.5-1.0
Low calorie jellies	gelation	kappa + iota kappa + galactomannans	0.5-1.0 0.5-1.0
Pet foods (canned)	fat stabilization, thickening, suspending, gelation	kappa + locust bean	
Fish gels	gelation	kappa + locust bean kappa + iota	0.5-1.0
Syrups	suspension, bodying	kappa, lambda	0.3-0.5
Fruit drink powders	bodying	Na+ kappa, lambda	0.1-0.2
Frozen concentrates	pulping effects	K+/Ca+ kappa	0.1-0.2
Relishes, pizza, BBQ sauce	bodying	kappa	0.2-0.5
Imitation milk	bodying, fat stabilization	iota, lambda	0.03-0.06
Imitation coffee cream	emulsion stabilization	lambda	0.1-0.2
Whipped topping	stabilize emulsion, overrun	kappa, iota	0.1-0.3
Puddings (nondairy)	emulsion stabilization	kappa	0.1-0.3

Though carrageenan has many uses it does however have limitations. The main limiting factor for carrageenan gum is its instability at low acidity. Once it is exposed to a pH at approximately 4.5 or below it loses gel strength and viscosity, thus limiting the products it can be used in. Also another limitation that carrageenan gum has is that it requires cations to induce gelling.

2.3 XANTHAN GUM

Xanthan gum is a hydrocolloid that is produced by the microorganism, *Xanthomonas campestris*. *Xanthomonas campestris* is a bacterium which is naturally found on the cabbage plant, which produces slimy and gummy colonies.

The microorganism produces these slimy and gummy colonies which are called extracellular polysaccharides. These polysaccharides are released from the bacterium cell because no covalent bonds are formed to the cell wall. The extracellular polysaccharide released from *Xanthomonas campestris* is called xanthan gum. Xanthan gum is produced by the process of submerged aerobic fermentation using glucose as the primary carbohydrate source. The xanthan gum is recovered, purified, dried and milled into a white powder.

2.3.1 Structure

Xanthan gum is an anionic linear hydrocolloid with a (1→4) linked β-D-glucose backbone, as seen in cellulose. However, unlike cellulose it has a large side unit on every other glucose unit at location C-3. The side unit, a trisaccharide, contains a glucuronic acid residue linked (1→4) to a terminal mannose unit and (1→2) to a second mannose which connects to the glucose backbone (Sworn 2000). The mannose unit connected to the backbone usually contains an acetyl group. Approximately 50% of the terminal mannose molecules carry a pyruvic acid residue. (Kovac P 1977; Zirnsak MA 1999; Sworn 2000). The primary structure is shown in Figure 5.

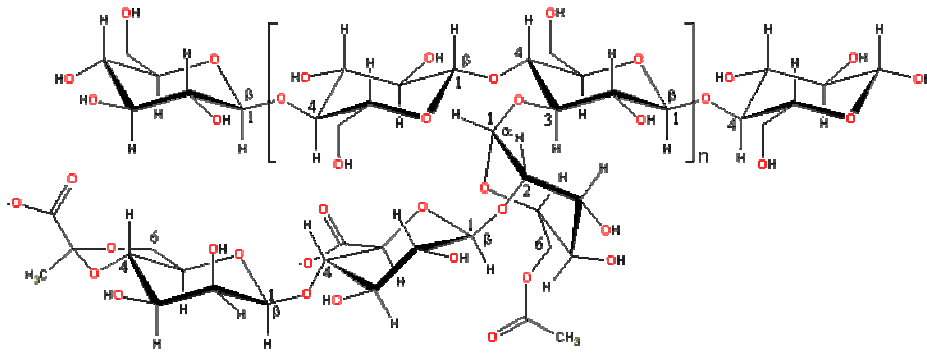


Figure 5: Molecular structure of xanthan gum

2.3.2 Properties

Xanthan gum is an excellent thickening agent. It exhibits pseudoplastic rheological characteristics, which means as shear is increased, viscosity is reduced. Once the shear is removed, the starting viscosity is recovered. The reason this occurs with xanthan gum is the ability of the xanthan molecules to form aggregates through hydrogen bonds and polymer entanglement (Sworn 2000). At low shear rates, xanthan solutions are highly ordered, entangled, stiff molecules. As shear is increased, the aggregates are interrupted and individual polymer molecules align in the direction of the shear force, which results in the pseudoplastic conditions.(Vanderbilt 2000; Deis 2001).

As little as 0.1% xanthan gum will significantly increase viscosity. When 1.0% xanthan gum is used, an almost gel-like consistency will be observed at rest (Sworn 2000; Vanderbilt 2000). However, when shear is applied, it exhibits the same rheological properties seen at a lower concentration.

Generally, xanthan gum is stable over the pH range 2 to 12 (Dziesak 1991; Sworn 2000; Vanderbilt 2000). At pH below 2 and above 12, viscosity tends to

decrease slightly. However, change in viscosity is dependent on the concentration of xanthan gum. The lower the concentration, the more profound the decrease in viscosity (Sworn 2000; Vanderbilt 2000).

Xanthan gum, unlike many other food gums, is stable at a range of temperatures. The viscosity will not change significantly between ambient temperature and a definitely “melting temperature”, which is usually around 60°C. (Sworn 2000; Vanderbilt 2000). At the melting temperature, a sharp decrease in viscosity is seen due to a reversible molecular conformation change (Sworn 2000). The specific “melting temperature” is dependent upon the ionic strength of the solution. If viscosity is lost due to an increase in temperature, it is reversible and as the solution cools, the initial viscosity will return.

Depending the concentration of xanthan gum, salts may either decrease or increase viscosity. At 0.25% xanthan gum concentration or below, monovalent salts may cause a slight decrease in viscosity. When a higher concentration is used, the salt actually increases the viscosity. Many divalent salts, such as calcium or magnesium, affect viscosity similarly (Sworn 2000).

Unlike most hydrocolloids, xanthan gum is not degraded by enzymes. Frequently enzymes, such as proteases, pectinases, cellulases and amylases, are found in many food systems. It is believed the arrangement of the trisaccharide side unit is responsible for this enzyme resistance (Sworn 2000). The side unit prevents enzymes from attacking the β -(1 \rightarrow 4) linkages located on the backbone. Therefore, xanthan gum can be used in food products containing active enzymes.

Although xanthan gum is not a gelling agent, it can form elastic, thermoreversible gels when combined with locust bean gum. High viscosities are achieved when combined with galactomannans such as locust bean gum and guar gum (Dziesak 1991).

2.3.3 Applications and Limitations

Xanthan gum is approved for food use as a stabilizer, emulsifier, thickener, suspending agent, and foam enhancer (Sanderson 1996). Since its introduction to the marketplace in the 1960s, it has been used in many food products including baked goods and pie fillings. Xanthan gum contributes to smoothness, air incorporation and retention for batters of cakes, muffins, biscuits, and bread mixes. It also adds volume and moisture, which leads to higher crumb strength with less crumbling. The use of xanthan gum in a microwave cake mix application facilitates better moisture retention, better stabilization and structure formation which help producing a more tender and moist cake (Anon 1989). Xanthan gum can be added to cold or hot processed bakery and fruit pie fillings in which it will improve texture and flavor release. It also can extend shelf life as well as syneresis control and stability during freeze-thaw cycles. Xanthan gum is used in wet prepared batters and batter coatings. In prepared batters, xanthan gum acts as a suspension agent and improves gas retention. Shrimp, chicken, fish, and onion rings can use xanthan gum in their batter formulations in order for consistent adhesion and stabilization. Frequently, xanthan gum is used in salad dressing. The pseudoplasticity of xanthan gum makes it flow easily when poured

and once the flow stops it recovers its viscosity, resulting in cling or adhesion. Small particles of xanthan gum can be added to dry mixes for milk shakes, sauces, gravies, dips, soups, and beverages. The xanthan gum can provide a very rapid viscosity development as well as enhancing body and evenly suspending particles. Xanthan gum provides stability, syneresis control and consistent viscosity when exposed to freeze-thaw cycles (Sanderson 1996). It can be added to frozen products like whipped toppings, batters, soufflés, gravies, and entrees. Another use of xanthan gum is in retorted products, due to the stability over a wide range of temperatures. Although the viscosity would be low at high retort temperatures, upon cooling the original viscosity would return. In addition to this reason, the xanthan can improve the filling process and reduce splashing (Sworn 2000). Syrups and toppings also have a use for xanthan gum. It allows these products to have excellent pouring and cling properties as well as good stability and uniform suspension of ingredients.

In general terms, xanthan thins under shear in the mouth, facilitating flavor release (Chinachoti 1995). Pseudoplasticity is also important for the mouthfeel and visual aesthetics of the product and for its utility as a processing aid.

Table 6: Food Applications of Xanthan Gum

Product	Functionality	Typical use level (%)	Ref
Ice cream	Stabilizer, viscosity and crystallization control of mix	0.05-0.2	Dziezak 1991, Urlacher and Noble 1997
Baked goods	Stabilizer, facilitates pumping	0.1-0.4	Garcia-Ochoa et al. 2000
Fruit gels	Adds body, prevents sticking		Dziezak 1991
Pizza sauces	Thickener, inhibits absorption by dough	0.1-0.2	Dziezak 1991, Urlacher and Noble 1997
Microwave cakes	Stabilizer, helps moisture retention	0.2	Anon 1989
Beverages	Stabilizer, mouthfeel modification	0.05-0.2	(Giese 1995)
Salad dressings	Stabilizer, suspending agent, emulsifier	0.1-0.5	Garcia-Ochoa et al. 2000
Dry mixes	Eases dispersion in hot or cold water, thickener	0.05-0.2	Garcia-Ochoa et al. 2000
Frozen foods	Improves freeze-thaw stability	0.05-0.2	Garcia-Ochoa et al. 2000
Syrups, toppings, relishes	Thickener, heat stability, uniform viscosity	0.05-0.2	Garcia-Ochoa et al. 2000
Cheese	Syneresis inhibitor	0.5-0.2	Garcia-Ochoa et al. 2000 Becker et al. 1998
Juice drinks	Suspending agent	0.05-0.2	Garcia-Ochoa et al. 2000, Becker et al. 1998
Sausage casings	Film formation	-	Becker et al. 1998
Icings and glazes	Adhesiveness	-	Becker et al. 1998
Gravies and sauces	Thickener, mouthfeel, flavor release, heat resistant	0.1-0.2	Urlacher and Noble 1997

Xanthan gum's pseudoplastic properties allow for easy mixing and pumping during the production of food products in addition to providing food systems with long-term stability. Xanthan gum is stable over a wide pH range, temperature, and exposure to enzymes. Therefore it can be used in many different products. However, xanthan gum is a thickening agent not a gelling agent. Therefore it cannot form a gel network.

2.3 Galactomannans

Other hydrocolloids used in the food industry, which come from a plant origin, include the galactomannans. These are widely used due to their ability to alter rheological properties of aqueous solutions, such as thickening and gelling behavior. The most common galactomannans are from the carob tree (*Ceratonia siliqua*), from the guar plant (*Cyamopsis tetragonoloba*) and the tara shrub (*Cesalpinia spinosa*), though the first two are used more extensively. All three types of galactomannans have identical backbone composed of linear (1→4)-β-D-mannan chains with varying concentrations of (1→6) linked D-galactose side units. Each galactomannan can be identified by the mannose-galactose ratios. Different quantities of galactose lead to different physical and chemical properties of each galactomannan. All three galactomannans mentioned are capable of interacting with other hydrocolloids such as agar-agar, Danish agar, carrageenan, and xanthan gum in order to form three dimensional structures.

2.4.1 Guar Gum

Guar gum is found in the endosperm of the seeds of the guar plant, *Cyamopsis tetragonoloba*, which is milled in order to obtain guar gum (Meer 1977; Wielinga 2000).

Guar gum is a neutral hydrocolloid with linear chains of D-mannopyranosyl units with D-galactopyranose substituents protruding by (1→6) linkages. For every galactose residue there are approximately two mannose residues.

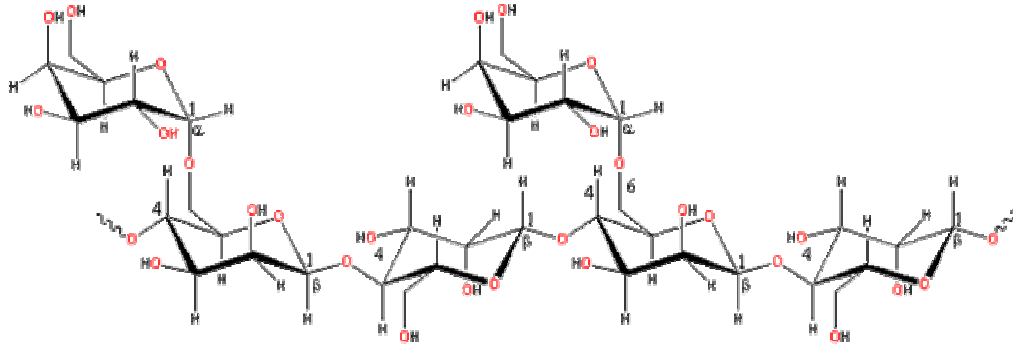


Figure 6: Molecular structure of guar gum

Guar gum is highly substituted which allows for good hydration and hydrogen-bonding activity. Water can easily “slip” between the molecules in order to hydrate or dissolve the gum. The molecular weight of guar gum is between 220,000 and 300,000 (Hoyt 1966). Guar gum has a higher degree of galactose substitution (40%) than locust bean gum (20-23%) (Maier 1992). The galactose content of galactomannans has been studied to show that it strongly influences the behavior of each hydrocolloid. Low galactose content leads to stronger synergistic interactions with other hydrocolloids as well as a stronger gelling capacity independently based upon interactions of smooth areas of the

mannan backbone (Dea 1977; McCleary 1985). The higher galactose content leads to prevention of strong cohesion of the main backbone, so no extensive junction zones or crystalline regions can be formed. Another factor that influences physical behavior of the galactomannan is the distribution of galactose units along the mannan backbone. Guar gum is evenly substituted, which means there are no smooth and hairy regions of the mannan backbone. On average, for every two molecules of mannose, a galactose side unit is attached (Meer 1977). A two to one mannose-galactose ratio leaves small galactose uninhibited mannose areas, which has been shown to have lesser functionality (McCleary 1979; Launay 1986). Whereas locust bean gum, on average, has a four to one ratio, which should exhibit greater functionality. Richardson et al (1998) reported that two galactomannans, with the same average galactose content but with different mannose-galactose ratios, would exhibit different degrees of functionality (Richardson 1998). The galactomannan with the broader distribution of galactose units would be more functional because they contain a greater proportion of chains with lower galactose content (McCleary 1979; Launay 1986).

2.4.1.1 Functions and Applications

Guar gum is used as a thickener and stabilizer in the food industry as a result of its hydration and water-binding properties. It is used as a stabilizer at a concentration of 3.0% in ice cream, ice pops, and sherbet. It improves the body, texture, chewiness, and heat-shock resistance by binding free water (Wielinga 2000). Guar gum is also used in cheese products. In cold-pack cheese it is used

at a concentration of 3.0% in order to prevent syneresis and weeping. In soft cheeses it is added to increase the yield of curd and to give the curds a better texture. Concentrations of .25-.35 are added to pasteurized cheeses in addition to locust bean gum and act as a stabilizer. Guar gum is also added to dessert and pastry products, such as pie fillings, icings, cake and donut mixes. It is added to pie fillings to thicken but prevent shrinking and cracking of the filling (Meer 1977; Wielinga 2000). In icing it is added to absorb free water, which prevents stickiness as well as not sticking to packaging materials. Meat and gravy sauces contain guar gum since it allows for reduction of the total solids in the product. Another use for guar gum is in canned meat products. It is used in conjunction with agar to prevent fat migration during storage as well as controlling syneresis. As a thickener it is sometimes added to salad dressings, pickle and relish sauces. Guar gum can also be used in dietetic beverages or low carbohydrate products due to its suspending ability and improving body of thin and watery products. (Meer 1977).

An advantage of guar gum is its cold water solubility which allows viscous pseudoplastic solutions to form when hydrated in cold water (Deis 2001). Its viscosity is dependent upon factors such as time, temperature, concentration, pH, ionic strength, and type of agitation. Maximum viscosity is reached during the temperature range of 25-40°C, with higher temperatures increasing the rate at which maximum viscosity is achieved. However, too high a temperature will degrade the gum and normal function will not be carried out. Guar gum is stable over a wide range of pHs, with its optimal rate of hydration between pH 7.5-9.

The maximum viscosity will remain stable between the pH range of 1 to 10.5. Another advantage of guar gum is its ability to be compatible with salts over a wide range of electrolyte concentrations. For instance, guar gum with borate ions, the borate ions act as cross-linking agents with guar gum to form structural gels. It is also a good emulsifier due to the amount of galactose substituents. Guar gum exhibits stability during freeze-thaw cycles as it is able to retard ice crystal growth by slowing mass transfer across solid and liquid interfaces (Chaplin 2003).

Though guar gum is easily hydrated and is an economical stabilizer and thickener, it has some limitations as well. Unlike locust bean gum, it does not form gels. Guar gum is stable over a wide pH range, however if both temperature and pH are at extreme points, it could lead to degradation. For instance, at a pH 3 and temperature of 50°C, guar gum starts to degrade.

2.4.2 Locust Bean Gum

Locust bean gum, also called carob bean gum, is produced from the evergreen carob tree, *Ceratonia siliqua*. Locust bean gum is found in the endosperm of the pods from the carob tree. The endosperm is separated from the hull and germ, which is then mechanically ground to produce locust bean gum. The slightly off-white powder consists of 88% galactomannan, 3-4% pentosan, and 5-6% protein, cellulose and ash (Griffiths 1952). The molecule weight of locust bean gum is approximately 310,000 (Kubal 1948).

2.4.2.1 Structure

Locust bean gum is a neutral galactomannan with linear chains of 1,4-linked beta-D-mannan backbone with 1,6-linked alpha-D-galactose side units.

For every galactose residue there are approximately 4 mannose residues (Wielinga 2000).

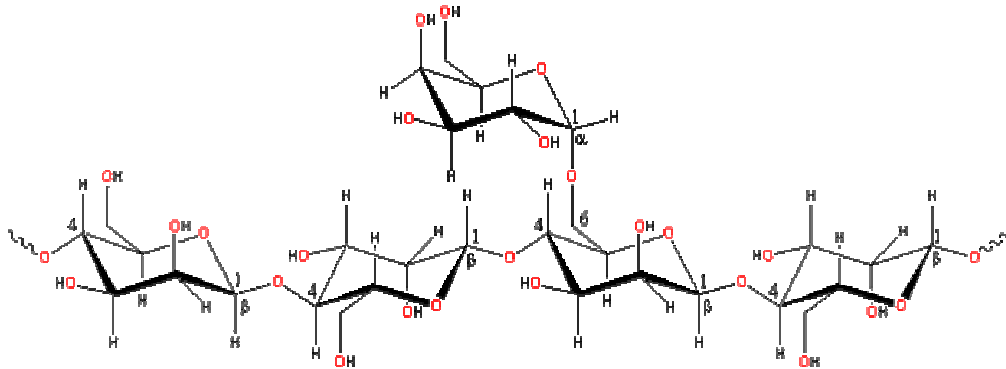


Figure 7: Molecular structure of locust bean gum

Locust bean gum is not as highly substituted as guar gum, but the galactose side units still allow for hydration and hydrogen-bonding activity. Locust bean gum has an approximate mannose-galactose ratio of 4:1, which is a relatively low galactose concentration. According to Dea et al (1977), this signifies stronger synergistic interactions with other food hydrocolloids in addition to stronger gelling abilities when used independently (Dea 1977). With such a high mannose-galactose ratio, this influences solubility of the hydrocolloid.

2.4.2.2 Properties

At ambient temperatures, locust bean gum is only partly soluble therefore heat treatment is required for maximum solubility (Hui 1964; Gaisford 1986; Maier 1992). Since locust bean gum is a neutral hydrocolloid it is stable over a wide pH range (3-11). Distribution of side units greatly influences the physical behavior of the galactomannan. Locust bean gum is unevenly substituted, which means there are smooth and hairy regions found on the mannan backbone. On

average, for every four molecules of mannose, one galactose side unit is attached (Meer 1977). A four to one mannose-galactose ratio leaves considerable smooth mannose backbone regions, which has been shown to have more functionality (McCleary 1979; Launay 1986). As Richardson et al (1998) reported locust bean gum should be more functional because it contains greater unsubstituted areas on the mannose backbone.

2.4.2.3 Applications and Limitations

Locust bean gum acts as a thickening agent, stabilizer, and a fat replacer in various food systems. It is an excellent stabilizer for dairy products, such as ice cream, due to its ability to bind free water and high swelling potential. It also has good heat-shock resistance and provides good body to the ice cream product (Meer 1977; Lazaridou A 2000). Locust bean gum is also used in processed meats, such as salami, bologna, and sausages, as a binding and stabilizing agent. It also provides a lubricating effect on the meat mixture and eases the extruding and filling operation. In addition to guar gum, locust bean gum is added to cheese products. Soft cheeses use locust bean gum in order to catalyze the coagulation step as well as increasing the yield of curd produced. It also contributes body and texture to the final cheese product. At low concentrations, approximately 0.2%, it is added to soup as a thickener. It is also added as a thickener to pie fillings, it also serves to produce a clear filling. Another category of food systems locust bean gum is added to are bakery products. When added to dough, it provides more uniformity with increased water-holding capacity, greater resiliency and

higher yields. Locust bean gum can also be added to cake and biscuit dough, in order to give higher yields as well as not needing to add as many eggs. It also allows the cake and biscuit to be softer, keep their freshness, and retain their shape during processing. Many prepared foods also have locust bean gum added such as soup bases, sauces, frozen batter, vegetable and fish dishes. In addition to those already stated, it is added to whipping cream, mayonnaise, ketchup, and salad dressings as a stabilizer.

Locust bean gum is an economic thickener and stabilizer, requiring only small concentrations to make highly viscous solutions. Locust bean gum is stable over a pH range of 3 to 11, so it is little affected by pH changes. Locust bean gum has the ability to form gels, unlike guar gum. Another advantage of locust bean gum is its ability to interact with other hydrocolloids to influence gelling properties (Meer 1977). For instance, locust bean gum has synergistic relationships with xanthan gum, carrageenan, and agarose. Locust bean gum is also capable of self-associating upon freeze-thaw cycles.

Though locust bean gum has many advantages, it has some limitations as well. Locust bean gum is not cold water soluble, so heat needs to be applied in order to fully hydrate the gum. Solution clarity can be a deciding factor when choosing food hydrocolloids. Locust bean gum produces a cloudy, off-white, and opaque solution.

2.5 CURDLAN GUM

Curdlan gum was discovered by Dr. Harada and coworkers in 1964. The name curdlan was given due to the ability of this substance to curdle when

heated (Harada 1966; Maeda 1967; Pszczola 1997; Nishinari 2000). Curdlan is an extracellular microbial polysaccharide produced by *Alcaligenes faecalis* var. *myxogenes*, which is today classified as *Agrobacterium* biovar 1 (Nakao 1997; Jezequal 1998). Curdlan is produced by a fermentation process using the microorganism *Alcaligenes faecalis* var. *myxogenes*, which was originally isolated from the soil. The aerobic fermentation process is described in U.S. patents 3,754,925 and 3,822,250 (Kimura 1973; Kimura 1974). Curdlan is the third microbial exopolysaccharide approved for use in the United States by the FDA, which was approved in 1996 (USFDA 1996). Over 100 tons of curdlan are produced annually even though curdlan is relatively expensive in comparison to other food gums (Chaplin 2003b).

2.5.1 Structure

Curdlan is composed of a minimum carbohydrate concentration of 90% and a maximum water content of 10% (Nakao 1997; Jezequal 1998). Curdlan is a neutral polysaccharide consisting of D-glucose with β -1,3 glucosidic linkages (Figure 8), which means there are repeating glucose subunits joined by a beta linkage between the first and third carbon of the glucose ring (Nakao 1997; Jezequal 1998; Funami 1999; Funami 1999b). The 1,3 β -D-linkage is similarly seen in other hydrocolloids such as carrageenan, agarose, and gellan gum, however curdlan does not possess any acidic components (Nishinari 2000). The D-glucose that makes up curdlan is similar to cellulose however, the linkages differ (Nishinari 2000).

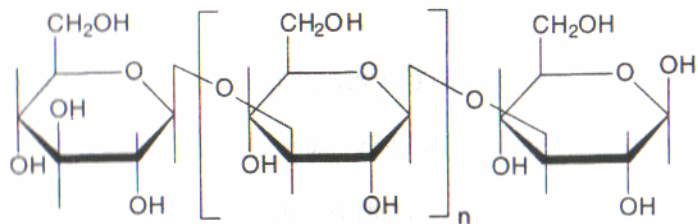


Figure 8: The Molecular Structure of Curdlan

Curdlan, in its solid state, may exist in a triple helix shown by ^{13}C NMR analysis (Nishinari 2000). It is in granular form similar to that of a donut shape. Curdlan is not water soluble although it can be dissolved in aqueous NaOH because of the ionization of hydrogen bonds. Upon introduction to aqueous NaOH, the bonds are broken due to swelling and the granular structure of curdlan is lost (Nishinari 2000).

2.5.2 Properties

Curdlan gum is not soluble in water, alcohol, and most organic solvents, however it is soluble in alkaline solutions such as sodium hydroxide and trisodium phosphate (Nakao Y 1991; Nakao 1994; Nishinari 2000). Ogawa et al (1972) studied curdlan conformation in various concentrated alkaline solutions. At low concentrations of sodium hydroxide (below 0.19 N NaOH), curdlan has an ordered (helical) conformation, however a significant change is seen once the sodium hydroxide concentration is increased to a concentration between 0.19 and 0.24 N NaOH (Ogawa K 1972). At a concentration higher than 0.2 N NaOH, curdlan is fully soluble and has a random structure. However, once this solution

is neutralized, the soluble turns to an order state which consists of single and triple helices (Ogawa K 1972).

Curdlan is a linear homopolymer chain, but forms complex tertiary structures believed to be caused by intramolecular and intermolecular hydrogen bonding (Nishinari 2000). It is these hydrogen bonds that may confirm why curdlan is not soluble in water. It acts somewhat similar to cellulose. Although curdlan is not soluble in water, an aqueous solution containing curdlan can form a gel depending on the heating temperature (Nakao Y 1991; Nakao 1994; Nakao 1997). Two types of curdlan gels can be formed: a low-set gel and a high-set gel. The low-set gel, which is thermo-reversible, can be created one of three ways: addition of the cations Ca^{++} or Mg^{++} , neutralization of an aqueous alkaline solution of curdlan, or by heating a curdlan solution between 55 and 60°C and then cooling it below 40°C (Kanzawa Y 1987; Kanzawa Y 1989). A low-set curdlan gel exhibits properties similar to those of carrageenan and agar-agar. The curdlan molecules swell around 55°C which results in partial rupture of intramolecular hydrogen bonding (Jezequal 1998). Therefore upon cooling, new hydrogen bonds cross-link curdlan micelles, which are occupied by molecules of a single-helix (Maeda 1967; Kimura 1973). If the aqueous solution is heated to temperatures exceeding 80°C a high-set gel will result, which is also identified as a thermo-irreversible gel (Pszczola 1997; Jezequal 1998). The high-set curdlan gel is a much stronger and more resilient gel than the low-set gel. The texture of the high-set gel is described as being between a soft, elastic gel as seen with gelatin and a hard brittle gel seen with agar-agar (Nakao 1997; Jezequal 1998). It

is believed the molecular mechanism for a high-set gel results from cross-linking between curdlan micelles with hydrophobic interactions (Fulton WS 1980). The curdlan micelles are occupied by molecules of multiple-chain helix or triple stranded helix (Marchessault 1979; Kasai 1980). The high set gel is stable at low temperatures, such as freezing as well as at high temperatures, as seen in processing conditions such as retorting. It is also resistant to enzymatic and acidic hydrolyses (Nakao Y 1991; Nakao 1997). It is possible to change a low-set gel into a high-set gel by increasing the temperature to 80°C (Nakao 1997). The formation of the two types of gels are seen in the figure below.

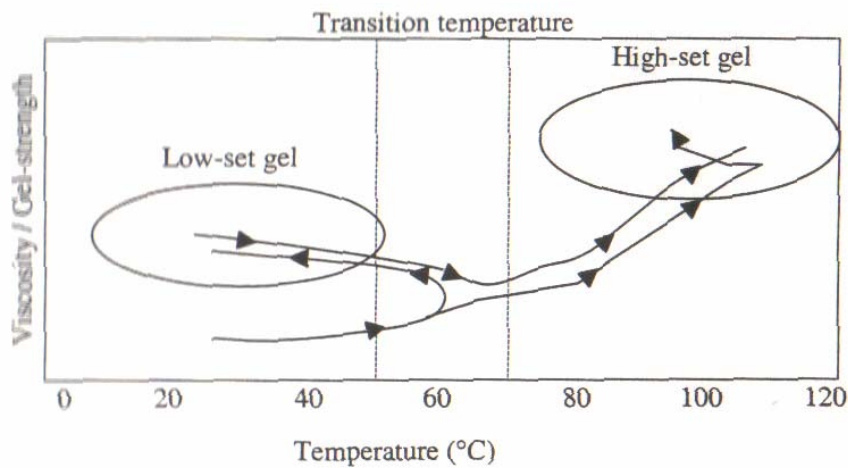


Figure 9: Effect of temperature on viscosity and gel strength (adapted from Nakao 1997)

Either type of curdlan gel does not add any color, smell, or taste to products, however, can make a profound difference when added in small amounts. A general property of curdlan gel is as the concentration of curdlan is increased, the gel strength is also increased. For higher strength gels, a higher concentration of curdlan is needed, however, if a low strength gel is needed; only a minimal amount of curdlan is needed. Gel strength is not only dependent on the

concentration of curdlan, but on the heating temperature and time as well. Gel strength increases with increasing temperature as well as heating time (Nakao 1997; Nishinari 2000). In addition to curdlan concentration, heating time and temperature, gel strength is stable over the pH range of 2-10 (Nakao 1997; Jezequal 1998). There are no significant effects on gel strength with addition of inorganic salts (Funami 1999).

2.5.3 Applications and Limitations

Curdlan, which is not soluble in water, can be made into a gel if heat is applied. The distinguishing characteristic of curdlan is that no other conditions need to be met to induce gel formation, such as pH, sugar concentration, and cation presence. Before heating though, the curdlan needs to be properly dispersed in water. Usually a high speed mixer or homogenizer would be sufficient (Nishinari 2000).

There are many potential uses for curdlan gel as it is a tasteless, odorless, and colorless gel. The gel is able to withstand the temperature extremes in the case of freezing and retorting. Curdlan is also capable of forming a gel when a large amount of lipids are used in a product. In noodle dough, the curdlan helps to prevent soluble ingredients from leaking out and overall softens the noodles, which results in a very clear soup broth (Nakao 1997; Nishinari 2000). Curdlan can also be added to tofu. When tofu is frozen without curdlan, upon thawing it, it possesses a rough texture that is not desirable. The addition of curdlan however, enables the tofu to keep a normal smooth texture that it possesses prior

to freezing. It is also used in surimi products, which is ground fish meat, as it contributes to the elasticity (Nishinari 2000). Curdlan is also used in frozen sweet products, such as cakes and ice cream. Curdlan contributes to the texture of the cakes and helps retain shape for ice cream. Another popular use for curdlan gel is in processed meat products. It can improve the water-holding capacity as well as positively altering the texture (Nakao 1997; Nishinari 2000). An additional use for curdlan is in freeze-dried foods. The curdlan can improve the rehydration time and the overall texture of the food product. Retorted products provide an ideal opportunity for curdlan use. The overall body and viscosity of retorted sauces can be greatly improved with a low concentration of curdlan gum. Curdlan can also be used in foods as a fat replacer (Jezequal 1998). Frequently, consumers desire healthier products, but do not want to give up the mouthfeel of their products. Curdlan mimics fat mouthfeel once it is hydrated and heated. Lastly, since curdlan can bind additional water, it can be added to food products to inhibit ice crystallization and moisture migration. Potential applications for curdlan are shown in Table 7.

Table 7: Potential Uses of Curdlan in Food Products

Product	Functionality	Typical use level (%)
Noodle	texture modifier	0.2-1
Kamaboko	texture modifier	0.2-1
Sausages, Ham	texture modifier, water holding	0.2-1
Processed cooked foods	binding agent, moisture retention	0.2-2
Processed rice cake	shape retention	4.0-6.0
Cakes	moisture retention	0.1-0.3
Ice cream	shape retention	0.1-0.3
Jellies	gelling agent, freeze-thaw stability	1.0-5.0
Fabricated Foods	gelling agent, freeze-thaw stability	1.0-5.0
Edible films	film formation	1.0-10
Dietetic foods	low-energy ingredient	30-100

Adapted from Nishinari 2000

Curdlan can be used in many food systems due to its ability to form two types of gels, retain its gel strength as well as being stable over a wide range of pH. Also important to mention is that it is a colorless, odorless, and tasteless substance that will not affect the final sensory outcome of food products. Frequently, hydrocolloids can influence final color, odor, or impart an undesirable taste. Though curdlan gum has many advantages, limitations are still present. The biggest limitation of curdlan is the cost. It is relatively expensive in comparison of other gums on the market. However, the cost is decreasing as technology is improving. Though curdlan is relatively new to the market (1996) there has been a lot of research done solely on curdlan. However, studies are lacking on the use of curdlan with other hydrocolloids currently used in food systems.

Chapter 3

OBJECTIVES

The ultimate goal of this study was to reveal and characterize the interactions of curdlan gum with four common hydrocolloids: carrageenan, xanthan, guar, and locust bean gum.

In order to achieve this goal, there were two specific objectives accomplished. The first objective was to evaluate the rheological and textural properties of the copolymers. Rheological studies included using steady shear and dynamic oscillatory shear measurements, to better understand the viscoelastic characteristics. Textural properties included measuring the gel strength and adhesiveness of all four copolymer solutions.

The second objective was to expose the copolymers to a wide range of temperatures as well as a series of freeze-thaw cycles to see if curdlan gum enhanced the stability of the copolymers.

Chapter 4

MATERIALS AND METHODS

4.1 Materials

Odorless and tasteless, free flowing curdlan powder was obtained from Tadeka USA (Orangeburg, New York).

Kappa carrageenan was provided by TIC Gums (Belcamp, MD) in the form of TIC Pretested Colloid F-390 Powder from Lot #: 5075. It is a white free flowing powder which is used between .8-1.5% for gel systems. It requires a temperature of 180°F in order to be soluble in water.

Xanthan Gum was provided by TIC Gums (Belcamp MD) in the form of TIC Pretested Ticaxan Xanthan Powder from Lot #5556. Its typical usage is .05-.35% and is cold water soluble.

TIC Gums also supplied guar gum in the form of TIC Pretested Gum Guar 8/22A NF (USP) Powder. It is typically used between 0.1 and 1.0% and is cold water soluble.

Locust bean gum was in the form of TIC Pretested Pre-Hydrated Locust Bean Gum Powder. It is usually used in a range of 0.15% and 0.75%. The pre-hydrated term in the name implies that when it is added to hot water, the locust bean gum will not lump.

4.2 Methods

The experimental design was completed using ECHIP Statistical Software for engineers and scientists (Hockessin DE). Curdlan was used with other

hydrocolloids, which produced a copolymer, and rheological properties were measured. The design variables were curdlan concentration and the concentration of the other four gums (carrageenan, xanthan, guar, and locust). ECHIP calculated the number of trials and designed a completely randomized continuous design. Levels of gums ranged from 0% (w/v) to 1% (w/v). The randomized trials are seen below. For each combination of gums, an ECHIP program was set up.

Trial	Carra_conc	Curdlan_conc	Trial	Xanth_conc	Curdlan_conc
2	0	0.5	10	1	0.667
5	1	0	9	1	0.333
7	0.667	0	2	0	0.5
1	0	1	1	0	1
3	0.5	1	2	0	0.5
8	0.333	0	11	0.333	0.667
11	0.333	0.667	4	1	1
9	1	0.333	3	0.5	1
4	1	1	1	0	1
2	0	0.5	5	1	0
1	0	1	4	1	1
5	1	0	3	0.5	1
3	0.5	1	6	0	0
4	1	1	7	0.667	0
10	1	0.667	8	0.333	0
6	0	0	5	1	0

Trial	Guar_conc	Curdlan_conc	Trial	Locust_conc	Curdlan_conc
4	1	1	4	1	1
7	0.667	0	5	1	0
5	1	0	1	0	1
1	0	1	4	1	1
9	1	0.333	5	1	0
5	1	0	3	0.5	1
6	0	0	2	0	0.5
2	0	0.5	7	0.667	0
3	0.5	1	8	0.333	0
11	0.333	0.667	1	0	1
2	0	0.5	2	0	0.5
3	0.5	1	11	0.333	0.667
4	1	1	3	0.5	1
10	1	0.667	9	1	0.333
8	0.333	0	10	1	0.667
1	0	1	6	0	0

4.2.1 Preparation of Copolymer Solutions

The hydrocolloid powders were weighed and dry blended at ambient temperature before being introduced to fast moving DI Water. Upon introduction to the DI Water, they were constantly stirred while the temperature reached 90°C. Once the temperature was met, the gums were removed from the heat and poured into 50 mL test tubes and allowed to cool to room temperature. They were covered and refrigerated overnight. Before analysis the following day, they each were set at room temperature for 30 minutes to adjust to the ambient temperature.

4.2.2 Rheological Testing

General and dynamic rheological measurements were carried out using the AR 2000 Rheometer (TA Instruments, New Castle DE) using a 40mm stainless steel parallel plate. Viscosity tests were conducted to see changes in viscosity as shear rate increased. Oscillation tests were done within the linear viscoelastic region (LVR) to determine storage and loss moduli. Frequency sweeps were conducted at a frequency of 1 Hz. Once results were collected, they were reported to ECHIP Statistical Modeling Software which calculated two and three dimensional contour plots.

4.2.3 Heat Stability Testing

The AR 2000 Rheometer was also used to conduct heat stability testing of the copolymer gels. Viscosity was measured as the temperature was ramped from 20°C to 80°C.

4.2.4 Gel Strength and Adhesiveness

The TA.XT2i Texture Analyzer by Texture Technologies, Inc (Scarsdale, NY) was used to determine the gel strength and adhesiveness profiles. A P/0.5R probe using a 5kg load cell was used. For this analysis, when 5g of force was detected by the probe, it continued to descend into the sample for 5 seconds and then returned to the starting position. The graph produced by the TA.XT2i can provide very valuable information such as the gel strength, the adhesiveness, as well as elasticity or brittleness of a particular gel.

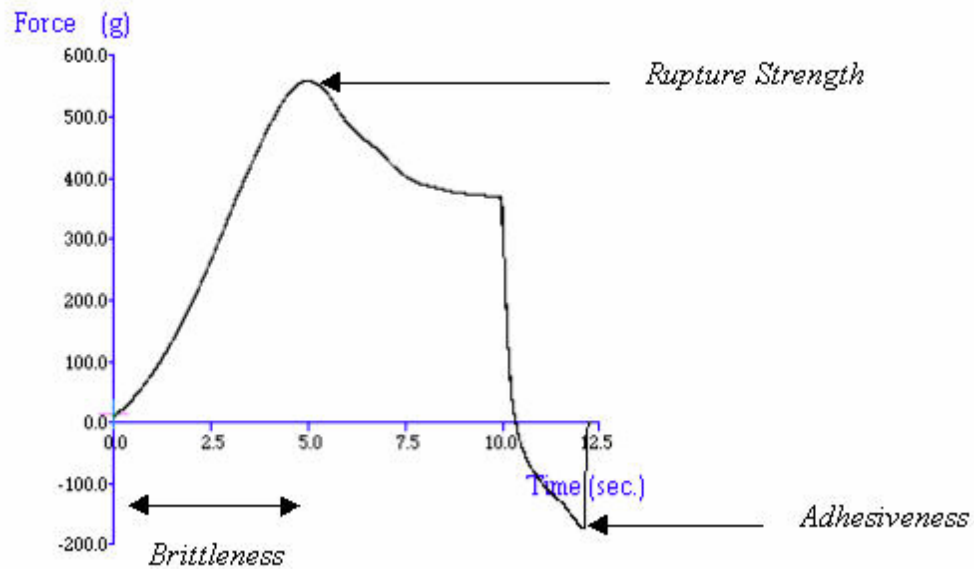


Figure 4.1: Typical graph from Texture Analyzer and the areas to find information on gel strength, adhesiveness, and brittleness

4.2.5 Syneresis Testing

Syneresis testing was completed by centrifuging the samples at 2200 rpm (707 x g) for 20 minutes in a Beckman Model TJ-6 centrifuge. The volume of the

exuded water was determined using a graduated cylinder. The percent of syneresis was defined as

$$(\text{volume of water exuded} / \text{total volume of sample}) \times 100$$

4.2.6 Freeze-Thaw Stability

Copolymerized hydrocolloidal solutions containing various concentrations of curdlan gum were prepared as above. The solutions were stored at 4°C for 24 hours. The samples were then subjected to five freeze-thaw cycles in which they were stored at -16°C for 18 hours and then at 25°C for 6 hours. The thawed samples were then tested for viscosity, storage and loss moduli, gel strength, adhesiveness, syneresis, and heat stability.

Chapter 5:

Results and Discussion

5.1 RHEOLOGICAL AND TEXTURAL CHARACTERISTICS

5.1.1 Viscosity

To elucidate the basic flow behavior of various combinations of hydrocolloids containing curdlan-based copolymers, the changes in the solution's apparent viscosity, η_a , which is defined as the resistance to flow with a material that follows the relationship shear stress divided by shear rate (Steffe 1996), were investigated. As an example, a set of solutions containing carrageenan/curdlan at different combinations were tested under increasing shear rates with constant strain (Figure 5.1). A typical shear-thinning behavior was observed, as the solution η_a decreased with increasing shear rate. As expected, the viscosity increased as the total gum concentration increased, and none of the solutions exhibited yield stress behavior. All hydrocolloidal copolymers investigated in the present study showed similar shear-thinning flow behavior, which is a desirable property for food hydrocolloids. Shear-thinning hydrocolloids are extensively used to improve or modify food texture. The reduction in solution η_a provides processing advantage during high-shear processing operations such as pumping and filling (Tada 1998), whereas the high apparent viscosity during mastication provides a desirable mouthfeel upon consumption (Reilly 1997).

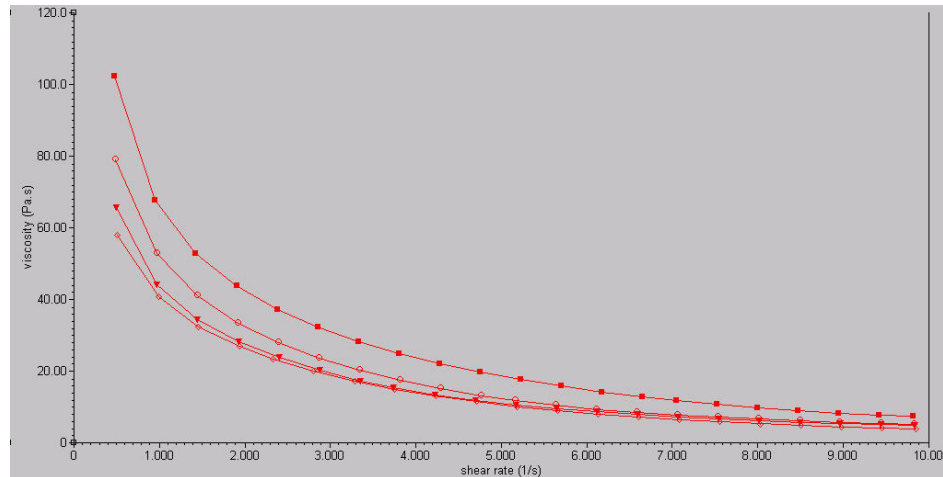


Figure 5.1: Changes in apparent viscosity as shear rate increases for Carrageenan/curdlan combinations (-◇-, 1.0% carrageenan; -▼-, 1.0% carrageenan with 0.33% curdlan; -○-, 1.0% carrageenan with 0.667% curdlan; -■-, 1.0% individual gums with 1.0% curdlan)

To further characterize and compare the contribution of each polymer to η_a in a copolymeric hydrocolloidal system, a set of experiments were conducted based on the response surface methodology (RSM) with a quadratic model and the results were illustrated in both three-dimensional (3D) and two-dimensional (2D) contour plots (Figure 5.2). In the present study, the values of η_a at 2 s^{-1} shear rate, a typical shear rate at which hydrocolloids are stirred-in in many food preparations, were recorded for each combination of copolymers.

As seen in the 3D contour plot, the highest viscosity occurred when 1.0% (w/v) curdlan was in combination with 1.0% (w/v) carrageenan (Figure 5.2a). It is also apparent that curdlan, when present alone in a solution, had the lowest viscosity at 1% (w/v) as compared to the other gums. Therefore, the 3D contour plot curved upward along the carrageenan axis steeper than the curdlan axis. The highest viscosity was found in the carrageenan/curdlan system, reaching 42.3 Pa·s

at 1%/1% combination. Similar trends were found when curdlan was combined with guar or locust bean gum (Figure 5.2c-d).

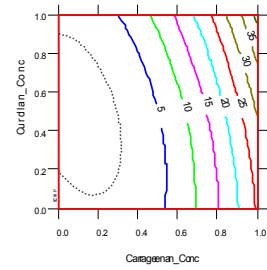
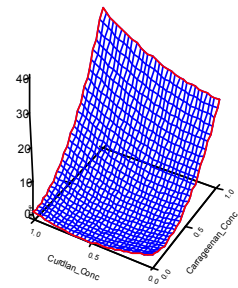
Conversely, the 3D viscosity contour plot of solutions containing xanthan/curdlan copolymers curved downward along the xanthan gum axis after steep increase at low concentration ranges up to 0.4% (w/v) (Figure 5.2b). This could be attributed to the high viscosity of xanthan gum even at very low concentration. For instance, 0.1% (w/v) xanthan gum solution gives 0.34 Pa·s. The food industry has taken advantage of such properties and used xanthan gum as a thickening agent to control and/or modify the texture of products in many food systems (Sworn 2000).

A synergistic relationship was found when locust bean gum was combined with curdlan gum, namely the viscosity of two gums combined were greater than the effect of each gum individually (Figure 5.2d). The viscosity of 1.0% (w/v) curdlan was 0.36 Pa·s and for 1.0% (w/v) locust the viscosity was 3.8 Pa·s. When they were added together at 1.0% (w/v) of each, the total viscosity was 13.80 Pa·s, greater than the sum of their respective viscosity at 1.0% (w/v).

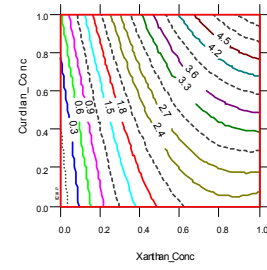
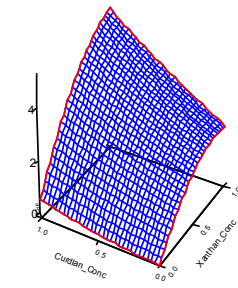
Synergism was also found with guar and curdlan combinations; however the effect was to a lesser extent compared with locust bean gum/curdlan. The viscosity of 1.0% of guar was 9.4 Pa·s and when it was mixed with 1.0% curdlan (viscosity 0.36 Pa·s); the viscosity reached 16.9 Pa·s. It is understood as a rule of thumb that by doubling the concentration of guar gum in an aqueous solution the viscosity would increase by 10 Pa·s (Wielinga 2000), i.e., if 2.0% (w/v) of guar

gum solution would be made, it would have a viscosity higher than 1.0% (w/v) guar gum combined with 1.0% (w/v) curdlan.

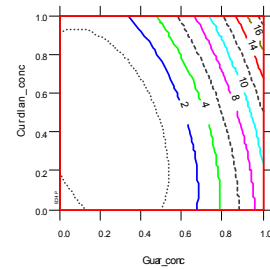
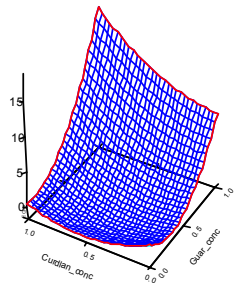
The difference in the degree of synergism between locust bean gum and guar gum could be attributed to the chemical structure of these two hydrocolloids. Both gums are galactomannans, which have an identical (1→4)-β-D-mannan backbones. However, there is a difference in the degree and type of substitution of these two hydrocolloids. Locust bean gum is unevenly substituted and has a low galactose content, but can lead to stronger synergistic interactions (Dea 1977; McCleary 1985). The unevenly substituted backbone allows for large smooth areas to be open for creating junction zones with adjacent molecules. In the case of guar gum, it is evenly substituted and has a higher galactose content, which means there are smaller areas on the backbone that are uninhibited, rendering less functionality (McCleary 1979; Launay 1986).



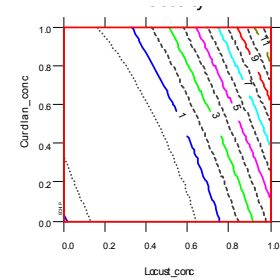
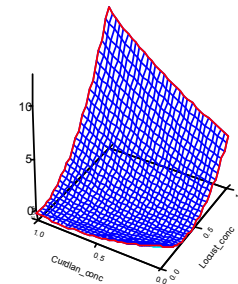
(a)



(b)



(c)



(d)

Figure 5.2: Comparison of 3-D and 2-D contour plots of apparent viscosity values for (a) Carrageenan/Curdlan (b) Xanthan/Curdlan (c) Guar/Curdlan and (d) Locust bean gum/Curdlan

5.1.2 Storage and Loss Modulus

To characterize the respective rheological capacity of curdlan gum copolymerized with carrageenan, xanthan, locust bean, and guar gum, the storage (G') and loss (G'') moduli of each combination were measured (Figure 5.3). In solutions containing carrageenan and curdlan copolymers at various concentrations, G' predominated over G'' at all frequencies studied, exhibiting more elastic than viscous behavior. At the higher frequencies studied (ca. 2 rad/s), G' decreased rapidly and the crossover points were found for 1.0% carrageenan alone and for 1.0% carrageenan with 0.33% curdlan (Figure 5.3a). However, crossover points would have occurred in a few radians per second higher for 1.0% carrageenan with 0.667% and 1.0% curdlan. It was observed that the crossover frequency increased with increasing curdlan concentration. In addition, as curdlan concentration increased, the values of G' and G'' increased. The crossover point signifies the frequency at which the characteristic behavior of the gels shifts from elastic to viscous (Lo 2003).

In solutions containing xanthan/curdlan copolymers, G' predominated at lower frequencies, indicating certain degrees of elastic behavior (Figure 5.3b). However, the crossover frequency occurred at a low frequency and it was observed as curdlan concentration increased so did the crossover frequency. The data illustrated that at lower frequencies, xanthan and curdlan combinations exhibited more elastic behavior. However, as frequency increased, more viscous behavior was displayed, as indicated by the increasing predomination of G'' at higher frequencies.

When guar and curdlan gum were combined, as curdlan concentration increased, so did the crossover point (Figure 5.3c). Guar gum in the solution all by itself showed slightly higher elastic properties at low frequencies; however, at those low frequencies, G' and G'' were overlapping. The loss modulus G'' predominated at higher frequencies, indicating more viscous behavior of the solution. Moreover, as curdlan concentration increased, so did the elastic behavior at low frequencies. At the higher frequencies G'' continued to predominate, in agreement with the very high viscosity observed in guar and curdlan combinations. On the other hand, locust gum, another galactomannan, in combination with curdlan in solution showed G'' predominant over G' for the entire frequency sweep. This observation suggests that the locust/curdlan combinations exhibited more viscous behavior than elastic. No crossover point was observed in any of the locust/curdlan combinations.

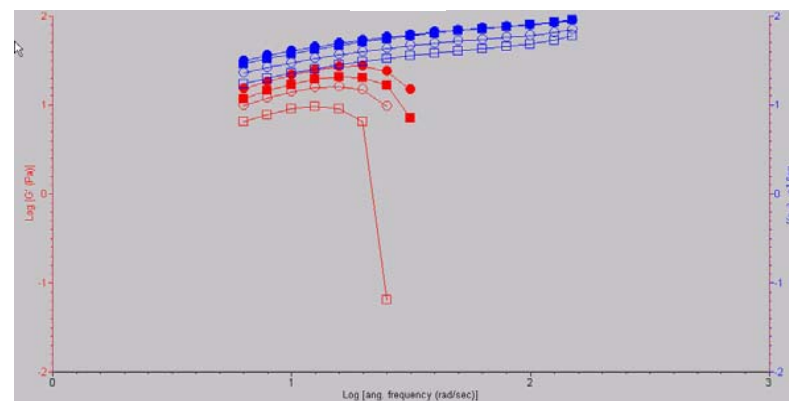
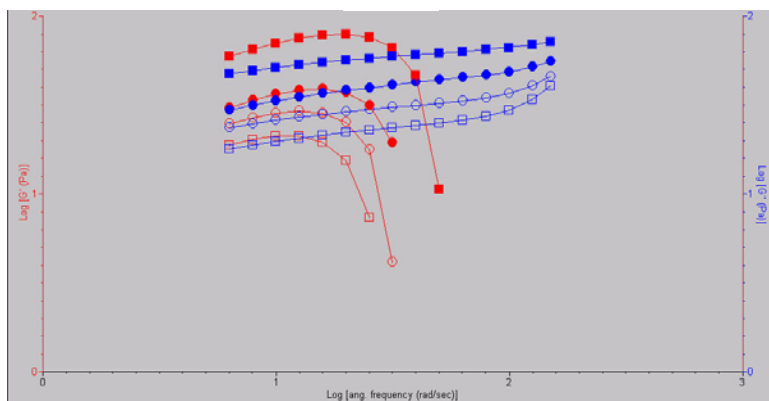
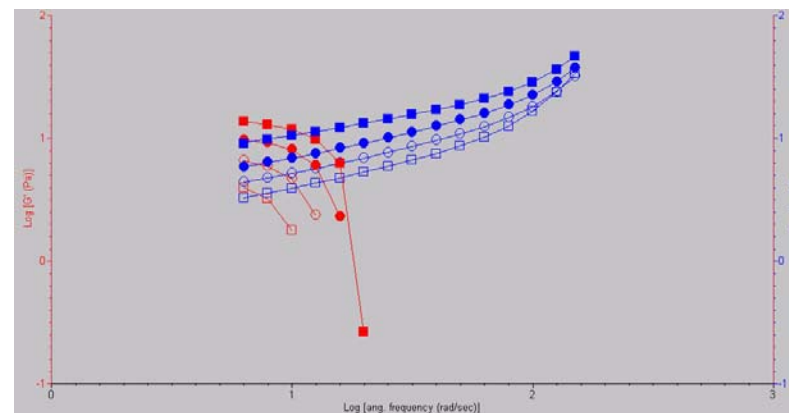
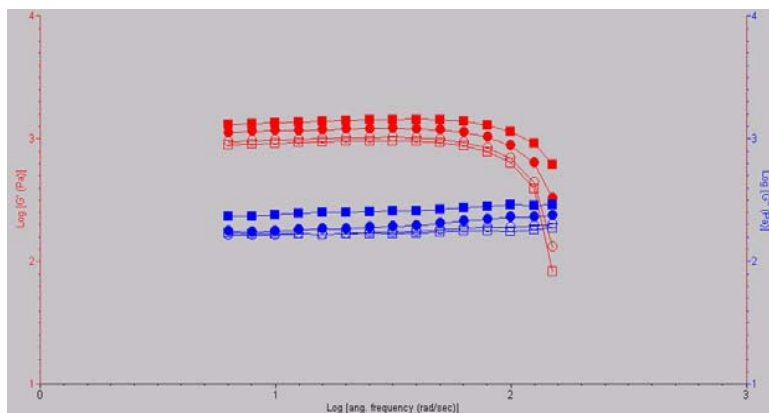


Figure 5.3: Storage and Loss Moduli for (a) Carrageenan/curdlan (b) Xanthan/curdlan (c) Guar/curdlan and (d) Locust/curdlan (-□-, 1.0% of individual gums; -○-, 1.0% individual gums with 0.33% curdlan; -●-, 1.0% individual gums with 0.667% curdlan; -■-, 1.0% individual gums with 1.0% curdlan)

5.1.3 Gel Strength

Gel strength is commonly measured to indicate the strength of a gel network. This can be a very important characteristic depending on what type of food system is being used. The graph produced can provide very valuable information such as the gel strength, the adhesiveness, as well as elasticity or brittleness of a particular gel (Fizman 2000; Hoefler 2004).

To illustrate how the gel strength of copolymers differs at various concentration combinations of curdlan and the other gums studied, both 3D and 2D contour plots were employed (Figure 5.4). In combinations that contained carrageenan/curdlan, guar/curdlan, and locust/curdlan, the highest gel strength was attained when there was 1.0% of each gum, making a total gum concentration of 2.0%. However, in the case of xanthan/curdlan, the maximum gel strength was reached at a curdlan concentration of 1.0% and a xanthan concentration of 0.64%, which showed higher gel strength than 1.0% of each. Out of all the combinations studied, only carrageenan/curdlan produced a real gel network, which also produced the highest gel strength.

It has been shown that the ability of gelling is due to the double helix formation of carrageenan (Anderson 1969; Rees 1969). In the present study, a temperature of 90°C was reached when preparing the solutions. Such a high temperature promoted the formation of random coils in the solution (Anderson 1969; Rees 1969; Rees 1970). Upon cooling, double helices formed junction zones, which produced a three-dimensional network. The gels were then placed in the refrigerator overnight, which induced aggregation of the junction zones by

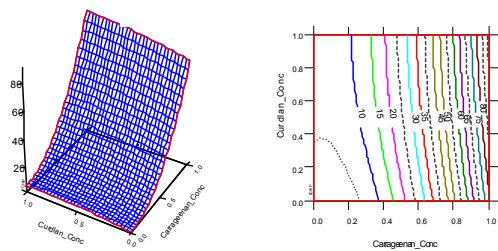
hydrogen bonding of adjacent double helices (Rees 1969; Moirano 1977; Hoefler 2001). Carrageenan with a 1.0% (w/v) concentration produced a gel network with relatively high gel strength. However, 1.0% (w/v) of curdlan alone had very low gel strength, again attributed to the low concentration of curdlan. Though the highest gel strength was reached when 1.0% (w/v) carrageenan mixed with 1.0% (w/v) curdlan, it appears that the interaction is more additive than synergistic. For all concentration combinations, no synergistic relationships were observed in regards to gel strength, only additive.

The results obtained in the present study help indicate the applications of these copolymers. Carrageenan is capable of forming a gel network upon cooling from high temperatures. Therefore it can be easily pumped through manufacturing equipment at high temperatures and able to form and shape upon cooling (Glicksman 1979; Pedersen 1979). This is observed in the case of chocolate and flavored milks, which uses very low levels of carrageenan (0.02-0.03%) (Hoefler 2004). The carrageenan is added to suspend cocoa particles and provide body to the milk. Carrageenan only dissolves in milk at temperatures above 50°C and contributes viscosity to the beverage only once the milk is cooled to below 30°C (Hoefler 2004). Therefore, the carrageenan can go through all the processing steps including pasteurization without contributing any increased viscosity. Primarily, carrageenan is used in products such as water dessert gels and milk puddings, due for the desirable gel-like texture (Glicksman 1979). Its gelling ability is the reason that carrageenan is the most common hydrocolloid used in meat processing. It is used predominately in poultry products, such as

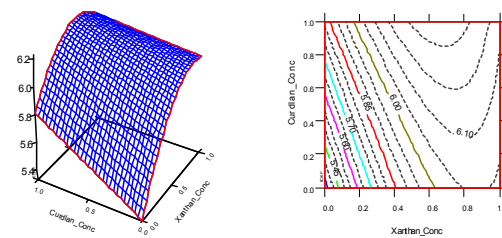
chicken breast, and precooked, reformed products such as deli meats (Imeson 2000). Carrageenan is not hydrated when introduced to the product. However, upon cooking the product, the carrageenan is hydrated and assists proteins in creating a gel network (Hoeffler 2004). The carrageenan also binds water in the gel and prevents it from running out during cooking. Therefore, carrageenan not only reinforces the gel network, but also improves the sliceability of the product, and minimizes syneresis (Imeson 2000; Hoeffler 2004).

The low gel strength of curdlan with xanthan, guar, and locust bean could find applications in products such as ice cream and salad dressings where added body is desired. Xanthan gum is most commonly used in salad dressings due to its ability to suspend herbs and spices while thickening and adding body to the product (Hoeffler 2004). Frequently, other hydrocolloids are added to salad dressings in addition to xanthan gum to further modify the texture (Sworn 2000; Hoeffler 2004). Therefore, curdlan combined with xanthan could be a potential combination.

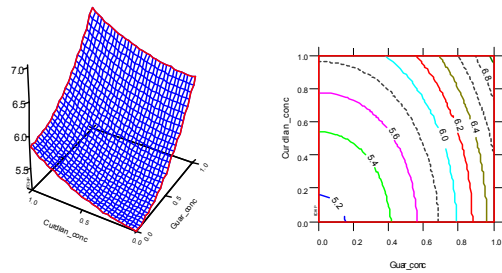
All four copolymers could be used as fat replacers as each provide either a thickening or gelling effect and can promote a creamy texture under the appropriate conditions (Hoeffler 2004).



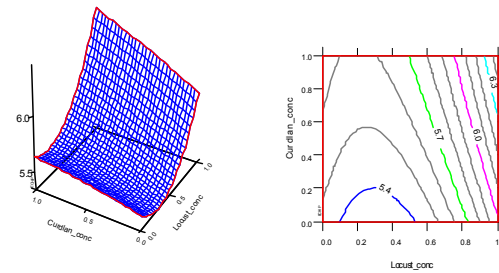
(a)



(b)



(c)



(d)

Figure 5.4: Comparison of gel strength for the following copolymers (a) Carrageenan/Curdlan (b) Xanthan/Curdlan (c) Guar/Curdlan and (d) Locust bean gum/Curdlan

5.1.4 Adhesiveness

It is apparent with the 3D and 2D contour plots that curdlan reduced the adhesiveness, which refers to amount of work needed to overcome the attractive forces between the surface of the food product and the surface of the material with which it comes in contact (Texture Technologies Corp), of the carrageenan/curdlan combinations (Figure 5.5). The highest degree of adhesiveness was observed when 1.0% (w/v) carrageenan was in the solution alone (Figure 5.5a). This reduction in adhesiveness is desirable in processing and manufacturing. However, quite the opposite was observed for combinations containing xanthan, guar, and locust bean gum.

In the xanthan/curdlan and locust/curdlan combinations, adhesiveness was the greatest when 1.0% (w/v) curdlan and 1.0% (w/v) of xanthan (Figure 5.5b) or locust bean gum (Figure 5.5d) was used. In all solutions, it was found that curdlan in the solution alone did not have good adhesive properties, whereas 1.0% (w/v) of each of the other gums by themselves showed higher adhesive properties than curdlan. Except for the carrageenan/curdlan mixture, when 1.0% (w/v) curdlan was combined with 1.0% (w/v) of the other gums, respectively, the solution adhesiveness was at its maximum. Among all combinations investigated in the present study, the locust/curdlan combination exhibited the highest degree of adhesiveness, which was supported by visual observations that a large amount of sample solution adhered to the tip of the probe on the Texture Analyzer.

Adhesiveness can be observed two different ways: adhesion to manufacturing equipment or sticking to fingers and parts of the mouth (Fizman

2000). Adhesiveness may be deemed a positive attribute in food products such as puddings, bakery products, and confectionery products (Fizman 2000; Fizman 2000). In the present study, curdlan combined with xanthan, guar, and locust bean gum had high levels of adhesiveness. These copolymers could potentially be used in salad dressing formulations. Manufacturers and consumers, in most cases, want a salad dressing which clings to the salad and won't quickly collect in the bottom of the bowl (Sworn 2000; Hoefler 2004). Therefore, this high adhesiveness would be desirable in this type of product.

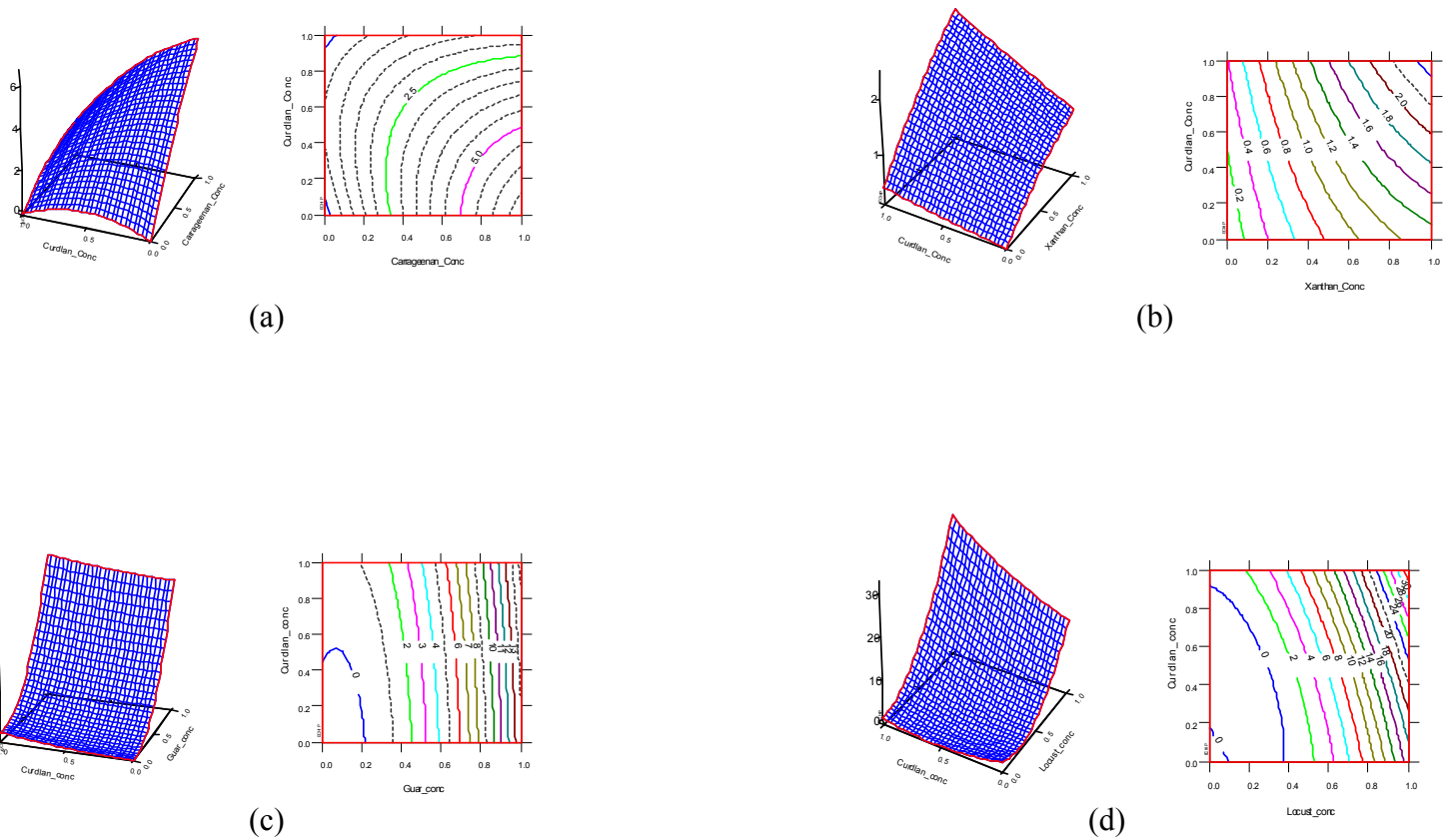


Figure 5.5: Three-dimensional and two-dimensional contour plots showing the comparison of adhesiveness between the copolymers of (a) Carrageenan/Curdlan solutions (b) Xanthan/Curdlan solutions (c) Guar/Curdlan solutions and (d) Locust bean gum/Curdlan solutions

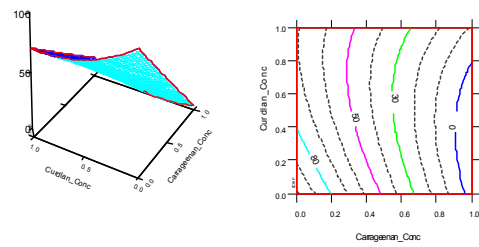
5.1.5 Syneresis

Syneresis, the separation of liquid from a gel, is a common problem with some food hydrocolloids in food applications. Without proper control or preventative measure, syneresis could result in significant loss of moisture, flavor, color, and eventually the quality of food (Glicksman 1977; Hoefler 2004). It has been researched that, by proper blending of hydrocolloids, the degree of syneresis could either be reduced or delayed (Imeson 2000; Hoefler 2004).

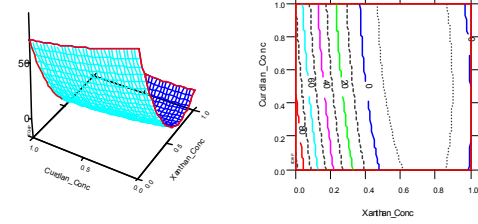
Measured by the percent of water secreted from the solutions during 20 minutes of centrifugal force ($707 \times g$), curdlan alone in the solution exhibited certain degrees of syneresis, due mainly to the relatively low concentration of curdlan and lack of a gel network. A gel-like network was only found in the bottom of the centrifuge tube after the supernatant was decanted. Since syneresis is, in most cases, an undesirable characteristic, a combination of hydrocolloids that could reduce or delay syneresis would be of great interest to the food industry.

In the case of carrageenan/curdlan, the optimal concentration combination that yielded the lowest amount of syneresis was found at 1.0% (w/v) carrageenan and 0.33% (w/v) curdlan (Figure 5.6a). Similarly, in the xanthan/curdlan mixture, the combination showing the least syneresis was found to be 0.68% (w/v) xanthan and 0.68% (w/v) curdlan. Moreover, all combinations containing xanthan and curdlan gum were very stable, which coincides with the results reported by Sanderson (1996).

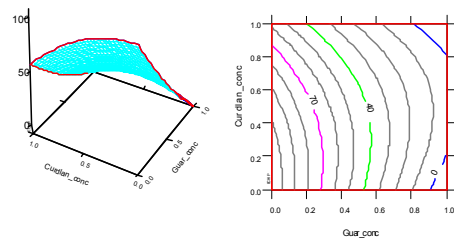
While guar gum or locust bean gum was used in combination with curdlan, the least syneresis was found when only guar gum (Figure 5.6c) or locust bean gum (Figure 5.6d) was present in the solution by themselves or used at 1.0% (w/v) in conjunction with 1.0% (w/v) curdlan, respectively. The degree of syneresis was reduced as guar or locust bean gum concentration was increased. These results suggest that, to avoid syneresis in copolymers containing curdlan and guar or locust bean gum, empirical measurements are required to fulfill the needs of each specific application. Interestingly, in all of the curdlan combinations, when curdlan was used in addition to another gum, the solutions were homogeneous before any centrifugal force was applied.



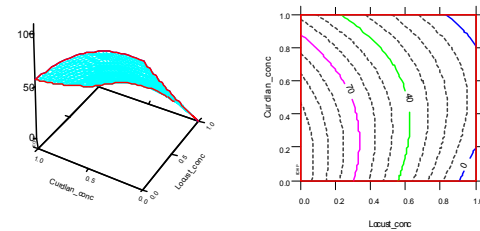
(a)



(b)



(c)



(d)

Figure 5.6: Contour Plots for Syneresis which is shown in % Water Lost for (a) Carrageenan/curdlan (b) Xanthan/curdlan (c) Guar/curdlan and (d) Locust/curdlan

5.1.6 Heat Stability

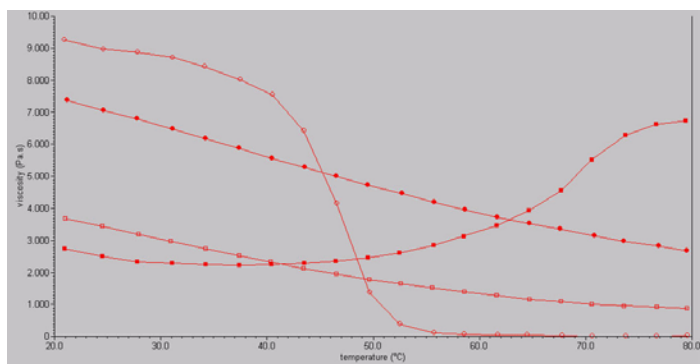
To understand the heat stability of each of the copolymers, the solution viscosity of various combinations of hydrocolloids in question was measured at a constant shear rate of 2 s^{-1} over a temperature range of 20°C to 80°C (Figure 5.7). Without combining with curdlan gum, carrageenan showed the most dramatic decrease in viscosity as temperature increased, with its steepest and quickest decrease starting around 40°C and reached below $0.02 \text{ Pa}\cdot\text{s}$ at 55°C (Figure 5.7a). The results are as expected since κ -carrageenan is known to create a thermo-reversible gel (Imeson 2000; Williams 2000). This means that at low temperatures a gel network is formed, however, at higher temperatures, the gel melts and becomes a liquid. Yet, upon cooling a gel network is reformed.

Both guar and locust bean gum also decreased in viscosity as heat increased, but the curve does not have a very steep slope. Furthermore, as opposed to carrageenan, guar and locust bean gum did not fall to extremely low viscosity. Overall guar showed good heat stability, but at too high a temperature the gum can degrade and become unable to function normally (Deis 2001). It has been reported that the viscosity of 1.0% (w/v) guar gum in aqueous solutions will decrease as temperature increases (Wielinga 2000). As temperature increases from 20° to 80°C a drop in viscosity should be approximately 50% . However, in the present study, when 1.0% (w/v) curdlan was added to the 1.0% (w/v) guar gum solution, the viscosity decreased only by 33% over the 20° to 80°C range (Figure 5.7d), showing enhanced heat stability.

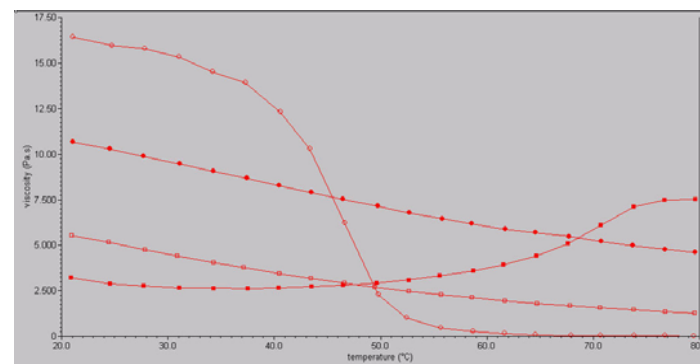
Xanthan gum, which is known for its stability over a wide temperature range (Pedersen 1979; Sworn 2000), is the only gum out of the four to have an overall increase in viscosity as temperature increased. There is approximately a 4 Pa·s viscosity difference from 20° to 80°C. This increase is primarily due to the intermolecular entanglement during the breakdown of the native conformation of xanthan molecules (Dea 1979). The phenomenon has been characterized spectroscopically using optical rotation and circular dichroism (Morris 1977). The xanthan molecules undergo a helix-coil transition as temperature increases. Once the xanthan is in coil form, the molecule would show the expected decrease in viscosity as seen in other hydrocolloids upon heating. If the temperature ramp would have been carried out to 100°C, a decrease in viscosity would have been observed after the increase in viscosity around 65°C (Dea 1977)

With increasing amounts of curdlan were added to 1.0% (w/v) of carrageenan, xanthan, guar, or locust bean gum, the effect of curdlan on heat stability could be identified (Figure 5.8b-d). It was found that, as curdlan concentration increased, so did initial and final viscosities. However, this was expected due to the higher total gum concentration. Carrageenan combinations, independent of added curdlan, still withheld its thermo-reversible gel network, which was unexpected because curdlan is thermo-irreversible when it is exposed to 80°C (Pszczola 1997; Jezequal 1998). Xanthan combined with curdlan did not change significantly except in the viscosity, but this is due to the increase in total gum concentration. Xanthan combinations still continued to increase at the higher temperatures. For the combinations that involved guar and locust bean gum, as

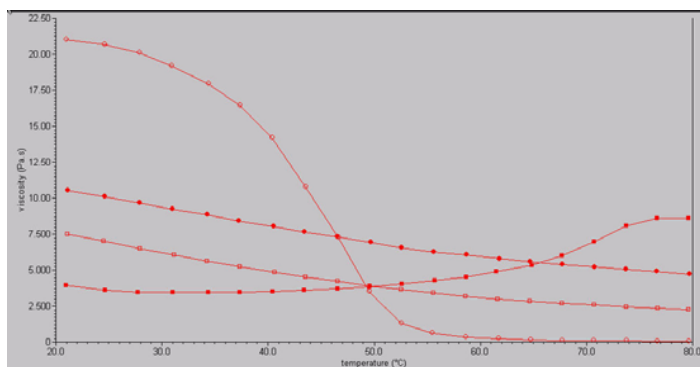
curdlan concentration increased, viscosity values did as well. This was also observed in terms of viscosity. For guar gum, the increase in total gum concentration is responsible for the viscosity increase. However, a synergistic relationship was observed with locust bean gum and curdlan gum for viscosity. For heat stability, the added curdlan increased the heat stability of the locust bean gum by over 10%. Therefore, curdlan added to the heat stability of guar and locust bean gums, but did not for xanthan or carrageenan.



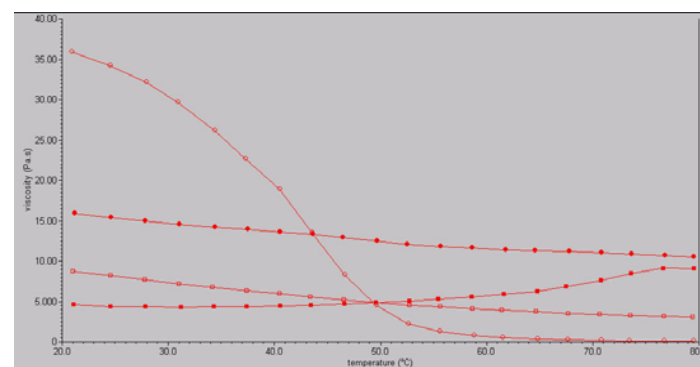
(a)



(b)



(c)



(d)

Figure 5.7: Heat Stability of (a) the individual gums at 1.0% (b) 1.0% individual gums with 0.33% curdlan (c) 1.0% individual gums with 0.667% curdlan and (d) 1.0% of the individual gums with 1.0% curdlan (-○-, carrageenan/curdlan; -■-, xanthan/curdlan; -●-, guar/curdlan; -□-, locust/curdlan)

5.2 FREEZE THAW STABILITY

Measurements for viscosity, storage and loss moduli, gel strength, adhesiveness, syneresis, and heat stability were taken after each individual freeze-thaw cycle. The results presented are from the combination of 1.0% (w/v) curdlan blended with 1.0% (w/v) of either carrageenan, xanthan, guar, or locust bean gum. This combination was chosen due to the results of the original data.

5.2.1 Viscosity

Apparent viscosity was reported as a single point at a shear rate of 2 s^{-1} (Figure 5.8). The viscosity for the carrageenan/curdlan combination decreased over the first two freeze-thaw cycles, but then increased slightly for the third through fifth cycle. The overall decrease in apparent viscosity was $10 \text{ Pa}\cdot\text{s}$. It is apparent that xanthan/curdlan combinations were the most stable over the freeze-thaw cycles as the viscosity was not altered significantly. A dramatic change in apparent viscosity was observed with the locust/curdlan combination. Upon the first freeze-thaw cycle, the locust/curdlan combination changed from a viscous liquid to a weak gel network, thus increasing the viscosity. The viscosity increased extensively during the first two freeze-thaw cycles, but decreased with the third freeze-thaw cycle. However, the viscosity after the fifth freeze-thaw cycle ($39.89 \text{ Pa}\cdot\text{s}$) was dramatically higher than before the solution was exposed to extreme temperatures ($11.97 \text{ Pa}\cdot\text{s}$). The gel network was produced due to the chemical structure of the galactomannan, locust bean gum. Locust bean gum is unevenly substituted which has smooth mannose backbone regions uninhibited.

These unsubstituted regions allow for the hydrocolloid to have more functionality (McCleary 1979; Launay 1986). In addition, Dea et al (1977) suggests that due to the low galactose concentration of locust bean gum, it signifies stronger synergistic interactions with other food hydrocolloids in addition to stronger gelling abilities when used independently. With freeze-thaw cycles, locust bean gum is known to self-associate, creating a weak gel (Wielinga 2000). The opposite was identified for guar/curdlan combinations. There was no viscosity increase following the first freeze/thaw cycle with solutions containing guar gum. Rather, the viscosity was maintained through the first freeze thaw cycle but then decreased beginning with the second cycle, which is in agreement with Dea (1979) and Wielinga (2000).

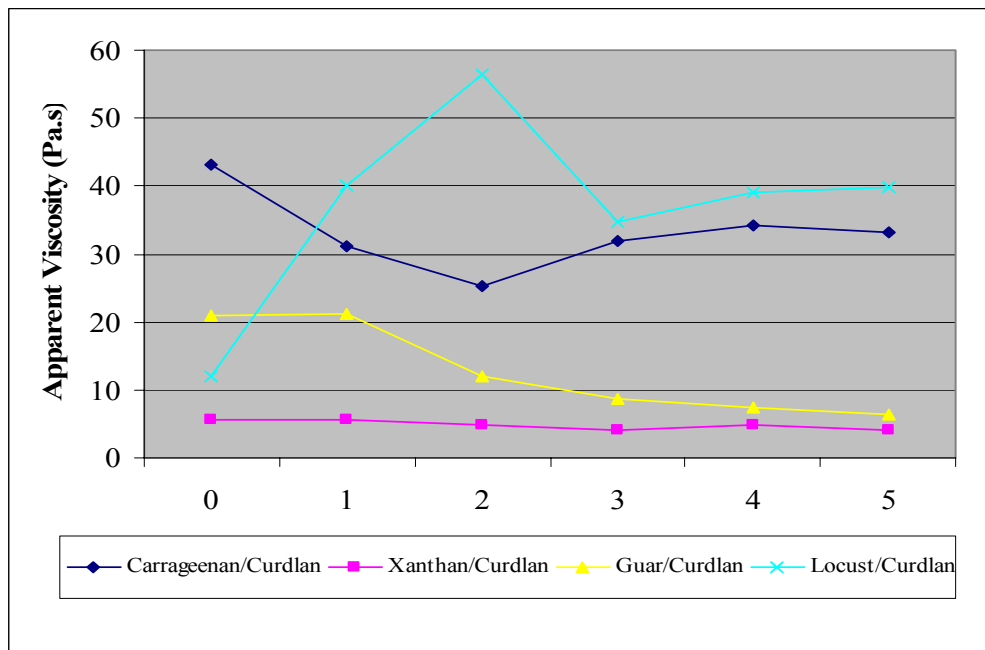


Figure 5.8: Apparent viscosity at $2s^{-1}$ shear rate for the copolymer blends over five freeze-thaw cycles

5.2.2 Storage and Loss Modulus

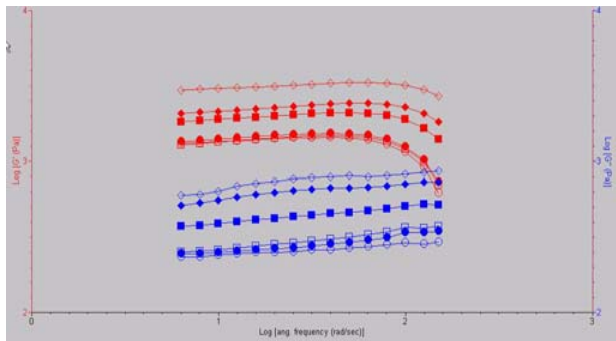
Stability of original characteristics regarding elasticity and viscosity components were compared over the five freeze-thaw cycles (Figure 5.9). In the carrageenan/curdlan combination (Figure 5.9a), during the first two cycles, the characteristics were similar to the solution prior to any freeze-thaw cycles. However, as frequencies and freeze-thaw cycles increased, G'' did as well. The storage modulus, G' , predominated over the entire frequency range studied and no crossover points were observed. Yet, as frequency increased, G'' increased and G' decreased, which was observed with the original data.

The xanthan/curdlan combination did not show a significant difference between any of the freeze-thaw cycles (Figure 5.9b). In past studies, which supports the present study, it suggests xanthan gum is a very stable hydrocolloid through a number of different environments, including freeze-thaw cycles (Pedersen 1979, Sanderson 1996, Sworn 2000). The only difference observed was a slight increase in G' at very low frequencies as freeze-thaw cycles continued, showing some increased elasticity.

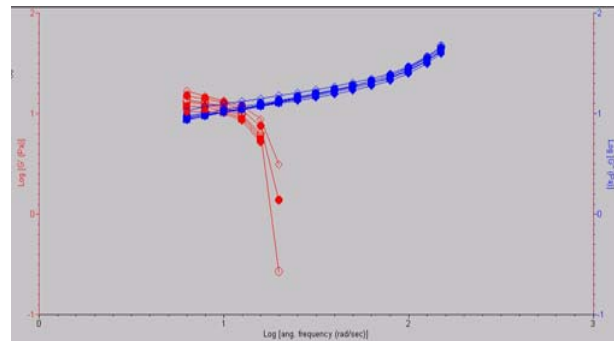
In the freeze-thaw cycles zero to four, G' predominated over G'' during exposure to low frequencies for the guar/curdlan combination (Figure 5.9c). As frequency increased, a crossover point was observed and viscous behavior predominated. The guar/curdlan solution not exposed to freeze-thaw treatment possessed the longest elastic curve; however, as the cycles continued a decrease in elasticity (G') was observed. By the fifth cycle, the solution displayed more

viscous behavior than elastic, seen by G'' predominating G' over the entire frequency sweep.

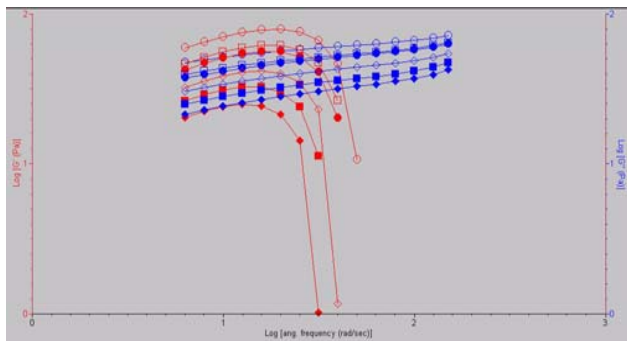
A dramatic change was observed for the locust/curdlan combination when it was exposed to the freeze/thaw conditions (Figure 5.9d). In the original data the loss modulus, G'' , predominated over the entire frequency sweep and no crossover point was observed. The solution was in liquid form prior to being exposed to freezing temperatures. However, after the first freeze-thaw cycle, the liquid changed into a gel network, which explains the significant change in the storage and loss moduli. Just after the first freeze-thaw cycle, G' and G'' increased by one decade. The storage modulus, G' , predominated at low frequencies and then at higher frequencies G'' predominated. This displayed a significant difference in the rheological properties after the freeze-thaw cycles. For cycles one through five, as frequency increased G' decreased and G'' continued to increase. This change is attributed to the self-association of locust bean gum, promoted by freeze concentration and ample time to thaw (Dea 1979).



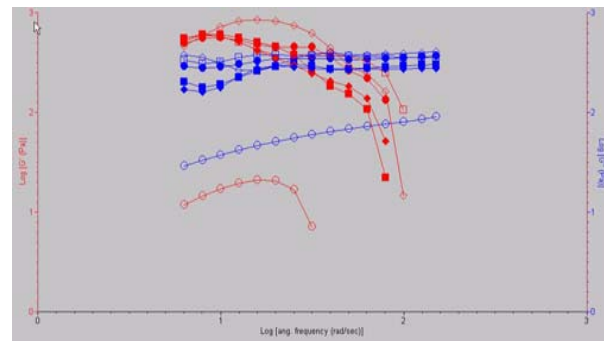
(a)



(b)



(c)



(d)

Figure 5.9: Frequency Sweep over the freeze-thaw cycles for (a) 1.0% carrageenan with 1.0% curdlan (b) 1.0% xanthan with 1.0% curdlan (c) 1.0% guar with 1.0% curdlan and (d) 1.0% locust with 1.0% curdlan (-o-, cycle 0; -●-, cycle 1; -□-, cycle 2; -■-, cycle 3; -◇-, cycle 4; -◆-, cycle 5)

5.2.3 Gel Strength

Over the course of five freeze-thaw cycles, guar/curdlan and xanthan/curdlan combinations, both in 2.0% (w/v) total gum concentrations, remained the most stable in gel strength, seen by consistent gel strength after each cycle (Figure 5.10). This combination could potentially be used in products that require freezing and thawing since there was not a large deviation in gel strength during the freeze-thaw cycles.

Locust with curdlan showed a sharp increase in gel strength, which was also observed in the viscosity results after the first freeze-thaw cycle. Again this is attributed to the formation of the gel network after the first freeze-thaw cycle. However, after the first freeze-thaw cycle the gel strength decreased and then remained relatively constant for the rest of the cycles. Overall though, it was observed that the gel strength at the end of the fifth freeze-thaw cycle (9.2g) was higher than before any freeze-thaw cycles occurred (6.51g).

The biggest decrease in gel strength was observed with the carrageenan/curdlan combination. Gel strength decreased dramatically during the first two freeze-thaw cycles and then slowly decreased each following cycle. The overall decrease in gel strength was 74.02 grams. Thus not showing carrageenan/curdlan to be a very stable combination, although κ -carrageenan is not freeze-thaw stable independently (Imeson 2000). A decrease was also seen for carrageenan/curdlan with viscosity measurements over the five freeze-thaw cycles. Therefore, 1% (w/v) carrageenan and 1.0% curdlan would not be an ideal

combination to use in food products that need to retain high gel strength during freeze-thaw cycles.

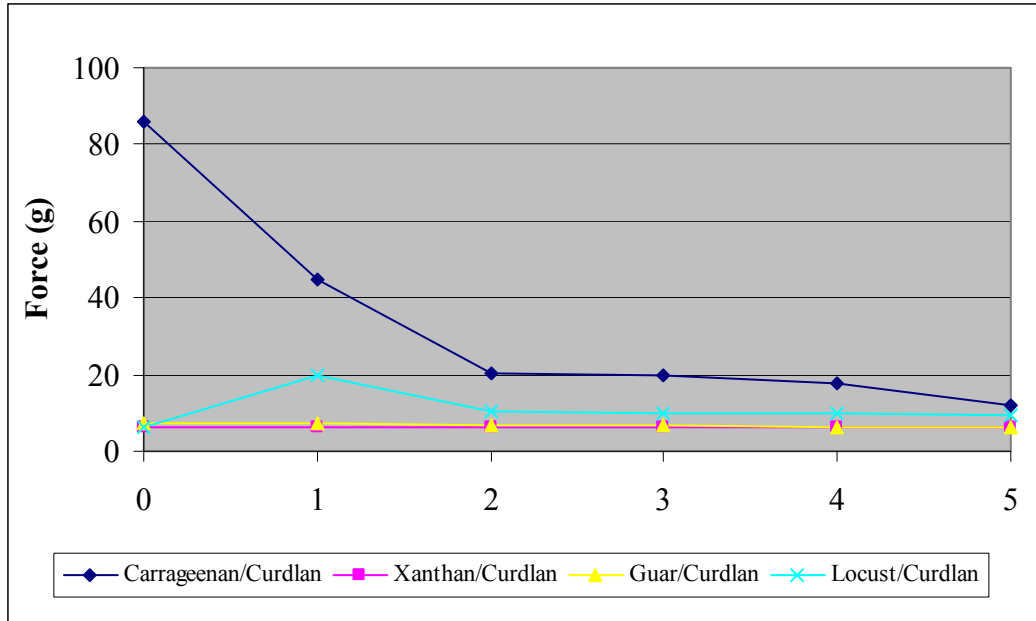


Figure 5.10: Gel Strength of the copolymers over five freeze-thaw cycles

5.2.4 Adhesiveness

Curdlan when combined with locust had the highest degree of adhesiveness prior to freeze-thaw cycles and carrageenan with curdlan had the lowest. However, after the first freeze-thaw cycle a shift was observed in the adhesiveness of locust with curdlan (Figure 5.11). Adhesiveness decreased from 33.65 g·mm to 0.59 g·mm. The reasoning is due to the development of a weak gel, which was also responsible for the increased viscosity and gel strength after the first freeze-thaw cycle.

The carrageenan/curdlan combination decreased in adhesiveness during the freeze-thaw cycles, thus again not showing a freeze-thaw stable combination.

Xanthan when combined with curdlan had the same degree of adhesiveness prior to and through the freeze-thaw cycles. Therefore, xanthan and curdlan combinations could be used in frozen food applications where adhesiveness is an important characteristic, such as the case with Cool-Whip. A decrease in adhesiveness was observed with the guar/curdlan combination as the freeze-thaw cycles continued. Though out of all the combinations, it had the highest adhesiveness after the freeze-thaw cycles. If adhesiveness is not a desirable characteristic in the frozen food system, as is the case for pastas, these copolymers could be used if they are stable in other aspects (Fizman 2000).

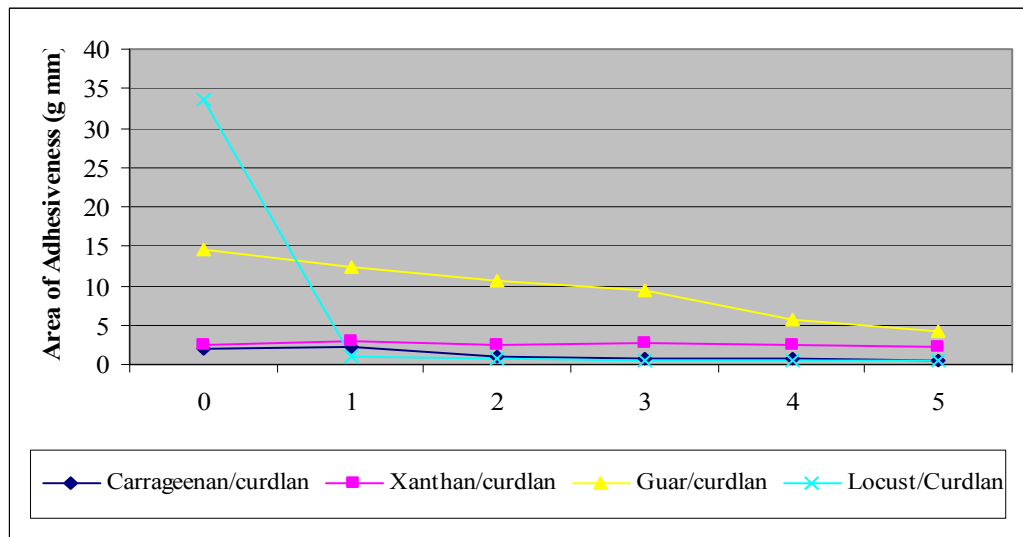


Figure 5.11: Comparison of adhesiveness properties of the copolymers over the five freeze-thaw cycles

5.2.5 Syneresis

Over the course of five freeze-thaw cycles (Figure 5.12), it is apparent that 1.0% (w/v) curdlan combined with 1.0% (w/v) xanthan or 1.0% (w/v) guar were the most stable combinations in the area of syneresis. During all five freeze-thaw

cycles, no water was excreted from the solutions, thus providing a very stable combination. All solutions which contained xanthan gum, independent if curdlan was added, were unaffected by centrifugal force. However, for the carrageenan/curdlan or locust/curdlan combinations syneresis did occur. The most pronounced syneresis was observed with the locust/curdlan combination, which released water as the cycles continued. Dea (1979) reports that “galactomannan gels are unstable and, on a second freeze-thaw cycle, synerese badly, often losing up to 50% of their water content”. Syneresis was very obvious in the solutions prior to centrifugal force as a weak gel network was surrounded by exuded water, which is characteristic for this galactomannan (Wielinga 2000). This was not only found in this particular combination, but in all combinations containing locust. However, of all combinations, the lowest degree of syneresis was observed by 1.0% (w/v) curdlan with 1.0% (w/v) locust in addition to 1.0% (w/v) locust with 0.667% (w/v) curdlan with syneresis percents at 55 and 54 respectively by the fifth cycle. Both of these combinations had much lower syneresis than 1.0% (w/v) of locust independently, which had a percent loss of 68.50 by the fifth freeze-thaw cycle. One percent (w/v) carrageenan and 1.0% (w/v) curdlan combinations exhibited no syneresis prior to any freeze-thaw cycle. However, after the first freeze-thaw cycle, close to 20% water was lost and this continued for the remainder of the freeze-thaw cycles. It is known that kappa-carrageenan is subject to syneresis, which causes gel shrinkage due to the loss of fluid (Imeson 2000). And because of this, kappa-carrageenan has very poor potential for good freeze-thaw stability. Similar to locust bean gum,

combinations containing 1.0% (w/v) carrageenan with 1.0% (w/v) curdlan and 1.0% (w/v) carrageenan with 0.667% (w/v) curdlan both had the lowest amounts of syneresis. The water lost for 1.0% (w/v) carrageenan alone was 47% by the fifth cycle, whereas the percent lost for 1.0% (w/v) carrageenan with 1.0% (w/v) curdlan was 13% by the fifth cycle. Therefore, curdlan helped stabilize both the locust/curdlan and carrageenan/curdlan combinations, but it is still not ideal for products that require freezing and thawing steps as the case with frozen pies.

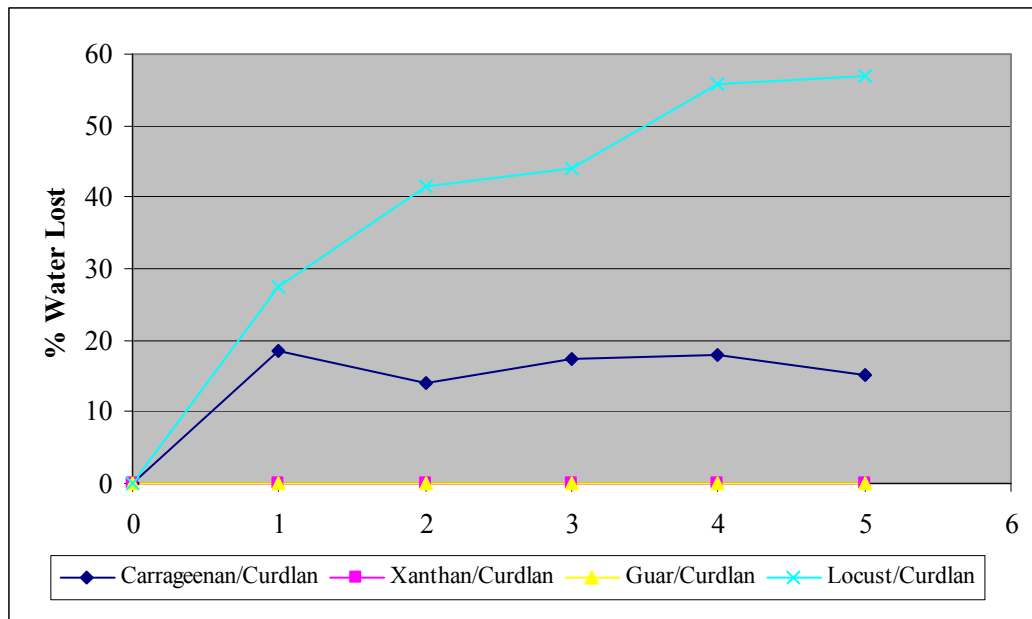


Figure 5.12: Syneresis over five freeze-thaw cycles for 1.0% individual gums combined with 1.0% curdlan gum

5.2.6 Heat Stability

Heat stability testing was also preformed after each freeze-thaw cycle. Results show the viscosity at 80°C during 2 s⁻¹ shear rate (Figure 5.13). Carrageenan with curdlan remained to have a very low viscosity at 80°C during

the freeze-thaw cycles, though as the cycles occurred the final viscosity did decrease.

Xanthan combined with curdlan remained to be very stable in the area of heat stability showing almost no differences in viscosity over the five cycles. Again supporting that xanthan gum is a freeze-thaw stable hydrocolloid (Sworn 2000). Guar when combined with curdlan also remained stable over the course of several cycles, however, by the fourth cycle, the viscosity began to decrease slightly and a further decrease was seen by the fifth cycle. During the first two freeze-thaw cycles, locust/curdlan had an increase in viscosity at 80°C, which was also seen by the viscosity data for freeze-thaw cycles. However, the viscosity at 80°C decreased in cycles three through five. This could be accepted as the unstableness of the galactomannan gel which is produced under freeze-thaw conditions (Dea 1979).

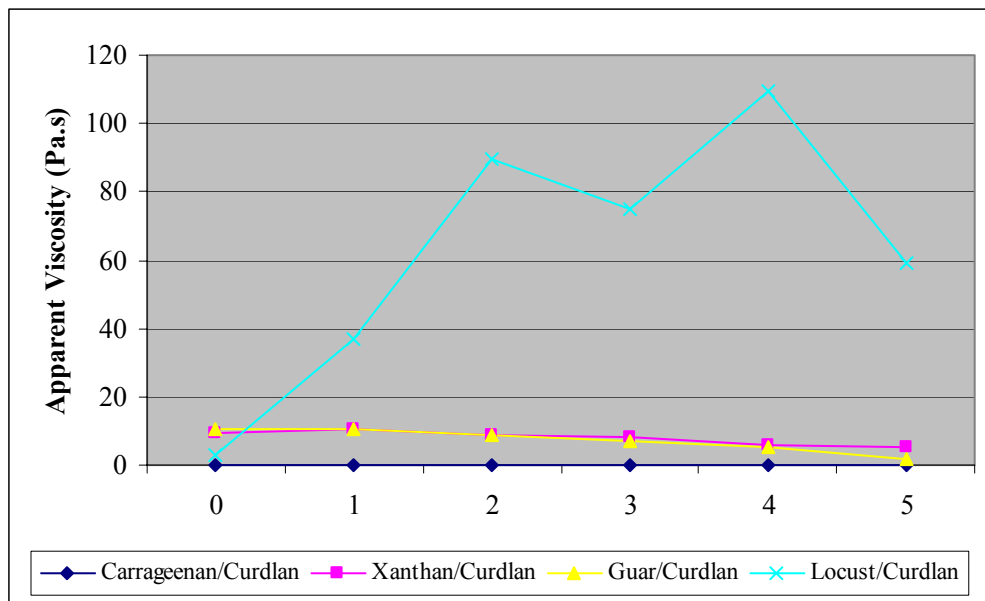
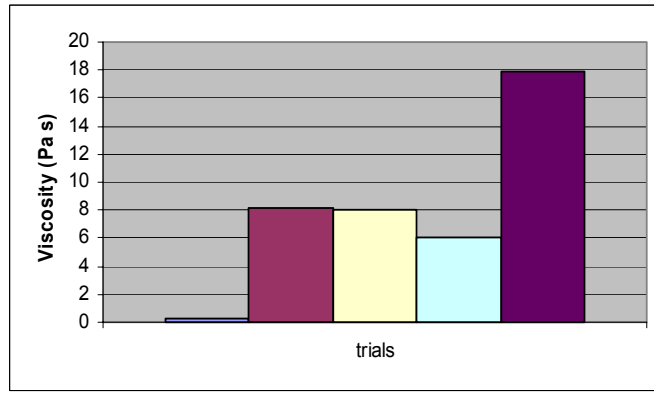


Figure 5.13: Viscosity at 80°C over five freeze-thaw cycles to determine heat stability

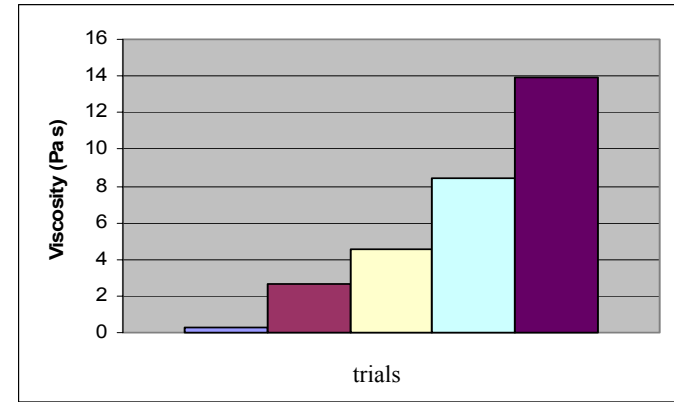
5.3 RHEOLOGICAL AND TEXTURAL CHARACTERISTICS USING SODIUM HYDROXIDE

5.3.1 Viscosity

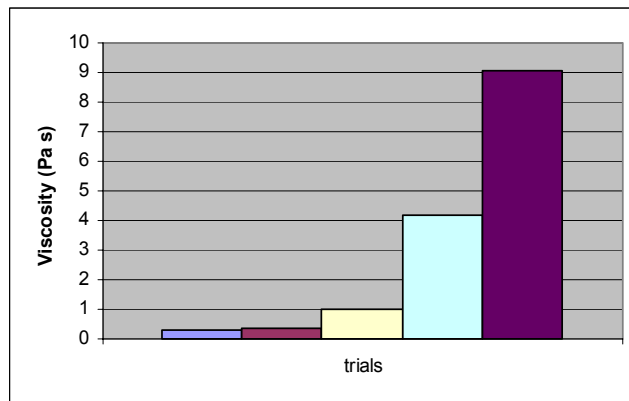
Apparent viscosity was reported as a single point at a shear rate of 2 s^{-1} (Figure 5.14). An increase in viscosity was observed for carrageenan/curdlan, xanthan/curdlan, and guar/curdlan combinations as curdlan concentration decreased. As carrageenan concentration increased (Figure 5.14a), viscosity increased significantly which is attributed to the gel network formed by carrageenan (Imeson 2000). In the locust bean/curdlan combination, when 0.5% curdlan was combined with 0.5% locust bean gum, the apparent viscosity observed was the lowest among all combinations studied. The results observed using sodium hydroxide did not reveal the same interactions for guar/curdlan and locust bean/curdlan combinations when DI water was used. This may be attributed to the difference in pH of the solutions, as both guar and locust bean are stable up to a pH of 10. Curdlan is not soluble in water at room temperature, but dissolves in an alkaline aqueous solution such as 0.1 M NaOH (Nishinari 2000). Therefore, this solubility difference might affect the interactions observed between different hydrocolloids.



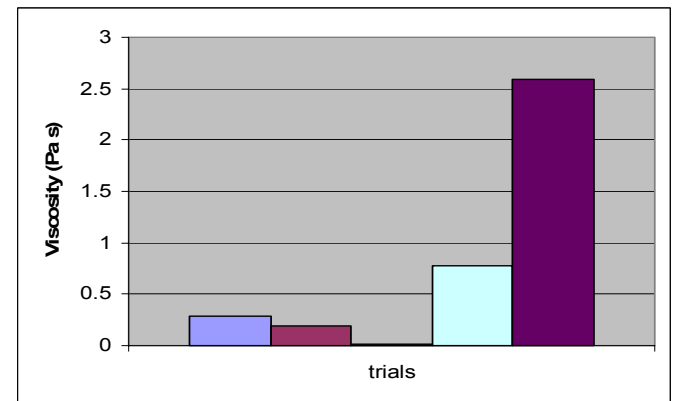
(a)



(b)



(c)



(d)

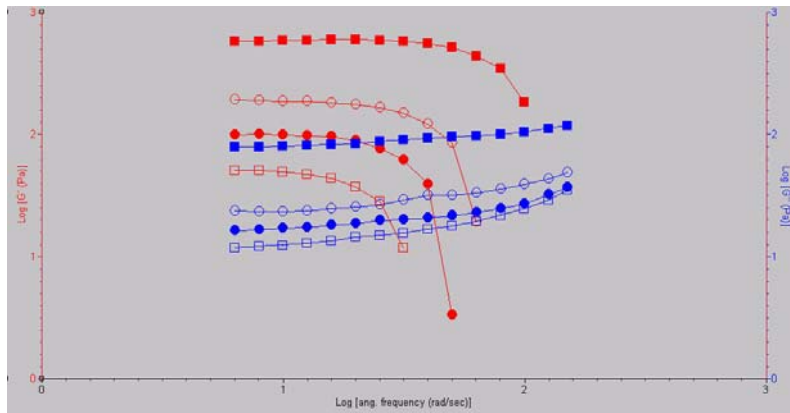
Figure 5.14 Apparent viscosity at shear rate 2/s of copolymers containing fixed concentrations of (a) Carrageenan/curdlan (b) xanthan/curdlan (c) guar/curdlan and (d) locust bean/ curdlan (■ 1.0% curdlan; ■ .7% curdlan, .3% other gum; ■ 5% curdlan, .5% other gum; ■ .3% curdlan, .7% other gum; ■ 1.0% other gum)

5.3.2 Storage and Loss Modulus

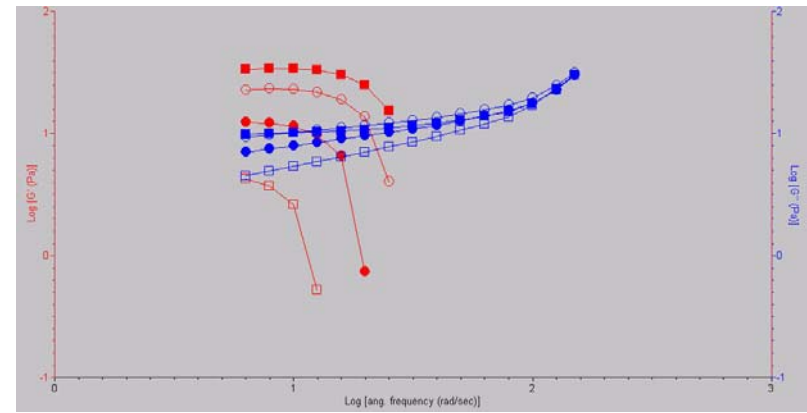
The storage (G') and loss (G'') moduli were measured to characterize the rheological properties of the copolymers in sodium hydroxide (Figure 5.15). When DI water was used as the solvent for the carrageenan/curdlan copolymer, G' predominated over the entire frequency sweep. However, when sodium hydroxide was used as the solvent, G' predominated at lower frequencies, with G'' predominating at higher frequencies (Figure 5.15a). As the curdlan concentration increased, the crossover point decreased. In addition, as the amount of carrageenan increased, higher decades were observed for both G' and G'' .

In solutions containing xanthan/curdlan copolymers, G' predominated at lower frequencies, showing some elastic components (Figure 5.15b). However, as the frequency increased, a crossover point was observed and G'' predominated. As xanthan gum increased, an increase in elasticity was observed, which contrast with results observed when DI water was used as a solvent.

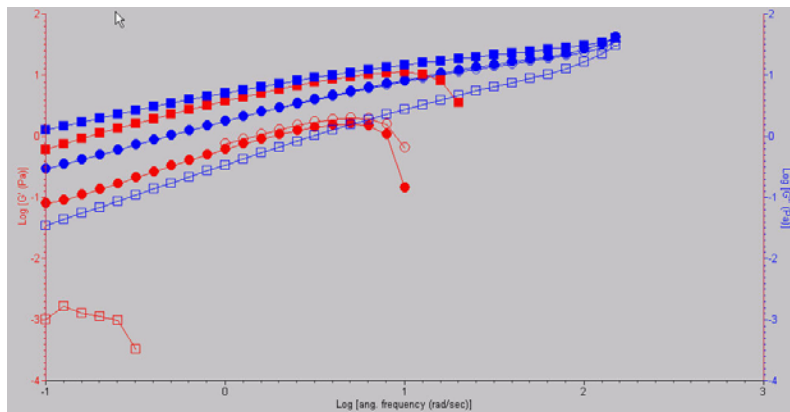
In both guar/curdlan (Figure 5.15c) and locust/curdlan (Figure 5.15d) all combinations evaluated had a predomination of G'' over the entire frequency sweep. In addition, as curdlan concentration decreased, there was an increase in the decades for G' and G'' . Results for solutions containing locust/curdlan were not very different between the two solvents. However, the results observed for guar/curdlan solutions were very different between the two solvents, DI water and sodium hydroxide. The results indicated differences in rheological properties of the copolymers as different solvents were used.



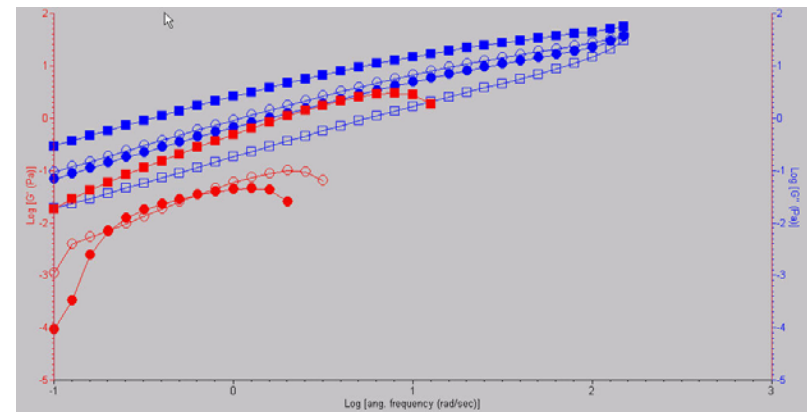
(a)



(b)



(c)

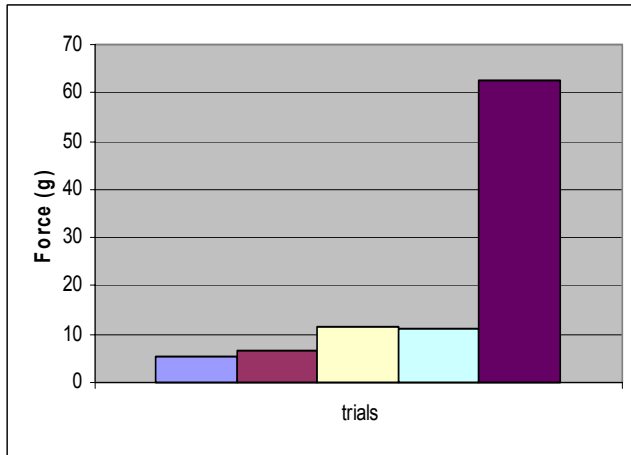


(d)

Figure 5.15 Storage and Loss Moduli for (a) Carrageenan/curdlan (b) Xanthan/curdlan (c) Guar/curdlan and (d) Locust/curdlan (-■-, 1.0% other gums (no curdlan); -○-, 0.7% other gums with 0.3% curdlan; -●-, 0.5% other gums with 0.5% curdlan; -□-, 0.3% other gums with 0.7% curdlan)

5.3.3 Gel Strength

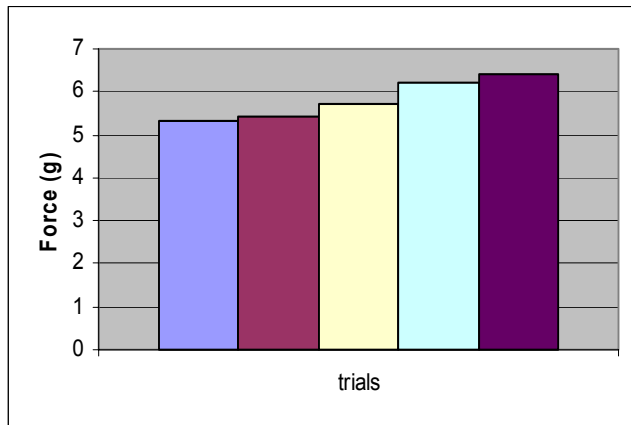
Gel strength was evaluated for the copolymers when sodium hydroxide was used as the solvent. In all combinations studied, the highest gel strength was attained when there was 1.0% (w/v) of carrageenan, xanthan, guar, or locust bean used without the addition of any curdlan gum. Unlike the carrageenan/curdlan results observed from when DI water was used, no additive or synergistic effect was observed. However, in the solutions containing xanthan/curdlan, guar/curdlan, and locust/curdlan, each of these displayed an additive effect in gel strength. For these particular combinations, this was also observed when DI water was used as the solvent.



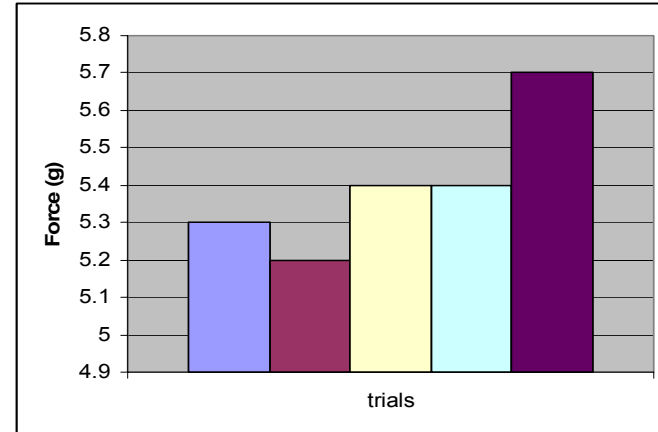
(a)



(b)



(c)



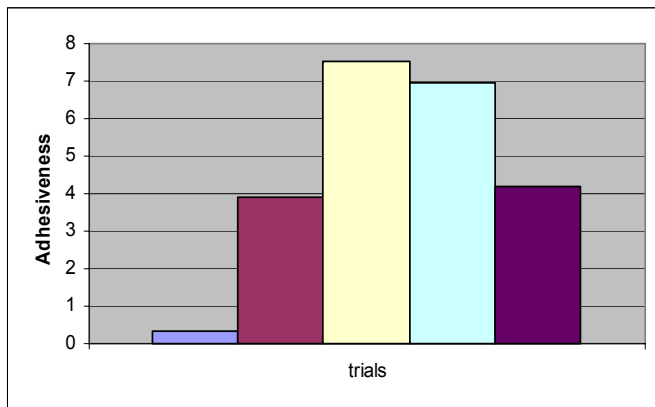
(d)

Figure 5.16 Gel strength of fixed concentrations of copolymers containing (a) Carrageenan/curdlan (b) xanthan/curdlan (c) guar/curdlan and (d) locust bean/ curdlan (■ 1.0% curdlan; ■ .7% curdlan, .3% other gum; ■ .5% curdlan, .5% other gum; ■ .3% curdlan, .7% other gum; ■ 1.0% other gum)

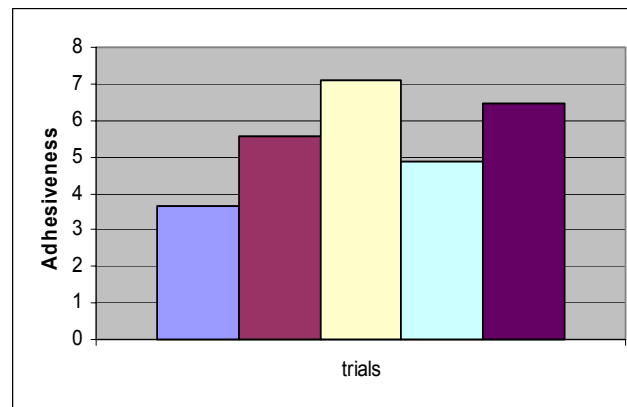
5.3.4 Adhesiveness

Adhesiveness is defined as the amount of work needed to overcome the attractive forces between the surface of the food product and the surface of the material in which it comes in contact (Texture Technologies Corp.). It is apparent that adhesiveness was increased when 0.5% (w/v) curdlan was combined with 0.5% (w/v) carrageenan when sodium hydroxide was used for the solvent (Figure 5.17a). However, quite the opposite was observed when DI water was used as the solvent, which indicated a sharp decrease in adhesiveness when the two gums were combined in equal amounts. Not only was an increase in adhesiveness observed for carrageenan/curdlan but also for the 0.5% xanthan with 0.5% curdlan combination. When compared to the results obtained using DI water, the xanthan/curdlan combination did not behave very differently.

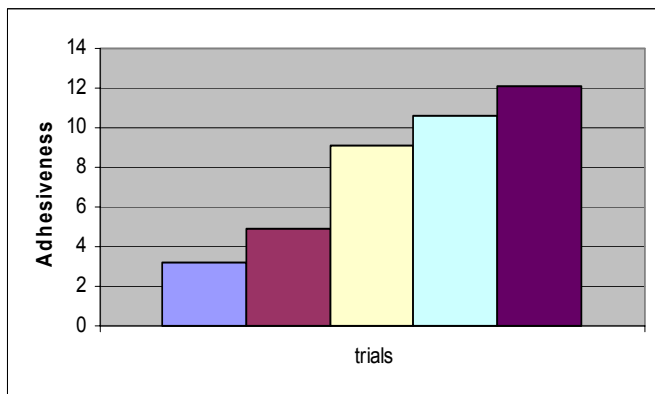
A combination where a large difference was observed was with the locust/curdlan combination (Figure 5.17d). When DI water was used as the solvent, equal amounts of locust bean and curdlan gum displayed the highest amount of adhesiveness over all the combinations evaluated. However, with the solvent sodium hydroxide, 1.0% locust bean gum displayed more adhesiveness than any combination of locust bean with curdlan gum. In addition, the 0.5% locust with 0.5% curdlan, had the lowest amount of adhesiveness compared to this combination with any other gum, which deviates from the results significantly when using DI water.



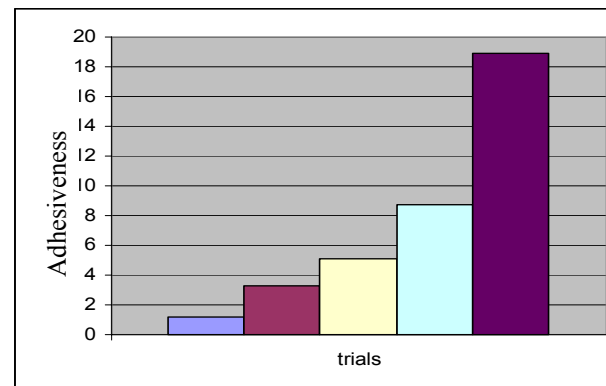
(a)



(b)



(c)



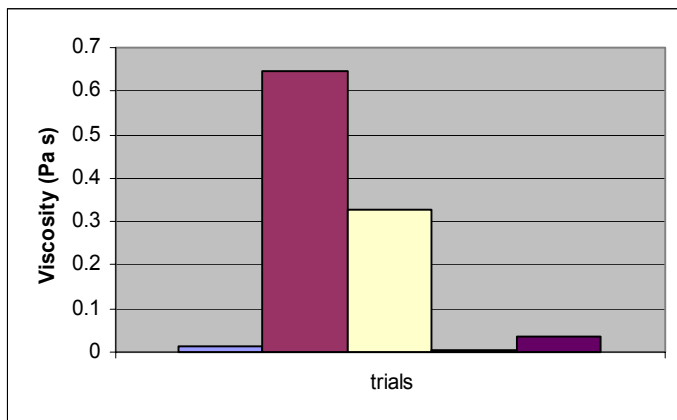
(d)

Figure 5.17 Adhesiveness of copolymers containing fixed concentrations of (a) Carrageenan/curdlan (b) xanthan/curdlan (c) guar/curdlan and (d) locust bean/ curdlan (■ 1.0% curdlan; ■ .7% curdlan, .3% other gum; ■ 5% curdlan, .5% other gum; ■ .3% curdlan, .7% other gum; ■ 1.0% other gum)

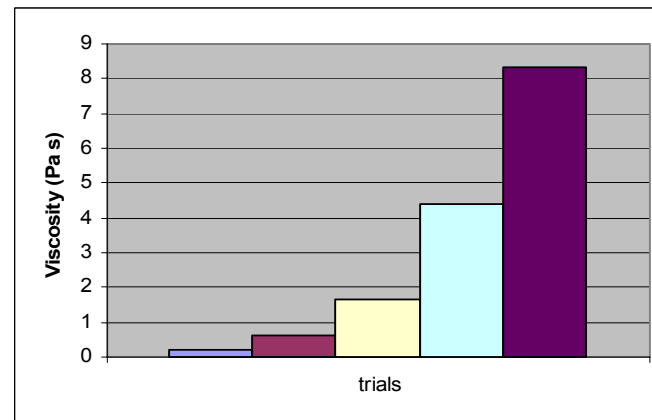
5.3.5 Heat Stability

The heat stability of each of the copolymers was evaluated under a constant shear rate of 2 s^{-1} over a temperature range of 20°C to 80°C (Figure 5.18). When carrageenan was combined with curdlan using DI water as the solvent, a thermoreversible gel was created. The results were expected since κ -carrageenan is known to create thermoreversible gels (Imeson 2000; Williams 2000). However, when sodium hydroxide was used, combinations of 0.7% curdlan, 0.3% carrageenan and 0.5% curdlan, 0.5% carrageenan, both had higher viscosities attained at 80°C . The combination that withstood viscosity best under high temperatures was the 0.7% curdlan with 0.3% carrageenan copolymer. This may be attributed to the ability of curdlan gum to produce thermo-irreversible gels (Nishinari 2000).

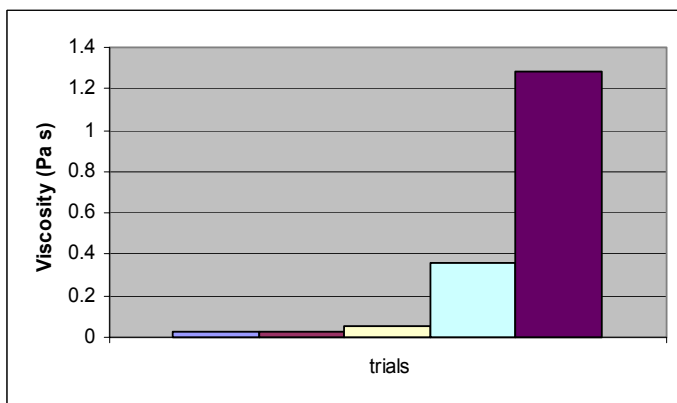
For the copolymers containing xanthan/curdlan, guar/curdlan, and locust/curdlan, the highest viscosity at 80°C was observed when curdlan was not included. For guar/curdlan and locust/curdlan these results deviate from those obtained when DI water was used as the solvent. In the aqueous solutions, the solutions containing curdlan gum with guar and locust bean gum displayed enhanced heat stability



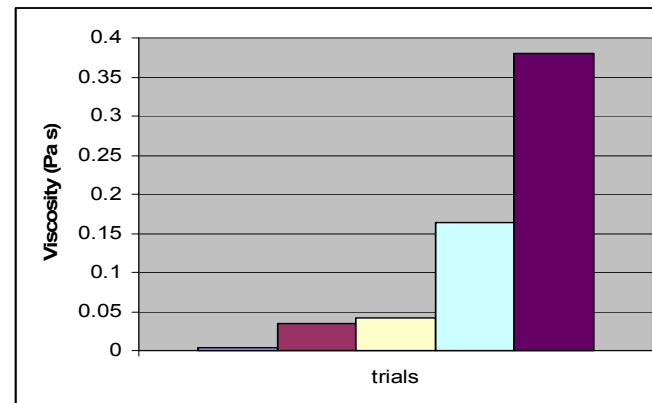
(a)



(b)



(c)



(d)

Figure 5.18 Apparent viscosity at 80°C under a shear rate 2/s for copolymers containing fixed concentrations of (a) Carrageenan/curdlan (b) xanthan/curdlan (c) guar/curdlan and (d) locust bean/ curdlan (■ 1.0% curdlan; ■ .7% curdlan, .3% other gum; ■ 5% curdlan, .5% other gum; ■ .3% curdlan, .7% other gum; ■ 1.0% other gum)

Chapter 6

Conclusions and Recommendations for Future Work

An AR2000 Rheometer was used to characterize the rheological properties of the copolymers. All combinations exhibited shear-thinning behavior with increasing shear rate. A synergistic relationship was observed for curdlan combined with guar and locust bean gum in apparent viscosity measurements. Storage and loss moduli were studied during a frequency sweep. For all copolymer blends, as curdlan concentration increased, the crossover frequency also increased, except for locust/curdlan combinations which exhibited no crossover point. An additive interaction was observed for gel strength in all cases of copolymers containing curdlan gum. Adhesiveness was also measured for all copolymer blends. In all combinations, except carrageenan/curdlan, curdlan increased adhesiveness of the copolymers. However, curdlan dramatically decreased adhesiveness for carrageenan gels. In addition, curdlan added to syneresis stability for all copolymers studied. Unexpectedly, curdlan did not increase the heat stability of carrageenan gels. Curdlan also did not enhance the heat stability of xanthan gum as xanthan gum is already extremely heat stable. However, heat stability was increased when curdlan was added to both guar and locust bean gum.

The freeze-stability of the copolymer solutions was also studied. Xanthan/curdlan blends remained very stable during the freeze-thaw cycles in all

aspects. Combinations with guar and curdlan were also stable in areas of gel strength, syneresis, and heat stability. Curdlan when combined with carrageenan and locust bean gum showed more stability than the gums independently. Even though curdlan increased the stability, the copolymers did not exhibit stability as in the case of xanthan/curdlan.

The use of sodium hydroxide as a solvent compared to DI water influenced the rheological and textural behavior of the copolymers.

Equipped with the knowledge of some basic aspects of copolymers containing curdlan gum, it is recommended future research be conducted using a higher curdlan gum concentration which would give a gel network. In addition, research could be conducted on the molecular level to analyze how the molecules are interacting. Now that some initial research has been completed on copolymers containing curdlan, it is also recommended to use a model food system to see how the copolymers interact with other food components. Lastly, it is recommended to further the knowledge of the stability of the copolymers under different conditions such as a wide range of pH.

APPENDIX A

RHEOLOGICAL AND TEXTURAL CHARACTERISTICS DATA

Table A.1 Apparent viscosity under increasing shear for carrageenan/curdlan (Figure 5.1)

1.0% car, 1.0% cur		1.0% car, 0.667% cur		1.0% car, 0.33% cur		1.0% car	
shear rate	viscosity	shear rate	viscosity	shear rate	viscosity	shear rate	viscosity
1/s	Pa.s	1/s	Pa.s	1/s	Pa.s	1/s	Pa.s
0.468	92.15	0.468	92.15	0.4947	84.88	0.4983	71.61
0.9428	61.7	0.9428	61.7	0.97	56.42	0.9735	47.95
1.418	49.07	1.418	49.07	1.444	43.76	1.447	37.37
1.893	41.2	1.893	41.2	1.92	35.51	1.923	30.46
2.369	35.4	2.369	35.4	2.395	29.44	2.398	25.47
2.844	31	2.844	31	2.871	24.68	2.874	21.73
3.319	27.24	3.319	27.24	3.346	21.07	3.269	19.31
3.793	23.95	3.793	23.95	3.821	17.91	3.825	16.4
4.27	21.2	4.27	21.2	4.295	15.55	4.22	14.84
4.744	18.55	4.744	18.55	4.693	13.77	4.695	13.14
5.22	16.42	5.22	16.42	5.166	12.1	5.171	11.88
5.694	14.31	5.694	14.31	5.642	10.76	5.645	10.61
6.169	12.84	6.169	12.84	6.117	9.678	6.121	9.506
6.644	11.62	6.644	11.62	6.593	8.774	6.595	8.544
7.119	10.41	7.119	10.41	7.066	7.925	7.071	7.673
7.594	9.48	7.594	9.48	7.542	7.278	7.545	6.957
7.989	8.827	7.989	8.827	8.017	6.733	8.02	6.327
8.466	7.976	8.466	7.976	8.492	6.278	8.495	5.735
8.939	7.316	8.939	7.316	8.967	5.82	8.971	5.306
9.415	6.828	9.415	6.828	9.442	5.472	9.445	4.949
9.811	6.502	9.811	6.502	9.838	5.248	9.842	4.608

Table A.2 Viscosity measurements for the four copolymer solutions (Figure 5.2)

Trial	Viscosity (Pa s) at 2 s ⁻¹			
	carrageenan/curdlan	xanthan/curdlan	guar/curdlan	locust/curdlan
1	0.35	0.35	0.35	0.35
2	0.02	0.02	0.02	0.02
3	10.47	4.10	2.80	1.02
4	42.30	5.20	21.00	14.10
5	26.65	2.50	9.50	3.90
6	0.00	0.00	0.00	0.00
7	9.97	1.80	1.61	0.89
8	1.32	1.20	0.20	0.10
9	23.70	3.20	10.85	6.00
10	33.01	4.00	11.20	9.20
11	3.20	2.40	0.53	0.15

Table A.3 Storage and Loss Moduli for the four copolymer solutions (Figure 5.3)

Part (a)

ang. Freq rad/sec	1.0% car, 1.0% cur		1.0% car, 0.667% cur		1.0% car, 0.33% cur		1.0% car	
	G' Pa	G'' Pa	G' Pa	G'' Pa	G' Pa	G'' Pa	G' Pa	G'' Pa
6.284	1302	233.2	1302	233.2	1118	174.7	949.4	162.9
7.912	1324	233.8	1324	233.8	1137	173	963.4	162
9.961	1345	239.2	1345	239.2	1153	175.6	976.8	163.8
12.54	1364	245.5	1364	245.5	1166	180	988	167.2
15.78	1383	249	1383	249	1180	182.3	1002	166.5
19.87	1406	248.9	1406	248.9	1195	183	1013	168.3
25.02	1421	252.6	1421	252.6	1203	188.1	1019	171.7
31.49	1431	259.2	1431	259.2	1207	192.2	1023	171.7
39.65	1436	258.9	1436	258.9	1202	195.4	1013	175.4
49.91	1421	266.6	1421	266.6	1177	202.8	987.3	180.9
62.81	1379	274.2	1379	274.2	1125	211.1	935.9	187.1
79.11	1295	280.8	1295	280.8	1030	217.6	840.3	189.9
99.57	1143	291	1143	291	876.4	228.6	693.1	189.8
125.4	913.3	284.3	913.3	284.3	631.5	229.5	439.2	194.2
150	617.5	291.4	617.5	291.4	326.8	234.2	129.8	200.6

Part (b)

ang. Freq rad/sec	1.0% xan, 1.0% cur		1.0% xan, 0.667% cur		1.0% xan, 0.33% cur		1.0% xan	
	G' Pa	G'' Pa	G' Pa	G'' Pa	G' Pa	G'' Pa	G' Pa	G'' Pa
6.284	9.618	5.813	13.65	9.089	6.527	4.376	3.977	3.254
7.912	9.141	6.288	12.88	9.785	5.873	4.734	3.194	3.541
9.961	8.065	6.829	11.74	10.5	4.618	5.158	1.788	3.887
12.54	6.006	7.473	9.793	11.28	2.34	5.644	-0.6726	4.284
15.78	2.302	8.218	6.234	12.18	-1.58	6.206	-4.73	4.728
19.87	-3.96	9.058	0.2651	13.18	-8.035	6.851	-11.29	5.284
25.02	-14.32	10	-9.931	14.27	-18.5	7.62	-21.97	5.896
31.49	-30.92	11.14	-26.44	15.54	-35.39	8.491	-39.07	6.614
39.65	-57.86	12.45	-53.26	16.99	-62.56	9.577	-66.57	7.498
49.91	-101.2	13.99	-96.86	18.72	-106.1	10.79	-110.8	8.607
62.81	-170.8	15.9	-165.7	21	-175.8	12.32	-180.5	10.14
79.11	-281.3	18.52	-275.9	23.95	-286.3	14.6	-291.6	12.51
99.57	-456.9	22.18	-451.4	28.4	-461.7	17.92	-467.9	16.47
125.4	-736.9	28.44	-733.3	36.11	-741.2	23.81	-750	23.58
150	-1069	37.07	-1066	46.53	-1072	31.58	-1082	33.55

Part (c)

ang. Freq rad/sec	1.0% gua, 1.0% cur		1.0% gua, 0.667% cur		1.0% gua, 0.33% cur		1.0% guar	
	G' Pa	G'' Pa	G' Pa	G'' Pa	G' Pa	G'' Pa	G' Pa	G'' Pa
6.284	59.38	47.15	30.32	29.65	24.85	23.58	18.82	17.87
7.912	65	49.25	33.49	31.48	26.85	24.75	20.22	18.81
9.961	70.36	51.29	36.24	33.22	28.52	25.95	21.11	19.7
12.54	74.91	53.12	38.22	34.9	29.15	26.97	21.08	20.54
15.78	78.11	54.85	38.82	36.5	28.32	27.95	19.56	21.36
19.87	78.94	56.42	37.05	38	25.13	28.92	15.49	22.14
25.02	75.71	57.78	31.47	39.47	17.77	29.78	7.405	22.86
31.49	66.46	59.23	19.27	40.89	4.143	30.62	-7.087	23.55
39.65	46.66	60.55	-2.945	42.29	-19.67	31.41	-31.74	24.31
49.91	10.58	61.7	-41.41	43.61	-59.82	32.25	-72.88	25.07
62.81	-51.1	63.13	-105.6	44.99	-126	33.29	-140.6	25.99
79.11	-154	64.6	-211.3	46.49	-233	34.56	-249.4	27.26
99.57	-322.8	66.49	-383.8	48.36	-404.6	36.6	-423.4	29.52
125.4	-599.6	68.95	-659.7	51.55	-679.9	40.43	-702.1	33.76
150	-923.5	71.91	-985.7	55.63	-1007	45.75	-1033	40.45

Part (d)

ang. Freq rad/sec	1.0% loc, 1.0% cur		1.0% loc, 0.667% cur		1.0% loc, 0.33% cur		1.0% loc	
	G' Pa	G'' Pa	G' Pa	G'' Pa	G' Pa	G'' Pa	G' Pa	G'' Pa
6.284	11.82	28.94	15	31.58	9.836	23	6.446	17.4
7.912	14.43	33.12	18.25	35.86	11.97	26.28	7.805	19.99
9.961	17.05	37.46	21.59	40.27	14	29.63	8.997	22.67
12.54	19.39	41.92	24.6	44.68	15.6	33.03	9.625	25.43
15.78	20.88	46.49	26.76	49.12	16.18	36.44	9.111	28.18
19.87	20.49	51.04	27.03	53.46	14.71	39.77	6.457	30.87
25.02	16.72	55.52	23.83	57.66	9.6	43.02	0.06491	33.52
31.49	7.175	59.96	14.85	61.69	-1.531	46.13	-12.4	36.02
39.65	-12.12	64.18	-4.063	65.53	-22.55	49.03	-34.85	38.43
49.91	-47.04	68.22	-38.74	69.17	-59.54	51.82	-73.56	40.81
62.81	-107.3	72.2	-98.77	72.64	-122.2	54.6	-137.8	43.13
79.11	-208.7	76.13	-200.4	76.14	-226.4	57.36	-243.4	45.58
99.57	-376.6	80.21	-368.6	79.76	-397.1	60.32	-416.1	48.45
125.4	-647	85.26	-639.9	84.26	-671.5	64.5	-692.6	52.98
150	-966.7	90.17	-961.8	89.2	-995.6	69.55	-1019	59.42

Table A.4 Gel strength measurements for the four copolymer solutions (Figure 5.4)

Trial	Gel Strength (force in grams)			
	carrageenan/curdlan	xanthan/curdlan	guar/curdlan	locust/curdlan
1	5.57	5.83	5.83	5.57
2	5.83	5.57	5.57	5.83
3	32.29	6.1	6.04	5.79
4	86.02	6.21	7.23	6.51
5	78.84	6.02	6.41	5.92
6	5.18	5.3	5.01	5.36
7	30.82	6.08	5.92	5.67
8	6.89	5.75	5.35	5.3
9	81.45	6.08	6.65	6.18
10	99.73	5.99	6.53	6.22
11	5.8	6.1	5.54	5.31

Table A.5 Adhesiveness measurements for the four copolymer solutions (Figure 5.5)

Trial	Adhesiveness			
	carrageenan/curdlan	xanthan/curdlan	guar/curdlan	locust/curdlan
1	0.35	0.35	0.35	0.35
2	0.3	0.3	0.3	0.3
3	0.87	1.58	4.87	9.01
4	1.89	2.56	14.56	33.65
5	5.11	1.35	14.43	17
6	0	0	0	0
7	7.89	1.06	4.98	5.37
8	1.41	0.58	0.61	0.52
9	9.59	1.6	13.27	20.16
10	2.03	2.07	15.56	26.47
11	0.69	1	0.96	0.82

Table A.6 Syneresis data for curdlan with carrageenan, xanthan, guar, and locust (Figure 5.6)

Trial	Syneresis (% Water Lost (v/v))			
	carrageenan/curdlan	xanthan/curdlan	guar/curdlan	locust/curdlan
1	63.53	63.53	63.53	63.53
2	85.56	85.56	85.56	85.56
3	59.26	0	0	0
4	0	0	0	0
5	0	0	0	0
6	100	100	100	100
7	8.95	0	0	0
8	74.29	0	89.5	94.29
9	0	0	0	0
10	0	0	0	0
11	14.29	0	71.36	81.43

Table A.7 Heat stability of trial 5, 9, 10, and 4 (Figure 5.7)

Carrageenan/curdlan results				
	1.0% car, 1.0% cur	1.0% car, 0.667% cur	1.0% car, 0.33% cur	1.0% car
temperature °C	viscosity Pa.s	viscosity Pa.s	viscosity Pa.s	viscosity Pa.s
21	35.87	21.02	16.4	9.257
24.6	34.21	20.67	15.95	8.964
27.8	32.17	20.09	15.77	8.876
30.9	29.65	19.19	15.33	8.708
34.4	26.19	17.93	14.53	8.428
37.4	22.66	16.46	13.9	8.019
40.4	18.93	14.21	12.31	7.551
43.5	13.55	10.79	10.28	6.405
46.6	8.334	7.275	6.194	4.149
49.5	4.522	3.497	2.298	1.362
52.5	2.252	1.327	1.01	0.3872
55.4	1.311	0.6212	0.4534	0.1125
58.6	0.8047	0.3538	0.2536	0.06786
61.7	0.551	0.2326	0.1453	0.04264
64.7	0.3424	0.1612	0.06782	0.03758
67.7	0.2299	0.1238	0.04532	0.0231
70.7	0.1572	0.09658	0.03583	0.01207
73.7	0.1221	0.08033	0.03383	0.01002
76.6	0.1154	0.07007	0.02921	0.0111
79.6	0.1066	0.06181	0.02309	0.01606

Xanthan/curdlan results				
	1.0% xan, 1.0% cur	1.0% xan, 0.667% cur	1.0% xan, 0.33% cur	1.0% xan
temperature °C	viscosity Pa.s	viscosity Pa.s	viscosity Pa.s	viscosity Pa.s
21.1	4.651	3.937	3.205	2.746
24.6	4.405	3.611	2.886	2.506
27.9	4.341	3.489	2.765	2.341
31.2	4.317	3.444	2.666	2.282
34.3	4.348	3.454	2.639	2.245
37.4	4.392	3.471	2.636	2.227
40.5	4.468	3.522	2.674	2.253
43.5	4.562	3.61	2.726	2.281
46.6	4.695	3.721	2.802	2.352
49.6	4.856	3.87	2.93	2.452
52.7	5.062	4.045	3.089	2.615
55.5	5.272	4.279	3.318	2.838
58.6	5.568	4.543	3.595	3.132
61.6	5.872	4.901	3.942	3.47
64.8	6.287	5.338	4.4	3.927
67.5	6.837	6.032	5.093	4.552
70.8	7.601	6.957	6.092	5.52
73.6	8.481	8.067	7.116	6.291
76.6	9.11	8.599	7.489	6.621
79.6	9.095	8.588	7.518	6.731

Guar/curdlan results

	1.0% gua, 1.0% cur	1.0% gua, 0.667% cur	1.0% gua, 0.33% cur	1.0% guar
temperature °C	viscosity Pa.s	viscosity Pa.s	viscosity Pa.s	viscosity Pa.s
17.2	21.1	10.51	8.95	7.825
16.52	24.6	10.08	8.653	7.506
15.84	27.8	9.657	8.326	7.174
15.15	31	9.231	8.061	6.866
14.72	34.4	8.826	7.737	6.499
14.29	37.4	8.396	7.449	6.205
13.93	40.3	8.033	7.118	5.876
13.48	43.5	7.635	6.829	5.568
13.09	46.6	7.292	6.49	5.231
12.57	49.8	6.929	6.191	4.964
12.17	52.6	6.567	5.874	4.662
11.85	55.6	6.269	5.614	4.405
11.61	58.5	6.048	5.379	4.156
11.46	61.6	5.8	5.148	3.925
11.35	64.7	5.589	4.906	3.709
11.18	67.6	5.407	4.72	3.506
11.08	70.7	5.22	4.508	3.302
10.97	73.6	5.052	4.373	3.128
10.76	76.9	4.892	4.137	2.966
10.57	79.5	4.705	3.997	2.879

Locust/curdlan results

	1.0% loc, 1.0% cur	1.0% loc, 0.667% cur	1.0% loc, 0.33% cur	1.0% locust
temperature °C	viscosity Pa.s	viscosity Pa.s	viscosity Pa.s	viscosity Pa.s
21.1	8.351	7.524	4.798	3.59
24.6	7.85	7	4.49	3.342
27.8	7.352	6.511	4.193	3.085
30.9	6.923	6.049	3.917	2.857
34.3	6.44	5.647	3.63	2.62
37.3	6.062	5.224	3.356	2.421
40.4	5.663	4.859	3.119	2.218
43.7	5.313	4.533	2.905	2.041
46.5	4.953	4.227	2.668	1.87
49.5	4.634	3.9	2.468	1.717
52.7	4.331	3.645	2.27	1.564
55.7	4.07	3.402	2.101	1.427
58.7	3.853	3.198	1.944	1.321
61.6	3.669	3.008	1.825	1.221
64.6	3.48	2.863	1.711	1.125
67.8	3.31	2.701	1.608	1.048
70.6	3.168	2.58	1.507	0.9587
73.8	3.043	2.468	1.426	0.8983
76.6	2.922	2.362	1.337	0.8201
79.7	2.815	2.259	1.285	0.7718

APPENDIX B

FREEZE-THAW STABILITY DATA

Table B.1 Viscosity over five freeze thaw cycles (Figure 5.8)

Freeze-thaw Cycles	Viscosity (Pa s) at 2 s ⁻¹			
	Carra/curdlan	Xan/curdlan	Guar/curdlan	Locust/curdlan
0	43.2	5.71	20.99	11.97
1	31.1	5.7	21.1	40
2	25.2	4.919	11.9	56.4
3	32	4.21	8.61	34.8
4	34.1	4.73	7.53	39
5	33.2	4.19	6.35	39.89

Table B.2 Storage and loss moduli over the freeze-thaw cycles (Figure 5.9)

Results for Carrageenan

ang. Freq rad/sec	Original		Cycle 1		Cycle 2		Cycle 3		Cycle 4		Cycle 5	
	G' Pa	G'' Pa	G' Pa	G'' Pa	G' Pa	G'' Pa	G' Pa	G'' Pa	G' Pa	G'' Pa	G' Pa	G'' Pa
6.284	1302	233.2	1342	244.8	1279	251.4	1821	373.1	2963	601.3	2074	512.6
7.912	1324	233.8	1370	246.3	1309	255.8	1856	377.7	3011	604.5	2104	531.4
9.961	1345	239.2	1400	249.4	1340	260.9	1892	389.9	3044	639.6	2138	556.3
12.54	1364	245.5	1426	254.6	1369	268.2	1926	401	3063	689.7	2175	582
15.78	1383	249	1452	259.6	1397	276.2	1962	411.5	3101	714	2219	603.3
19.87	1406	248.9	1478	264.6	1425	284.2	1999	422.5	3144	737.6	2265	621.6
25.02	1421	252.6	1501	269	1449	289.9	2032	435	3185	769.4	2310	641.8
31.49	1431	259.2	1515	276.2	1466	299.8	2064	442.9	3231	785.6	2356	655.8
39.65	1436	258.9	1523	283	1477	307	2085	456.5	3281	789.5	2398	665.2
49.91	1421	266.6	1514	291.1	1470	316.9	2098	461.3	3310	808.4	2431	670
62.81	1379	274.2	1478	301.1	1438	327.8	2078	473	3323	789.9	2430	672.8
79.11	1295	280.8	1399	314.9	1363	343.3	2023	486.3	3286	802.5	2387	689.8
99.57	1143	291	1243	340.1	1209	365.2	1891	507.6	3184	825.6	2283	707
125.4	913.3	284.3	1018	339.6	986.6	364.8	1659	524.5	2975	843.2	2065	728.1
150	617.5	291.4	730.8	347.2	700.9	372.8	1403	518.5	2701	863.6	1815	731.5

Results for Xanthan (Figure 5.9)

ang. Freq rad/sec	Original		Cycle 1		Cycle 2		Cycle 3		Cycle 4		Cycle 5	
	G' Pa	G'' Pa	G' Pa	G'' Pa	G' Pa	G'' Pa	G' Pa	G'' Pa	G' Pa	G'' Pa	G' Pa	G'' Pa
6.284	13.65	9.089	14.93	9.474	13.03	8.885	11.68	8.803	16.74	10.69	10.25	8.579
7.912	12.88	9.785	13.95	10.23	12.43	9.626	11.55	9.686	14.9	11.69	10.69	9.428
9.961	11.74	10.5	12.78	10.94	11.31	10.36	10.63	10.49	13.44	12.46	10.11	10.23
12.54	9.793	11.28	10.88	11.7	9.423	11.12	8.875	11.29	11.94	13.22	8.457	10.97
15.78	6.234	12.18	7.433	12.55	5.895	11.99	5.513	12.15	8.835	14.09	5.168	11.78
19.87	0.2651	13.18	1.357	13.5	-0.2062	12.93	-0.4372	13.05	3.14	15.04	-0.7828	12.59
25.02	-9.931	14.27	-8.666	14.58	-10.23	13.97	-10.33	14.03	-6.513	16.1	-10.58	13.49
31.49	-26.44	15.54	-25.07	15.8	-26.66	15.14	-26.63	15.14	-22.61	17.27	-26.84	14.49
39.65	-53.26	16.99	-51.79	17.21	-53.36	16.5	-53.2	16.43	-49.03	18.64	-53.33	15.66
49.91	-96.86	18.72	-95.11	18.89	-96.65	18.09	-96.31	17.92	-92.1	20.26	-96.39	17.03
62.81	-165.7	21	-163.5	21.05	-164.9	20.08	-164.5	19.88	-160.6	22.32	-164.4	18.85
79.11	-275.9	23.95	-273.3	23.91	-274.6	22.87	-274	22.5	-270.1	25.11	-273.8	21.26
99.57	-451.4	28.4	-448.1	28.09	-449	26.83	-448.1	26.39	-444.9	29.31	-447.8	24.94
125.4	-733.3	36.11	-728.7	35.17	-728.9	33.62	-727.6	33.15	-726.1	36.41	-727.2	31.26
150	-1066	46.53	-1061	44.42	-1060	42.36	-1058	41.88	-1058	46.34	-1057	39.74

Results for Guar (Figure 5.9)

ang. Freq rad/sec	Original		Cycle 1		Cycle 2		Cycle 3		Cycle 4		Cycle 5	
	G' Pa	G'' Pa	G' Pa	G'' Pa	G' Pa	G'' Pa	G' Pa	G'' Pa	G' Pa	G'' Pa	G' Pa	G'' Pa
6.284	59.38	47.15	42.29	37.32	46.66	39.45	26.14	25.02	32.15	30.32	20.39	21.31
7.912	65	49.25	46.71	39.43	51.37	41.48	28.83	26.6	35.56	32.16	22.47	22.79
9.961	70.36	51.29	50.81	41.44	55.72	43.44	31.06	28.09	38.58	33.92	24.08	24.18
12.54	74.91	53.12	54.26	43.4	59.52	45.38	32.51	29.54	40.79	35.6	24.88	25.52
15.78	78.11	54.85	56.19	45.16	61.68	47.04	32.51	30.9	41.64	37.15	24.27	26.83
19.87	78.94	56.42	55.79	46.79	61.49	48.59	30.15	32.2	40.1	38.64	21.28	28.09
25.02	75.71	57.78	51.53	48.32	57.4	49.98	23.95	33.44	34.8	40.04	14.32	29.32
31.49	66.46	59.23	41.05	49.85	47.31	51.47	11.3	34.73	23	41.41	1.02	30.5
39.65	46.66	60.55	20.17	51.34	26.53	52.85	-11.75	35.93	1.172	42.8	-22.69	31.68
49.91	10.58	61.7	-16.82	52.82	-10.12	54.23	-50.85	37.1	-36.98	44.12	-62.46	32.8
62.81	-51.1	63.13	-79.14	54.24	-72.37	55.51	-115.7	38.3	-100.6	45.43	-128	34.01
79.11	-154	64.6	-182.5	55.77	-175.8	57.04	-221.7	39.75	-205.8	47	-234.7	35.53
99.57	-322.8	66.49	-351.6	57.72	-344.8	58.9	-393.2	41.56	-376.3	48.83	-406.6	37.17
125.4	-599.6	68.95	-628	60.17	-622.2	61.52	-671	44	-653.8	51.17	-685.2	39.47
150	-923.5	71.91	-950.4	62.92	-944.7	64.26	-995	47.11	-977.9	54.17	-1010	42.36

Results for Locust (Figure 5.9)

ang. Freq rad/sec	Original		Cycle 1		Cycle 2		Cycle 3		Cycle 4		Cycle 5	
	G' Pa	G'' Pa	G' Pa	G'' Pa	G' Pa	G'' Pa	G' Pa	G'' Pa	G' Pa	G'' Pa	G' Pa	G'' Pa
6.284	11.82	28.94	495.8	288	18.12	40.5	558	203.7	462.1	376.2	243.7	111.8
7.912	14.43	33.12	551.1	276.8	19.52	42.32	608.2	176.9	591.9	357.3	161.7	144.7
9.961	17.05	37.46	561	284.3	22.99	45.57	603	191.8	727.7	309.9	120.3	145.9
12.54	19.39	41.92	530.7	304.6	27.12	49.49	561.1	226.4	823.2	265.7	111.2	144.9
15.78	20.88	46.49	481.6	327.7	28.59	52.52	509	261.2	846.1	264.7	118.8	145.2
19.87	20.49	51.04	449.2	343.4	25.82	54.56	454.8	290.5	820.8	293.2	125.8	146.2
25.02	16.72	55.52	452.3	348.1	19.59	56.6	378	302	747.1	343.4	130.8	148.3
31.49	7.175	59.96	449.6	347.5	7.496	58.62	266.6	293.9	627.9	383.4	126.6	148.8
39.65	-12.12	64.18	363.9	346.9	-15.23	60.31	183.1	273.1	446.2	398.3	115.5	149.5
49.91	-47.04	68.22	262.9	334.5	-54.18	61.95	152.5	274.7	292.6	375.1	87.84	149.3
62.81	-107.3	72.2	218.4	339	-118.9	63.89	107.9	281	243	377.5	32.11	148.4
79.11	-208.7	76.13	133.3	344.7	-224.7	66.28	22.31	286.9	162.4	383.5	-63.63	148
99.57	-376.6	80.21	-17.51	351.4	-396.2	69.51	-132.2	291.7	14.62	390.2	-226.8	148.3
125.4	-647	85.26	-268.7	358.9	-668.6	74.27	-390	296.8	-235	397.6	-492.3	149.6
150	-966.7	90.17	-575.4	365.9	-988.9	79.71	-699.6	302.5	-543.3	404.9	-804.4	152.4

Table B.3 Gel strength over the five freeze-thaw cycles (Figure 5.10)

Cycles	Gel Strength (force in grams)			
	Carrageenan/curdlan	Xanthan/curdlan	Guar/curdlan	Locust/curdlan
0	86.02	6.21	7.23	6.51
1	44.54	6.46	7.04	19.89
2	20.3	6.42	6.68	10.27
3	19.74	6.42	6.67	10.01
4	17.58	6.47	6.43	10
5	12	6.26	6.25	9.2

Table B.4 Adhesiveness differences over freeze-thaw cycles (Figure 5.11)

Cycles	Adhesiveness			
	Carrageenan/curdlan	Xanthan/curdlan	Guar/curdlan	Locust/curdlan
0	1.89	2.56	14.56	33.65
1	2.1	2.86	12.4	1.11
2	0.94	2.36	10.69	0.72
3	0.66	2.78	9.42	0.61
4	0.62	2.49	5.72	0.59
5	0.45	2.12	4.25	0.51

Table B.5 Percent water lost over the freeze-thaw cycles (Figure 5.12)

Cycles	Percent Water Lost (v/v)			
	Carrageenan/curdlan	Xanthan/curdlan	Guar/curdlan	Locust/curdlan
0	0	0	0	0
1	18.57	0	0	27.5
2	14.09	0	0	41.43
3	17.27	0	0	44.09
4	18	0	0	55.71
5	15.01	0	0	57

Table B.6 Viscosity at 80° to determine heat stability (Figure 5.13)

Freeze-thaw Cycles	Viscosity (Pa s) at 80°C			
	Carrageenan/curdlan	Xanthan/curdlan	Guar/curdlan	Locust/curdlan
0	0.1066	9.095	10.5	3.047
1	0.1217	10.42	10.29	36.74
2	0.1308	8.599	8.604	89.48
3	0.1156	7.966	7.299	74.85
4	0.0481	6.029	5.33	109.7
5	0.1175	5.267	1.692	59.19

APPENDIX C

RHEOLOGICAL AND TEXTURAL CHARACTERISTICS USING SODIUM HYDROXIDE DATA

Table C.1 Information for the following Figures:

Apparent viscosity at shear rate 2/s of copolymers containing fixed concentrations (Figure 5.14)

Gel strength of fixed concentrations of copolymers (Figure 5.16)

Adhesiveness of copolymers containing fixed concentrations (Figure 5.17)

Apparent viscosity at 80°C under a shear rate 2/s for copolymers containing fixed concentrations (Figure 5.18)

Carrageenan/Curdlan

Trial	Force (g)	Adhesiveness	Viscosity	Viscosity (Pa.s) at 80°
1.0 Cu/ 0 Ca	5.3	0.3455	0.2916	0.01123
.7 Cu/ .3 Ca	6.5	3.891	8.213	0.6468
.5 Cu/ .5 Ca	11.7	7.515	7.986	0.3285
.3 Cu/ .7 Ca	11.3	6.954	5.998	0.005079
0 Cu/ 1.0 Ca	62.6	4.208	17.85	0.03586

Xanthan/Curdlan

Trial	Force (g)	Adhesiveness	Viscosity	Viscosity (Pa.s) at 80°
1.0 C/ 0 X	5.3	3.662	0.2916	0.1824
.7 C/ .3 X	6.1	5.581	2.676	0.6321
.5 C/ .5 X	6.1	7.11	4.561	1.681
.3 C/ .7 X	6.6	4.862	8.451	4.418
0 C/ 1.0 X	6.9	6.469	13.892	8.322

Guar/Curdlan

Trial	Force (g)	Adhesiveness	Viscosity	Viscosity (Pa.s) at 80°
1.0 C/ 0 G	5.3	3.203	0.2916	0.02779
.7 C/ .3 G	5.4	4.862	0.3587	0.029
.5 C/ .5 G	5.7	9.118	1.019	0.05828
.3 C/ .7 G	6.2	10.64	4.192	0.3594
0 C/ 1.0 G	6.4	12.12	9.081	1.285

Locust/Curdlan

Trial	Force (g)	Adhesiveness	Viscosity	Viscosity (Pa.s) at 80°
1.0 C/ 0 L	5.3	1.151	0.2916	0.002935
.7 C/ .3 L	5.2	3.287	0.1964	0.03409
.5 C/ .5 L	5.4	5.068	0.01121	0.04193
.3 C/ .7 L	5.4	8.734	0.7743	0.1641
0 C/ 1.0 L	5.7	18.9	2.589	0.3802

Table C.2 Storage and Loss Moduli (Figure 5.15)

Carrageenan (Ca)/Curdlan (Cu)								
	1.0 Ca/ 0 Cu		.7 Ca/ .3 Cu		.5 Ca/ .5 Cu		.3 Ca/ .7 Cu	
ang. frequency rad/sec	G'	G''	G'	G''	G'	G''	G'	G''
	Pa	Pa	Pa	Pa	Pa	Pa	Pa	Pa
6.284	575.3	79.46	575.3	79.46	190.7	23.5	99.32	16.29
7.912	580.5	78.77	580.5	78.77	188.9	23.16	99.39	16.58
9.961	586.9	79.58	586.9	79.58	186.9	23.3	98.99	17.07
12.54	591.2	81.16	591.2	81.16	184.7	23.69	97.8	17.41
15.78	592.6	82.62	592.6	82.62	181.6	24.49	95.08	17.98
19.87	592.8	84.26	592.8	84.26	175.8	25.46	89.15	18.58
25.02	588.7	87.27	588.7	87.27	166.3	26.63	76.19	19.88
31.49	577.6	89.71	577.6	89.71	149.5	28.82	61.78	20.04
39.65	555.8	92.49	555.8	92.49	121.4	31.46	39.18	20.69
49.91	514.2	95	514.2	95	84.51	31.46	3.33	21.54
62.81	437.9	96.97	437.9	96.97	19.13	33.28	-58.61	22.87
79.11	344.2	99.44	344.2	99.44	-87.1	35.75	-158.3	24.53
99.57	183.6	105.1	183.6	105.1	-258	38.83	-317.4	26.97
125.4	-79.3	111.8	-79.3	111.8	-529.8	43.4	-573.2	32
150	-391.4	117.2	-391.4	117.2	-851.3	48.72	-874.3	36.75

Xanthan (Xan)/Curdlan (Cu)								
	1.0 Xan/ 0 Cu		.7 Xan/ .3 Cu		.5 Xan/ .5 Cu		.3 Xan/ .7 Cu	
ang. frequency rad/sec	G'	G''	G'	G''	G'	G''	G'	G''
	Pa	Pa	Pa	Pa	Pa	Pa	Pa	Pa
6.284	4.252	4.502	33.57	9.862	22.64	9.354	12.25	7.064
7.912	3.735	4.911	34.21	9.998	23.1	9.734	12.14	7.488
9.961	2.618	5.37	34.19	10.15	22.94	10.14	11.44	7.945
12.54	0.5256	5.871	33.1	10.32	21.72	10.56	9.774	8.433
15.78	-3.163	6.431	30.31	10.53	18.9	11.02	6.527	8.968
19.87	-9.46	7.074	24.88	10.79	13.54	11.54	0.7393	9.534
25.02	-19.77	7.759	15.24	11.12	4.021	12.1	-9.209	10.18
31.49	-36.54	8.558	-1.109	11.55	-12.1	12.76	-25.58	10.86
39.65	-63.62	9.492	-27.87	12.08	-38.46	13.5	-52.35	11.64
49.91	-107	10.55	-71.05	12.77	-81.42	14.38	-95.33	12.59
62.81	-176.4	11.92	-140.2	13.76	-150.2	15.5	-164.1	13.77
79.11	-288.7	13.68	-251.5	15.1	-260.9	17.07	-274.8	15.3
99.57	-465.5	17.05	-430.3	17.59	-439.3	19.51	-453.3	17.62
125.4	-747	23.35	-712.1	22.93	-720.8	24.44	-735.3	22.52
150	-1074	30.15	-1043	30.09	-1051	31.11	-1066	29.88

Guar (Gu)/Curdlan (Cu)

	1.0 Gu/ 0 Cu		.7 Gu/ .3 Cu		.5 Gu/ .5 Cu		.3 Gu/ .7 Cu	
ang. frequency rad/sec	G' Pa	G'' Pa	G' Pa	G'' Pa	G' Pa	G'' Pa	G' Pa	G'' Pa
0.1	0.6123	1.255	0.6123	1.255	0.7385	1.776	0.07959	0.2895
0.1259	0.75	1.466	0.75	1.466	0.8925	2.099	0.09	0.3415
0.1585	0.9174	1.708	0.9174	1.708	1.072	2.47	0.1084	0.4093
0.1995	1.114	1.983	1.114	1.983	1.279	2.899	0.1339	0.4927
0.2512	1.348	2.295	1.348	2.295	1.496	3.387	0.1667	0.5936
0.3163	1.62	2.645	1.62	2.645	1.711	3.947	0.208	0.7151
0.3982	1.936	3.04	1.936	3.04	1.89	4.562	0.2594	0.8602
0.5013	2.308	3.487	2.308	3.487	1.987	5.248	0.3238	1.034
0.631	2.728	3.978	2.728	3.978	1.92	6.025	0.4021	1.239
0.7944	3.207	4.519	3.207	4.519	1.55	6.877	0.4975	1.485
1	3.756	5.122	3.756	5.122	0.6391	7.814	0.6128	1.773
1.259	4.378	5.786	4.378	5.786	-1.175	8.821	0.7445	2.105
1.586	5.085	6.512	5.085	6.512	-4.497	9.915	0.8899	2.491
1.995	5.867	7.301	5.867	7.301	-10.35	11.13	1.048	2.93
2.512	6.726	8.161	6.726	8.161	-20.21	12.38	1.219	3.441
3.163	7.649	9.081	7.649	9.081	-36.43	13.76	1.384	4.02
3.98	8.608	10.06	8.608	10.06	-62.84	15.19	1.522	4.683
5.011	9.554	11.11	9.554	11.11	-105.5	16.84	1.582	5.436
6.309	10.39	12.22	10.39	12.22	-174.4	18.62	1.475	6.271
7.943	11	13.4	11	13.4	-285.9	20.74	1.075	7.204
10	11.12	14.61	11.12	14.61	-463.1	23.57	0.141	8.237
12.59	10.4	15.87	10.4	15.87	-744.6	28.39	-1.692	9.351
15.84	8.221	17.19	8.221	17.19	-1068	34.15	-5.04	10.57
19.95	3.599	18.55	3.599	18.55	na	na	-10.84	11.87
25.12	-5.079	19.97	-5.079	19.97	na	na	-20.62	13.26
31.63	-20.16	21.4	-20.16	21.4	na	na	-36.77	14.75
39.81	-45.44	22.87	-45.44	22.87	na	na	-63.1	16.34
50.11	-87.02	24.45	-87.02	24.45	na	na	-106	18.05
63.09	-154.5	26.12	-154.5	26.12	na	na	-175.3	20.01
79.43	-264.9	28.02	-264.9	28.02	na	na	-285.5	22.46
100	-440.9	30.58	-440.9	30.58	na	na	-461.9	26.14
125.9	-720.6	34.66	-720.6	34.66	na	na	-742.9	32.05
150	-1044	39.76	-1044	39.76	na	na	-1067	41.47

Locust (Loc)/Curdlan (Cu)

	1.0 Loc/ 0 Cu		.7 Loc/ .3 Cu		.5 Loc/ .5 Cu		.3 Loc/ .7 Cu	
ang. frequency rad/sec	G' Pa	G'' Pa	G' Pa	G'' Pa	G' Pa	G'' Pa	G' Pa	G'' Pa
0.1	0.01845	0.2921	0.01845	0.2921	1.09E-03	0.09085	9.06E-05	0.06743
0.1259	0.02894	0.367	0.02894	0.367	3.92E-03	0.1154	3.28E-04	0.08677
0.1585	0.04186	0.4604	0.04186	0.4604	5.36E-03	0.1464	2.41E-03	0.1111
0.1995	0.05905	0.5755	0.05905	0.5755	6.90E-03	0.1854	6.77E-03	0.1408
0.2512	0.08171	0.7182	0.08171	0.7182	9.35E-03	0.2345	0.01219	0.177
0.3163	0.1118	0.894	0.1118	0.894	0.01316	0.2957	0.01747	0.2215
0.3982	0.1521	1.109	0.1521	1.109	0.01845	0.3718	0.02253	0.2762
0.5013	0.2053	1.374	0.2053	1.374	0.02528	0.4666	0.02795	0.3438
0.631	0.2759	1.696	0.2759	1.696	0.03416	0.5841	0.03349	0.4271
0.7944	0.3677	2.084	0.3677	2.084	0.04506	0.7291	0.03872	0.5303
1	0.4893	2.557	0.4893	2.557	0.05803	0.9074	0.04347	0.6572
1.259	0.6436	3.123	0.6436	3.123	0.0731	1.128	0.04527	0.8131
1.586	0.8417	3.802	0.8417	3.802	0.0871	1.396	0.04124	1.005
1.995	1.09	4.602	1.09	4.602	0.09708	1.722	0.02534	1.238
2.512	1.386	5.531	1.386	5.531	0.09287	2.117	-0.01343	1.521
3.163	1.734	6.617	1.734	6.617	0.06414	2.595	-0.08721	1.866
3.98	2.121	7.879	2.121	7.879	-0.0222	3.171	-0.2321	2.284
5.011	2.515	9.316	2.515	9.316	-0.2065	3.846	-0.5007	2.783
6.309	2.854	10.93	2.854	10.93	-0.5703	4.644	-0.9828	3.36
7.943	3.016	12.75	3.016	12.75	-1.259	5.566	-1.821	4.032
10	2.803	14.77	2.803	14.77	-2.483	6.62	-3.231	4.819
12.59	1.862	16.96	1.862	16.96	-4.605	7.819	-5.589	5.717
15.84	-0.4067	19.36	-0.4067	19.36	-8.207	9.18	-9.497	6.738
19.95	-4.958	21.91	-4.958	21.91	-14.29	10.7	-15.9	7.908
25.12	-13.28	24.61	-13.28	24.61	-24.28	12.36	-26.28	9.21
31.63	-27.74	27.45	-27.74	27.45	-40.6	14.18	-43.08	10.65
39.81	-52.19	30.4	-52.19	30.4	-67.02	16.21	-70.04	12.29
50.11	-92.66	33.49	-92.66	33.49	-109.6	18.39	-113.3	14.18
63.09	-159	36.8	-159	36.8	-178.2	20.85	-183	16.15
79.43	-267.5	40.41	-267.5	40.41	-289.2	23.54	-294.5	18.83
100	-441.5	44.51	-441.5	44.51	-465.9	27.21	-471.4	22.32
125.9	-719	50.34	-719	5.727	-746.2	32.35	-752.8	28.58
150	-1040	56.48	-1040	6.941	-1069	38.4	-1076	35.11

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