EFFECT OF FLAXSEED GUM ON MUFFIN AND SALAD DRESSING QUALITY AND STABILITY

By

Sandra Stewart

A Thesis
Submitted to the University of Manitoba
in partial fulfillment of the
requirements for the degree of

MASTER OF SCIENCE

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The rung of a ladder was never meant to rest upon, but only to hold a man's foot long enough to put the other somewhat higher.

Thomas Huxley

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ABSTRACT

Flaxseed gum was isolated from cv. Norman and Linola™ using an optimal extraction process followed by a concentration step. The gums had good yields (ca. 5%) of high carbohydrate (ca. > 80%) and low protein material. Aqueous dispersions exhibited shear thinning behaviour. Under dynamic oscillatory rheology, the 2% (w/v) dispersions exhibited typical viscoelastic behaviour. Two types of food emulsions (muffins and model salad dressings) were evaluated to determine the potential of flaxseed gum as a feasible alternative to two commercial gums, xanthan and guar gum.

Flaxseed gum improved muffin height and volume with no significant changes in texture as measured by instrumental and sensory test methods. Surprisingly, both flaxseed gums and both commercial gums did not appear to significantly increase moisture retention in the muffins or retard staling. The primary effect of hydrocolloids in the muffins was to maintain higher batter viscosity during heating. Higher viscosity values reduce gas diffusion and migration of the air cells as well as protect the batter from shocks or vibrations which may cause the emulsion to rupture resulting in a bakery product of low volume. Flaxseed gum (0.5% flour weight basis) could easily replace xanthan gum or guar gum used at the 0.1% fwb level to produce muffins of good volume and texture.

Flaxseed gum appears to act as a steric stabilizer in the model salad dressing due to its surface active ability. For stabilization, sufficient adsorbing flaxseed gum (> 0.45% w/w) was required to cover the particle surface or else bridging flocculation occurred. Solvent quality affected the stability of the model oil in water emulsions. Flaxseed gum stabilized emulsions were stable at pHs greater than 2.8. Values lower than this caused the polysaccharide to have a compact configuration or cause cleavage of the polymer creating instability. Larger mean droplet size and creaming were observed when the pH is too low or the gum concentration is not sufficient

for coverage. Salt addition greatly affected the rheological properties of the polysaccharide; however, the electrolyte improves the emulsifying capabilities of the egg yolk protein. Aging weakened the polymer network structure as shown by a decrease in the creep viscosity, Newtonian viscosity and instantaneous elastic modulus. As well, the increase in phase angle as the emulsion aged confirmed the transformation to a more fluid system. The changes in the creep measurements as the emulsion ages depended on whether crosslinking of the polysaccharide (dependent on the configuration of the polysaccharide) or droplet coalescence was the dominant process.

There was no observed difference in emulsion stability (with regard to creaming, mean droplet size, complex viscosity, phase angle, Newtonian viscosity and instantaneous elastic modulus) when cv. Norman flaxseed gum was replaced with Linola™. Xanthan gum formulated emulsions displayed higher viscosities and the possibility of increased network structure. As expected, there was a difference in colour when fresh egg yolk replaced dried egg yolk. Both emulsions had similar dynamic parameters but differed in Newtonian viscosity. No obvious explanation is apparent. Fresh egg yolk stabilized emulsions did have a significantly smaller mean droplet size. When dried egg yolk was replaced with fresh egg yolk under the conditions of pH 4 and 2.5% (w/w) salt, there were no obvious interactions occurring between the protein and the polysaccharide.

1. INTRODUCTION

Hydrocolloids or water soluble gums are encountered in a variety of biological sources (Glicksman, 1982). These include plant extracts, seed extracts, plant exudates, microbial by-products as well as chemically modified products. The physical characteristics of each hydrocolloid are governed by their molecular weight, configuration and individual component properties (Pomeranz, 1985). Polysaccharides comprise an important segment of the water soluble polymer market as they are finding appeal in an increasing range of applications (Ward and Andon, 1993). Based on their key function to texturize and/or stabilize food systems, hydrocolloids are used in a wide range of food products. Functions such as adhesive agent, binder, bodying agent and crystallization inhibitor are only a few of the possibilities for hydrocolloids in food systems (Pomeranz, 1985). Hydrocolloids are biocompatible, biodegradable and non-toxic which makes them an ideal choice for today's applications.

Flaxseed (*Linum usitatissimum* L.) is used to commercially produce both fibre and oil. However, flaxseed is grown in North America principally to obtain flaxseed oil. The outer layer of the hull contains a mucilaginous substance which is composed primarily of polysaccharides (Hunt and Jones, 1962). When fully hydrated, the gum imparts high viscosity to solutions and it has been shown to have considerable potential for food and non food uses (BeMiller, 1973).

Flaxseed gum has been reported to replace gum arabic in emulsions with concentrations required to stabilize the emulsion from 0.5 to 1.5% (BeMiller, 1973). The gum has been considered a potential substitute for egg whites in bakery products and ice cream (Nikkila, 1965). Flaxseed gum with its demulcent and emollient properties, is reported to make a natural skin lotion and cosmetic ingredient (McCredie and Whistler, 1959). Due to its low cost of production, bland taste, high lubrication and retention, flaxseed gum has been considered in

medicinal preparations (Boichinov, 1967), a saliva substitute and an antibiotic carrier for oral applications (Attström, 1993). There are also patents for flaxseed gum glue preparations (Maton and Maton, 1962) and water paint formulations (Bolley and McCormack, 1952).

Information on the physicochemical properties of the gum has been extensively documented (Mazza and Biliaderis, 1989; Fedeniuk and Biliaderis, 1994; Cui *et al.*, 1994ab; Cui *et al.*, 1996). There is a lack of information on flaxseed gum functionality in typical food applications. The aim of this study was to generate new information on potential food applications for flaxseed gum using model systems. Specifically, the goal was to determine the potential of flaxseed gum as a feasible alternative to such traditional gums as xanthan and guar gum in two types of food emulsions, muffins and salad dressings.

2. LITERATURE REVIEW

2.1. Composition of Flaxseed

Flaxseed (*Linum usitatissimum* L.) is extensively used for the commercial productions of both fibre and oil. Mature seeds are flat and oval in shape with their dimensions ranging from 3 to 6 mm in length and between 2 and 3.5 mm in diameter (Freeman, 1995). Flaxseed contains a seed coat (hull) with a thin endosperm, an embryo axis and two cotyledons comprising 36%, 4%, and 55% respectively of the total seed weight (Bhatty and Cherdkiatgumchai, 1990). The surface of the flaxseed can vary in colour from dark brown to light yellow.

Flaxseed is used primarily for production of industrial oil. The development of a low linolenic acid flaxseed allows the possibility of marketing a food grade flaxseed oil (Prentice, 1992). The Flax Council of Canada adopted the generic term "solin" for low (5% by weight) linolenic acid varieties of flaxseed. Flaxseed contains anti-nutritional factors such as cyanogenic glucosides (Mazza and Oomah, 1995). Toxicity of cyanogenic glucosides is due to the release of a potent respiratory inhibitor, hydrogen cyanide. Mechanically separated hulls, independent of seed colour, contain a high level of the cyanogenic glucoside, neolinustatin, whereas the endosperm is rich in linustatin (Mazza and Oomah, 1995). Variability in seed yields and quality are dependent upon cultivar, growing conditions and processing. Attempts have been made to remove the cyanogenic compounds. Procedures range from a complicated acid treatment to a relatively simple isopropanol extraction (Madhusudhan and Singh, 1985; Dev and Quensel, 1988).

Flaxseed hull is composed mainly of polysaccharides with some protein and oil (20% and < 1%, respectively) due to contamination by the endosperm and cotyledons when fracturing (Bhatty and Cherdkiatgumchai, 1990). The highly polished seed coat (testa) of the flaxseed hull consists

of five distinct layers with the outer most surface layer (epiderm) incorporating a mucilaginous carbohydrate material (Freeman, 1995). The gum accounts for approximately 8% of the flaxseed weight (BeMiller, 1973; Mazza and Biliaderis, 1989). Extraction and quantitative determination of flaxseed gum have been reported (Bhatty and Cherdkiatgumchai, 1990; Cui *et al.*, 1994; Fedeniuk and Biliaderis, 1994). Flaxseed gum can be easily isolated from whole seeds or meal using a simple aqueous extraction followed by ethanol precipitation. Depending on the cultivar and extraction conditions, flaxseed gum can vary in composition from 30 to 80% carbohydrate; 8 to 24% protein and 9 to 12% ash (Mazza and Biliaderis, 1989; Wanneberger *et al.*, 1991; Bhatty, 1993). This dried, colourless product is composed primarily of polysaccharides that on hydrolysis yield L-galactose, D-xylose, L-arabinose, L-rhamnose, D-galacturonic acid with traces of D-glucose (BeMiller, 1973;Cui *et al.*, 1994a).

2.2. Composition of Flaxseed Gum

Flaxseed gum consists of a mixture of two fractions: an acidic polymer containing high galacturonic content and a neutral polymer with low galacturonic content (Hunt and Jones, 1962; Cui *et al.*, 1994a; Fedeniuk and Biliaderis, 1994). The branched neutral fraction contains a (1→4) β D-xylose backbone (Hunt and Jones, 1962) to which L-arabinose and D-galactose side chains are attached at positions 2 and/or 3 (Muralikrishna *et al.*, 1987). The neutral fraction accounts for about 32% of the extracted gum (Cui *et al.*, 1994b).

The average molecular weights, estimated by gel chromatography, are about 500 000 daltons and 600 000 daltons for the neutral and acidic fractions, respectively (Muralikrishna *et al.*, 1987). The large molecular-size, neutral fraction displays shear thinning flow behaviour at high concentrations (Cui *et al.*, 1994a). It has a rheological pattern similar to typical viscoelastic

fluids and is comparable to guar gum solutions at similar concentrations (Cui *et al.*, 1994ab; Fedeniuk and Biliaderis, 1994). On the other hand, the pectic-like acidic fraction exhibits Newtonian like flow behaviour at concentrations up to 2% (Cui *et al.*, 1994ab). This profile may be due to the lower molecular size of the polymer since high molecular size polysaccharides display more pronounced shear thinning than smaller sized molecules (Izydorczyk and Biliaderis, 1992).

The acidic fraction of flaxseed gum contains: L-rhamnose, L-fucose, L-galactose and D-galacturonic acid (Hunt and Jones, 1962). Hunt and Jones (1962) were able to separate the acidic polymer further into two components (CuI and CuII) using a cupric acetate solution. The CuI fraction contained L-rhamnose, L-galactose and D-galacturonic acid. The polymer is composed of a main chain of L-rhamnose units with L-galactose units attached as non reducing end groups. The D-galacturonic acid was present either in the rhamnose backbone or as part of the side chains. Fraction CuII contained L-rhamnose backbone with L-fucose and L-galactose attachments. Using partial acid hydrolysis, Muralikrishna and coworkers (1987) isolated the acidic polymer and described its structure as having a main chain consisting of (1-2) linked α-L-rhamnopyranosyl and (1-4) linked D-galactopyranosyluronic acid residues from which fucose and galactose units were linked.

2.3. Properties of Flaxseed Gum

Rheological properties of flaxseed gum are influenced by several factors especially extraction conditions and cultivar (Cui *et al.*, 1996). The range of viscosity from an almost viscous fluid (cv. Liflora) to that of a nearly elastic gel (cv. Szegedi 62) are due to variations in polysaccharide content, branching and molecular weight (Wanneberger *et al.*, 1991). As well, the type of

polysaccharide, that is, the relative amounts of neutral to acidic fraction affects the viscoelastic properties of each gum cultivar solution (Cui *et al.*, 1996). Extraction conditions such as pH, temperature and water:seed ratio also have a substantial influence on flaxseed gum yield, composition and rheological properties (Cui *et al.*, 1994c; Fedeniuk and Biliaderis, 1994).

At low concentrations, flow curves of flaxseed gum exhibit Newtonian behaviour. Above 0.2% concentrations, the dispersions exhibit typical pseudoplastic profiles (Mazza and Biliaderis, 1989; Cui *et al.*, 1994ab). Mazza and Biliaderis (1989) observed that flaxseed gum viscosity at low shear rates falls between gum arabic and galactomannan gums such as guar and locust bean. Fedeniuk and Biliaderis (1994) confirmed the rheological properties of flaxseed gum resemble those of guar gum. It is the branched neutral fraction of flaxseed gum that has the typical viscoelastic properties similar to those observed by guar gum (Cui *et al.*, 1994ab; Fedeniuk and Biliaderis, 1994). Flaxseed gum can form a gel-like material in the presence of sucrose (Susheelamma *et al.*, 1991).

Flaxseed gum is an anionic polymer due to the charged groups on the galacturonic acid. The gum's viscosity, therefore, will vary as a function of ionic strength and pH of the medium (Mazza and Biliaderis, 1989). A strong electrolyte effect suppresses the charges of the polymer to favour intra-molecular interactions, which will result in polymer folding thus occupying less volume (Buttle, 1960). Resistance to shear is lower for smaller molecules; therefore, viscosity is reduced. In addition, the neutralization of the negative charges on the polymer tends to accelerate the relaxation process after the polymer chains are stretched. The observed effect is a reduction in the relaxation time resulting in a less elastic system (Tam and Tiu, 1989). The variation in viscosity depends heavily on salt type. Sodium and potassium chloride decrease flaxseed gum viscosity by 10% (Susheelamma, 1987). Calcium chloride reduces the viscosity by 20% whereas ferric salts reduce it by 50%. Similar rheological profiles of flaxseed gum

containing either NaCl or $CaCl_2$ indicate that a Ca^{2+} mediated cross link commonly observed for pectins or alginates, does not occur for this hydrocolloid (Fedeniuk and Biliaderis, 1994). Potassium iodide decreases the viscosity; however, calcium or magnesium carbonate at concentrations around 0.5 M, actually increases flaxseed gum viscosity by 15 to 20%. Other salts that reduce the viscosity of the polysaccharide are sodium, potassium, calcium, magnesium and ferrous sulphate; sodium, potassium and ferric phosphates. Ferrous ammonium sulphate influences the viscosity of flaxseed gum the greatest with a 75% reduction (Susheelamma, 1987). Organic salts such as sodium acetate, sodium potassium tartrate, sodium citrate, potassium citrate as well as ferric citrate all reduce flaxseed gum viscosity by at least 25% (Susheelamma, 1987).

The pH of the environment significantly affects flaxseed gum viscosity. The optimum viscosity is around the pH range of 6 to 8 (Mazza and Biliaderis, 1989; Fedeniuk and Biliaderis, 1994). Dispersions around this range exhibit the greatest apparent viscosity and the greatest degree of shear thinning at high shear rates due to an extended chain conformation. As is the case with electrolytes, changes in flaxseed gum viscosity with varying pH are due to a reduction in the effective volume caused by suppression of the electrostatic charge (Mazza and Biliaderis, 1989). Below the optimum range, the carboxylate groups of the acidic fraction become increasingly undissociated. The overall charge is reduced and a decrease in viscosity is observed. Above the optimum pH range, viscosity gradually decreases perhaps on account of alkaline depolymerization reactions (Aspinall, 1982).

The effect of temperature on flaxseed gum at a 0.3% w/v concentration follows a typical Arrhenius type equation with an apparent activation energy of around 13 $kJ.mol^{-1}$ (Mazza and Biliaderis, 1989). At temperatures ranging from 10 to 55 °C, water-vapour adsorption isotherms of flaxseed gum dispersions display characteristic sigmoidal profiles (Mazza and

Biliaderis, 1989). The monolayer moisture content of flaxseed gum decreases with increasing temperature. Overall, this value is higher than that of locust bean and guar gums. An increase in temperature which in turn generates an increase in water activity at a constant moisture content, implies that the product may be more susceptible to microbial, nutritional and aesthetic deterioration (Mazza and Oomah, 1995). A high heat of sorption value suggests that at 25 °C locust bean and guar gums hold water molecules at the monolayer more tightly than flaxseed gum (Mazza and Biliaderis, 1989).

Water binding capacity of flaxseed gum (2 500 g of H_2O/100g of solids) as determined by the Baumann Capillary Apparatus, falls between that of xanthan gum (32 000 g of H_2O/100g of solids) and the 2 200 g of H_2O/100g of solids recorded for guar gum (Fedeniuk and Biliaderis, 1994). Solubility of a 0.5% (w/v) flaxseed gum dispersion ranges from 70 to 90% (Mazza and Biliaderis, 1989). The foam capacity and stability of flaxseed gum solutions decrease with decreasing gum concentration (Mazza and Biliaderis, 1989).

2.4. Hydrocolloids in Bakery Products

Hydrocolloids are frequently added to cake batters to improve grain and volume of the final product. Usefulness of a hydrocolloid in a specific formulation depends on a thorough understanding of the physical and chemical properties of the gum plus the potential interactions that may occur with other components in the formulation (Ward and Andon, 1993). Shelke and coworkers (1990) reported increased batter viscosity at ambient temperatures over the control values when xanthan, guar and carboxymethylcellulose (CMC) were added. All hydrocolloid containing formulations produced cake volumes greater than the control and this was most likely due to the higher viscosity during heating which allows for better retention of the

expanding gas cells. According to Garden-Robinson (1994), flaxseed gum at levels between 0.5 and 1.0% (flour weight basis) enhances viscosity, aids in foam stability and increases absorption in bread while improving the loaf volume and bread storage quality.

2.4.1. Dynamics of cake batter

There appears to be a lack of published information on the baking dynamics of muffin batter. Cake batter was used as a comparable model to muffin batter on account of the extensive research of its baking dynamics and their relatively similar formulations. Cakes as well as some muffins are characterised by a high level of sugar and fat in the formula. Gluten is not developed in cake batters to such an extent as in bread dough, primarily due to three factors: lower protein content of the flour (8 to 12%), higher sugar content and a basic pH environment (Pyler, 1988). In a muffin formulation, gluten can partially develop with slight mixing even though the formulation still contains a low protein content (8 to 12%). Thus the degree of mixing of the batter is important when developing a tender crumb.

To produce a cake that consists of a light and tender crumb along with a uniform grain, the batter must retain the gases produced by the leavening agents (Mizukoshi *et al.*, 1980). The gas phase is incorporated into the cake batter during the mixing step. These small bubbles act as nucleation sites for the gas produced by the leavening agents. Without these sites, the cake would not develop the characteristic uniform grain.

Bubble mechanics states that:

$$p = 2\,\gamma/r \qquad [1]$$

where p is the pressure inside a gas cell, r is the radius of the cell and γ is the interfacial tension (Handleman *et al.*, 1961). As a bubble radius becomes smaller, the internal pressure of the bubble becomes immensely larger. Solubility of a gas increases with increasing pressure. Therefore, the equilibrium concentration of dissolved CO_2 is higher in a smaller bubble than in a larger one. Due to thermodynamics, the dissolved gas moves from the area of high concentration to an area of low concentration. This raises the concentration of dissolved gas around the larger bubble above the level in equilibrium and causes the gas to come out of solution and into the bubble. This in turn, causes the bubble to expand to restore the balance. Large bubbles become larger, eventually attaining the critical buoyancy that allows them to rise to the top of the batter. Therefore, on standing, bubbles in cake batters appear to increase in size but decrease in number to produce cakes with a coarser texture and lower volume (Handleman *et al.*, 1961).

Cake batter viscosity represents a significant part in the final product quality (Hoseney, 1984). Reduction in gas diffusion and retention of expanding gas cells increase due to reduced migration within a viscous system (Handleman *et al.*, 1961). Starch granules also resist settling out and forming a separate layer in a viscous formulation (Pomeranz, 1988). The number of air cells in a cake batter can decrease either by coalescence or by decreasing the size of the air cell until it simply disappears. The volume of the cake depends on the initial number of air bubbles in the batter and, to some extent, on their size distribution since buoyancy forces increase with increasing bubble diameter. Due to the high pressure requirements needed to create new gas cell nuclei, no new gas cells are formed after mixing (Handleman *et al.*, 1961). Therefore, it is important to incorporate and maintain as many air cells as possible in the batter prior to baking. A simple two stage creaming method where the fat, sugar and egg ingredients are mixed prior to adding the flour and leavening components can successfully incorporate a large number of air cells into cake batters (Pyler, 1988).

2.4.2. Dynamics of Gas Cell Expansion

At the beginning of baking, heat enters the cake mainly through the pan (Pomeranz, 1988). Small gas cells are embedded in a continuous starch-protein matrix. As the temperature begins to increase, batter volume increases starting from the periphery of the pan. The expansion of the batter is due to the increased water vapour pressure in the air bubbles caused by the high temperatures. Under normal baking conditions, a small initial loss of CO_2 is observed. Diffusion of the gas to the external surface is retarded due to the gluten; however, how the gluten actually slows the rate of carbon dioxide diffusion remains a mystery (Hoseney, 1984). As the temperature of the system continues to increase, the starch begins to swell and gelatinize. A sharp increase in the rate of gas loss is observed at the end of the baking process. Protein coagulation, starch gelatinization, completion of bubble expansion and gas release occur at or about the same temperature (Mizukoshi *et al.*, 1980). The explanation for the gas release is thought to be due to the rupturing of the interconnection between adjacent gas cells (Gan *et al.*, 1995). During baking, cake batter begins to change from the fluid sol to the characteristic gel like cake structure. Setting of the batter coincides with starch gelatinization (Shelke *et al.*, 1990). Additives that delay starch gelatinization, increase cake volume by altering the setting point temperature of the starch granule (Mizukoshi *et al.*, 1980). Formation of the sponge structure inhibits the expanding gas cells. The increasing pressure within the cell causes the cell to rupture at the weakest point, primarily at the thin starch-protein membrane which separates adjacent gas cells. The membrane ruptures and causes the gas to be released (Mizukoshi *et al.*, 1980). At this point, further expansion of the cake is no longer possible. Continued heating only coagulates the proteins further and strengthens the cake structure.

Gan and coworkers (1995) indicated that an interfacial film involvement at the gas/liquid

interface plays a significant role in gas retention. Hypothetically, as the gas cells expand, a thin liquid film develops between adjacent cells. The interconnection between adjacent cells can rupture while the baking process continues. Not until the tensile stress on the system increases to the point where the liquid film ruptures, is the carbon dioxide gas actually released. It is the rupturing of this film and not the starch/protein matrix that signals the end of gas cell expansion (Gan *et al.*, 1995). Pentosans, comprised of mainly arabinoxylans and arabinogalactans, may contribute positively to gas retention by stabilizing the liquid film to allow it to expand to a larger surface area without rupturing (Izydorczyk *et al.*, 1991).

2.4.3. Analytical Techniques for Assessing Muffin Quality

The main acceptability factors for evaluating foods are appearance, flavour, texture, odour and temperature (Bourne, 1990). If any of these factors fail to reach a consumer's expectation, it will not be consumed or at the very least, it will leave a negative impression on the consumer. Therefore, assessing the quality of a product via chemical, physical or sensory evaluation prior to reaching the consumer is essential.

2.4.3.1. Instrumental Texture Analysis

Texture is a multidimensional attribute related to deformation, disintegration and flow of the sample under force (Szczesniak *et al.*, 1963). Food textural parameters are measured as functions of mass, distance, pressure and time (Bourne, 1990). The compression test involves measuring the force required to compress a food a set distance. The texture profile analysis (TPA) consists of compressing the sample twice in reciprocating motion in an attempt to mimic

the action of the jaw. The resulting force-time curve produces a number of textural parameters that can be used to assess texture (Bourne, 1978):

i) Hardness is defined as the peak force during the first compression cycle. It is often referred to as first bite. It's units are in kg force or N.

ii) Cohesiveness is defined as the ratio of the positive force area during the second compression to the positive force area during the first compression. It is a dimensionless parameter.

iii) Springiness or elasticity is defined as the height that the food recovers after the end of the first bite.

iv) Gumminess is defined as the product of hardness x cohesiveness

v) Chewiness is defined as the product of gumminess x springiness.

An instrumental method of assessing food texture is of limited value if it does not correlate with human appraisals. Each of the above parameters have been found to correlate with sensory evaluations (Szczesniak *et al*, 1963).

2.4.3.2. Scanning Electron Microscopy

Scanning electron microscopy (SEM) is a technique gaining popularity for studying the ultrastructure of food products. Sample preparation is easier and introduces fewer artifacts than other commonly used techniques such as transmission electron microscopy or light microscopy. Specimens are scanned with a lower energy electron beam and the secondary backscattered electrons that come from the sample's surface are collected by the detector to produce a three dimensional image. Fracturing the sample and then coating it with a very thin electron reflective layer of heavy metal, allow for surface and internal structure to be examined (Faridi and Faubion, 1990).

Several drawbacks, however, to the use of SEM remain. Because the samples are exposed to a high vacuum, sample preparation is a critical factor in producing quality images. For proper interpretation, the sample's integral components should be practically undisturbed during sample preparation to minimize the possibility of artifactual structures. Doughs fixed in solutions of glutaraldehyde and osmium tetroxide with or without chemical dehydration show evidence of structural distortion under SEM (Varriano-Marston, 1977; Chabot *et al.*, 1979; Freeman *et al.*, 1991). Starch granules and proteinaceous material appear to be separated entities; as well, an obvious loss of spatial relationship between the major components of the dough is observed when using these sample preparation techniques. Air dried dough samples show evidence of structural distortion most likely due to the high interfacial tension during drying (Varriano-Marston, 1977). Recently, the rapid freezing of samples in a liquid nitrogen slush and sublimation on a cold stage has been successfully used in examining the ultrastructure of wheat glutens with minimal loss or alteration of the native structure (Freeman *et al.*, 1991). The successful key to this technique is the extremely rapid freezing of the sample to avoid the formation of large, structure disrupting ice crystals.

2.4.3.3. Shelf Life Evaluations

Staling is a generic term used to describe deleterious changes that affect colour, flavour or textural properties of a product. Consumers associate staling with the changes that occur to textural properties; therefore, any treatment that maintains a feel of moistness at all stages of storage is perceived by the consumer as contributing to the freshness (Kulp *et al.*, 1959; Willhoft, 1973). With bread crumb, the starch fraction which undergoes retrogradation over time, contributes the greatest to the staling effect (Willhoft, 1973). Unlike bread which can be refreshened by heating, there may be a two-mechanism approach to the overall firming

process in cakes. The first process is the intrinsic firming of the cell wall material that appears to have a negative temperature correlation; the second firming effect is due to the overall loss of moisture that is positively correlated to temperature. The maximum overall firming rate of cake crumb, therefore, is found at 21 to 25 °C (Guy, 1983). Approximately one-fourth of the total firming of yellow cakes occurred on the first day and one half within the first four days (Kulp *et al.*, 1959). Because of their ability to bind water, hydrocolloids should theoretically increase the antistaling properties of baked goods (Anderson and Andon, 1988). Hydrocolloids such as gum arabic are used in bakery formulations to extend the shelf life of the product due to the ability of the gum to bind water (Bayfield, 1958). Flaxseed gum has been reported to be part of a formula for shelf stable bread (Garden-Robinson, 1994).

A second concern for food processors is molding of baked products. Mold causes a discoloured, fuzzy appearance along with an off odour that affects the appeal of the product. Mold spores are present in the air. Settling on the surface of baked goods, the spores will germinate and proliferate under many environmental conditions. The most common types of bread mold are *Aspergillus*, *Penicillium*, *Rhizopus* and *Mucor* (Potter, 1986).

2.4.3.4. Differential Scanning Calorimetry

The major driving force for protein-polysaccharide interactions is electrostatic in nature (Imeson *et al.*, 1977; Ledward, 1994). Ionic interactions occurring between xanthan gum and gluten to increase dough stability have been reported (Huebner and Wall, 1979). Carboxymethylcellulose gum (CMC) has been reported to interact with egg white protein to precipitate it out of solution (Clark and Glatze, 1987). Since flaxseed gum contains ca. 70% of the acidic fraction (Cui *et al.*, 1994b), interaction between the gum with one or all of the muffin's major protein components

is possible. Differential Scanning Calorimetry (DSC) is capable of detecting an interaction if there is a significant change in the thermal properties of the protein involved (Biliaderis, 1983). DSC is a thermoanalytical technique for monitoring changes in physical or chemical properties of materials as a function of temperature (Biliaderis, 1983). In our muffin formulation, gluten, casein and ovalbumin were the dominant proteins. Gluten and casein were not examined in this study due to their inability to show a denaturation peak when examined under DSC (Hoseney *et al.*, 1986; Paulsson and Dejmek, 1990). The denaturation of ovalbumin is strongly pH dependent with the most intensive denaturation occurring at extreme pH values (Sajdok *et al.*, 1989). The average pH value of commercial angel cake is 5.7 and white cake is 7.5 (Lowe, 1955). The pH chosen for this experiment was 6, and this value falls between the range of typical cake systems. At this pH, ovalbumin will have a negative charge (pI = 4.6) as will flaxseed gum; therefore, the electrostatic interaction between the protein and polysaccharide will be minimal.

2.5. Hydrocolloids in Salad Dressings

Quality is multi-faceted with consistency being one critical concern facing the industry. Hydrocolloids are generally used to improve or manipulate the texture of food products. In salad dressings, gums provide thickness, cling, suspension of particles as well as prevent the separation of the two phase system (Andres, 1987). Using hydrocolloids in a salad dressing formulation allows the food technologist to maintain quality under a wide range of processing and storage conditions. The most successful application of the hydrocolloid, xanthan gum, is as a stabilizer for salad dressings (Gordon, 1990). When used in salad dressing formulation, the xanthan gum is effective in preventing agglomeration and creaming of oil droplets by holding them within the weak gel matrix. This weak network readily breaks down to become a pourable dressing. On contact with food, the pseudoplastic intermolecular network reforms to provide

"cling" rather than draining off (Gordon, 1990).

2.5.1. Formation of Emulsions

An emulsion is a dispersed system whose droplet diameter, in general, exceeds 0.1 μm and it is characterised by an interfacial boundary that separates two or more immiscible phases (Dickinson, 1989). There are two types of fluid emulsions. An oil in water (o/w) emulsion has the oil in the dispersed or discontinuous phase; whereas the reverse is true of a water in oil (w/o) emulsion.

Emulsions are usually achieved by mechanical means although viscous forces can also form small dispersed droplets. The theory behind both processes involves the interface between two immiscible liquids deforming to the point at which a droplet will form (Walstra, 1983). In order to form a droplet of diameter, d, the deformation must overcome Laplace pressure, given by $4\gamma/d$ where γ is the interfacial tension (Walstra, 1987). The natural tendency is for the discontinuous phase to coalesce. This reduces the total pressure of the system producing two distinct phases (Walstra, 1983). To create a stable emulsion, a barrier to this type of coalescence must be devised. An emulsifier can lower the surface tension thereby reducing Laplace pressure to facilitate deformation (Walstra, 1987).

The primary stabilisation in a food emulsion is usually based on the presence of an adsorbed layer of protein at the oil/water interface (Dickinson, 1989). Being surface active materials, all soluble proteins exhibit emulsifying and foaming properties. The main thermodynamic driving force for protein adsorption is the removal of protein's hydrophobic amino acid side chains from the aqueous phase which releases the ordered water molecules surrounding the protein. Egg yolk proteins have been used for years to stabilize oil in water emulsions.

Gums, historically, have been thought to promote emulsion stability by increasing the viscosity of the aqueous phase. Addition of a thickener creates a force opposite to the movement of the dispersed particles which slows separation thereby, retarding but not preventing coalescence. Some studies (Kislalioglou *et al.*, 1971; Vernon-Carter and Sherman, 1980) have shown that certain gums are also surface active. This allows the gum to contribute to emulsion stability both by surface activity as well as by viscosity. Viscoelastic films can form at the oil/water interface due to the hydrogen bonded crosslinking of adsorbed molecules (Vernon-Carter and Sherman, 1980). The films are hydrated with the degree of hydration being minimal at the oil interface with steadily increasing hydration reached at the last layer of adsorbed polymer molecules. The degree of crosslinking at any location within the adsorbed layer is inversely proportional to the degree of hydration of the molecule (Kislalioglou *et al.*, 1971).

2.5.2. Types of Instability

Emulsions are inherently unstable. Even a system that appears stable visually, has the total number of droplets, their size distribution and their spacial arrangement constantly evolving (Dickinson and Stainsby, 1988). The primary types of instability for an oil in water emulsion are creaming, flocculation and coalescence (Figure 2.01).

2.5.2.1. Creaming

Creaming, by definition, is the separation of the dispersed phase under the influence of gravity. No change in the droplet size or integrity occurs in creaming (Jaynes, 1985). It is a potential problem when the droplet diameter in an emulsion exceeds 0.5 μm (Dickinson, 1988). An oil in

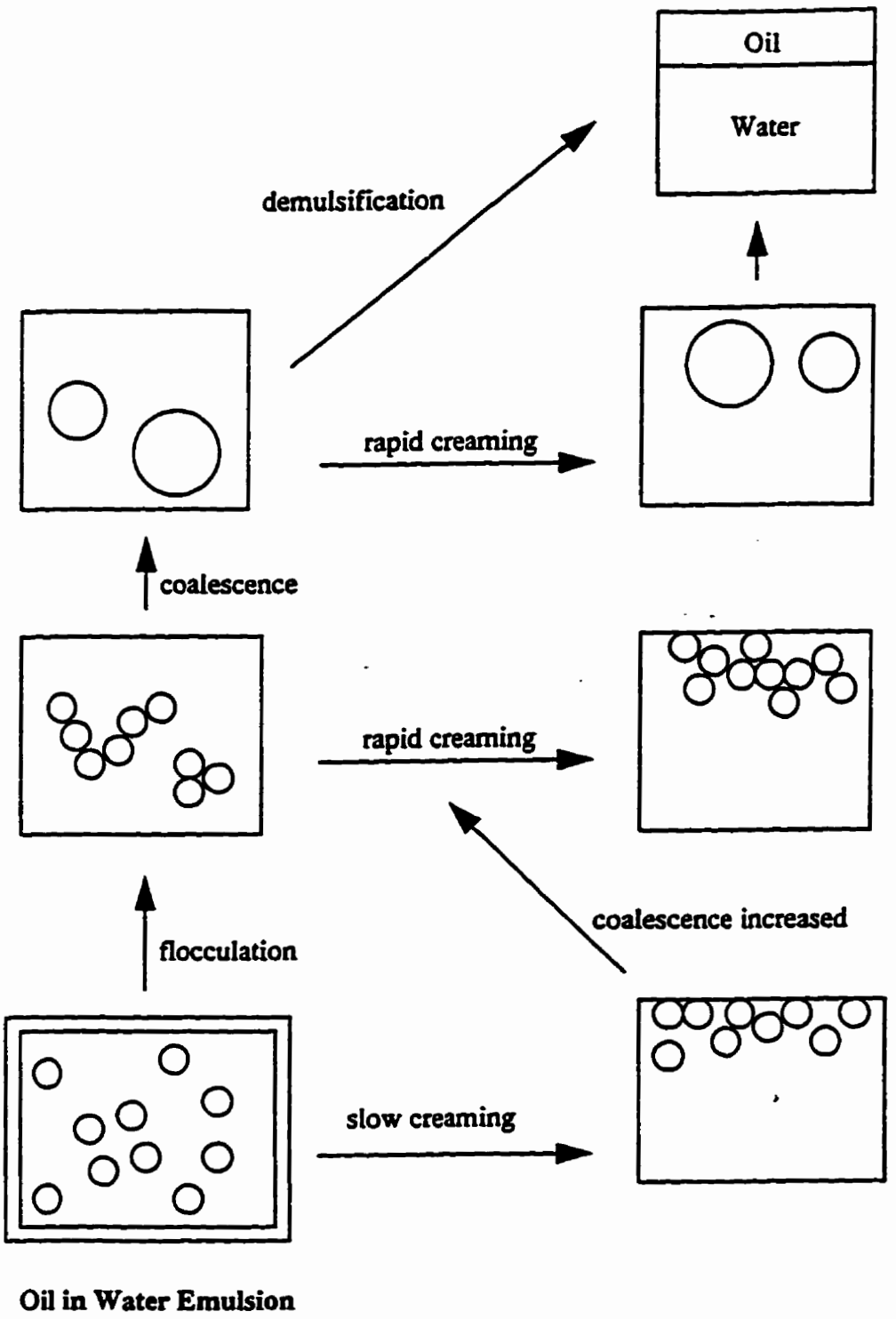


Figure 2.01. Different types of instability for an o/w emulsion (Adapted from Walstra, 1987)

water emulsion creams because the dispersed droplets are of a lower density than the continuous phase. Large droplets may have an effective density closer to that of the oil phase, whereas very small droplets may have an effective density larger than the continuous phase so that creaming will never occur even under centrifugal conditions (Dickinson and Stainsby, 1988)

In principle, creaming can be inhibited by matching the droplet density to that of the aqueous phase. Creaming influences the heterogeneous distribution of dispersed droplets. In the early stages of creaming, a vertical concentration gradient forms in the emulsion; however, a distinct boundary between an upper cream layer and a lower depleted emulsion layer can be observed after a period. Creaming is reversible. That is, the original conditions of the emulsion will return with gentle mixing. An emulsion droplet surrounded by a viscoelastic film behaves hydrodynamically like a rigid sphere. It can be modelled after Stokes' Law:

$$V_s = \frac{a\,(\rho_d - \rho_c)\,d^2}{18\,\eta} \qquad [2]$$

where V_s is the velocity of an isolated particle, a is 9.81 m.s $^{-2}$ for gravitational creaming, d is the particle diameter, η is the medium viscosity and ρ_d and ρ_c are the densities of the disperse and continuous phase respectively (Walstra, 1987).

Employing Stokes' Law, there are three ways of increasing emulsion stability with respect to creaming: reduce the dispersed droplet size, match the phase densities or increase the viscosity of the dispersed phase (Dickinson and Stainsby, 1988). The first condition can be satisfied by simply homogenizing the emulsion at high pressure using a high ratio of emulsifier to oil. The

second and third conditions involve product formulation modifications. Creaming can be retarded by increasing the viscosity of the continuous phase with the use of hydrocolloids (Dickinson, 1988). The crucial factor in this relationship is the apparent shear viscosity in the presence of very low applied stress. This weak gel network can be reinforced if the hydrocolloid interacts with the protein adsorbed on to the oil droplet; conversely, it may be less effective if the hydrocolloid is thermodynamically incompatible with the protein (Dickinson, 1988). The use of a hydrocolloid thickening agent to retard creaming can be easily undermined if the hydrocolloid induces droplet flocculation (Dickinson and Stainsby, 1988).

2.5.2.2. Flocculation

Flocculation is a thermodynamically spontaneous clustering of dispersed droplets without a change in the droplet size (Dickinson, 1988). At high volume fractions, all emulsions flocculate in the sense that neighbouring droplets are in close proximity of each other. On the other hand, flocculation at low volume fractions depends on the strength of interactions between the dispersed droplets. This in turn depends on factors such as the structure of the absorbed layer and the thermodynamic quality of the solvent.

In thermodynamic terms, the interaction energy (G_{int}) is the free energy needed to bring two droplets from a certain distance apart to some closer distance 'h' (Walstra, 1987). This energy consists of three components: Van der Waals' attraction, electrostatic repulsion and steric repulsion. The extent of droplet flocculation can be regulated by electrostatic or steric stabilization (or a combination of the two). In electrostatic stabilization, droplets are separated by a repulsion between their charged surfaces. In steric stabilization, the dispersed droplets are separated by osmotic repulsion where there is a high concentration of polymer in the

overlapping region to physically prevent two macromolecules from coming together (Dickinson and Stainsby, 1988). Solvent quality, pH and ionic strength of the emulsion will influence how significant electrostatic repulsion will be at inhibiting flocculation on account of their effect on droplet surface charge. Polymer conformation, on the other hand, will influence the role of steric repulsion in controlling stability.

Proteins can provide both types of stabilization. Electrostatic stabilization is favoured by low ionic strength environments and pH that is well away from the proteins' isoelectric point. For steric stabilization, high amounts of emulsifier are required to ensure complete coverage of the droplet surface. If the protein concentration is not high enough to supply complete coverage, then bridging flocculation can occur. In this type of flocculation, the biopolymer adsorbed on one droplet is shared with another droplet, bringing the two together. With protein stabilized emulsions, any process that causes a protein to aggregate will induce flocculation (Dickinson, 1988).

Non-adsorbed polymers may also influence stability. Depletion flocculation (or depletion stabilization) arises whenever two particles are close enough together that other polymer molecules are excluded from the region. An osmotic pressure gradient results causing the two particles to come together spontaneously. Instability due to flocculation is closely linked with that due to creaming (Dickinson, 1988).

2.5.2.3. Coalescence

Unlike the other two types of instability, coalescence is always irreversible. When two droplets contact each other, a thin film forms between them. Coalescence results from the rupture of the

film (Tadros and Vincent, 1983). When the dispersed phase is entirely liquid, free oil can appear at the surface of the emulsion. The rate of coalescence largely follows first order kinetics; flocculation on the other hand, is typically a second order reaction (Walstra, 1988).

The rate of coalescence in emulsions under ambient conditions is often so slow that accelerated tests such as high temperature and/or high gravitational forces are used for quality control. These methods may describe an emulsion as unstable even if long term storage does not. High temperatures can produce conformational changes in the proteins that do not occur at ambient temperatures (Jaynes, 1985). Centrifugation can rupture an oil/water interface that would not break under normal gravitational forces. If hydrolysis due to a low pH or enzymatic activity were to change the nature of the protein interface, this may not be revealed by an accelerated method. Therefore, long term storage tests should supplement quick scanning methods. Extended storage tests provide quantitative and reliable evaluation of emulsion stability by studying the kinetics of oil drop coalescence (Sherman, 1968).

2.5.3. Experimental Techniques for Assessing Emulsion Stability

2.5.3.1. Rheological Properties of Emulsion

Rheology is the science of deformation and flow of matter (Tung, 1988). Rheological properties form the basis of textural attributes. Shear stress is defined as shear force per unit area with units of Nm^{-2} or Pa. Shear rate is the rate of change of strain per unit thickness of fluid as a function of time. Its units are expressed as s^{-1}. The shear rate obtained from an applied shear stress is dependent upon the material's resistance to flow; therefore, the flow behaviour, or viscosity of a sample, is defined as shear stress over shear rate (Morris, 1984).

From a rheological standpoint, materials are grouped into ideal solids, liquids or plastics. When an ideal elastic or solid material is subjected to small deformation, strain of the material is directly proportional to the stress applied. An ideal viscous or Newtonian fluid will continue to deform if the stress is continued to be applied and no elastic recovery is observed after the stress is removed. Its viscosity is constant and independent of the shear rate; furthermore, the shear stress is proportional to shear rate. The ideal plastic (or Bingham plastic) material behaves as a solid until it is stressed beyond its yield point then flows as a liquid. In the wide spectrum of food, few can be classified by ideal rheological standards. Non-Newtonian fluids are grouped in three broad categories: time independent, time dependent and viscoelastic fluids (Tung, 1988).

Time independent non-Newtonian fluids display a flow curve where the ratio of shear stress to shear rate is not constant. The most common type is pseudoplastic flow. This fluid exhibits shear thinning over a wide range of shear rates. A comparatively small group of fluids termed dilatant fluids, exhibits an increase resistance to flow with increasing shear rate. The power law is often used to describe a material's flow under a small range of shear rates. The relationship of

$$\sigma = m\,\dot{\gamma}^{n} \qquad [3]$$

where σ is the shear stress, $\dot{\gamma}$ is the shear rate and m and n are parameters called the consistency coefficient and the flow behavior index, respectively. This model can indicate whether the fluid behaves in a Newtonian ($n = 1$), shear thinning ($n < 1$) or shear thickening fashion ($n > 1$) (Morris, 1984).

With time independent behaviour, the fluid is dependent only on the shear rate. Some fluids,

however, exhibit a time delay. Sometimes, this change may or may not be reversible upon rest. Thixotropic fluid experiences a decrease in shear stress and apparent viscosity; whereas a rheopectic fluid shows an increase in shear stress and apparent viscosity at a constant shear rate and temperature. The major difference between thixotropic versus pseudoplastic and dilatant versus rheopectic systems is the time required to restore the original structure when shear stresses are removed. Rheodestructive fluids are another type of time dependent fluid. The time dependent loss of structure is not recoverable and a permanent loss of structure is experienced (Tung, 1988).

Viscoelastic behaviour of materials exhibits partial elastic recovery upon removal of shear stress. This dual nature is observed in polymer dispersions (Dickinson, 1988). The viscoelastic aspect of the solution is particularly relevant when considering textural attributes, processing properties, stability characteristics or the fundamental molecular nature of the system.

Rheological properties of hydrocolloids may be influenced by several factors. Rheological properties are often very sensitive to changes in concentration. For high concentration solutions, an increasing interaction between particles would increase the observed viscosity of the sample. For anionic polymers, pH and ionic strength changes will significantly affect the rheological properties due to conformational changes in the polymer.

2.5.3.1.1. Creep Compliance

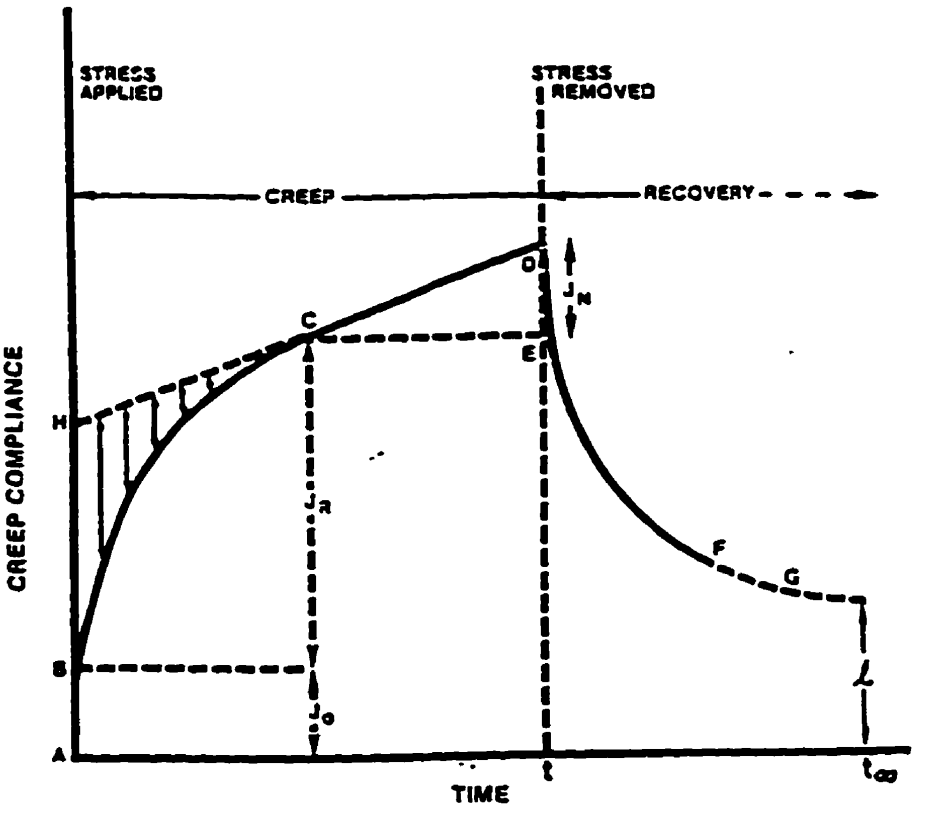
At low strains, the elastic component in a viscoelastic material will play a major role in contributing to the materials' behaviour. A creep test is the slow deformation of material measured under constant stress (Sherman, 1983). This stress should be well below the yield

stress of the sample. In this region of stress, the material will exhibit the characteristics of both solids (elastic component) and fluids (viscous component). By applying small stresses, it is possible to mimic gravitational effects to assist in predicting sedimentation.

In creep testing, a selected shear stress is applied to an emulsion and the resultant strain is monitored as a function of time. After some predetermined time, the stress is removed and the strain is again monitored. Since the change in strain (ie. deformation) is dependent upon the applied stress, the notation, compliance, is used rather than strain when discussing results. Creep compliance is the ratio of the strain to the applied constant stress. Creep/recovery profiles can therefore be directly compared even if they were not measured under the same applied stress assuming that the stresses are within the viscoelastic range of the samples (Sherman, 1968).

The creep/recovery curve has three distinct regions (Figure 2.02). At the very start of the test, there is an immediate strain represented by AB. The data relates primarily to a pure elastic deformation referred to as the instantaneous elastic compliance (J_o). If the stress is removed shortly after, the emulsion undergoes no permanent change. However, after a short period of stress, the compliance curvature decreases. Eventually, the compliance increases linearly with time (CD). The linear region represents Newtonian compliance (J_N) whereas the area between J_O and J_N (BC) represents the retarded elastic compliance (J_R) (Sherman, 1983). The retarded elastic compliance region incorporates the response of a wide spectrum of bond strengths to the applied stress. Initially only the weakest bonds are broken but at longer times, stronger bonds rupture although no change in the applied stress occurs (Sherman, 1983). The total number of broken bonds depends on the magnitude of applied stress.

Recovery must be monitored for at least as long as the creep test to guarantee that all the



where AB = instantaneous elastic compliance (J_O)
region BC = retarded elastic compliance (J_R)
region CD = Newtonian compliance (J_N)
Stress is removed at point D:
DE = instantaneous elastic recovery
EF= retarded elastic recovery
l = represents the nonrecoverable strain per unit shear stress.

Figure 2.02. Creep compliance time behaviour of a typical emulsion displaying viscoelasticity (Adapted from Sherman, 1983)

elasticity of the material has been recovered. When the stress is removed (D), strain recovery follows a similar sequence as the compliance (Figure 2.02). An instantaneous elastic recovery (DE) followed by retarded elastic recovery (EF) and an eventual flattening of the curve (Sherman, 1983). The degree of structural alteration incurred by the sample due to the stress is represented by the vertical distance from the flattened curve to the x axis of the time line. The viscoelastic parameters of the emulsion are determined from the analysis of the creep compliance curve. The emulsion's creep behaviour, therefore, is given by:

$$J(t) = J_O + J_R + J_N \qquad [4]$$

where Jo is the instantaneous elastic compliance, J_R is the retarded elastic compliance and J_N is the Newtonian compliance. Provided that the emulsion exhibits linear viscoelasticity, the data can be analyzed by the following:

$$J_O = \frac{1}{E_O} \quad , \quad J_N = \frac{t}{\eta_N} \qquad [5]$$

where E_O is the instantaneous elastic modulus and η_N is the Newtonian viscosity (Sherman, 1968). The retarded creep compliance can be represented by:

$$J_R = \Sigma\ 1/E_i\ [1 - e^{(-t/\tau i)}] \qquad [6]$$

where E_i is the retarded elastic modulus for a given element, τi ($= \eta_i/E_i$) is the retardation time, and η_i is the coefficient of viscosity for the same element. The analysis of creep behaviour of visco-elastic foods, therefore, yields the rheological properties of elasticity, E_i, Newtonian viscosity, η_N, and the viscosity of individual elements, η_i (Sherman, 1968). The viscoelastic parameters, E_o and η_N are the main parameters mentioned when describing o/w emulsions (Vernon-Carter and Sherman, 1980; Kiosseoglou and Sherman, 1983). For ease of discussion and comparison, only these two parameters were examined in this study.

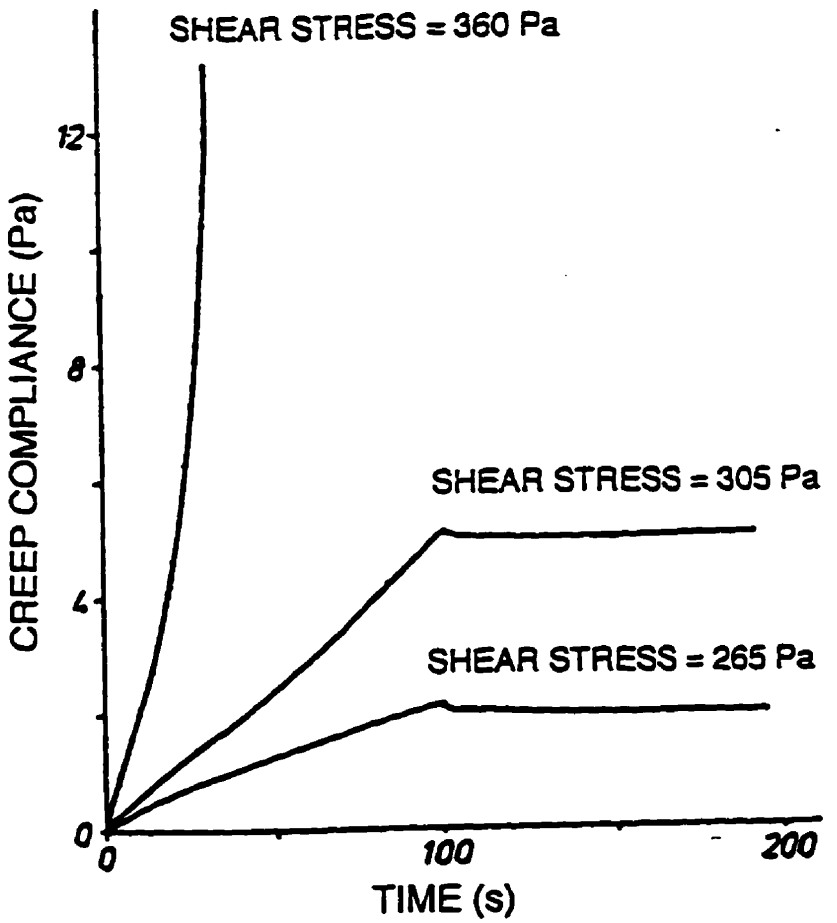


Figure 2.03. Effect of shear stress on creep and recovery curves of a polymer latex (Source: Zosel, 1982)

Outside of the samples' viscoelastic range, creep compliance becomes dependent on stress (Figure 2.03). Creep curves showing an upward curvature indicates the network structure is breaking down rapidly (Zosel, 1982). This sample would show liquid behaviour with a relatively low viscosity and with minimal elastic properties. Creep curves showing a levelling off to a horizontal line indicates that the sample's yield stress is greater than the stress applied. The sample deforms due to its viscoelastic properties but it will not flow.

Carrillo and Kokini (1988) showed that creep compliance curves are very useful in studying the behaviour of emulsions. Any formulation that reduces the compliance value corresponds to an emulsion having increasing levels of structure and a higher storage stability. For example, addition of salt to a constant egg yolk level stabilizes the oil in water emulsion as shown by a low compliance value (Figure 2.04). Aging also destabilizes the emulsion as shown by a shift of the compliance curve towards a higher value (Figure 2.04).

2.5.3.1.2. Dynamic Testing

Viscoelastic properties can be studied by the response to a stress that varies periodically with time. When a stress is applied at a given frequency, the strain amplitude will be proportional to the stress amplitude if the emulsion has linear viscoelastic properties. The strain alternates sinusoidally as does the stress but it will be out of phase with the stress. The data can be interpreted as a complex shear modulus (G*), which is the ratio of stress amplitude over strain amplitude. It can be expressed as the sum of two components:

$$G^* = G' + i\,G'' \qquad [7]$$

where G' is the storage modulus which is the sum of the elastic component, and G" is the loss modulus which is the loss of energy through permanent deformation of the sample. In addition,

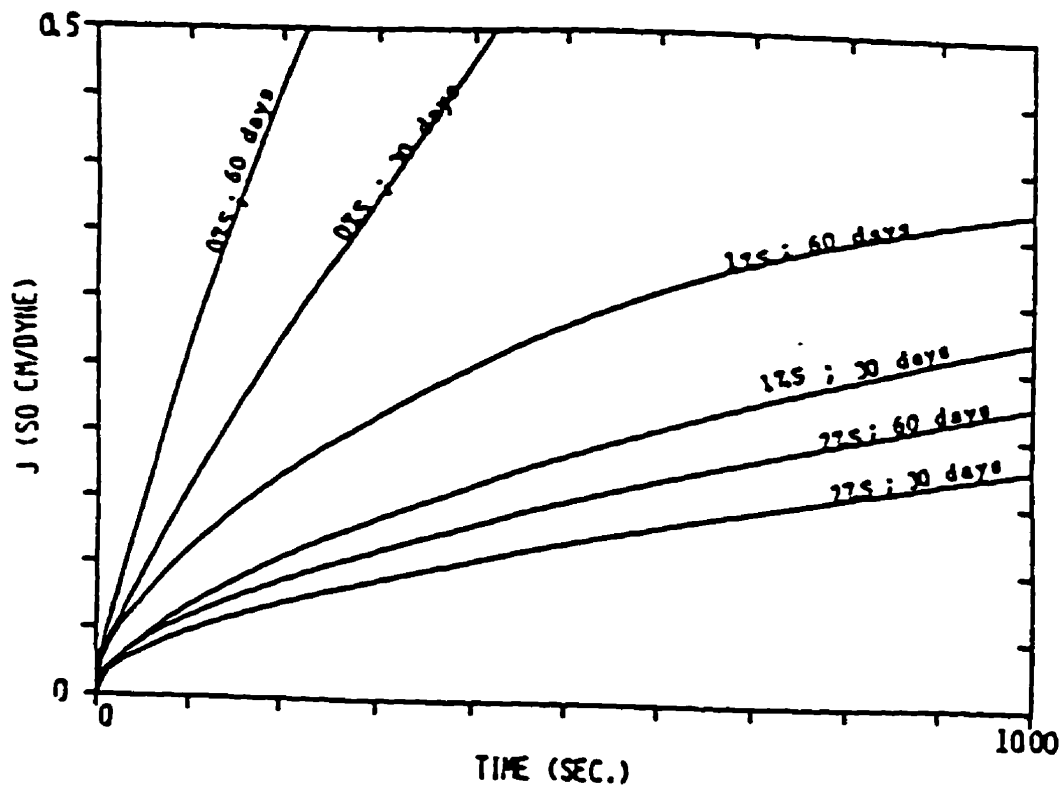


Figure 2.04. Effect of aging time on averaged creep data curves for 1% egg yolk and 0%, 1%, and 2% salt oil in water emulsions (Source: Carrillo and Kokini, 1988)

$G''/G' = \tan \delta$, where $\tan \delta$ is the loss tangent. Viscoelastic materials also exhibit a complex viscosity (η^*) which is represented by:

$$\eta^* = G^*/\omega \qquad [8]$$

where G^* is the complex shear modulus and ω is the frequency. The combination of viscous and elastic components in a material will respond differently depending on the speed at which the sample is moved (Morris, 1984). By oscillating over a wide range of frequencies, the characteristics of the sample can be determined. Figure 2.05 shows three idealized mechanical spectra of a non covalent cross linked gel, a concentrated polymer solution, and a dilute solution. In polymeric gels, the behaviour approximates a permanent network where G' is greater than G" over the entire frequency range (Figure 2.05a). In contrast, the dilute polymer solutions G" predominates over the entire frequency range (Figure 2.05c). In concentrated solutions, a crossover point occurs at which G' becomes greater than G" (Figure 2.05b).

During a shear stress amplitude sweep, emulsions stabilized with hydrocolloids can show a limiting viscosity or Newtonian plateau at low shear stresses. Identification and quantification of this low shear viscosity plateau is useful when predicting emulsion stability. Shear rates and stresses experienced by oil droplets undergoing gravitational separation or flocculation would be observed in the small range (Pettitt *et al.*, 1995). Pettitt and coworkers observed increasing limiting viscosity with the addition of xanthan gum (Figure 2.06). This increase, they believed, corresponded to a more stable emulsion.

2.5.3.1.3. Rheological Changes During Emulsion Storage

When freshly prepared emulsions are stored at ambient temperatures, the droplets flocculate

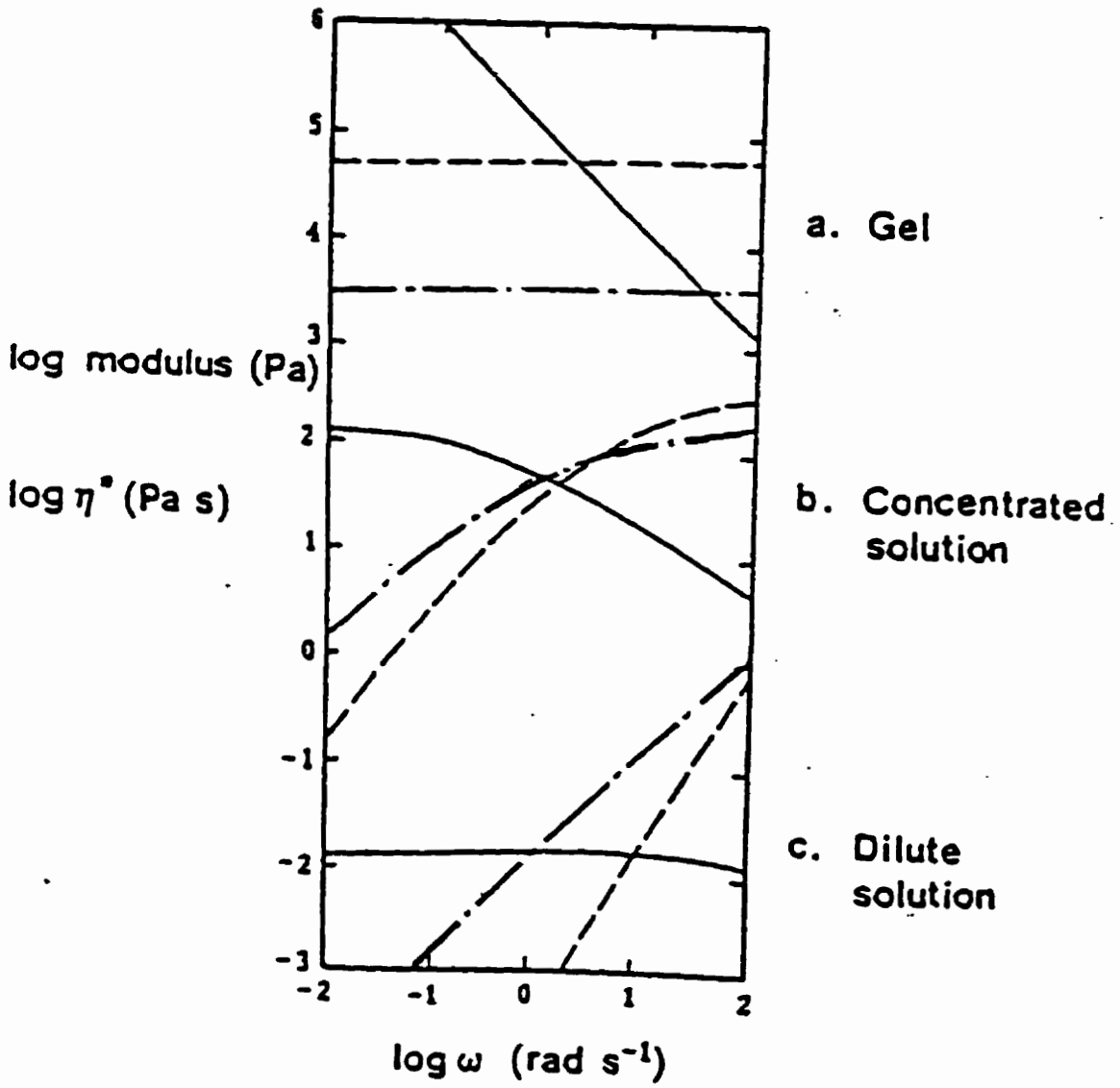


Figure 2.05. Frequency (ω) dependence of G' (– – –), G" (– · – · –) and η* (——) for
a) a strong gel (2% w/v agar)
b) a concentrated solution (5% w/v λ-carrageenan)
c) a dilute solution (5% w/v dextran)
(Source: Morris, 1984)

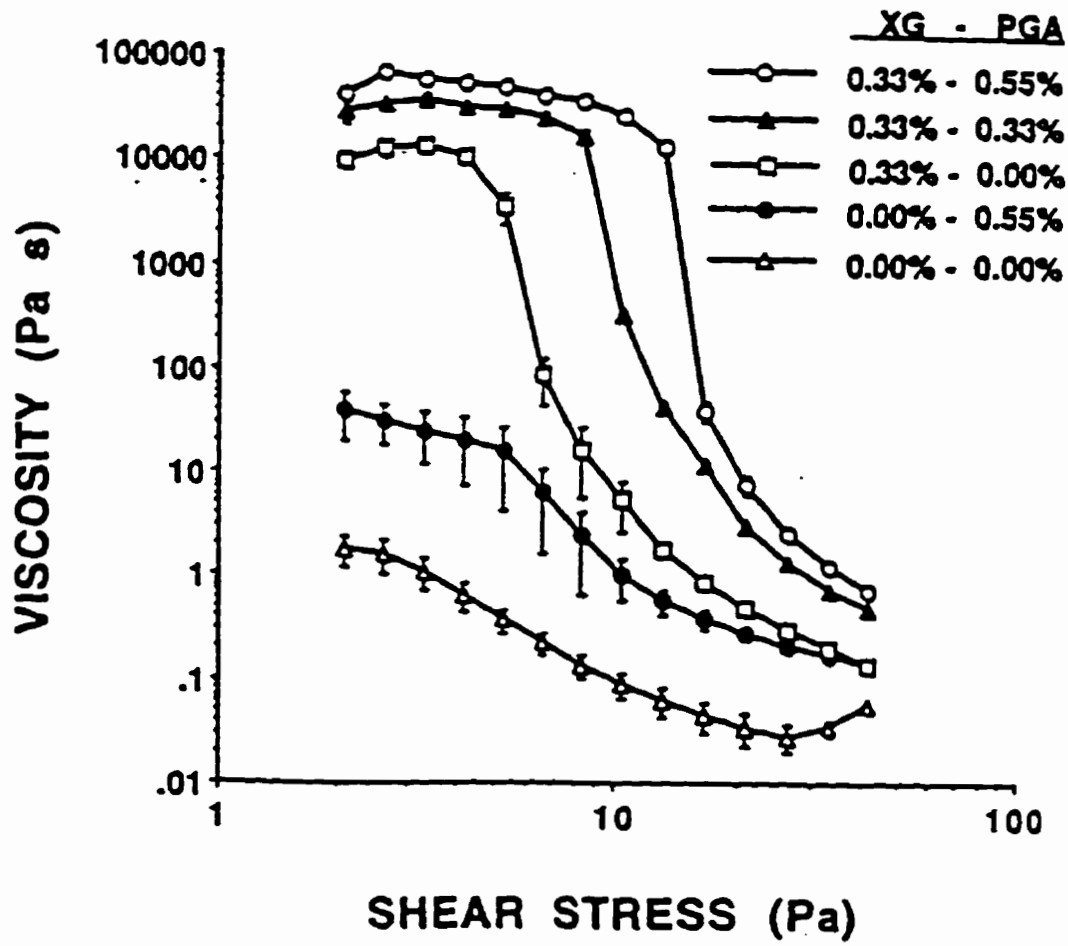


Figure 2.06. Effect of adding propylene glycol alginate (PGA) and xanthan gum (XG) on viscosities of oil in water emulsions containing 40% oil. (Source: Pettitt *et al.*, 1995).

and coalesce for a period before visual signs appear. These flocculated droplets form three dimensional networks that exhibit viscoelastic behavior. The distance that separates the droplets depends on Van der Waals' attraction, electrostatic and steric repulsion potentials.

Viscosity measurements made at high shear rate, decrease sharply with storage time probably due to increase in mean droplet diameter (Sherman, 1983). Mean droplet diameter (D_V) can be derived from the equation:

$$D_v = \sqrt[3]{\Sigma\ n_i\ \ d_i^3\ /\ \Sigma n} \qquad [9]$$

where n_i is the number of drops with diameter d. The rate of drop coalescence (K) can be calculated by applying the equation :

$$N_t = N_0 \exp(-Kt) \qquad [10]$$

where N_t and N_0 are the numbers of drops per ml emulsion at time t and t=0, respectively. The numbers of drops per ml emulsion can be determined using the equation:

$$N_t = \frac{6\phi}{\pi\ D_v^3}\ x\ 10^{12} \qquad [11]$$

where ϕ is the volume fraction of oil. The slower the coalescence rate, the more stable is the emulsion.

With creep compliance time tests, the value of each parameter decreases with storage time (Vernon-Carter and Sherman, 1980; Kiosseoglou and Sherman, 1983). During the first few days of storage the values of all parameters increase and then decrease subsequently. The general trend is therefore in agreement to that observed for viscosity measurements at low shear rates.

An increase in viscosity on aging is due to the entrapment of the continuous phase between droplets. The decrease in viscosity is due to drainage of the film surrounding the droplets from gravitational forces and coalescence as well as the breakdown of aggregates resulting in decreased effective phase ratio.

3. CHARACTERIZATION OF FLAXSEED GUM

3.1. Introduction

New food applications continue to be developed as consumer demands change in terms of convenience, nutrition and cost as new processing techniques and product economics evolve. System components, such as acids, salts, proteins and fats can interact with hydrocolloids chosen for specific products. These components are often critical when choosing the hydrocolloid and optimizing its use. Processing techniques as well as other considerations such as cost, nutrition and availability are just as important to the commercial success of a gum in a competitive hydrocolloid market as its physico-chemical properties (Sanderson, 1990).

In this experiment, two types of flaxseed gum were extracted having similar viscoelastic properties (Mazza *et al.*, 1994; Cui and Mazza, 1996). Linola™ 947 is a form of flaxseed, belonging to the same botanical species as cv. Norman. The major difference between Linola™ and cv. Norman is the fatty acid composition of the oil (Linola Grower's Guide, 1996). Most flaxseed cultivars contain higher proportions of polyunsaturated linolenic acid (Bhatty, 1995). An obvious difference between the two extracted flaxseed gums is colour; the gum from flaxseed cv. Norman is light brown whereas Linola™ is pale yellow (Appendix A). The object of this experiment was to produce a high quality (ie. high carbohydrate, low contaminant) product with good yield and favourable rheological behaviour.

3.2. Materials

Flaxseed (cvs. Norman and Linola™947) grown commercially in southern Manitoba, Canada

in 1994 was used. Xanthan gum and guar gum were obtained from Kelco (San Diego, CA) and Indian Gum Industries (Prescott Canada Distributors, ON), respectively. All chemicals used were reagent grade unless otherwise specified.

3.3. Methods

3.3.1. Extraction

Flaxseed gum was extracted by an aqueous process described by Cui *et al.* (1994c). The aqueous extract was concentrated prior to precipitation with one volume of 95% ethanol by using an Alpha-Laval concentrator (CentriTherm model CTIB-2, Lund, Sweden) under the following conditions: feed rate 38-40%; feed temp 40-45°C; concentrate temp ca. 60 °C; and steam temp ca. 90 °C.

3.3.2. Chemical Analysis

Crude flaxseed gum was analysed using the following methods: moisture content by the vacuum oven method (925.09), ash (923.03), oil content by the soxhlet method (22-033) (AOAC, 1995); crude protein was determined by the Micro-Kjeldahl method (960.52) (AOAC, 1995). Cyanogenic glucosides in flaxseed gum were determined by the method of Oomah *et al.* (1992). All tests were done in triplicate unless otherwise stated.

3.3.3. Rheological Measurements

The steady shear flow curves and dynamic rheological measurements of flaxseed gum solutions

were carried out using a controlled stress rheometer (Bohlin Model CVO; Bohlin Instruments, NJ). Measurement geometry was a 6 cm diameter cone and plate with a 2° cone angle (0.07 mm gap setting). Polymer solutions (pH 6.5) were hydrated in double distilled water overnight prior to testing. Commercial gums (xanthan and guar) and flaxseed gums (cv. Norman and Linola ™) were prepared at 1% (w/v) and 2% (w/v) solutions for the steady shear rheological measurements and for the small strain oscillatory tests (frequency 0.01 to 15 Hz, less than 4% strain). A low viscosity silicon oil was applied to the exposed surfaces to prevent drying.

3.4. Results & Discussion

The method used by Cui *et al.*, (1994c) was slightly modified. One volume of 95% ethanol removed the majority of cyanogenic glucosides (ca. > 83%) with additional ethanol washes deemed redundant (Figure 3.01). Consistent with reports from Wanasundara and coworkers (1993), an alkanol wash was an effective method of extracting the cyanogenic glucosides. Cyanogenic glycosides are capable of liberating hydrogen cyanide upon hydrolysis (Mazza and Oomah, 1995). The accepted limit for human consumption of flaxseed is 50 g per day (Bhatty, 1995). Considering that flaxseed contains approximately 30 to 40 mg of total hydrogen cyanide equivilant (THCN) per 100 grams of seed (Oomah *et al.*, 1992), a consumption of 15 to 20 mg HCN per day is within the acceptable limits. No processing of the gum after extraction (that is, no ethanol precipitation), left behind 238 mg HCN per 100 grams of flaxseed gum. This corresponds to a safe consumption between 6 and 8 grams of flaxseed gum per day (Figure 3.01). After one wash with 95% ethanol, 44.5 mg of HCN per 100 g of flaxseed gum remained which represents a safe consumption of 30 to 40 grams per day. Ethanol wash improved the functionality of the flaxseed gum. Linustatin and neolinustatin were the dominant cyanogenic glucosides found in flaxseed gum (Figure 3.02). Frehner *et al.*, (1990) indicated that mature

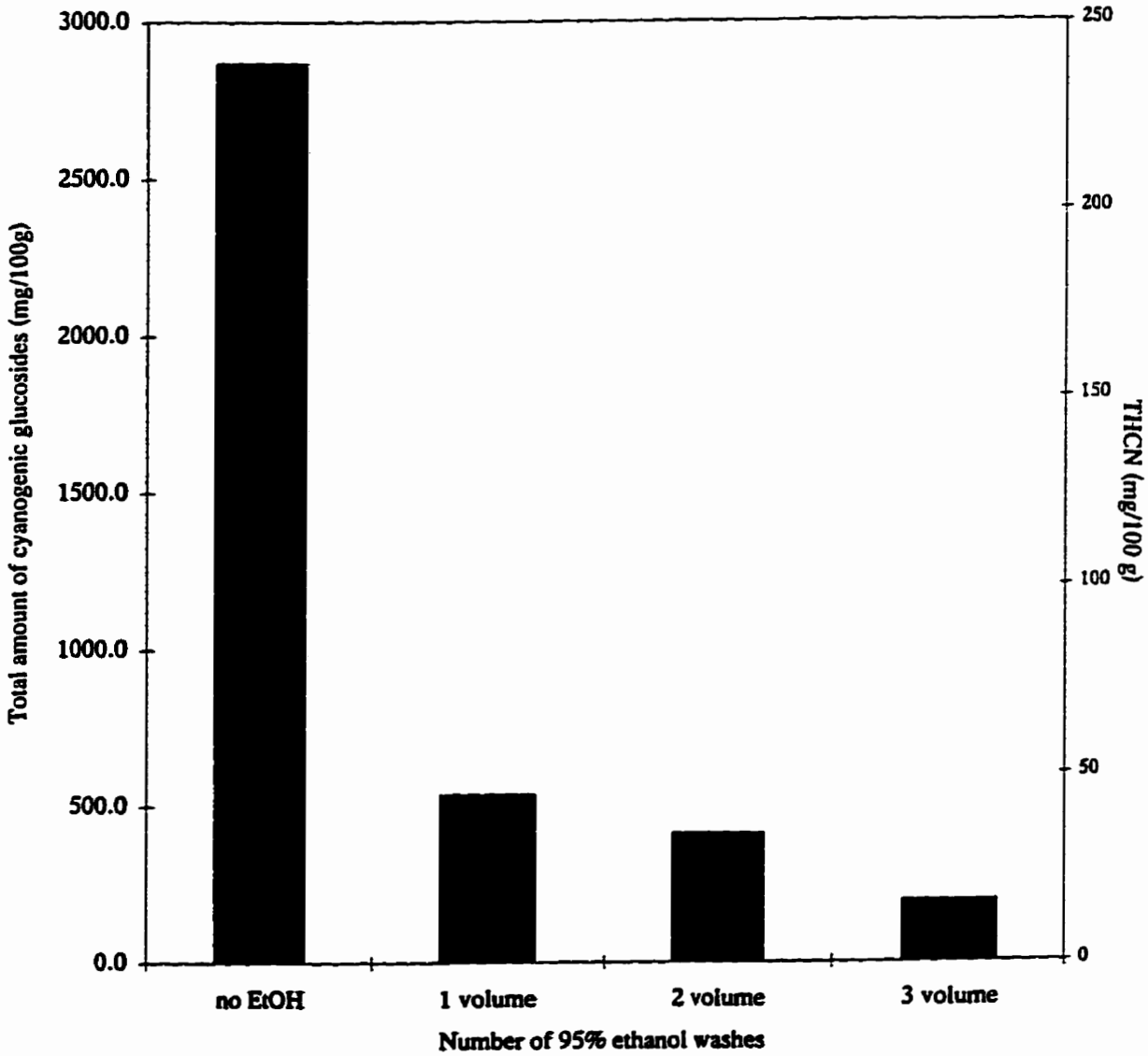


Figure 3.01. Effect of 95% ethanol washes on removal of cyanogenic glucosides from flaxseed gum cv. Norman

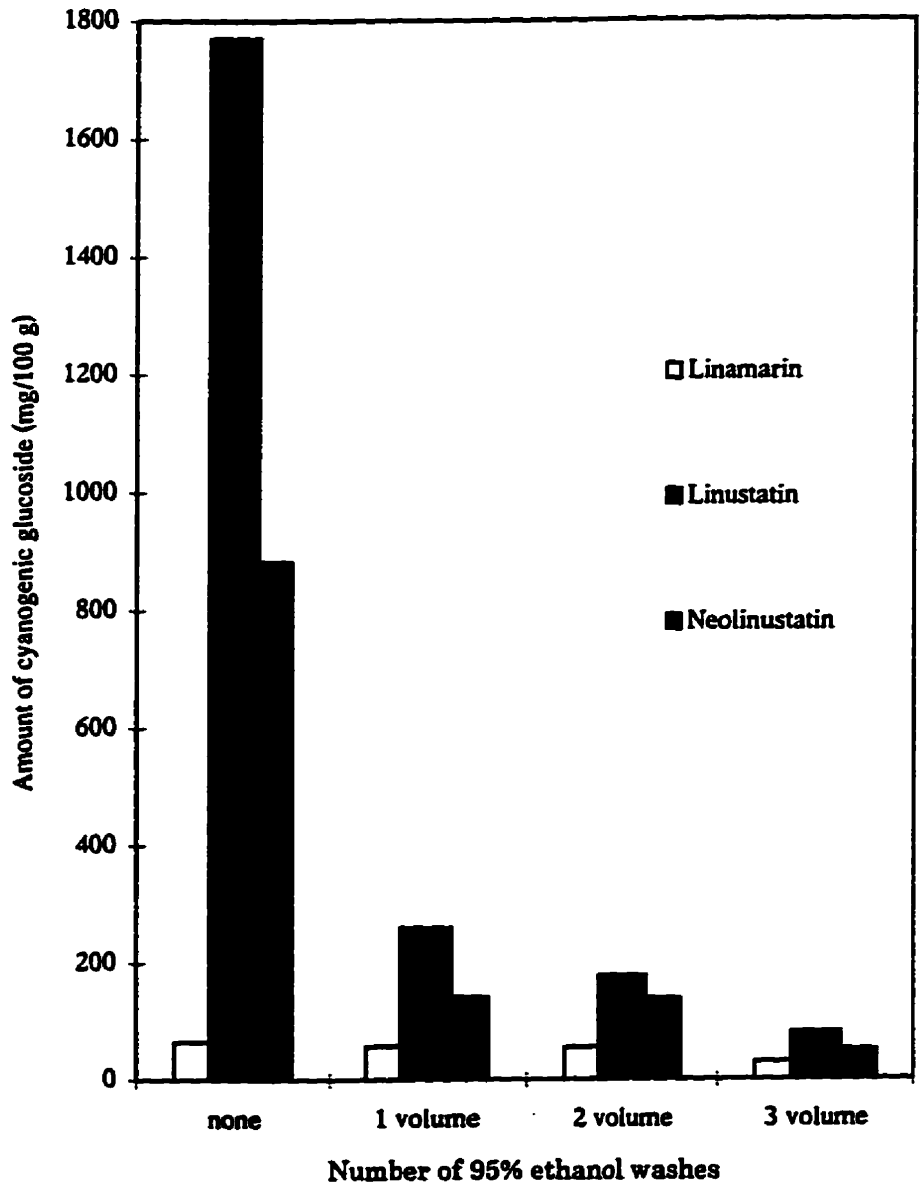


Figure 3.02. Effect of 95% ethanol washes on removal of individual cyanogenic glucosides from crude flaxseed gum cv. Norman

seeds predominantly contain these two glycosides. Linustatin accounts for 54-76% of the total cyanogenic glycoside content (Mazza and Oomah, 1995).

The yields and composition values for the gum extracted from cv. Norman and Linola™ flaxseed together with commercial xanthan and guar gum are given in Table 3.01. Gum yields were slightly lower for Linola™ than for cv. Norman. Linola™ has a seed coat that is slightly thinner than most flax cultivars (Linola Grower's Guide, 1996). It is assumed, theoretically that Linola™ would also have a lower gum content. A similar observation for yellow seeded canola hulls being lower in fiber and lignan than those from brown seeded types has been reported (Slominski *et al.*, 1994). A modified production technique which employed an Alpha Laval CentriTherm concentrator was used to concentrate the flaxseed gum prior to ethanol precipitation. High water content makes it easier to extract the polysaccharide due to the low viscosity; however, it resulted in large volumes of extract which required a large volume of ethanol to precipitate the gum. Partial concentration of the extract with the Alpha-Laval CentriTherm concentrator was performed to remove some of the water prior to the ethanol extraction. Conceivably, the reduced yield of gum could have resulted from the concentration step of the production process. Due to the pale seed coat colour of Linola™, it was difficult to determine the onset of gum concentration using the Alpha-Laval centritherm. Extractions of Linola™ and cv. Norman flaxseed at optimum conditions produced yields comparable with that from the brown seeded cv. Linott (5-8%) determined by Mazza and Biliaderis (1989) and Fedeniuk and Biliaderis (1994). Moisture content of the flaxseed gums were similar to that reported for cv. Norman (6.5%) by Cui and coworkers (1994).

Table 3.01. Yield and composition of crude flaxseed gum cv. Norman and Linola™ along with xanthan and guar gum.

Component (on dry basis)	Hydrocolloidal Gums			
	Norman	Linola™ 947	Guar gum	Xanthan gum
yield (%)	5.5 ± 0.5	4.4 ± 0.4	ND	ND
moisture (%)	7.9 ± 0.1	8.6 ± 0.4	9.6 ± 0.1	7.6 ± 0.1
protein (%)	10.3 ± 0.3	10.6 ± 0.2	1.4 ± 0.1	1.0 ± 0.05
oil (%)	0.3 ± 0.05	0.4 ± 0.05	ND	ND
ash (%)	7.1 ● 0.2	7.8 ● 0.3	0.7 ± 0.1	10.6 ● 0.3
carbohydrate[a] (%)	82.3	81.2	97.9	88.4

[a] determined by difference
ND, not determined

Because of the flaxseed gums were concentrated at high temperatures (steam temperature was 90 °C), it is possible that chain cleavage could have occurred to the flaxseed gum which would effectively lower gum viscosity. Rheology measurements were taken at 1% and 2% solutions and compared with published data. The shear rate dependent flow behaviour of xanthan (1% w/v), guar (1% w/v), Norman (1% and 2% w/v) and Linola™ (1% and 2% w/v) flaxseed gums were determined. Shear thinning behaviour was observed for all polymers at concentrations examined (Figure 3.03). Differences in shear thinning behaviour were quantified using the power law model, $\sigma = m\dot{\gamma}^a$ (Tung, 1988). The consistency index (m), and the flow behaviour index, (n), were determined for the concentrated solutions (Table 3.02). As concentration increased, the value for m increased while n decreased. For gum from cv. Norman flaxseed an increase in gum concentration from a 1% (w/v) to 2% (w/v) resulted in a shift of the m value from 0.22 to 2.08 and n from 0.75 to 0.60. Fedeniuk and Biliaderis (1994) reported a 2% (w/w) dispersion of cv. Linott flaxseed gum having a flow behaviour index (n) of 0.63 and a consistency index (m) of 1.68. The increase of m as the flaxseed gum dispersions increased from 1% (w/v)

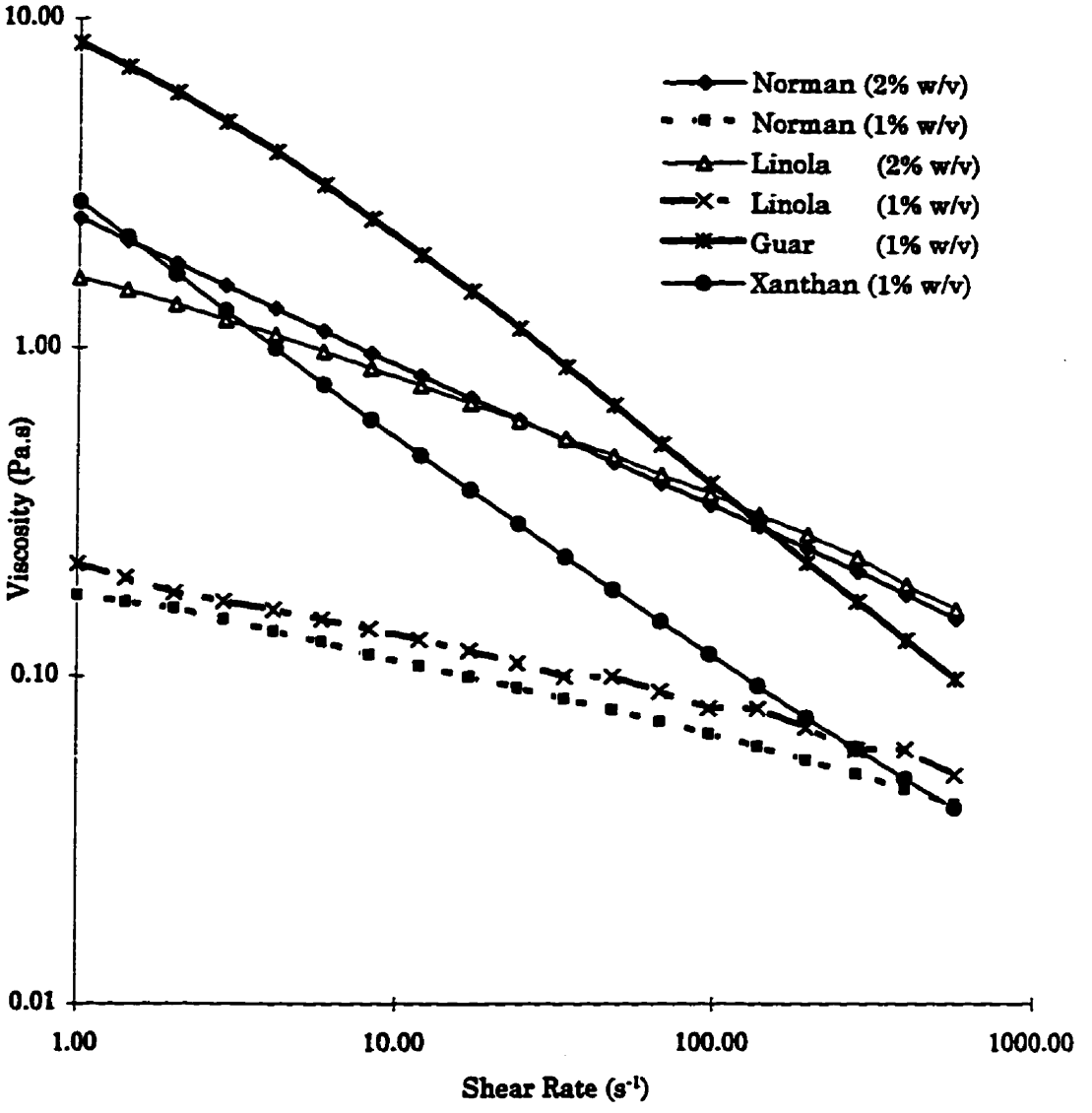


Figure 3.03. The effect of shear rate on the apparent viscosity of commercial food gums and flaxseed gum (pH 6.5; 25°C)

to 2% (w/v) indicates that a more viscous solution is obtained at higher gum concentrations. The decrease in n confirmed a more pronounced shear thinning (Tung, 1988). Both flaxseed cultivars displayed similar shear thinning profiles (Table 3.02, Figure 3.03). This was to be expected on account of flaxseed gum cv. Norman and Linola™ are reported to be rheologically similar (Mazza *et al.*, 1994). Guar gum exhibited the highest m (9.72) and the lowest n (0.28) values. Fedeniuk and Biliaderis, (1994) recorded values of m being 18.07 and n equalling 0.28 for 1.5% (w/w) guar gum dispersions. Xanthan gum recorded a consistency coefficient (m) of 2.68 and a flow behaviour index (n) of 0.32. These were consistent with values reported by Fedeniuk and Biliaderis (1994) for xanthan gum.

Table 3.02. Consistency coefficient (m) and flow behaviour index (n) of commercial gums and flaxseed gum solutions (25 °C) according to the power law model ($\eta = m\dot{\gamma}^n$).

Polymer	m	n
Guar gum (1% w/v)	9.72	0.28
Xanthan gum (1% w/v)	2.68	0.32
Norman flaxseed gum (1% w/v)	0.22	0.75
Linola™ flaxseed gum (1% w/v)	0.22	0.76
Norman flaxseed gum (2% w/v)	2.08	0.60
Linola™ flaxseed gum (2% w/v)	2.02	0.61

n=3, $R^2 > 0.99$

Small deformation oscillatory rheological tests are useful in examining the molecular origin of of polymer solutions. As was to be expected, 1% and 2% (w/v) solutions of Linola™ and Norman had similar dynamic profiles (Figures 3.04 C and E; D and F, respectively). Figure 3.04 D and F, shows the flaxseed gum dispersions exhibited a concentrated solution profile where the storage modulus (G') crosses over and exceeds the loss (G") modulus around the 20 Hz point.

The mechanical spectrum is much weaker than previously reported values. Cui *et al.*, (1994) reported typical "weak gel" properties of 2% (w/w) cv. Norman dispersions where the storage modulus exceeded the loss modulus over the entire frequency range. Evidently, concentration of the flaxseed gum using the Alpha-Laval concentrator affected the polymer's ability to form a network. It was possible that heating to 60°C cleaved some of the high molecular sized, branched neutral fraction. It is this fraction which is thought to be responsible for the typical viscoelastic behaviour of the gum (Cui *et al.*, 1994ab). Fedeniuk and Biliaderis (1994) however, reported lower values for the cv. Linott under extraction conditions of 80°C where the loss modulus exceeded the storage modulus over the entire frequency range. Xanthan gum (Figure 3.04A) exhibited behaviour typical of a weak gel, with G' exceeding G" over the frequency range investigated. Both moduli were relatively independent of frequency which is in agreement with Morris (1990). Guar gum (Figure 3.04B) exhibited typical viscoelastic behaviour as is evident by G" exceeding G' at low frequencies but crossing over at higher frequencies. The mechanical spectra of 2% (w/v) Linola™ and cv. Norman flaxseed gum, therefore, resemble that of guar gum. This is in agreement of findings from Mazza and Biliaderis (1989) and Fedeniuk and Biliaderis (1994).

Protein content of flaxseed gum was between 10.3 to 10.6% on a dry weight basis. These values are consistent with 9 to 13% protein levels reported for flaxseed gum cultivars by Mazza and Biliaderis, (1989), Fedeniuk and Biliaderis (1994), Cui *et al.*, (1994). A certain amount of protein contamination in flaxseed gum can be viewed as favourable. Since proteins are primarily responsible for surface active properties, flaxseed gum has the added possibility as acting as an emulsifier in a food system (Dickinson, 1988). Dev and Quensel (1989) reported that high mucilage protein concentrates performed as excellent emulsifying/stabilising ingredients compared to their low mucilage counterparts. The ash contents for both flaxseed

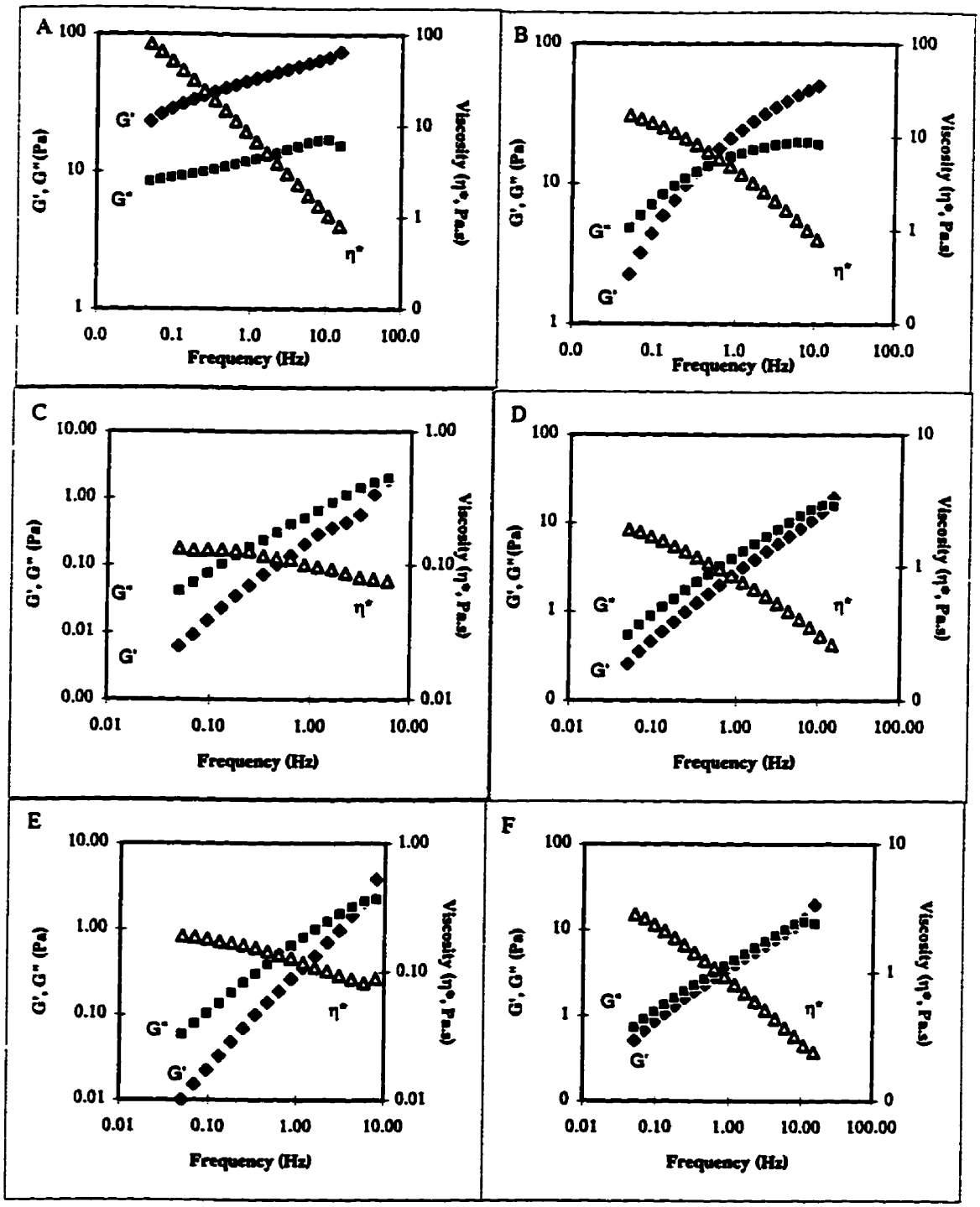


Figure 3.04. Frequency dependence of storage (G') and loss (G") moduli and complex viscosity (η*) of commercial food gums and flaxseed gums (pH 6.5; 25°C).

A) 1% (w/v) xanthan gum
B) 1% (w/v) guar gum
C) 1% (w/v) Linola flaxseed gum
D) 2% (w/v) Linola flaxseed gum
E) 1% (w/v) Norman flaxseed gum
F) 2% (w/v) Norman flaxseed gum

gums are comparable to those reported for flaxseed cv. Linott (6.3%) extracted at 80 °C using an ethanol precipitation (Fedeniuk and Biliaderis, 1994). Compared to commercial guar gum, flaxseed mucilage extracts contained more ash. The commercial xanthan gum contained considerably higher amounts of ash than the flaxseed gums. Oil contamination from the flaxseeds' endosperm were low (ca. < 0.5% on a dry basis). These values were comparable to the results obtained from cv. Linott (0.4%) by Mazza and Biliaderis (1989) and cv. Norman (0.9%) by Bhatty and Cherdkiatgumchai (1990).

3.5. Conclusions

On the basis of the chemical analysis, results reveal that flaxseed gum, obtained by an aqueous extraction process, followed by concentration, precipitation with ethanol and drying, produces good yields (ca. 5 %) of carbohydrate rich (ca. > 80%) material. Previously reported work (Mazza and Biliaderis, 1989; Cui *et al.*, 1994ab; Fedeniuk and Biliaderis, 1994) indicates that flaxseed gum exhibits pronounced shear thinning and weak gel properties observed at concentrations greater than 2%. The data from this study supports data of pronounced shear thinning but weak gel properties at this concentration were mot observed. Apparently, some sort of polymer cleavage occurred during the concentration step to weaken the "weak gel" properties. Flaxseed cv. Norman and Linola™ gums displayed similar shear thinning and dynamic profiles at 1% and 2% (w/v) concentrations. The difference observed in apparent viscosity is generally attributed to differences in the structural and molecular size of each polymer since these intrinsic parameters are the determining factors for the polysaccharide's hydrodynamic volume. The higher the hydrodynamic volume, the more viscous is the aqueous solution.

Due to the simple extraction procedure and the gum's favourable physico-chemical characteristics, flaxseed gum makes a feasible alternative to traditionally used gums. The next stage, therefore, in assessing flaxseed gum as a potential food gum, was to evaluate the gum in typical hydrocolloid environments: specifically, in the sector of the food industry focussing on bakery products and salad dressings.

4. EFFECT OF FLAXSEED GUM ON MUFFIN QUALITY

4.1. Introduction

Flaxseed (*Linum usitatissimum* L.) has been reported to have potential as a food gum (BeMiller, 1973; Mazza and Biliaderis, 1989). Garden-Robinson (1994) found that adding 1% flaxseed gum to bread mixes significantly improved volume, grain and texture. Texture is important in the acceptance and repeat purchase of food items. It is directly associated with the formulation, processing and storage of bakery products. A thorough understanding of the physical and chemical properties of hydrocolloids and their possible interactions with formula components is required when considering new formulations.

Fat, sugar, egg and flour are the principal raw materials used in cake formulations. Shortening performs three basic functions: it entraps air during creaming to aid in aeration, it coats the protein and starch particles thereby tenderizing the crumb, and it emulsifies large amounts of liquid (Pyler, 1988). Sugar increases the temperature at which starch gelatinizes as well as affecting batter viscosity (Hoseney, 1994). Eggs in a cake formulation contribute to binding, leavening, tenderizing, flavour and colour (Pyler, 1988). The function of leavening agents is to evolve carbon dioxide thus aerating the batter to produce a light and porous end product (Hoseney, 1994). Hydrocolloids are used in cake batters as a viscosity stabilizer and moisture absorbent. Average use levels are between 0.25% to 0.4% flour weight basis (fwb) and usually the liquid in the batter must be increased (Pyler, 1988).

Generally, batters can be considered an oil in water emulsion. In the initial batter stage, oil is mixed in an aqueous phase containing air, dissolved sugar, eggs and suspended flour particles (Krog *et al.*, 1985). During baking, the batter is converted to an expanded, porous foam. This

spongelike structure provides the cake's characteristic softness and mouthfeel. It is generally believed that hydrocolloids improve cake volume and texture by increasing the minimum batter viscosity required to retain expanded air nuclei and to resist starch settlement (Hoseney, 1984; Shelke *et al.*, 1990). Still, the baking mechanism of products containing hydrocolloids is not fully understood (Gan *et al.*, 1995).

Batter volume increases due to thermal expansion of bubbles on account of the increased vapour pressure of water and air in the bubble (Mizukoshi *et al.*, 1980). The surface elastical properties of the membrane that surrounds the air cell at this point is critical. It is believed that the increased viscosity of the batter due to the addition of high molecular weight polysaccharides, strengthens the boundaries of the expanding air cells and stabilises the foam during thermal expansion (Dziezak, 1991; Hoseney, 1984). This allows the batter to encapsulate the evolved gas and retain it in the cell because of a slower diffusion rate. A recent theory suggests that the polysaccharides form a liquid film on the inside of the air pocket. This film allows the foam structure to expand to a larger extent before rupturing and ending cake expansion (Gan *et al.*, 1995). The cake structure does not collapse as the air cells rupture on account of starch gelatinization which strengthens the foam structure (Mizukoshi *et al.*, 1980).

The objectives of this study were:

1. to investigate the effects of flaxseed gum on the sensory and physico-chemical characteristics of plain muffins.
2. to study the effect of aging on the quality of muffins stored for one week at room temperature.
3. to compare these effects with muffins containing commercially available gums normally used in bakery products.
4. to provide insight on the hydrocolloid effect via electron microscopic techniques.

4.2. Materials

Flaxseed gum was extracted from seed Linola™947 produced commercially in southern Manitoba, Canada in the 1994 growing season. The method for preparing the gum was described previously (Section 3). Xanthan gum and guar gum were obtained from Kelco (San Diego, CA) and Indian Gum Industries (Prescott Canada Distributors, ON). Bakery ingredients were purchased from a local supermarket. Ovalbumin was provided by Dr. S. Arntfield (University of Manitoba, Winnipeg, MB). All chemicals used were reagent grade unless otherwise specified.

4.3. Methods

4.3.1. Preparation of Muffins

A standard plain muffin formulation with a modification in the amount of more liquid being required for the formulation containing the hydrocolloid was adopted from Onwulata *et al.* (1995). The basic control mix had the following composition: flour (Rogers, all-purpose), 240g; white sugar (Rogers, granulated), 50g; milk (Lucerne, fluid, 2%), 250g; whole egg (Lucerne, fresh), 51g; vegetable oil (Becel), 50g; baking powder (Magic Baking Powder, single acting, anhydrous monocalcium phosphate), 10g; and salt (Windsor), 5g. The dry and liquid ingredients were mixed lightly by hand (ca. 15 stirs), eleven (55 ● 0.3 grams) muffins were placed in standard sized, 12 count aluminum tins and baked for 25 minutes at 204 °C (400 °F) which coincided with the muffin's light brown appearance. After cooling for 5 minutes, the muffins were removed from the tins and cooled 30 minutes on a wire rack. The cooled muffins were weighed, sealed in polyethylene bags and stored at -30 °C. Before testing, muffins were thawed for 4 hours at room temperature in their bags.

4.3.2. Experimental Design

Five formulations were evaluated: flaxseed gum, xanthan gum or guar gum at 0.1% levels (of the total batch weight); 0.5% levels of flaxseed gum, and the above formulation with no gum as the control. Based on product information, the percentage of gum added for xanthan and guar gum fell between the optimum ranges used in commercial bakery products (0.1%-0.3% fwb, 0.15%-0.5% fwb, respectively). The levels of flaxseed gum were selected based on the quality of muffins obtained during preliminary testing. Volume displacement was taken as the primary indicator of baking performance in preliminary experiments (Table 4.01).

Two treatments were baked in the conventional oven at one time. Each treatment was baked an equal number of times on the left-hand side in the oven as they were on the right-hand side. Each treatment was baked with the other treatments eight times (Appendix B1).

Table 4.01. Preliminary mean values for the effect of concentration of flaxseed gum on muffin quality.

Treatment	Volume[1] (cm^3)	Weight[1] (g)	Height[1] (mm)
5.0%	70.07^{c}	46.73^{a}	35.89^{c}
1.0%	90.51^{b}	45.90^{ab}	41.15^{ab}
0.5%	96.56^{a}	44.99^{b}	42.26^{a}
0.1%	91.95^{b}	45.82^{ab}	40.77^{b}

$^{a-c}$ means in the same column bearing the same superscript are not significantly different ($p < 0.05$) according to Tukey's Studentized Range test.
[1] mean of 5 muffins per batch x 2 batches.

4.3.3. Evaluation of Muffins

4.3.3.1. Physical Measurements

Muffins were weighed after baking to compute loss of moisture during baking. Volumes were determined by rapeseed displacement (Onwulata *et al.*, 1995). Height of whole muffins was measured in millimetres from the bottom of the muffin to the top of the cap using an electronic Digimatic micrometer (Mitutoyo MFG. Co. Ltd., Japan). Moisture content of two gram samples (duplicate) of ground muffins from each treatment was determined by the modified vacuum oven AACC Method 44-40 (AACC,1983). Water activity measurements were measured using a Rotronic-hygroscop DT (Rotronic Instrument Corp., NY) functioning in the range 50 to 95% humidity. Muffins were stored at room temperature (22 to 25 °C) in polyethylene bags during the seven day storage period.

Force compression curves were obtained using an Instron Universal Testing Machine (Model 4201) equipped with a 5 N compression load cell. Using a modification of the method described by Sych *et al.*, (1987), all samples were compressed twice in sequence to an approximate muffin depth of 60% with a 0.6 cm diameter anvil. The Instron was operated at a crosshead speed of 5 cm/min using a chart speed of 20 cm/min. Force compression curves were analysed for hardness, springiness, cohesiveness and chewiness as described by Bourne (1978). For cohesiveness, the areas, A1 and A2 (Figure 4.01) were digitially scanned in as a series of x, y points using a digitizing pad (Grid Master, Numonics, NJ). The force compression curves were approximated as a series of rectangles and triangles with the areas calculated using the standard geometrical formula of area equalling length times width.

Four measurements were taken per muffin and averaged (centre compression plus three compressions at 120 rotation around the centre). Sample size was approximately 3 cm in depth

(top removed), placed cut face down on an aluminum block with a Teflon coating. Muffins were first weighed then volumes were measured for each muffin (by rapeseed displacement, sample placed face down to prevent seeds from lodging in the cells) after cutting off the top but before placing them in the Instron. Five muffins per batch were tested on days 0, 1, 2 and 4. Three separate batches per treatment per day were sampled.

4.3.3.2. Sensory Evaluation

The sensory characteristics of the muffins were evaluated by a trained panel of 12 graduate students and staff (7 male; 5 female). Training consisted of two orientation sessions to define the attributes to be evaluated and to familiarize the panelists with the testing procedures. By panelist consensus during the training sessions, seven quality characteristics were defined. These attributes were exterior muffin top colour, extent of browning, surface roughness of muffin tops, degree of tunnelling, sponginess, chewiness and gumminess (Appendix B2). A 15 cm unstructured line scale anchored with one reference sample (control muffin at day 0) and two end points was used for each characteristic (Poste *et al.*, 1991). The positioning of the reference sample on the line scale was determined during the panel training by taking the mean of the panelists score. Panelists evaluated samples in individual booths under fluorescent light. Five samples plus a reference sample were presented in plastic wrap in random order. The sample size used was one half muffin cut vertically. Samples were coded with three digit random numbers and were presented to the panelists in a randomized block order. Panelists evaluated day 0 muffins (stored in the freezer and allowed to thaw for 4 hours). Panelists repeated their evaluations in the afternoon. Panelists evaluated one day old muffins on the following day (am and pm testing). Distilled water and unsalted crackers were provided for rinsing and clearing the mouth between samples. Score cards were quantified by measuring the distance the mark

was placed on the 15 cm line scale.

4.3.3.3. Rheological Measurements of the Batter

Rheological measurements on the muffin batters were performed with a controlled strain rheometer (Bohlin VOR; Bohlin Reologi, Edison, NJ). Using a modification of the procedure described by Khatkar *et al.* (1995), batter samples were placed on parallel plates (25 mm radii) with a gap separation of 2 mm. All measurements were conducted using a 93.2 g.cm torsion bar. Excess batter was trimmed off and a low viscosity silicon oil was applied to the exposed surfaces to prevent drying. The samples were allowed to rest for 30 minutes to allow stresses induced during sample handling to relax (Khatkar *et al.*, 1995). Batter was heated from 25 °C to 80 °C at a rate of 5 °C/min with the rheological data being collected every 60 seconds. At that point, the experiment was stopped due to the batter showing signs of baking onto the plates corresponding to a dramatic increase in viscosity. A strain sweep was performed on muffin batter at a frequency of 1 Hz to determine the linear viscoelastic region, required to maintain the molecular structure of the sample. Based on the results of the analysis, a maximum strain of 2% and a frequency of 1 Hz was used in the study. Two samples from each duplicate were tested per treatment (n=4).

4.3.3.4. Differential Scanning Calorimetry Measurements

To determine whether there was a flaxseed gum/egg protein interaction during muffin baking, the thermal properties of ovalbumin were studied using a Dupont 990 Thermal Analyzer with a 910 Differential Scanning Calorimeter cell base (Westec Industrial Ltd., Mississauga, ON). Measurements were carried out in hermetically sealed Dupont coated aluminum pans (Numbers

900790.901 and 900796.901). A silicon heat sink compound (Dow Corning Corp., Midland, MN) was used to improve contact between the pans and the thermocouple detector. Using a modification of the method described by Imeson *et al.*, (1977), the protein with and without flaxseed gum was studied in the temperature region of 30 to 120 °C at a scanning rate of 10 °C/min. Protein slurries (10% w/v) were prepared and 8-12 mg were placed in pre-weighed DSC pan. A higher concentration of protein (10% w/v versus 5% w/v) was used compared to the original method in order to display better denaturation peaks. The temperature at which protein denaturation occurred, T_D, was taken at the intersection of the extrapolated lower and higher temperature side of the DSC peak. The temperature at which the protein denaturation initially began, T_i, was taken as the extrapolated onset temperature of the endothermic peak and the enthalpy involved, ΔH_D, was calculated from the peak area. Data presented are means of triplicate measurements.

4.3.3.5. Mold Studies

Mold was removed from spoiled muffins, purified and cultivated on potato dextrose agar (PDA) (Appendix B 3). A small petri plate (diameter 4 cm, depth 1 cm) containing PDA was inoculated with mold spores and incubated for seven days in a 25 °C incubator. On the day of the test, treatments (control and 0.5% flaxseed gum formulated muffins) were baked. Muffins were cooled in the fume hood under UV light for 40 minutes. Latex gloves were worn to prevent contamination. A serrated knife wiped with EndBac 256 (SC Johnson, Ltd., Branford, Ont.) was used to cut the muffins into a 3.5 cm square (1 cm thick) sample size. Samples were taken from approximately the centre of each muffin. Samples were placed in small petri plates and placed on top of a test tube rack inside of a plastic container (30 cm long by 12 cm wide by 14 cm high) modified with a battery operated fan on one end. Along with the opened muffin samples, an

opened petri plate containing the purified mold was placed closest to the fan (Appendix B4). The container was closed and the fan was turned on for 15 minutes. At the end of the inoculation period, the lids were put back on the plates containing the muffins. The samples were wrapped in parafilm to prevent moisture loss and stored at 25 °C.

4.3.3.6. Scanning Electron Microscopy

A modified method described by Freeman *et al.*, (1991) was employed. A 3 mm x 2 mm sample was removed from the middle of a freshly baked muffin and fixed on a stub using a conductive glue (Tissue Tek #172, J. B. EM services, Inc., QC). Using the emitek K-1250 (Emitek, UK) low temp SEM protocol, the samples were rapidly frozen to -210 °C using a liquid nitrogen slush then freeze fractured. Each sample was sublimed for 4 minutes at -95°C then the temperature was reduced to -195 °C. The sample was sputter coated with gold, cryotransferred into the cold stage and examined under low temperature and high vacuum SEM (Jeol JSM-840A, Japan).

4.3.3.7. Statistical Analysis

Data was analyzed using analysis of variance using PROC GLM (SAS Institute, Inc, 1991.) to determine the variance due to treatment and day effects and their interactions. Significant differences between the treatment means were determined using Tukey's Studentized Range Test.

4.4. Results & Discussion

4.4.1. Physical Characteristics

4.4.1.1. Volume

Muffin volumes were influenced by treatment. All muffins containing hydrocolloid gums showed an increase in volume compared to the control (Table 4.02). Guar gum, xanthan gum and 0.5% flaxseed gum showed the greatest volume increases of 6.0%, 6.1% and 6.9%, respectively compared to the control. According to Gan *et al.*, (1995) batter volume is increased due to expansion of bubbles from increased vapour pressure. It is believed that hydrocolloids have a volume enhancing effect on baked products by increasing the viscosity of the batter which stabilizes the liquid film so that it can expand to a larger extent without rupturing the cells and hence, end cake expansion (Gan *et al.*, 1995). At equal concentrations, guar gum had a higher viscosity than flaxseed gum (Figure 3.03, 3.04). It would be expected that muffins

Table 4.02. Effect of gum type and concentration on physical characteristics of muffins.

Treatment	Volume[1] (cm^3)	Height[1] (mm)	Weight[1] (g)
control	92.49^{c}	40.1^{b}	45.26^{a}
0.5% flaxseed gum	98.53^{a}	42.8^{a}	45.11^{a}
0.1% flaxseed gum	94.17^{b}	40.7^{b}	45.25^{a}
0.1% xanthan gum	98.15^{a}	41.7^{ab}	45.27^{a}
0.1% guar gum	98.04^{a}	39.8^{b}	45.25^{a}

$^{a-c}$ values in the same column bearing the same superscript are not significantly different ($p<0.05$) according to Tukey's Studentized Range test.
[1] mean of 5 muffins per batch x 4 batches.

containing guar gum would produce muffins of larger volume compared to muffins containing equal concentrations of flaxseed gum if batter viscosity was a factor involved in the volume improving effect. The optimal concentration for commercial gums with regard to baking performance was not equal to the optimal levels for flaxseed gum. For this particular application, five times more flaxseed gum was required to produce muffins with similar volumes to that of the commercial gums.

4.4.1.2. Muffin Height and Weight

The formulation containing 0.5% flaxseed gum registered the highest muffin height at 42.8 mm (Table 4.02). It is possible that muffin tunnelling due to over mixing of the batter may have caused the increased height in this treatment. The sensory panel, however, found only slight variation in the amount of tunnelling between treatments. The muffins containing 0.5% flaxseed gum were significantly higher than the control (40.1 mm) and muffins containing 0.1% flaxseed (40.7 mm) or guar gum (39.8 mm). No explanation for the difference, however is apparent. No significant differences were observed in heights of muffins baked with the 0.1% gums and the control. All muffins imparted similar post bake weights having lost approximately 10% moisture from baking regardless of treatment (Table 4.02).

4.4.1.3. Muffin Water Activity and Moisture Content

A decrease in water activity was observed for all treatments over the seven day period (Table 4.03). However, the change was minimal. This was likely due to the storage environment. Cakes tend to equilibrate to the relative humidity of the storage environment and moisture proof packaging can retard staling significantly (Kulp *et al.*, 1959). Our results are comparable

Table 4.03. Effect of gum type and concentration on water activity of muffins stored over a seven day period at room temperature .

Treatment	Water activity measured over time* (h)				
	4	24	48	96	168
control	.955 ± .002[a]	.954 ± .002[a]	.952 ± .001[a]	.947 ± .009[a]	.948 ± .005[a]
0.5% flaxseed gum	.956 ± .001[a]	.954 ± .003[a]	.954 ± .002[a]	.945 ± .008[a]	.950 ± .001[a]
0.1% flaxseed gum	.956 ± .001[a]	.955 ± .003[a]	.951 ± .001[a]	.950 ± .011[a]	.951 ± .001[a]
0.1% xanthan gum	.957 ± .004[a]	.952 ± .003[a]	.951 ± .002[a]	.953 ± .008[a]	.953 ± .002[a]
0.1% guar gum	.954 ± .004[a]	.951 ± .002[a]	.953 ± .001[a]	.950 ± .005[a]	.951 ± .001[a]

*Time after removal from freezer
[a] means ± SD in the same column followed by the same letter are not significantly different ($p<0.05$) according to Tukey's Studentized Range test.
[1] average of 2 muffins per 3 batches

Table 4.04. Effect of gum type and concentration on moisture content of muffin stored over a seven day period at room temperature.

Treatment	Treatment Moisture Content (%) over time* (h)				
	4	24	48	96	168
control	34.5 ± 1.5[a]	35.1 ± 0.4[a]	33.9 ± 1.0[a]	33.5 ± 1.5[a]	31.7 ± 1.7[a]
0.5% flaxseed gum	35.4 ± 0.5[a]	33.6 ± 0.6[b]	33.8 ± 0.4[a]	33.1 ± 1.3[a]	32.3 ± 1.4[a]
0.1% flaxseed gum	34.4 ± 0.3[a]	34.3 ± 0.2[ab]	33.2 ± 1.1[a]	33.0 ± 1.3[a]	31.5 ± 1.7[a]
0.1% xanthan gum	34.3 ± 1.5[a]	35.3 ± 0.6[a]	33.6 ± 1.0[a]	33.7 ± 0.2[a]	32.7 ± 1.3[a]
0.1% guar gum	34.6 ± 0.1[a]	33.8 ± 0.8[ab]	33.9 ± 0.9[a]	32.7 ± 1.6[a]	31.2 ± 1.1[a]

*Time after removal from freezer
[a-b] means ± SD in the same column followed by the same letter are not significantly different ($p<0.05$) according to Tukey's Studentized Range test.
[1] average of 2 muffins per 3 batches.

to those of Sych *et al.* (1987) who reported very slight variation in water activity of layer cakes during a 42 day period. Moisture content and water activity values of muffins stored at room temperature for a seven day period revealed that neither gum type nor concentration of the gum in the batter significantly affected shelf life of the muffins (Table 4.03, 4.04). No significant improvement in shelf life of muffins containing hydrocolloids was observed. Even though gums are able to bind water and in theory, extend shelf life of bakery products, the staling characteristics of the muffins containing gums were similar to those of the control muffins. This is in agreement with Hippleheuser *et al.*, (1995) who reported no improvement in shelf life for baked goods containing xanthan gum. Under similar conditions as this experiment, Garden-Robinson (1994) reported significant improvement in reducing the staling of bread when flaxseed gum was used at 1% (flour weight basis). Evidently, the apparent improvement in the antistaling characteristics may not be dependent on gum selection and the other formulation variables may play a more important role.

4.4.1.4. Texture

A typical force compression curve obtained for the muffins is shown in Figure 4.01. Bottom crust hardness was defined as the peak force during which the plunger broke through the crust during the first compression. Crumb hardness was defined as the second peak force at maximum compression during the first compression. Springiness was the time elapsed from the end of the first bite to the start of the second bite (distance between b to c). Cohesiveness was defined as the ratio of the force area during the second compression to that during the first compression (A_2/A_1) (Bourne 1978). Chewiness was the product of hardness times springiness times cohesiveness. Adhesiveness was not analyzed even though it was visible (A_3). Adhesiveness represents the work necessary to pull the compressing plunger away from the

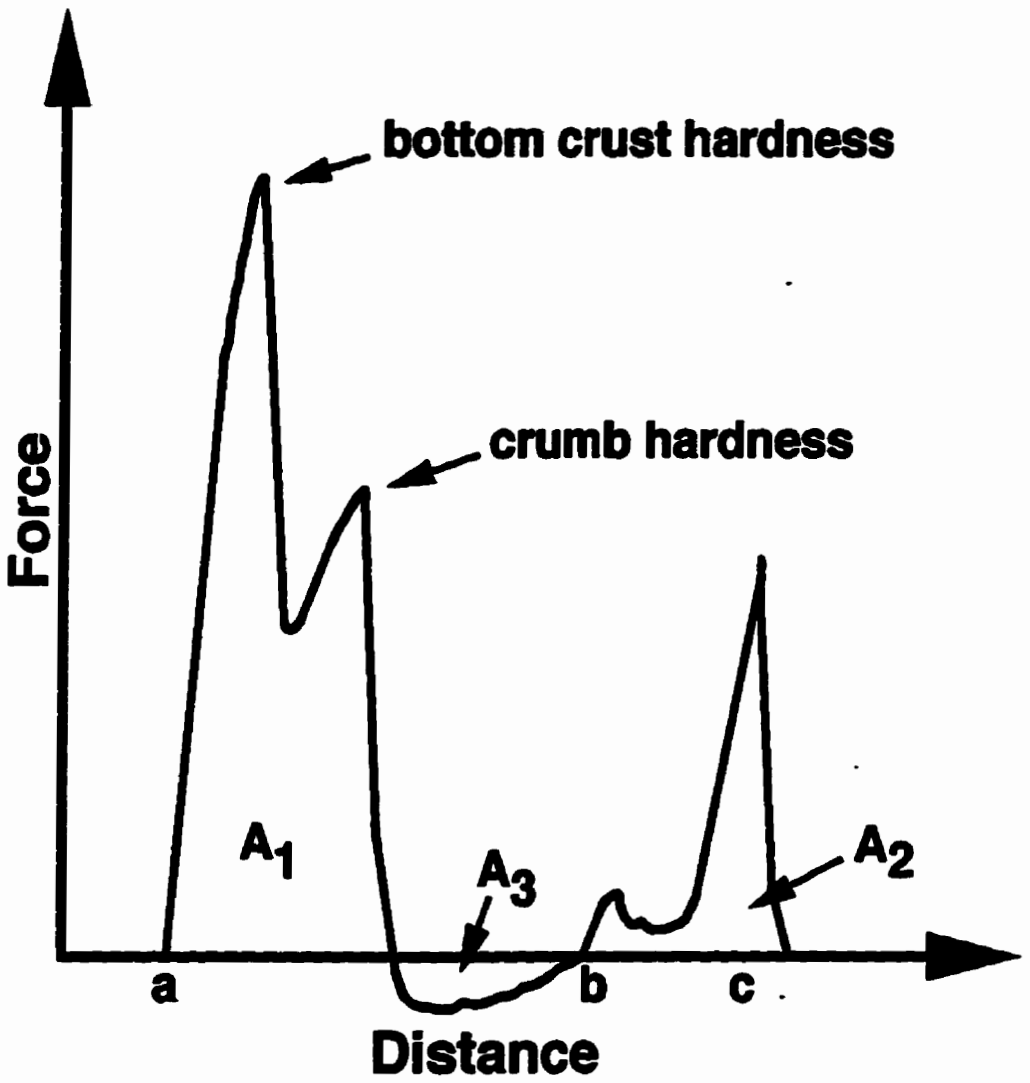


Figure 4.01. Typical force compression profile of control muffin (day one).

sample (Bourne, 1978). The plunger was not always easily removed from the muffins. On occasion the muffin had to be held down when the plunger was on the upswing thereby making the area under the curve not reliable.

The analysis of variance for the Instron textural parameters is presented in Tables 4.05. All attributes recorded significant day effects at the 1% level. The linear trend of storage time was significant at the 1% level for crumb hardness, bottom crust hardness and springiness. This aging trend is in agreement with results found for layer cakes (Sych *et al.*, 1987). Cohesiveness of the muffins tended to decrease in both linear and quadratic terms. Sych and coworkers (1987) observed significant linear and quadratic terms for cake cohesiveness. Treatment x day interactions were insignificant at the 5% level for the textural attributes: bottom crust and crumb hardness, springiness and cohesiveness but were significant for the attribute, chewiness (Table 4.05).

The xanthan gum formulation consistently ranked the highest in each of the textural attributes (Table 4.06 and 4.07). The 0.5% flaxseed gum formulation recorded the lowest bottom crust hardness (0.275 kg) and a low crumb hardness of 0.205 kg (Table 4.06). The most likely reason would be due to the high volume to muffin weight for this formulation thereby less force would be required for compression. Xanthan muffins required the greatest amount of force for compression (0.297 kg for bottom crust and 0.233 kg for crumb hardness) ;even though, it was assumed that this formulation would produce similar results to the 0.5% flaxseed formulation having registered similar volumes. Evidently, the polysaccharide is providing added strength to the muffin wall. Xanthan gum when added to wheat starch can produce a bread like structure without the aid of gluten due to the gum is able to support the foam wall structure to produce loaves with good volume and crumb structure (Christianson *et al.*, 1974). It has been shown that xanthan gum can effectively increase the peak time and dough stability of soft

Table 4.05. Mean square values for analysis of variance of muffin instrumental textural attributes

Source of variation	df	bottom crust hardness	crumb hardness	springiness	cohesiveness	chewiness
treatment	4	.0007*	.0018**	.0446	.0007*	.0458
batch(trt)	10	.0002	.0003**	.3920**	.0002	.0183*
day	3	.0030**	.0207**	1.750**	.0136**	.2401**
trt*day	12	.0004	.0001	.1163	.0003	.0220**
error	30	.0003	.0001	.0999	.0001	.0075
Aging Profile:						
day linear	1	.0078**	.0082**	4.900**	.0337**	.4153**
day quadratic	1	.0013*	.0008	.2422	.0062**	.2895**
day cubic	1	.0000	.0000	.1078	.0008*	.1539

*, ** Denotes a significant difference at $p<0.05$ and $p<0.01$ respectively

Table 4.06. Mean values for main effect of gum type on Instron attributes: bottom crust hardness, crumb hardness, springiness and cohesiveness of muffins[1] stored at room temperature for 0, 1, 2 and 4 days.

Attribute	Treatment[1]				
	control	0.5% flaxseed	0.1% flaxseed	0.1% xanthan	0.1% guar
bottom crust hardness (kg)	0.284^{ab}	0.275^{b}	0.283^{ab}	0.297^{a}	0.287^{ab}
crumb hardness (kg)	0.206^{c}	$.205^{c}$	$.217^{b}$	$.233^{a}$	$.207^{bc}$
springiness (mm)	15.66^{a}	15.82^{a}	15.77^{a}	15.72^{a}	15.73^{a}
cohesiveness	0.254^{b}	0.263^{ab}	0.263^{ab}	0.277^{a}	0.266^{ab}

[a-c] values in the same row with the same superscript are not significantly different ($p<0.05$) according to Tukey's Studentized Range test.
[1]average of 3 batches x 4 days.

wheat flour via interaction with the gluten protein (Huebner and Wall, 1979). That is, hydrogen bonding between the carboxyl groups on the xanthan polymer and the amide as well as other groups on the gluten protein can enhance soft wheat flour performance to approximate strong wheat flours.

Guar gum and both flaxseed treatments recorded textural profiles similar to that of the control for textural characteristics bottom crust hardness and crumb hardness (Table 4.06). No significant treatment effect for springiness and chewiness which is dependent on springiness, was observed for the treatments (Table 4.05). Crumb springiness can be described as the rate at which a deformed material goes back to its original condition after the deforming force is removed (Szczesniak, 1963). It is positively correlated with moisture content in cakes (Sych *et al.*, 1987). Therefore, it was expected that all treatments would have similar springiness values since the muffins had similar moisture content (Table 4.04). There was a significant day x treatment interaction for chewiness (Table 4.05). Table 4.07 shows the change in chewiness over the four day period for each treatment. No obvious explanation is apparent for the differences in time and treatment. Chewiness is dependent on hardness, cohesiveness and springiness. Xanthan gum formulated muffins registered minimal chewiness loss having kept their chewiness throughout the four day period (Table 4.07). There was a significant treatment effect for cohesiveness (Table 4.05). As discussed by Szczesniak (1963), the mechanical parameter cohesiveness represents the strength of the internal bonds which make up the food product. Xanthan gum containing muffins recorded the largest cohesiveness value (0.277) and the control registered the lowest (0.254) indicating that the xanthan gum formulation had a stronger internal bond structure than the control; even though the xanthan gum formulation had a lower density compared to the control. This suggests that the xanthan gum in the muffin formulation is somehow strengthening the cell wall of the air vacuole which is consistent with the bottom crust and crumb hardness results. Instrumental results show that the addition of

0.5% flaxseed gum yielded muffins of approximately equal textural quality to that of the control. Xanthan gum formulated muffins resulted in muffins of poorer texture than the control since softer, less cohesive muffins are considered to be of higher quality.

Table 4.07. Effect of gum treatment and storage time on muffin chewiness as determined by an Instron Universal Testing Machine.

Treatment	Chewiness (kg.mm)			
	Day 0	Day 1	Day 2	Day 4
Control	1.201[a]	1.243[a]	1.061[a]	1.007[bc]
0.5% flaxseed gum	1.420[a]	1.081[a]	1.120[a]	0.981[c]
0.1% flaxseed gum	1.354[a]	1.121[a]	1.107[a]	1.106[abc]
0.1% xanthan gum	1.423[a]	1.225[a]	1.197[a]	1.304[a]
0.1% guar gum	1.470[a]	1.133[a]	1.027[a]	1.173[abc]

[a-c] values in the same column bearing the same superscript are not significantly different ($p<0.05$) according to Tukey's Studentized Range test.
[1] mean of 4 punches per muffin x 5 muffins per batch x 3 batches.

4.4.2. Sensory Characteristics

Preliminary evaluation on panel performance was conducted and tabulated in Table 4.08. As expected, judges were a significant source of variation as seen by the significant judge effect for all attributes. While judge differences are well accepted in the literature, the judge*trt and judge*rep effects are key to the evaluation of panel performance. A significant judge*trt interaction for sponginess indicates that for this attribute the panel was not consistent. That is, some judges did not agree on the order for ranking sponginess for the treatments. A judge*repeat interaction was found for the attributes: exterior top colour, extent of muffin top browning, muffin top surface roughness, chewiness, and gumminess indicating that the panel

Table 4.08. Preliminary mean square values for analysis of variance for sensory characteristics of muffin

Source of Variation	df	Exterior top colour	extent of browning	surface roughness	tunnels	sponginess	chewiness	gumminess
Trt	4	86.2**	79.9**	23.8**	17.4*	4.1	10.5**	8.1*
Day	1	43.2**	73.0**	12.3*	42.3**	67.3**	10.2*	19.9*
Trt*day	4	47.6**	41.9**	10.6**	15.9**	3.2	9.6**	5.1
Judge	11	18.2**	34.7**	21.4**	17.4**	74.7**	35.7**	59.5**
Judge*trt	44	3.0	3.7	3.8	4.2	6.3**	2.9	4.4
Judge*day	11	7.5**	5.0	2.9	2.9	29.2**	11.1**	8.5**
Judge*trt*day	44	2.8	3.1	2.3	4.5	2.4	1.9	2.7
Rep	1	3.2	8.6	3.0	1.7	0.4	6.8	3.5
Judge*rep	11	15.2**	11.8**	6.0*	7.6	4.7	5.2**	8.3**
Trt*rep	4	7.1	9.1	3.8	5.7	0.8	3.4	1.3
Day*rep	1	1.1	2.8	0.3	21.7*	1.2	16.7**	8.3
Trt*day*rep	4	3.2	9.6	4.8	7.7	1.1	1.6	4.7
Error	99	3.0	4.3	2.8	5.2	2.7	2.1	3.1

*, ** Denotes a significant difference at $p<0.05$ and $p<0.01$ respectively

results were not reproducible from am to pm testing.

Because of these performance problems, principle component analysis for all judges and samples was performed to screen for potential judge 'outliers' (Figure 4.02 and 4.03). On the basis of these results, panelists 2, 11 and 12 were removed from further analysis. In addition, preliminary analysis revealed significant treatment x day interactions for exterior colour, extent of browning, surface roughness, tunnelling and chewiness; that is, the judges scored the treatments differently on the two days. On the basis that one would not expect any day to day differences for the attributes exterior top colour, extent of browning, muffin top surface roughness and tunnelling, panelists were found to be inconsistent when rating the muffins from day to day. This made comparison between day zero and day one muffins very difficult. Therefore a new analysis of variance for the nine panelists was conducted, these models were simplified by eliminating all non-significant ($p>0.05$) interactions for the fresh and day old muffins (Table 4.09 and 4.10, respectively).

For fresh muffins, main effects and interactions on muffin quality are presented in Table 4.09. Exterior top colour, extent of browning, muffin top surface roughness, tunnelling, sponginess, chewiness and gumminess were all significant for hydrocolloid treatment (Table 4.09). The two colour attributes showed some inconsistency with the panel having a significant judge*trt and judge*rep interaction for exterior top colour and a significant judge*rep interaction for extent of browning. However, despite these inconsistencies as shown by a significant mean square value, the inconsistencies were relatively small compared to the magnitude of the main effect. When recalculating a new F value using judge*trt as the error term, main effects are still significant. All attributes except exterior muffin top colour and gumminess for fresh muffins and chewiness for one day old muffins displayed no significant judge*trt interaction; hence panelists were in agreement with the ratings.

Xanthan gum formulations were visually distinct from the other muffin formulations (Table 4.11). They rated the highest for exterior colour (9.3), extent of browning (7.3) and surface roughness (5.1). The increased browning may be due to the increased presence of glucose units from the addition of xanthan gum, a β 1,4 linked glucose polymer carrying a trisaccharide side chain on alternating glucose units (Anderson and Andon, 1988). Due to non-enzymatic browning, the high glucose content may explain the darkening effect in the xanthan gum formulated muffins (Potter, 1986).

The panel distinguished a significantly greater degree of tunnelling (6.0) for the control muffins than for the 0.1% xanthan gum treatment (Table 4.11). Since hydrocolloids increase batter viscosity (Glicksman, 1982), it is speculated that the viscosity of the control treatment was lower than the other treatment. Lower batter viscosity (thin) would accelerate the rate of bubble rise and enhance migration of the gas cells (Handleman *et al.*, 1961). Increased migration of the air bubbles would amplify the possibility of having the bubbles collide with a sufficient amount of force to cause coalescence (Pomeranz, 1988). Eventually, this would lead to an increased bubble size which would correspond to an increase in percieved tunnelling.

In contrast, the 0.5% flaxseed gum formulations were not significantly different compared to the control in all attributes (Table 4.11). Perceived differences in chewiness among the formulations were consistent with observed differences in instrumental evaluations (Table 4.06). Xanthan gum and guar gum formulations were significantly chewier than the control (5.5) having scored 7.1 and 7.0, respectively. In contrast, both flaxseed gum treatments had similar chewiness to that of the control (Table 4.11).

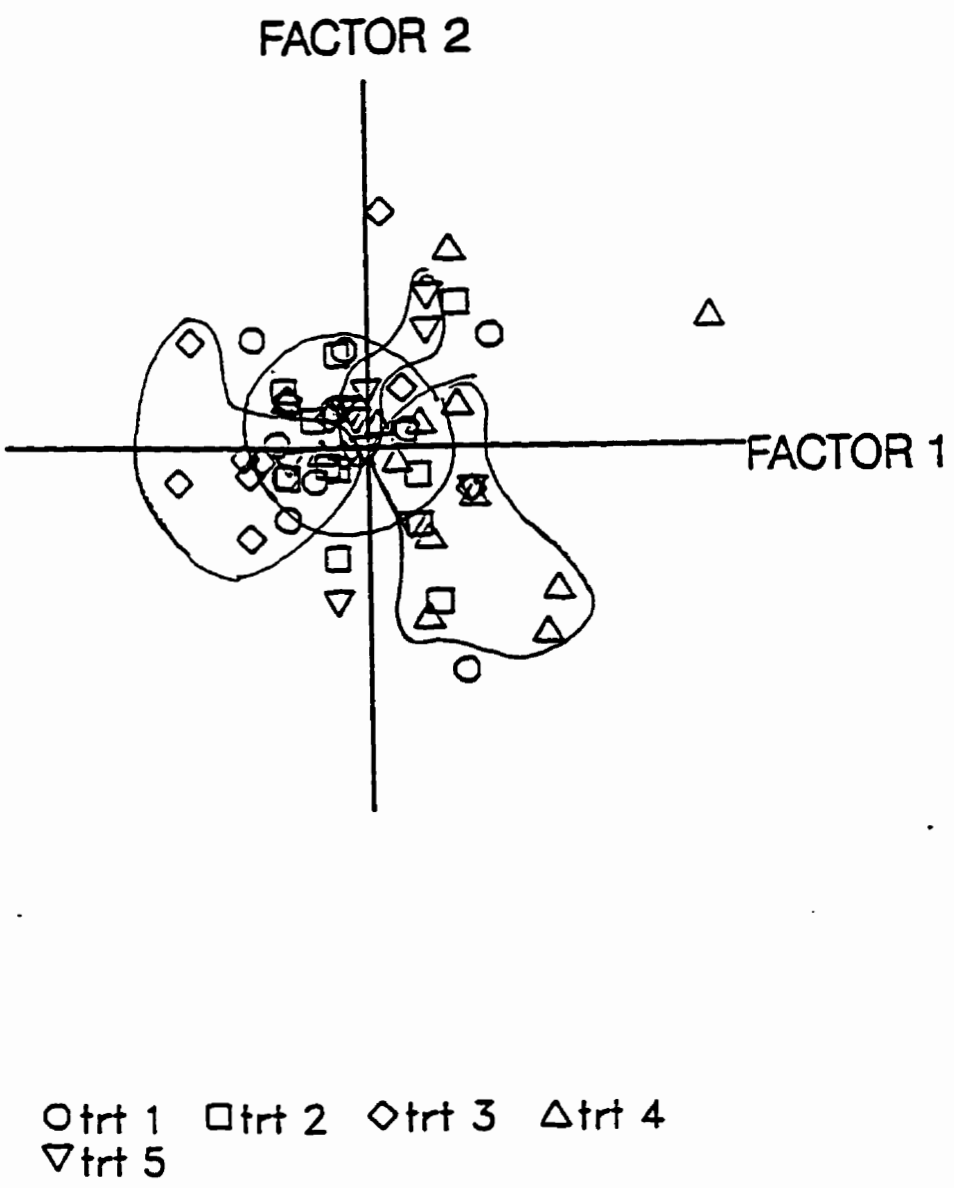


Figure 4.02. Principal component analysis by treatment

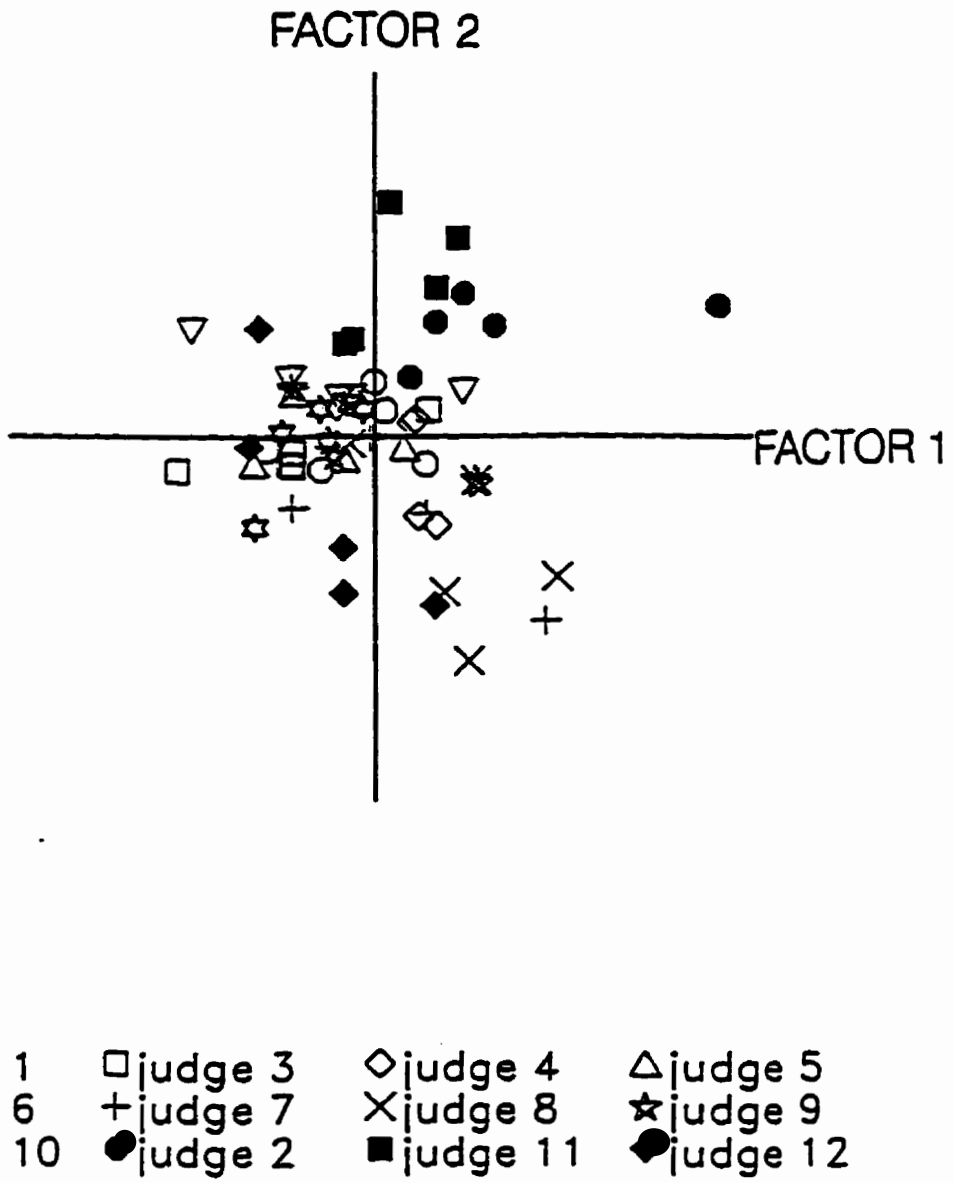


Figure 4.03. Principal component analysis by judge

Table 4.09. Mean square values for analysis of variance for sensory muffin characteristics ('fresh')

Source of Variation	df	exterior top colour	extent of browning	surface roughness	tunnelling	sponginess	chewiness	gumminess
Trt	4	66.2**	54.6**	21.0**	14.2*	11.0*	10.3**	6.9
Judge	8	22.9**	28.9**	14.8**	6.1	7.3*	4.0*	9.4**
Judge*trt	32	3.7*	3.9	2.1	5.2	3.8	2.4	4.9*
Repeat	1	15.5**	4.5	2.9	3.1	1.9	3.3	0.3
Judge*rep	8	10.6**	9.5**	8.5*	13.5*	6.3	1.9	3.4
Error	36	2.0	3.0	3.2	5.0	3.2	1.4	3.1

*, ** Denotes a significant difference at $p<0.05$ and $p<0.01$ respectively

Table 4.10. Mean square values of analysis of variance for sensory muffin characteristics (day old)

Source of Variation	df	exterior top colour	extent of browning	surface roughness	tunnelling	sponginess	chewiness	gumminess
Trt	4	31.5**	24.1**	2.4	5.9	2.4	4.2	0.4
Judge	8	8.5*	10.0**	13.5**	3.8	68.5**	14.4**	32.7**
Judge*trt	32	1.7	2.7	2.2	1.7	1.6	1.8**	2.3
Repeat	1	1.3	16.1*	3.0	12.3*	0.2	14.2	0.7
Judge*rep	8	9.1*	9.4**	4.1	6.7*	0.8	8.2**	7.2**
Error	36	3.0	2.9	2.4	2..7	2.2	1.7	1.4

*, ** Denotes a significant difference at $p<0.05$ and $p<0.01$ respectively

Gumminess was not significant for treatment at the 5% level (Table 4.09). The narrow range in scores between treatments for this attributes for fresh muffins suggests that the samples may not have been noticeably different for this attribute. There was a significant difference ($p < 0.05$) in sponginess between treatments. Formulations containing 0.5% flaxseed gum was significantly more spongy (5.5) than the formulation containing 0.1% flaxseed gum (Table 4.11). This may be related to the change in volume. It is speculated that adding 0.5% flaxseed gum to the muffin formulation decreased the density of the muffin, thereby reducing the force needed for compression. Even though there was a force difference detected by instrumental means (Table 4.06), panelists could not distinguish the difference in sponginess between xanthan and 0.5% flaxseed gum muffins.

With day old muffins, there were no significant treatments effects for muffin top surface roughness, tunnelling, sponginess, chewiness or gumminess (Table 4.10). It appears that panelists had difficulty evaluating the treatments on the second day of testing having been able to distinguish fresh treatments with relative ease. It is possible that the staling effect on the one day old muffins may have accounted for the panelists' inability to distinguish between samples since this factor was not evaluated separately.

In summary, xanthan gum containing muffins were rated consistently higher in exterior colour, extent of browning, muffin top surface roughness, sponginess, chewiness and gumminess but had the lowest tunnelling. In contrast, those muffins containing flaxseed or guar gum rated intermediate values for the muffin attributes. The control muffins that contained no hydrocolloid in the formulation, were perceived to have the lowest chewiness and gumminess as well as a high amount of tunnelling.

Table 4.11. Mean scores[1] for main effects of gum type and concentration on sensory characteristics of day 0 muffins stored at room temperature.(n=18; 9 judges x 2 reps)

Characteristic	Treatment				
	Control	0.5% Flaxseed	0.1% Flaxseed	0.1% Xanthan	0.1% Guar
exterior colour	5.6^{b}	6.5^{b}	4.0^{c}	9.3^{a}	6.8^{b}
extent brown.	4.0^{bc}	4.6^{b}	2.4^{c}	7.3^{a}	4.8^{b}
roughness	3.9^{ab}	5.0^{a}	2.4^{b}	5.1^{a}	3.8^{ab}
tunnelling	6.0^{a}	4.6^{ab}	5.3^{ab}	3.6^{b}	4.7^{ab}
sponginess	4.9^{ab}	5.5^{a}	3.5^{b}	5.2^{ab}	5.1^{ab}
chewiness	5.5^{c}	5.9^{bc}	5.7^{c}	7.1^{a}	7.0^{ab}
gumminess	4.6^{a}	5.7^{a}	4.5^{a}	5.9^{a}	5.4^{a}

[1]higher value represents a more intense attribute.
[a-c] values in the same row with the same superscript are not significantly different ($p<0.05$) according to Tukey's Studentized Range Test

Table 4.12. Mean scores[1] for main effects of gum type and concentration on sensory characteristics of day old muffins stored at room temperature. (n = 18; 9 judges x 2 reps)

Characteristic	Treatment				
	Control	0.5% Flaxseed	0.1% Flaxseed	0.1% Xanthan	0.1% Guar
exterior colour	4.2^{b}	4.0^{b}	6.1^{a}	6.4^{a}	6.9^{a}
extent brown.	2.4^{bc}	2.3^{c}	3.9^{ab}	4.4^{a}	4.7^{a}
roughness	3.0^{a}	3.3^{a}	3.2^{a}	3.8^{a}	3.8^{a}
tunnelling	4.2^{a}	4.2^{a}	3.0^{a}	3.7^{a}	4.5^{a}
sponginess	3.5^{a}	4.2^{a}	3.3^{a}	3.3^{a}	3.4^{a}
chewiness	5.7^{a}	5.3^{a}	6.4^{a}	5.4^{a}	6.1^{a}
gumminess	4.8^{a}	4.8^{a}	4.9^{a}	5.0^{a}	5.2^{a}

[1] higher value represents a more intense attribute.
[a-c] values in the same row with the same superscript are not significantly different ($p<0.05$) according to Tukey's Studentized Range Test

4.4.3. Viscosity of the Muffin Batter

The effect of gum type and concentration on apparent viscosity of muffin batter is presented in Figure 4.04. As was expected, the control batter displayed the lowest apparent viscosity (27 Pa.s) at 25 to 80°C. Formulations containing guar gum, xanthan gum and 0.1% flaxseed gum had similar starting viscosities (64.3 Pa.s, 57 Pa.s and 56.2 Pa.s, respectively). All treatments displayed an apparent viscosity decrease as the samples were heated. At the minimum of the apparent viscosity curve, the dough is more fluid which facilitates expansion during baking (Bloksma, 1986). Miller and Hoseney (1993) recorded similar viscosity profiles for cakes formulated with and without 0.5% or 1% (flour weight basis) xanthan gum. Their initial batter viscosity was approximately 2 000 cp or 2 Pa.s. The difference in viscosity would be expected due to formulation differences. The apparent viscosity for the xanthan containing muffin batter and the control batter remained practically constant during heating. When all treatments were compared, the profile for the control and the xanthan gum containing batter appeared flat. At minimum apparent viscosity, a low batter viscosity can easily lose gas as a result of shocks and vibrations which results in a low product volume (Bloksma, 1986). Shelke and coworkers (1990) reported xanthan gum formulated layer cakes maintained a higher batter viscosity compared to those containing guar or carboxymethylcellulose (CMC) at equal concentrations at the minimum point of heated batter viscosity (ca. 70 °C). This is in agreement with the findings of this study. At 70°C, xanthan gum formulated muffin batters maintained a higher viscosity (50.6 Pa.s) than 0.1% guar gum (40.6 Pa.s) or 0.1% flaxseed (35.5 Pa.s) formulated batters. At 75°C, xanthan gum and 0.5% flaxseed gum batters had similar viscosities (46.8 and 58.2, respectively). Treatments containing hydrocolloids had initial batter viscosities that were higher than the control. As well, the hydrocolloid containing batters were able to maintain a higher viscosity compared to the control throughout the heating which is consistent with results reported for layer cakes by Shelke and coworkers (1990) and Miller and Hoseney (1993).

Shelke and coworkers (1990) observed that the primary effect of hydrocolloids is the maintenance of higher minimum viscosities during heating but before starch gelatinization. In this experiment, xanthan gum and 0.5% flaxseed gum containing batters both had the highest minimum viscosities between the 65 to 75° C range. These two treatments also produced muffins with the highest volume (Table 4.02).

Guar gum and flaxseed gum formulated batters showed an initial increase in viscosity as the batter was heated (Figure 4.04). This initial increase was not observed for the 0.1% xanthan gum formulated muffin batter or for the control. Cake batters containing xanthan gum have been reported to have significantly slower rates of initial viscosity increase compared to those containing guar or CMC gum (Shelke *et al.*, 1990). This is to be expected due to xanthan gum's unique ability to maintain viscosity across a wide temperature and pH range (Dziezak, 1994). The apparent viscosity of both guar and flaxseed formulations peaked around 40 - 44°C and then decreased. The initial increase in viscosity for the 0.1% guar gum and 0.1% and 0.5% flaxseed gum containing muffin batters presumably reflects the limited availability of water for full hydration of these gums contained in the batter. Both guar gum and flaxseed gum have lower water binding capacity than xanthan gum (Mazza and Biliaderis, 1989); therefore, they find it difficult to compete with the starch, gluten and sugar components for the water available during the initial mixing. Guar gum and flaxseed gum containing batters drastically decrease in viscosity after ca. 45 °C. Both hydrocolloids are sensitive to temperatures. Flaxseed gum follows the usual Arrhenius type of temperature dependence (Mazza and Biliaderis, 1989). Guar gum's viscosity also decreases with increasing temperature (Glicksman, 1982).

At equal concentrations, guar gum and flaxseed gum initially show similar profiles. The 0.1% guar gum formulation however maintained a higher apparent viscosity after 40 °C compared to the 0.1% flaxseed formulated muffin batters. At this point the viscosity for the 0.1% flaxseed

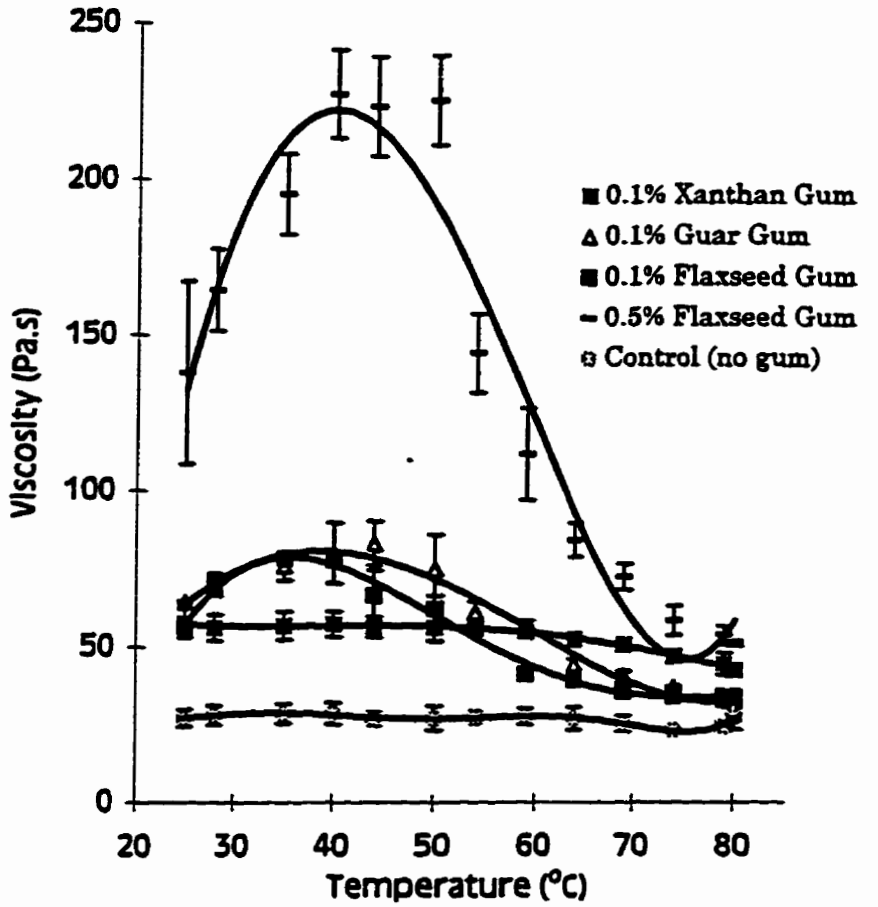


Figure 4.04. Effect of temperature on the apparent viscosity of muffin batter with or without commercial gums and flaxseed gum heated 5°C/min.

gum decreased at a faster rate. This may explain why 0.1% guar gum formulated muffins had a higher volume than muffins prepared with flaxseed gum at equal concentrations. The decreased viscosity may have influenced the rate at which air bubbles migrated to the surface and/or collided with each other before the foam structure sets. The rate of bubble rise on account of its buoyancy is proportional to the square of the bubble radius and is inversely proportional to the viscosity (Handleman *et al.*, 1961). The end result, batters with lower viscosity would contain fewer and larger bubbles which results in smaller muffin volumes. At the peak of highest viscosity, 0.5% flaxseed gum formulations had a viscosity approximately 4 times greater (ca. 230 Pa.s) than the 0.1% flaxseed gum formulation (ca. 75 Pa.s). As the temperature reaches 75 °C, 0.5% flaxseed gum formulated batters are less than twice (58.2 Pa.s) the viscosity of 0.1% flaxseed gum formulated batters (34 Pa.s).

4.4.4. Differential Scanning Calorimetry

Table 4.13 shows the results from the DSC analyses of ovalbumin with and without flaxseed gum in various ionic strengths. The endotherm for ovalbumin resulted in a denaturation temperature between 79.7 °C to 80.6 °C depending on the ionic strength of the solution (Table 4.13). This is in agreement with the denaturation temperature of 84 °C reported by Donovan *et al.*, (1975) and 81 °C reported by Beveridge *et al.*, (1985) for this protein. Variations in the positions of the endothermic peaks were dependent on heating rate with the faster rate corresponding to a higher temperature value (Donovan *et al.*, 1975). Enthalpy of denaturation (ΔH_D) of the egg white protein, ovalbumin, was 3.66 cal/g (Table 4.13). This is consistent with reported values of 3.64 ± 0.15 cal/g (Donovan *et al.*, 1975). The addition of salt stabilized ovalbumin as observed by the increase in enthalpy of denaturation (from 3.66 cal/g to 4.04 and 3.72 cal/g) and the increase in temperature of denaturation (79.68 to 80.6 °C). Addition of salt

has been shown to increase heat stability of individual proteins in whole egg (Woodward and Cotterill, 1983). Salt increases the ionic strength of the liquid surrounding the proteins and stabilizes them against denaturation. Anions stabilized egg white proteins to heat with nitrates, chlorides and sulfates being capable of protecting against heat damage (Nakamura *et al.*, 1979). The greater the heat sensitivity of the protein, the better protection given by the salts.

Addition of 1% flaxseed gum had little effect on the heat stability of ovalbumin in terms of denaturation temperature or enthalpy of denaturation at an ionic strength of 0.025 (Table 4.13). As the ionic strength increases, the denaturation temperature did not alter significantly; however, the enthalpy of denaturation decreased. The size of a denaturation peak is a measure of the heat flow required to denature the protein (Biliaderis, 1983). The flaxseed gum effectively lowered the ΔH_D thereby destabilizing the protein. Evidently, the destabilization was not electrostatic in nature since the 1% flaxseed gum sample was greater than a sample without at 0.2 ionic strength (difference of 0.25 cal/g) than at 0.025 ionic strength (difference of 0.03 cal/g). This was to be expected considering both protein and polysaccharide had a negative charge at this pH. Flaxseed gum did however appear to be interacting with the protein since there was an observed decrease in ΔH_D. It is possible that weak hydrogen, hydrophobic bonds or Van der Waal's attraction forces between the polysaccharide and the protein destabilized the protein (Ledward, 1994). The contribution of the salt may likely be to expose the hydrophobic groups in the interior of the native protein, allowing the flaxseed gum to interact and denaturation to occur more readily.

Table 4.13. Effect of flaxseed gum (1% w/v) on the temperature (T_D) and enthalpy (ΔH_D) of denaturation of approximately 10% (w/v) ovalbumin (oval) protein suspended in phosphate buffers (pH 6.0) of known ionic strength.

Presence of Polysaccharide	Ionic strength	T_i (°C)	ΔH_D (cal/g)	T_D (°C)
none	0.025	72.74 ± .41	3.66 ± .014	79.68 ± .20
gum	0.025	73.45 ± .38	3.63 ± .022	80.10 ± .20
none	0.05	72.57 ± .23	4.04 ± .027	79.62 ± .21
gum	0.05	74.23 ± .26	3.78 ± .020	80.11 ± .25
none	0.2	73.75 ± .28	3.72 ± .007	80.64 ± .34
gum	0.2	74.25 ± .36	3.47 ± .002	80.50 ± .25

n=3
Ti was the extrapolated onset temperature of the endothermic peak

4.4.5. Mold Studies of the Muffins

Preliminary experiments suggested that flaxseed gum may inhibit mold growth on the muffin surface. However, further examination under controlled conditions showed no statistically significant difference of the inhibition of mold between 0.5% flaxseed gum muffin treatment and the control (Table 4.14).

Table 4.14. Effect of 0.5% flaxseed gum on mold inhibition on muffin surfaces.

Treatment	mold counts per 3.5 cm^2 muffin surface
control	5.5 ± 3.1[a]
0.5% flaxseed gum	3.6 ± 2.6[a]

n = 3 batches x 2 muffins
[a] value in the same column with the same superscript are not significantly different ($p < 0.05$) according to Tukey's Studentized Range Test.

4.4.6. Scanning Electron Microscopy

The appearance of the internal crumb of muffins with or without added hydrocolloid gums were compared at low magnification (Figures 4.05 and 4.06). Xanthan, guar and 0.5% flaxseed gum formulated muffins have an open , porous appearance with numerous, relatively uniform gas cells (Fig. 4.05 and 4.06a). The control showed large, cup-like gas cells with thick cell walls separating individual cells (Fig. 4.06b), indicating that muffins containing gums were able to stabilize the foam structure better than the control thereby providing greater gas retention and resulting in enhanced volume. Muffins containing 0.1% guar gum or 0.1% xanthan gum had sharp angular edges to the fractured surface compared to the surfaces of flaxseed gum muffins and the control. Seemingly, the strength of the muffin crumb in the 0.1% guar gum and the 0.1% xanthan gum treatments were affected for unknown reasons (Veto, 1997). This is consistent with the instrumental results (Table 4.06) which suggests that xanthan and guar gum may have a stronger internal bond structure compared to the control.

Freeze fracturing permitted examination of the interior of the gas cell at higher magnification. Comparison of these photomicrographs with dough and bread ultrastructure studies using thin-sectioning and SEM techniques (Chabot *et al.*, 1979; Fretzdorff *et al.*, 1982; Pomeranz and Meyer, 1984) suggests the following interpretations. Wheat starch granules are bimodal with either spherical shapes between 15 and 25 μm or smaller granules with diameters of 2 to 5 μm (Fretzdorff *et al.*, 1982; Jane *et al.*, 1994). As has been observed in many SEM ultrastructure studies, all samples containing hydrocolloids show swollen starch granules embedded in a protein matrix inside the air pocket with a veil-like protein and/or colloidal film enveloping the starch granules (Figure 4.07a) (Chabot *et al.*, 1979; Varriano-Marston, 1977). Chabot and coworkers (1979) concluded that during the baking process starch granules gelatinized and adjust around the gas cells but due to the limited available water in the system, the granules

are swollen yet identifiable. The control sample had a smoother air pocket suggesting that the starch granules were completely modified (Figure 4.07b). Similar conclusions have been documented (Fretzdorff *et al.*, 1982; Pomeranz and Meyer, 1984).

Interestingly, pearl-like chains were found inside the air pockets of all treatments independent of hydrocolloid treatment (Figure 4.08a). This may be an artifact caused by sampling technique; however, these chains were observed only in air pockets and on or near the starch granules (Figure 4.08b). The presence of these chains in dough and bread has been attributed to probable protein-starch interactions (Fretzdorff *et al.*, 1982; Pomeranz *et al.*, 1984).

Figure 4.05. Scanning electron micrograph of muffins containing guar gum (a) and xanthan gum (b).

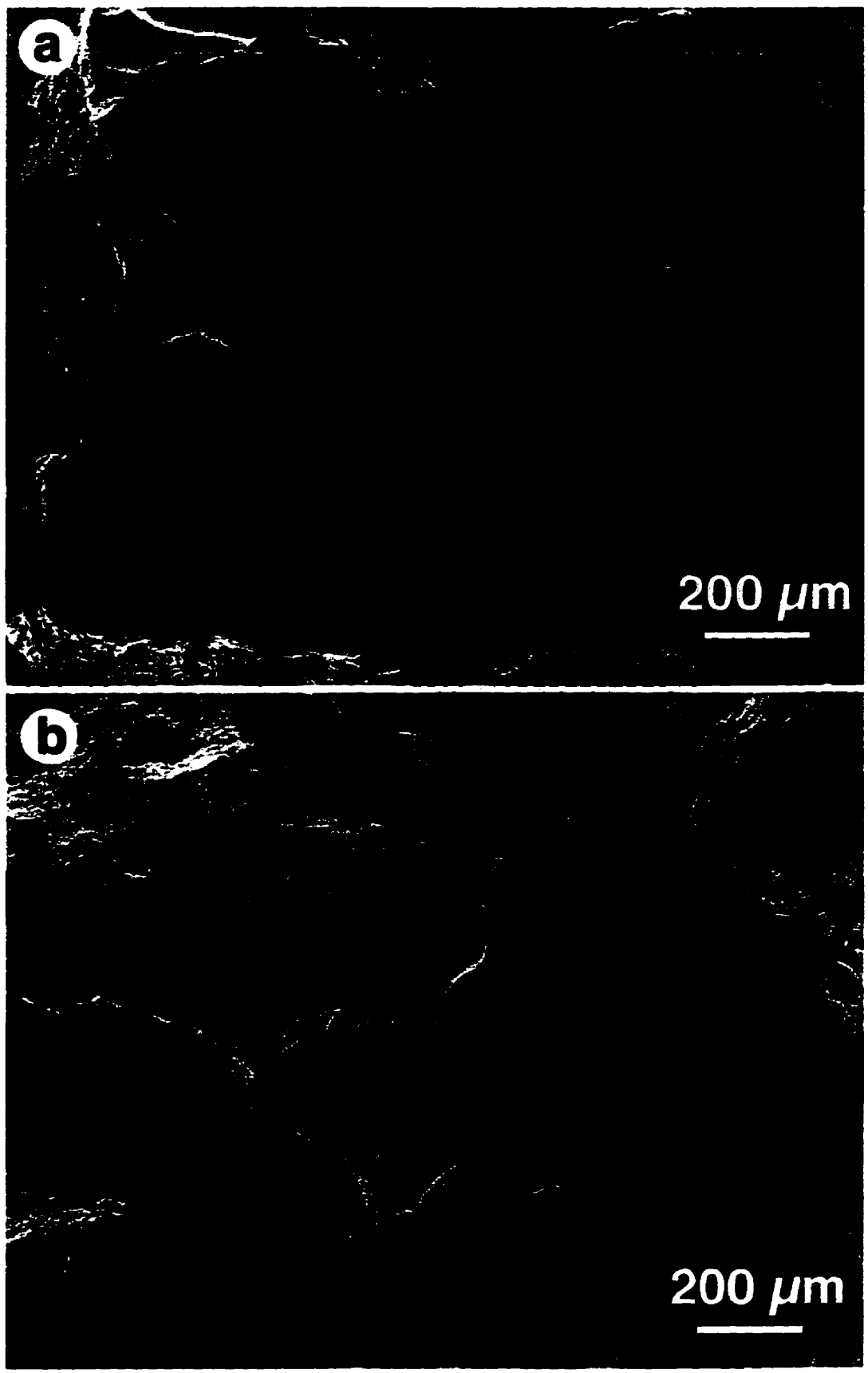

a
200 μm
b
200 μm

Figure 4.06. Scanning electron micrograph of muffins containing 0.5% flaxseed gum (a) and control (b).

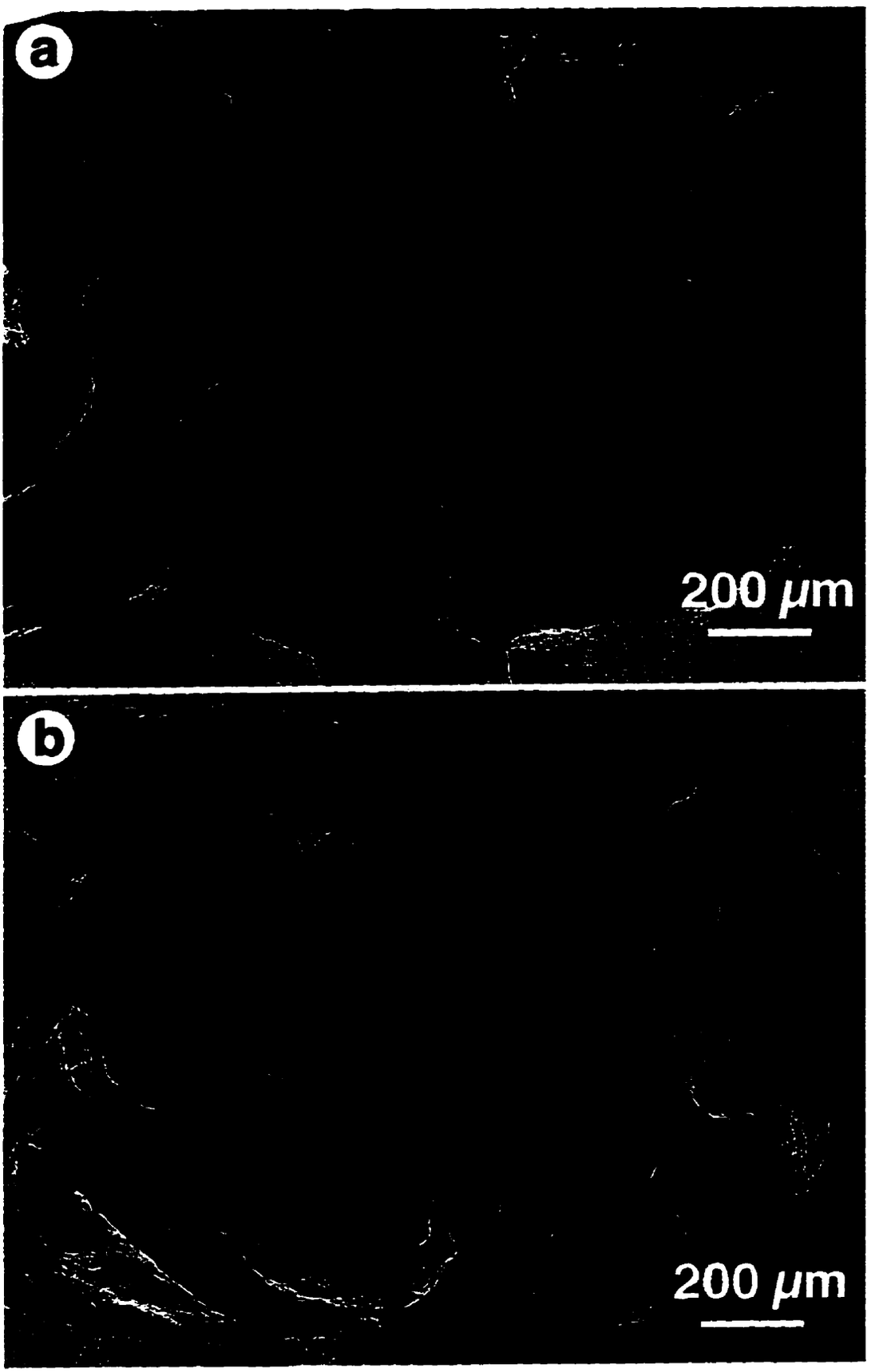

a
200 μm
b
200 μm

Figure 4.07. Scanning electron micrograph of air pocket of freshly baked muffins. 0.5% flaxseed gum muffin (a); control (b)

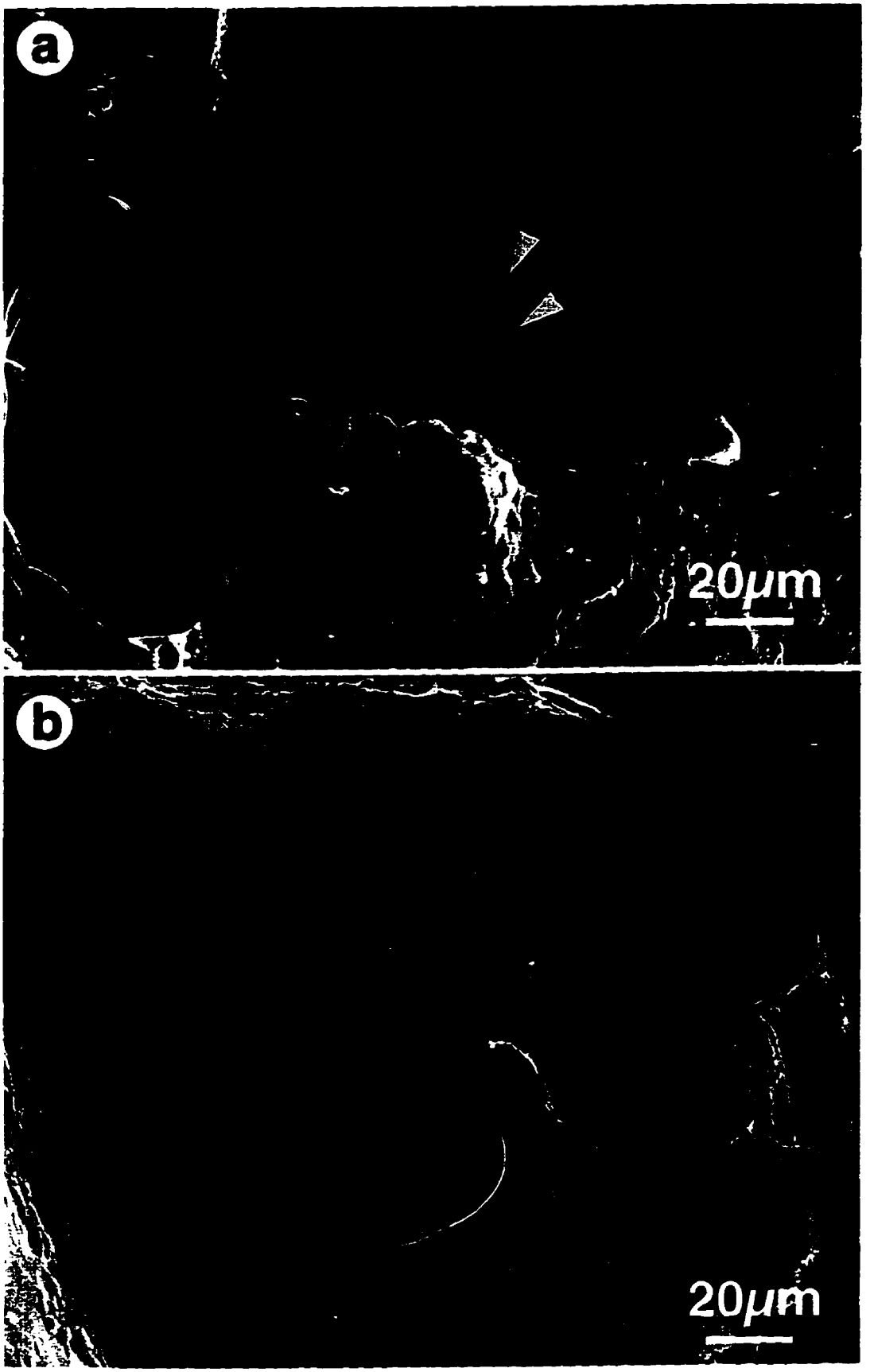
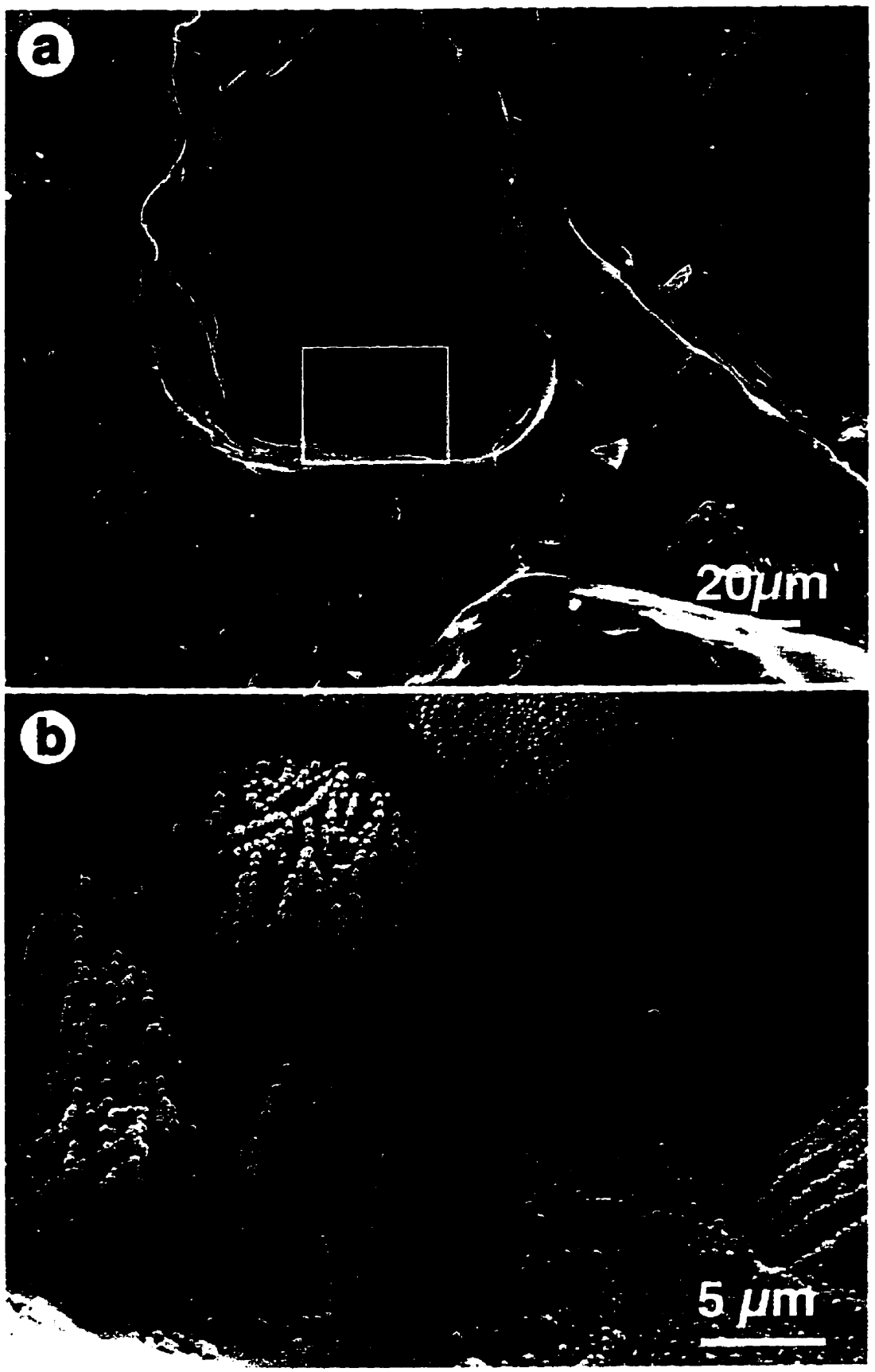

a
20μm
b
20μm

Figure 4.08. Scanning electron micrograph of muffin air pocket at low magnification (a). At high magnification (b).


a
20μm
b
5 μm

4.5. Conclusions

Flaxseed gum improved muffin height and volume with no significant changes in texture as measured by instrumental and sensory methods. The primary effect of hydrocolloids appears to be maintaining higher minimum batter viscosities during heating. The mechanism for the improvement may be due to the batter maintaining the foam structure until protein coagulation occurs. Flaxseed gum at 0.5% levels and xanthan gum at 0.1% had the highest minimum viscosity at 65 to 75°C and they also produced muffins with the greatest volume. Higher viscosity results in a reduction in gas diffusion and retention of expanding gas cells due to reduced migration within the system. Flaxseed gum and guar gum batters had initially similar viscosities at equal concentrations; however as baking proceeded, the viscosity for flaxseed gum containing batters decreased compared to the guar gum batters. Heating significantly affected the viscosity of the flaxseed and guar gum polymers.

Surprisingly, hydrocolloids did not appear to significantly increase moisture retention or retard staling in this muffin formulation. This is contradictory to the reports of flaxseed gum improving the shelf life of bread (Garden-Robinson, 1994). It is possible that the success to improving shelf life in terms of antistaling is only partially dependent on gum selection. Formulation variables may play an equally vital function in extending shelf life of bakery products. Overall, flaxseed gum at 0.5% levels could easily replace both guar gum and xanthan gum at 0.1% levels in this type of bakery product.

5. EFFECT OF FLAXSEED GUM ON QUALITY AND STABILITY OF A MODEL SALAD DRESSING

5.1. Introduction

The composition of mayonnaise and salad dressing differs in that salad dressings can contain a lower volume fraction of oil. Hydrocolloids are used in salad dressings to provide attributes such as improved mouth feel, thickness, cling-ability as well as functional attributes such as suspension of particles and prevention of an oil/water layer (Andres, 1987). Because of their low hydrophobicity and their limited chain flexibility which ultimately restricts adsorption onto a liquid interface, most polysaccharides do not function to reduce the emulsion interfacial tension as is the case with an emulsifier. Instead they form viscous, ordered network in the continuous phase to physically prevent oil separation (Dickinson, 1988). Choosing which hydrocolloid to use in an emulsion, therefore, becomes a matter of knowing its physico-chemical properties and how the gum interacts with other components in the formulation.

A hydrocolloid that is thermodynamically incompatible with a protein will be distributed differently within the system from a hydrocolloid that forms a chemical complex with the protein (Dickinson, 1988). Equally important when considering which hydrocolloid to use in an emulsion formulation is the solvent quality which influences the interactions of the colloid with itself as well as its environment. Variables commonly affecting solvent quality are pH, ionic strength, solute content and temperature. Stability or emulsifying efficiency of the macromolecules is related to their degree of hydration in the aqueous system (Dickinson, 1988). Any change in the character of the polymer due to the above variables will be reflected in its emulsifying or stabilizing ability.

The objectives of this study were:

1. To determine the effect of flaxseed gum concentration, salt concentration and pH on the initial quality and the stability of oil in water salad dressings.
2. To compare the optimal results from objective #1 with results using a commercial stabilizer at both equal gum concentrations and approximately equal viscosities; to assess potential protein-polysaccharide interactions of the flaxseed gum with the protein emulsifier using fresh egg yolk versus dried egg yolk; and to compare two types of flaxseed gums (cv. Norman and Linola ™ 947) on the stability of emulsions.

5.2. Materials

All ingredients used in this study were from commercial sources used in the manufacture of salad dressings unless otherwise stated. Xanthan gum was a commercial grade from Kelco, Division of Merck; dried egg yolk was supplied by Innovatec (Abbortsford, BC); the other ingredients were salt (Windsor, ON) and soybean oil (Hain, CA). Reagent grade glacial acetic acid was used to adjust the pH of the emulsion. Fresh egg yolk was prepared from grade A white eggs using the procedure by Davey *et al.* (1969). Eggs were carefully broken. The yolk was separated from the albumen, rinsed with distilled water then gently rolled on adsorbent tissue to remove traces of albumen. After the vitellin membrane was punctured, the liquid yolk was collected. Fresh egg yolk contained ca. 50 % water. This value was taken into account when substituting the fresh egg yolk for the dried yolk so that both treatments had equal solids concentration. Flaxseed gum was prepared as stated in section 3.

5.3. Methods

5.3.1. Preparation of Model Emulsions

The composition of the emulsion was a simple formula provided by Carrillo and Kokini (1988). Egg yolk powder was added to the emulsion at a 2% concentration. The phase ratio was maintained at a constant 0.4 (oil volume/emulsion volume) for every formulation (see appendix C1).

Pre-emulsification was done using a Waring Commercial food blender. Gums were first dispersed in the appropriate amount of water overnight to insure full hydration. To retard microbial growth, 0.1% (wt basis) sodium azide was added to the aqueous phase. The next day, salt and glacial acetic acid was added and the pH of the solution recorded. Soybean oil was then added and mixed in a Waring Blender (Model 700) for 120 seconds at high speed. Final emulsification was achieved using a Colloid Mill (Model 2F, Gaulin Corp., MA) with a gap setting of 0.008 inches (0.2 mm). All emulsions were stored in 500 mL high density polyethylene jars at room temperature (22-25°C) for a 40 day period.

5.3.2. Experimental Design

Response Surface Methodology (RSM) was used to examine the influence of flaxseed gum on the emulsion stability of a model salad dressing. Gum concentration, salt concentration, pH were the independent variables selected. The experiment was carried out according to a central composite design with three factors and five levels (Haaland, 1989). The complete design consisted of 18 experimental points that included four replications of the centre point. The 18 emulsions were prepared in random order to eliminate any order effects. End and central

values were chosen from the results of preliminary tests.

Seven dependent response variables were selected to measure the effect of ingredient levels on performance. Responses monitored were creep measurements (Newtonian viscosity, η_N, and instantaneous elastic modulus, E_0), dynamic measurements (complex viscosity in the low shear viscosity plateau and phase angle), surface tension, mean droplet size and colour. Treatments assessed over time were creep parameters, dynamic parameters and droplet size. Surface tension and colour, however, were tested only on day one of aging.

Under the assumption that the RSM central values for the three independent variables were in the optimal area for emulsion stability, further independent variables were evaluated. These included exchanging dried egg yolk for fresh egg yolk (concentration of fresh egg yolk was adjusted for moisture content); cv. Norman flaxseed gum for Linola™; and Norman flaxseed gum for xanthan gum at equal concentrations (0.75% w/w) and approximately equal viscosity basis (0.3% w/w). These treatments were done in duplicate and randomized along with the RSM evaluation.

5.3.3. Evaluation of Model Emulsions

5.3.3.1. Surface Tension Measurements

The influence of pH, salt and gum concentration on emulsion surface tension was examined with a Fisher surface tensiomat (Fisher Scientific, Wpg. MB). Emulsions were placed in a glass dish (diameter 7.5 cm; depth 4 cm). The solution was allowed to stand 30 minutes to equilibrate (Coia and Stauffer, 1987). The surface tension of distilled water was 72.0 ± 1 dyne/cm at 25°C. Measurements were conducted in triplicate.

5.3.3.2. Creaming

Emulsion stability was visually assessed using the method described by Hennock *et al.*, (1984). Measured amounts of the model emulsion were poured into 15 mL cylinders and stored at room temperature (22-25°C). The height of the clear liquid at the bottom of the tube was measure periodically over a 40 day period.

5.3.3.3. Emulsion Droplet Size

Viscosity of an emulsion is proportional to the droplet's mean volume diameter (D_V) (Walstra, 1987). To determine the D_V, photomicrographs of the emulsions under phase contrast at 500 x magnification were taken using a Zeiss standard WL microscope with a MC 63 automatic photomicrograph camera attachment (Zeiss, West Germany). At least 500 oil droplets were used in the calculation of mean volume droplet size (from eq. 9) and the corresponding coalescence rate (eq. 10 & 11).

5.5.5.4. Colour Measurements of Emulsions

Model salad dressings were assessed for colour differences using a HunterLab tristimulus colorimeter (model D25L-9; Hunter Associates Lab., Inc., VA). Twenty five millilitres of emulsion were placed in a dish (diameter 9 cm; depth 1 cm). Values were expressed in terms of lightness (L), redness/greenness (± a) and yellowness/blueness (± b) then converted to a single colour function called colour difference by using the following relationship (MacKinney and Little, 1962):

$$\Delta E = \sqrt{(\Delta L)^2 + (\Delta a)^2 + (\Delta b)^2} \quad [12]$$

The total difference is a measure of the distance in colour space between two colours but it does not indicate the direction in which the colour differs. The white standard was used as a reference to measure the difference between emulsion samples. The standard tile had the values: L = 90.76, a = -1.4, b = -1.5 (C2-18593, Hunters Associates Lab).

5.3.3.5. Rheological Properties

Rheological properties were determined on a controlled stress Bohlin CVO Rheometer (Bohlin Instruments, NJ). Dynamic oscillatory measurements were carried out using a measurement geometry of a 6 cm cone and plate with a 2 cone angle (0.07 mm gap setting). Homogenous samples were obtained by gently inverting the jars five times prior to sampling. All the o/w emulsions exhibited linear viscoelastic behaviour. Amplitude sweeps were carried out at shear stress values of 0.1 to 5 or 50 Pa depending on the degree of viscoelasticity of the sample. Frequency sweeps from 0.01 to 20 Hz were performed on the emulsions after establishing the linear viscoelastic range. For all samples, strain was set not greater than 4%. Values for storage (G') and loss (G") moduli, phase angle as well as complex viscosity (η^*) were obtained using the software analysis programs of the Bohlin Rheometer. Duplicate runs were performed on all samples. To prevent dehydration, a thin layer of silicon oil was applied to the exposed perimeter of all samples.

5.3.3.6. Creep Measurements

Using the same geometry as in the dynamic testing, the constant shear stress applied in the creep/recovery compliance studies was 0.45 Pa. This stress was at the high end range of the linear profile for the weakly viscoelastic samples. The small stress, however, did not allow the higher viscosity samples to reach viscous flow (see Figure 5.05a, high viscosity sample). A higher stress, 6.25 Pa, was also used in this situation. Creep compliance was monitored for 1 000 seconds followed by a 1 000 seconds of recovery. The Bohlin software was set up so that if an emulsion reached steady state Newtonian flow before the 1 000 second time frame, the recovery program would automatically initiate. Values for the Instantaneous elastic modulus (Eo) and the Newtonian viscosity (η_N) were obtained using the software analysis programs of the Bohlin Rheometer. At least duplicate runs were performed on all samples.

5.3.3.7. Statistical Analysis

For the response surface methodology design, data were analysed by multiple regression to fit the following second order (quadratic) polynomial model (Haaland, 1989):

$$Y_k = \beta_{kO} + \sum_{i=1}^{3} \beta_{ki} X_i + \sum_{i=1}^{3} \beta_{kii} X^2_{ii} + \sum_{i=1}^{3} \beta_{kij} X_{kij} X_i X_j \qquad [13]$$

where β_{kO}, β_{ki} and β_{kij} are constant regression coefficients of the model, while X_i, X_j, X_k are the coded independent variables. The RSREG (Response Surface REGression) program was used for the polynomial regression (SAS Institute, Inc., 1991).

5.4. Results & Discussion

The second order polynomial equation [13] was fitted to the experimental data from day one (Table 5.01). The results of the analysis and the empirical equations for each of the three independent variables are summarized in Table 5.02. Significance of lack of fit error term, R^2 value, coefficient of variation (CV) and model significance were used to judge the adequacy of the model fit.

5.4.1. Surface Tension Measurements

The developed model for surface tension of model emulsions was not predictive because of a low R^2 value (R^2=0.65), a non significant model term ($p > 0.15$) and a lack of fit error term ($p < .01$) (Table 5.02). Lack of model significance may be due to a number of reasons. Thickness of the viscous film adhering to the plate can create error in the measurements creating an erroneous decrease in surface tension (Yilmazer *et al.*, 1991). The situation is obviously more complicated than the three independent variables originally chosen meaning more parameters are needed to describe surface tension of model salad dressings.

On account of the difficulties in measuring surface tension of the emulsions, surface tensions of the individual hydrocolloid dispersions were determined over a range of concentrations. Changes in surface tension of the hydrocolloid dispersions as a function of gum concentration is show in Figure 5.01. The surface tension of water decreased dramatically with addition of flaxseed gum, to level off at a value of ca. 50 dynes/cm. Fedeniuk and Biliaderis (1994) observed surface tensions of ca. 52 dynes/cm for 0.3% to 0.6% (w/v) solutions of flaxseed gum cv. Linott.

Table 5.01. Process variables and experimental data for the three factor, five level response surface design of model flaxseed gum emulsions at day one.

Run	Gum conc.	pH	Salt conc.	colour	Surface tension	Droplet	Dynamic measurements		Creep parameters	
Order	(%w/w)		(% w/w)	difference	(dynes/cm)	Size (μm)	complex viscosity (Pa.s)	Phase angle	Newtonian viscosity (Pa.s)	Elastic modulus (Pa)
1	-1 (0.3)	-1 (2.81)	- 1 (1)	14.8	36.70	1.75	0.12	84.1	0.06	0.21
2	-1 (0.3)	-1 (2.81)	+ 1 (4)	12.2	58.17	1.34	0.22	78.6	0.39	1.29
3	-1 (0.3)	+1 (5.12)	- 1 (1)	9.17	45.27	1.29	0.44	71.9	0.48	1.82
4	-1 (0.3)	+1 (5.12)	+ 1 (4)	8.71	45.93	0.79	0.72	65.7	0.60	2.06
5	+1 (1.2)	+1 (5.12)	-1 (1)	31.7	31.13	2.60	2.63	62.1	23.4	0.93
6	+1 (1.2)	-1 (2.81)	+ 1 (4)	29.9	47.40	3.20	3.52	49.0	17 700	63.7
7	+1 (1.2)	+1 (5.12)	-1 (1)	10.4	55.70	0.89	23.13	32.6	47 500	47.6
8	+1 (1.2)	+1 (5.12)	+ 1 (4)	11.1	64.00	1.01	24.01	30.6	64 100	106
9	-1.68 (0)	0 (4)	0 (2.5)	9.9	ND	1.31	0.12	68.6	0.14	0
10	+1.68 (1.5)	0 (4)	0 (2.5)	11.8	35.70	0.88	37.20	32.7	129 250	167
11	0 (0.75)	-1.68 (2)	0 (2.5)	40.6	ND	3.53	1.05	65.5	1.06	0.83
12	0 (0.75)	+1.68 (6)	0 (2.5)	11.2	52.23	0.79	8.32	46.6	48 000	30
13	0 (0.75)	0 (4)	- 1.68 (0)	11.4	75.90	0.98	68.03	19.3	47 680	87.3
14	0 (0.75)	0 (4)	+ 1.68 (5)	11.2	50.33	0.90	5.49	34.8	20 878	27.9
15	0 (0.75)	0 (4)	0 (2.5)	11.4	46.97	1.02	6.76	36.4	25 246	28.7
16	0 (0.75)	0 (4)	0 (2.5)	11.0	47.77	0.86	9.60	35.3	33 000	49.4
17	0 (0.75)	0 (4)	0 (2.5)	10.9	48.27	0.90	6.61	36.9	29 437	31.4
18	0 (0.75)	0 (4)	0 (2.5)	11	47.57	0.88	5.36	35.2	28 790	25.5

ND, not detected due to emulsion separation within the 30 minute equilibrate time

Table 5.02. Regression coefficient and analysis of variance of the second order polynomial for the response variables: colour difference (ΔE), surface tension, mean droplet diameter, phase angle (δ), complex viscosity (η*), Newtonian viscosity (η_N) and instantaneous elastic modulus (Eo) on day one of testing.

	Dependent Response Variables						
	Y_1 (ΔE)	Y_2 (surface tension)	Y_3 (Droplet size)	Y_4 (δ)	Y_5 (η*)	Y_6 (η_N)	Y_7 (Eo)
β_0	70.226****	34.492	7.237***	212.378****	2.002	-55273	-56.946
Linear							
β_1	36.976***	-5.307	1.702**	-70.633*	-28.205	-103771	-147.65
β_2	-30.37****	5.667	-2.904****	-61.441***	17.794	33249	60.951
β_3	-1.879	-4.234	-0.160	-2.833	-21.390	7862.7	-19.110
Quadratic							
β_{11}	-0.707	-23.815	0.481	42.055***	4.871	34974	59.032
β_{22}	3.642****	-0.558	0.375****	7.138***	-2.684	-4943.7	-8.336
β_{33}	.008	2.553	0.017	.009	3.334	-1707.7	1.253
Interaction							
β_{12}	-7.548****	10.786	-0.703****	-5.362	9.770	23109	21.286
β_{13}	0.363	0.463	0.302***	-0.630	0.256	6347.1	22.115
β_{23}	0.338	-2.181	-0.041	0.807	-0.124	-50.748	-0.645
R^2	0.944	0.653	0.960	0.842	0.624	0.793	0.773
CV	21.15	20.53	16.97	22.79	137.79	79.94	84.39
F-Ratio (model)	14.905****	1.253	21.21****	4.748***	2.574	3.398***	3.018**
F-Ratio (Lack of Fit)	323.1****	707.8****	21.08***	288.4****	120.1****	74.9***	13.15***

Model in which X1 = gum concentration, X2 = pH, X3 = salt concentration

**** Significant at 0.01 level
*** Significant at 0.05 level
** Significant at 0.10 level
* Significant at 0.15 level

Izydorczyk *et al.* (1991) documented surface tension of 0.5% (w/v) solutions of pentosans and arabinoxylans to vary from 42 to 59 dynes/cm. The results for flaxseed gum were consistent with these earlier reports suggesting that flaxseed gum is surface active. Both flaxseed gums (cv. Norman and Linola™) show similar trends as was expected since Norman flaxseed and Linola™ have been reported to have similar rheological and structural nature (Mazza *et al.*, 1994). The surface activity is most likely due to the protein contamination during the extraction process since proteins are primarily responsible for surface active properties (Dickinson, 1988). The surface tension of xanthan gum dispersions were typical of previous reports indicating limited surface active capabilities (Yilmazer *et al.*, 1991; Mancini, 1992).

5.4.2. Creaming

Separation or creaming is a partitioning of the dispersed phase as a function of time (Dickinson, 1988). Creaming usually occurs when there is a significant density difference between the dispersed and the continuous phase. Creaming occurred in eight of the 18 prepared emulsions. All other emulsions were stable with regard to creaming over the 40 day period. Figure 5.02 shows the height of the sharp boundary between flocculated emulsion and the clear serum as a function of time.

Consistent with earlier reports, three regions for creaming were observed: an initial delay period then a linear creaming region followed by a period of cream compression (Parker *et al.*, 1995)The delay period varied from a few hours to several days. Generally, the interface started to rise immediately, levelling off as a concentrated cream was formed due to buoyancy forces. For the sample containing 1.2% gum, 4% salt with a pH of 2.81 (run 6), a significant delay period

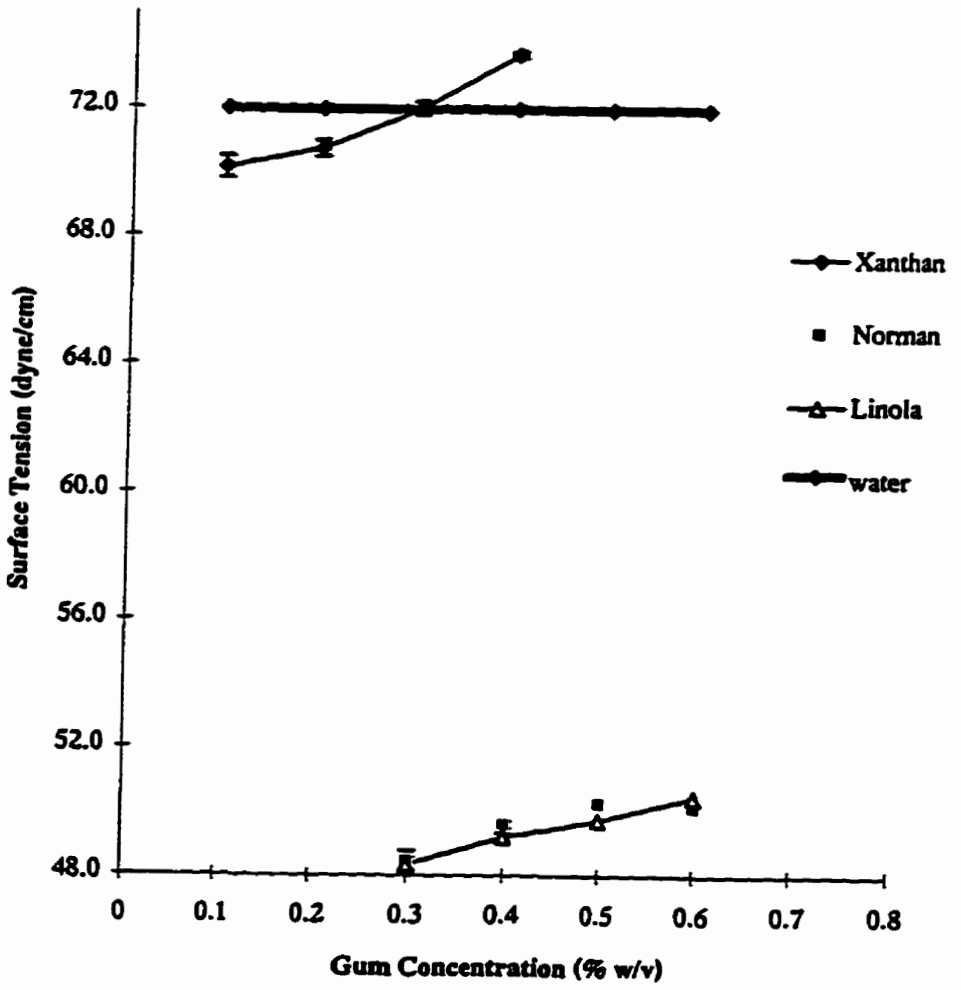


Figure 5.01. Changes in surface tension of water in response to changes in gum concentration (xanthan gum and flaxseed gums at pH 6.5; 25°C)

was observed before the linear creaming initiated. For this delay period to be observed, the model salad dressing must have had an initial yield stress which decreased with time. A critical point is reached where the yield stress is too small to prevent the buoyancy forces from becoming the predominant force hence creaming begins (Parker *et al.*, 1995). At low pH, there is the potential for depolymerization of the polysaccharide due to acid hydrolysis (Cui *et al.*, 1994b). Disordered coils are more susceptible to chain cleavage than ordered polysaccharide such as xanthan gum which has a pH range of 2 to 8 (Gordon, 1990) Run 5 (1.2% flaxseed gum, 1% salt; pH 2.81) displayed no significant delay period in creaming even though it's formula was similar to run 6 except for a salt content of 1% (w/w). No apparent reason is obvious for the difference in creaming. It may be that the low salt concentration reduces the ability of the egg protein to act as an good emulsifier. The combination of poor protein and compact polysaccharide makes this formulation less stable with regards to creaming than the same gum and pH formulation with higher salt levels.

Colloid concentration plays a critical role in creaming. Samples that contained 0.3% flaxseed gum independent of solvent quality accelerated creaming compared to the control (0% hydrocolloid) which suggests that either bridging or depletion flocculation had occurred. From the results of the surface tension which indicates flaxseed gum displays surface activity, the gum is more than likely to adsorb on to the oil interface rather than be excluded as would be the case for depletion flocculation. Non-complexing polysaccharides usually induce flocculation and enhance creaming when present at low concentrations (Cao *et al.*, 1990).

The independent variable, pH, also played a role in emulsion creaming as shown by all runs having a pH of 2.81 or lower resulted in separation (Figure 5.02). In low pH environments

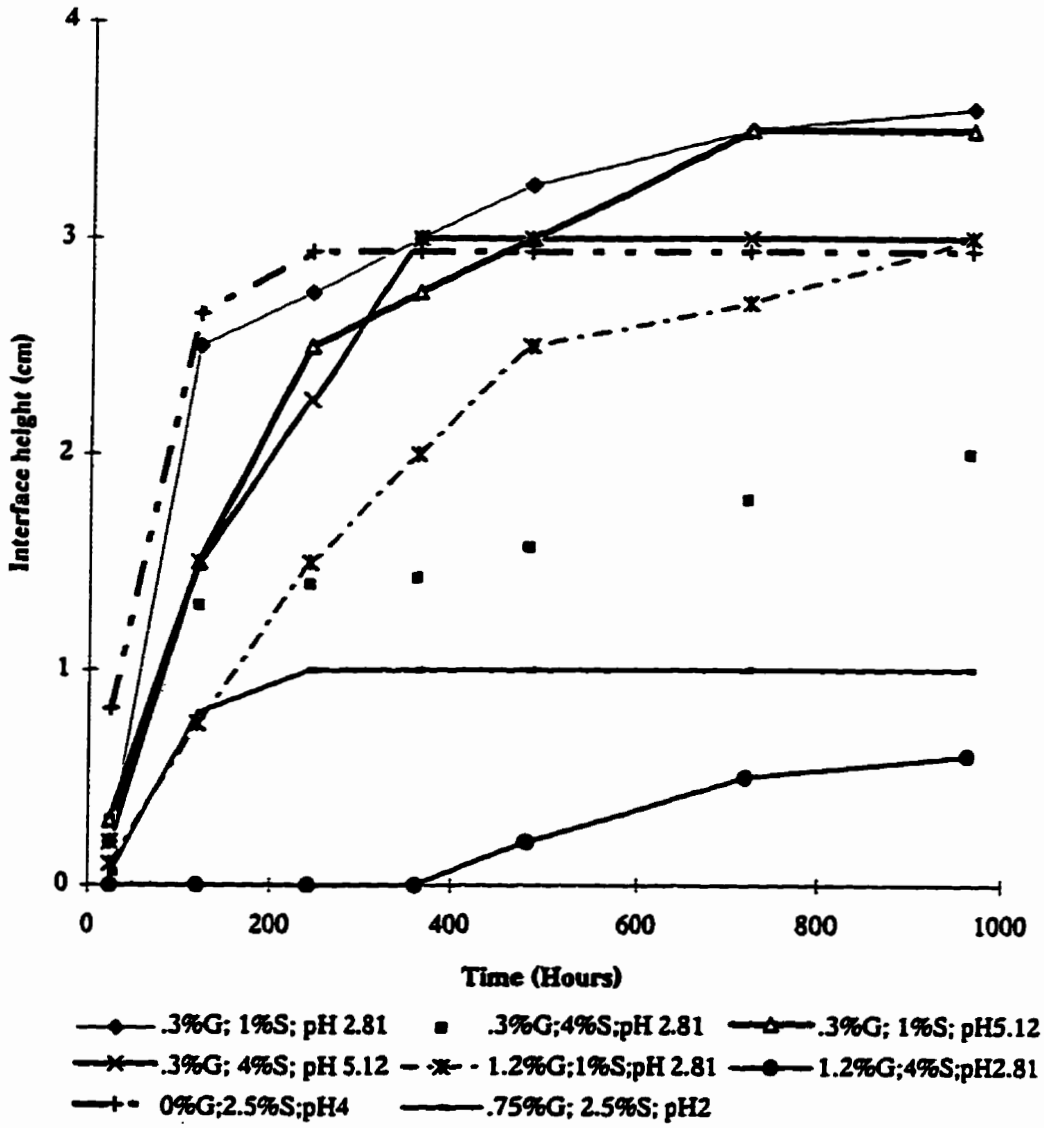


Figure 5.02. Evolution of serum height of salad dressings stored at 25 C for 1 to 40 days. Total sample height, 10 cm.

regardless of gum concentration, the solvent quality is lowered and the hydrocolloid becomes more compact. Adjacent polymer entanglement and inter-molecular hydrogen bonding is reduced resulting in a diminished polymer network (Dickinson and Stainsby, 1988). Run 11 creamed soon after emulsifying (although it contains 0.75% flaxseed gum in the formula) on account of the low pH (pH 2).

Run 9 (0% flaxseed gum, 2.5% salt and pH 4) was not stable with regard to creaming (Figure 5.02). Carrillo and Kokini (1988) recommended 2% egg yolk protein for stable emulsions. Normally with a mixture of surface active polymer and protein, a partial displacement at the oil/ water interface of the hydrophilic polymer (polysaccharide) by the hydrophobic polymer (egg yolk protein) is observed (Dickinson, 1989). The surface load for the egg protein alone evidently is too low for this formulation on account of the rapid onset of creaming.

Of the eight samples which exhibited creaming, one also displayed oiling off. That is, the oil droplets coalesced to become larger droplets with eventually an oil layer being produced at the top of the emulsion. Evidently, the original emulsion sample of 0.75% gum, 2.5% salt and pH 2 (run 11) was destroyed. The possibility of reduced surface activity of the egg protein and/or flaxseed gum due to the extremely low pH increases the probability of oiling off (Coia and Stauffer, 1987). Acid hydrolysis of hydrocolloids has been published for low pH mediums (Paredes *et al.*, 1989). It has also been reported that proteins can be desorbed wholly or in part by adjusting the pH or ionic concentration (Dickinson *et al.*, 1988). The reduced protein load at the oil/water interface can cause coalescence (Dickinson, 1988).

5.4.3. Emulsion Droplet Size

The larger the mean droplet size, the higher the creaming rate, coalescence rate and the probability of flocculation (Walstra, 1987). Smaller droplets produce greater emulsion stability with respect to coalescence (Walstra, 1988). The analyses of variance for mean droplet volume at day one is presented in Table 5.02. The predictive model was considered adequate because of the high R^2 (0.96), relatively low CV and significant model F ratio ($p< 0.01$). Although there was a significant lack of fit, a response surface plot was still generated. The model still offered a reasonable and meaningful interpretation of the variables.

Figure 5.03 shows the response surface plot for emulsion droplet size as a function of gum concentration and pH at a salt concentration of 2.5% (w/w). Gum concentration was significant ($p<0.10$) (Table 5.02). Mean droplet diameter decreased as gum concentration increased (Table 5.03). At day zero, the diameter decreased from 1.3 μm at 0% gum concentration (run 9) to 0.88 μm at 1.5% flaxseed gum concentrations (run 10). At day 40, the droplet diameter shifted from 1.78 μm (run 9) to 1.34 μm (run 10) as the gum concentration increased from 0% to 1.5% (w/w)

.

The independent variable, pH, had the greatest effect ($p<.01$) on mean droplet volume diameter (Table 5.03). The order of increasing drop size with pH independent of time was:

$$6<4<2$$

which was consistent with the values reported by Kiosseoglou and Sherman (1983). The diameter went from 3.5 μm at pH 2 (run 11) to 0.79 μm at pH 6 (run 12) on day one. At day 40, the trend continued with the mean droplet diameter decreasing as pH increased (from 3.70 μm at pH 2 to 1.13 μm at pH 6). Examining Figure 5.03, the smallest mean volume diameters were recorded around the isoelectric point of the egg protein (pI 4.6) which is consistent with Kiosseoglou and Sherman's (1983) findings. Away from the isoelectric point, the egg protein

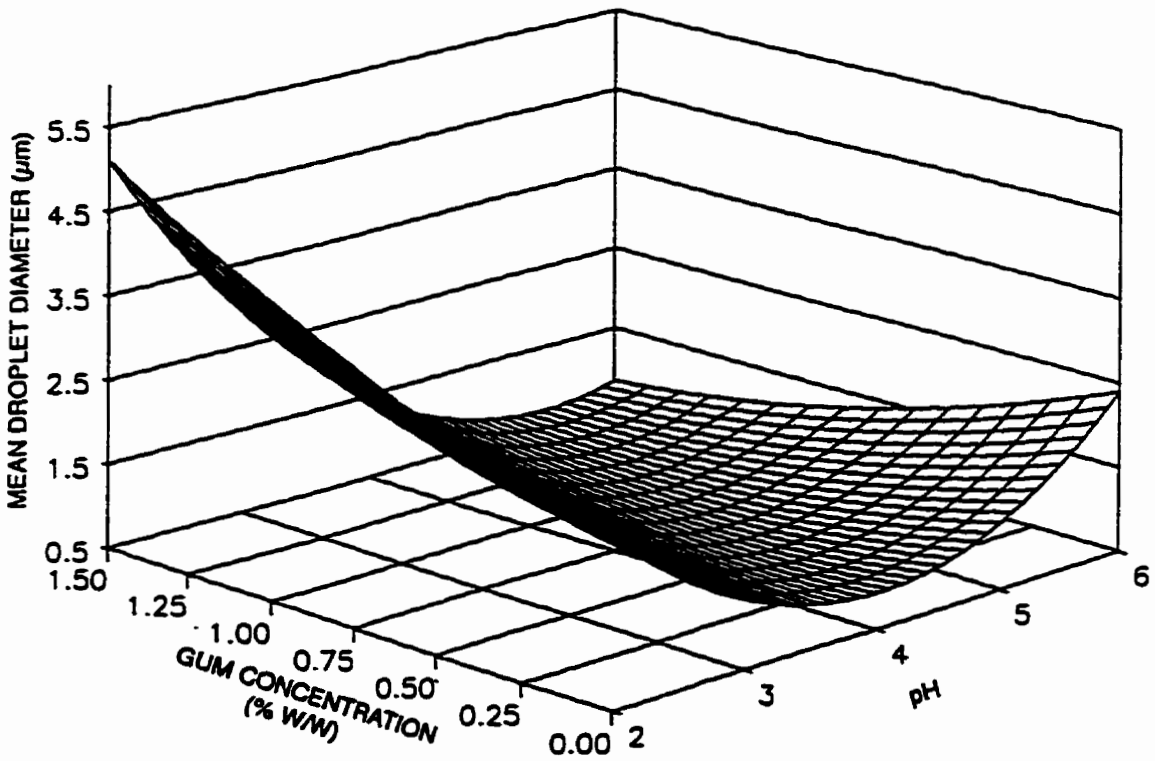


Figure 5.03. Response surface for the effect of gum concentration and pH on mean droplet size (μm) at 2.5% salt concentration on day one of testing.

molecules adsorbed on the oil droplet surfaces are charged which leads to greater disruption of the micelles and more pronounced unfolding (Kiosseoglou and Sherman, 1983). However, the apo-lipoprotein remains in the residual structure so that many of the hydrophobic groups are guarded in the interior of the structure surrounded by ionized hydrophilic groups (Kiosseoglou and Sherman, 1983). This results in a considerable decrease in the number of adsorbed segments projecting from the oil droplet. Therefore at pH's away from the egg protein's pI, reduced interlinking and network formation occurs which results in increased mean droplet diameter.

Table 5.03. Influence of the independent variables (pH; salt and gum concentration) on the mean droplet size and the rate of drop coalescence.

Formulation	Droplet Size day 0 (μm)	Droplet Size day 40 (μm)	Rate of Drop Coalescence ($s^{-1} \times 10^{-7}$)
0% gum; 2.5% salt; pH 4	1.31	1.78	2.69
1.5% gum; 2.5 % salt; pH 4	0.88	1.34	3.68
0.75% gum; 2.5% salt; pH 4	0.92*	0.97*	0.44*
0.75% gum; 0% salt; pH 4	0.98	1.10	1.00
0.75% gum; 5% salt; pH 4	0.90	1.03	1.16
0.75% gum; 2.5% salt; pH 2	3.53	3.70	0.41
0.75% gum; 2.5% salt; pH 6	0.79	1.13	3.13

* mean of the centre points (runs 15 thru 18)

The addition of salt shifted the average droplet size to smaller values. That is, from 0.98 μm at 0% salt levels to 0.90 μm at 5% (w/w) levels (Table 5.03). This was consistent with reports by Carrillo and Kokini (1988) and Kioseoglou and Sherman (1983). The latter researchers suggested the mechanism is due to the increased surface active egg yolk material.

All treatments showed some signs of coalescence. Smaller droplets are more stable to coalescence than larger ones (Walstra, 1988). The rate of drop coalescence of some of the formulations is presented in Table 5.03. Drop coalescence rates were influenced by electrolytes and gum concentration. The most stable emulsion with regards to coalescence was at the midpoint of the design. The treatment containing 0.75% gum, 2.5% salt at pH 4 had a rate of drop coalescence of 0.44×10^{-7} s^{-1} (Table 5.03). The particle size distribution changed very little over the 40 day period suggesting that the mechanism of viscosity change during the aging process is through a build up and break down of oil droplet aggregates and not coalescence. The treatments containing 0% gum (coalescence rate of 2.69×10^{-7} s^{-1}) and pH 2 (coalescence rate of 0.41×10^{-7} s^{-1}) are a little misleading. Both of these treatments were unstable within a matter of hours having recorded the largest inital and final mean droplet size (Figure 5.02). Even though the treatment containing a pH 2 was stable with regards to coalescence, it was not stable with regards to creaming. Creaming, itself, is not indicative of emulsion breakdown but it can facilitate coalescence.

5.4.4. Colour Measurements

The predictive model developed for colour difference was considered adequate because it possessed a high R^2 value ($R^2 = 0.94$), a low CV and a model that was significant at the 1% level (Table 5.02). Even though there was a significant lack of fit, the model still offered a reasonable explanation in the effort to model colour response. As shown in Figure 5.04, both gum concentration and pH influenced the colour of the emulsion. Increasing the gum concentration and/or decreasing the pH of the emulsion resulted in a darker coloured emulsion compared to the standard white tile. As gum concentration moves from 0% to 1.5% (w/w) , colour difference (ΔE) shifted away from the standard white tile, from 9.9 to 11.8. Flaxseed cv. Norman is a

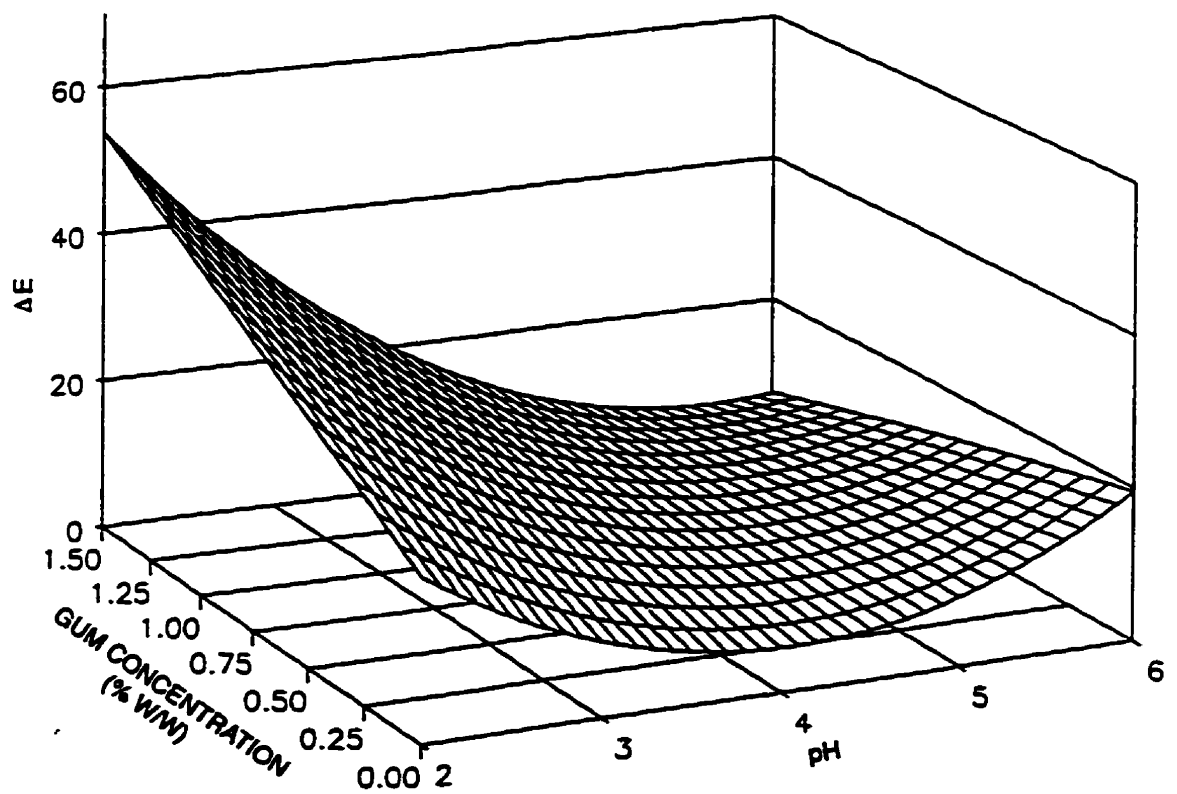


Figure 5.04. Response surface plot for the effect of gum concentration versus pH on ΔE at 2.5% salt concentration. Day one of testing.

brown coloured seed. During the gum extraction process, some of the pigment is retained in the gum; eventhough the ethanol precipitation removes a significant portion of the colour. It was therefore expected that the emulsion colour would deviate from the standard white tile as more of the light brown gum was added.

The independent variable, pH, significantly ($p < 0.01$) affected colour difference (Table 5.02). At pH 6, the model emulsion deviated from the standard white tile by 11.2 points. In contrast, at pH 2 the emulsion deviated from the standard white tile almost 41 points. Reports of pH significantly influencing colour in cereals have been documented (Mazza and Miniati, 1993). As the pH of the solution increases, the colour fades. At pH 6, most anthocyanins appear colourless (Mazza and Miniati, 1993). As expected, the variable salt had little influence on emulsion colour. It was insignificant ($p > 0.15$).

For droplet sizes, there may be a significant interaction between the size of the droplet and the wavelength of light. Greater coalescence resulting from low pH may reduce the amount of scattering and therefore, decrease the amount of light reflected back into the instrument, thereby changing the colour difference values. For this reason, the L, a, b values were recorded (Appendix C 2).

5.4.5. Dynamic Measurements

Typical viscosity versus shear stress curves for oil/water emulsions are presented in Figure 5.05. All emulsions displayed a low shear Newtonian plateau which varied with the viscosity of the emulsion. For all emulsions,as gum concentration increased, the complex viscosity in the low shear plateau, as well as the overall range of the plateau increased. The higher the value for

complex viscosity in the low shear range, the more stable is the emulsion (Cao *et al.*, 1990). The predictive model developed for complex viscosity in the low shear Newtonian plateau was considered unsatisfactory because it possessed only a moderate R^2, a high CV, did not have a significant model term ($p>0.15$) and had a significant lack of fit (Table 5.02).

Table 5.04 shows the effect of gum concentration and aging on the dynamic measurement: complex viscosity (η^*) and phase angle (δ). As expected and shown in Figure 5.05, η^* increases with increasing gum concentration. Complex viscosity increases from 0.13 Pa.s (0% gum) to 6.61 Pa.s (0.75% gum) to finally 37.2 Pa.s (1.5% gum) (Table 5.04). Changes in viscosity for the 0.75% gum concentration as the emulsion aged was likely due to a buildup and breakdown of aggregates versus drop coalescence on account of the low rate of coalescence (Table 5.03). Changes in viscosity for the 0% and the 1.5% gum formulation was likely due to droplet coalescence .

Aging also reduced the region of the plateau (Figure 5.06). Shear stresses within the Newtonian plateau produced small deformations which were within the linear viscoelastic range of the sample. Stresses beyond the plateau resulted in rapidly decreasing viscosities. The point where rapid breakdown begins can be viewed as being similar to a yield stress (Pettitt *et al.*, 1995). As the emulsion ages, the point where the break down in structure is observed shifts to the left. Less stress, therefore, is needed to break down the structure as the sample ages indicating a change in network formation.

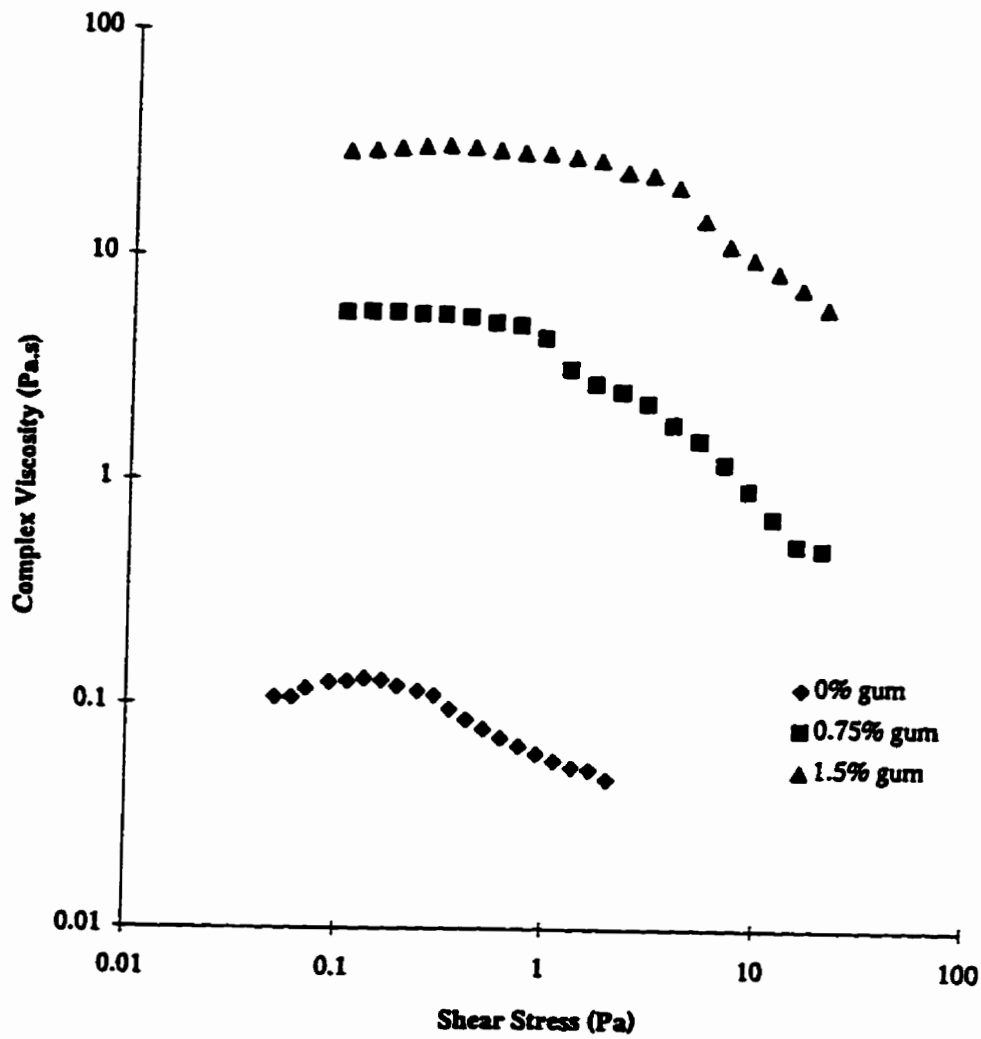


Figure 5.05. Effect of flaxseed gum concentration on complex viscosity of o/w emulsions at day one aging (2.5% salt; pH 4).

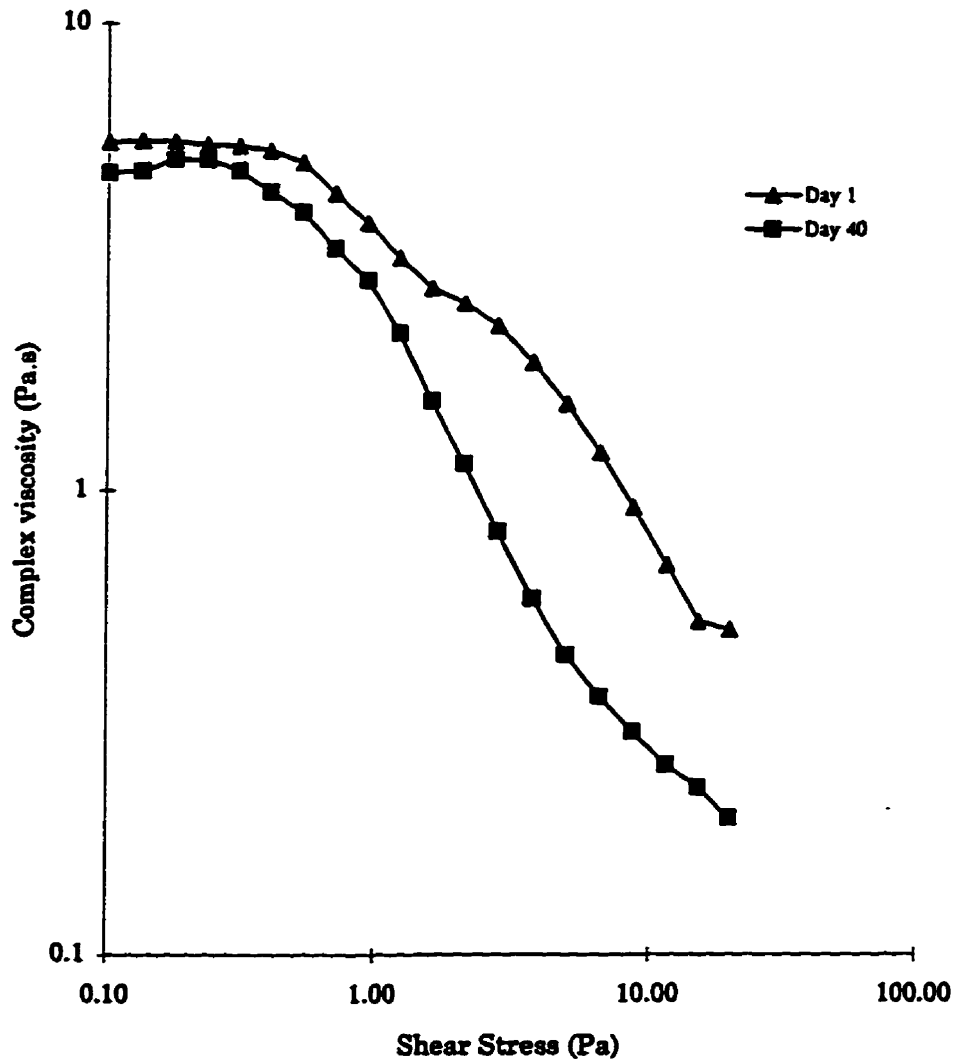


Figure 5.06. Effect of aging on complex viscosity of sample containing 0.75% flaxseed gum; 2.5% salt at pH 4.

Table 5.04. Effect of gum concentration at a constant pH 4 and salt concentration 2.5% on dynamic measurements: phase angle (δ) and complex viscosity (η*)

Day	Treatment					
	0% gum		0.75% gum		1.5% gum	
	δ	η*(Pa.s)	δ	η*(Pa.s)	δ	η*(Pa.s)
1	68.6	0.13	36.9	6.61	29.7	37.2
5	75.0	0.09	39.3	6.41	31.8	39.0
10	77.2	0.08	46.3	5.07	33.0	36.9
20	78.6	0.07	47.9	4.81	33.1	33.3
30	79.8	0.06	50.4	4.72	35.1	33.2
40	86.7	0.08	55.1	4.81	35.4	32.1

The effect of pH and aging on the dynamic properties is shown in Table 5.05. The order of increasing viscosity with pH, independent of time, was:

$$pH\ 2 < 4 < 6$$

which corresponds to decreasing mean droplet size. The smaller the mean droplet size, the greater the viscosity (Kiosseoglou and Sherman, 1983; Yilmazer *et al.*, 1991).

Table 5.05. Effect of pH at a constant gum concentration (0.75% w/w) and salt concentration (2.5% w/w) on dynamic measurements: phase angle (δ) and complex viscosity (η*) of emulsions.

Day	Treatment					
	pH 2		pH 4		pH 6	
	δ	η* (Pa.s)	δ	η* (Pa.s)	δ	η* (Pa.s)
1	65.5	1.05	36.9	6.61	46.6	8.32
5	78.3	0.66	39.3	6.41	41.5	10.9
10	78.4	0.60	46.3	5.07	43.2	10.5
30	79.0	0.51	50.4	4.72	47.1	10.2
40	79.9	0.47	55.1	4.81	46.3	10.1

The effect of salt concentration and aging is shown in Table 5.06. As expected, the absence of salt influenced the rheological properties of flaxseed gum containing emulsions. Flaxseed gum is sensitive to electrolytes with a significant viscosity loss observed in the presence of electrolytes (Mazza and Biliaderis, 1989). This would explain why η* is almost 10x greater at 0% (w/w) salt concentration compared to 2.5% (w/w) or 5% (w/w) salt levels. In contrast, there was little difference observed for η* with 2.5% (w/w) or 5% (w/w) salt levels (6.61 Pa.s and 5.49 Pa.s, respectively).

Applying a sinusoidally varying stress in a sample will induce a sinusoidally varying strain response. The difference of phase between the measured strain wave compared to the stress wave which created it is termed the phase angle. In the case of a pure solid, the strain is directly related to the stress applied (Tung, 1988). The strain is said to be in phase with the applied stress and the phase angle is = 0°. If the material is a pure viscous liquid, the strain rate will follow the applied stress. The resultant strain is said to be out of phase with the

Table 5.06. Effect of salt concentration at a constant gum concentration (0.75% w/w) and pH 4 on dynamic measurements: phase angle (δ) and complex viscosity (η*) of oil/water emulsions.

Day	Treatment					
	0% salt		2.5% salt		5% salt	
	δ	η* (Pa.s)	δ	η* (Pa.s)	δ	η* (Pa.s)
1	17.3	68.0	36.9	6.61	34.8	5.49
5	18.9	58.9	39.3	6.41	41.8	4.21
10	18.2	52.3	46.3	5.07	47.1	3.68
30	17.6	51.3	50.4	4.72	49.9	4.73
40	17.9	51.8	55.1	4.81	48.2	4.53

applied stress and the phase angle = 90°. Most real materials combine both components. The closer the phase angle is to 90° , the more fluid like is the sample's behaviour. The predictive model developed for phase angle was considered adequate since it had a high R^2 value (0.84), a low CV and had a significant model term at the 5% level; however, phase angle did show a significant lack of fit, suggesting that the second order model was not adequate for this parameter. Superimposing the predicted and the residual values, discrepancies of a size that was important at the extremes of the experimental design were observed (Appendix C3); therefore, interpretation at these values will be avoided. Response surface plots were generated even though a significant lack of fit was found for the model. The model developed offered a reasonable interpretation in the effort to model phase angle responses in model salad dressings, especially around the centre point of the design.

As shown in Figure 5.07, gum concentration and pH had a significant effect on phase angle. As would be expected, increasing the gum concentration changed the sample from a viscous (high

δ) to a predominantly elastic system (low δ). The exception was at pH 2 where gum concentration had little effect on the phase angle. At this pH, solvent quality is significantly reduced hampering the gum's ability to extend its chain conformation resulting in a reduced effect volume (Mazza and Biliaderis, 1989). As gum concentration increased from 0% to 1.5% (w/w), the phase angle decreased from 68.6 (fluid system) to 29.7 (Table 5.04). Phase angle mimics the results obtained for complex viscosity in terms of pH and salt effect. As the pH increased, an increase in structure on account of an extended polymer chain conformation is observed. A lower phase angle results. As salt increased, the emulsion shifted from a more solid material (δ = 17.3) to a more fluid system (δ = 34.8). The most stable pH in terms of low phase angle is at a pH 4.6, the pH around the egg protein's isoelectric point.

Phase angle increased with aging regardless of independent variable, shifting from an elastic to a more prominently viscous material regardless of treatment (Table 5.04, 5.05 and 5.06). Changes in phase angle and complex viscosity as the emulsion ages are attributed to a loss of network structure in the sample due to either flocculation or coalescence (Pettitt *et al.*, 1995). The loss of structure is reflected in changes in phase angle as well as the other viscoelastic parameters as the sample ages (Vernon-Carter and Sherman, 1980).

Along with phase angle and complex viscosity, all model salad dressings were assessed using frequency sweeps to further elucidate their viscoelastic profile. The storage modulus (G') increased with increasing concentration of gum. Three typical dynamic profiles were observed for the treatments. Table 5.07 shows three treatments displaying the three typical profiles and the effect of aging on these emulsions. The low viscosity samples exhibited typical dilute solution response with the loss modulus (G") being greater than the storage modulus (G') over the entire frequency range tested (Table 5.07). This profile did not alter over the storage period.

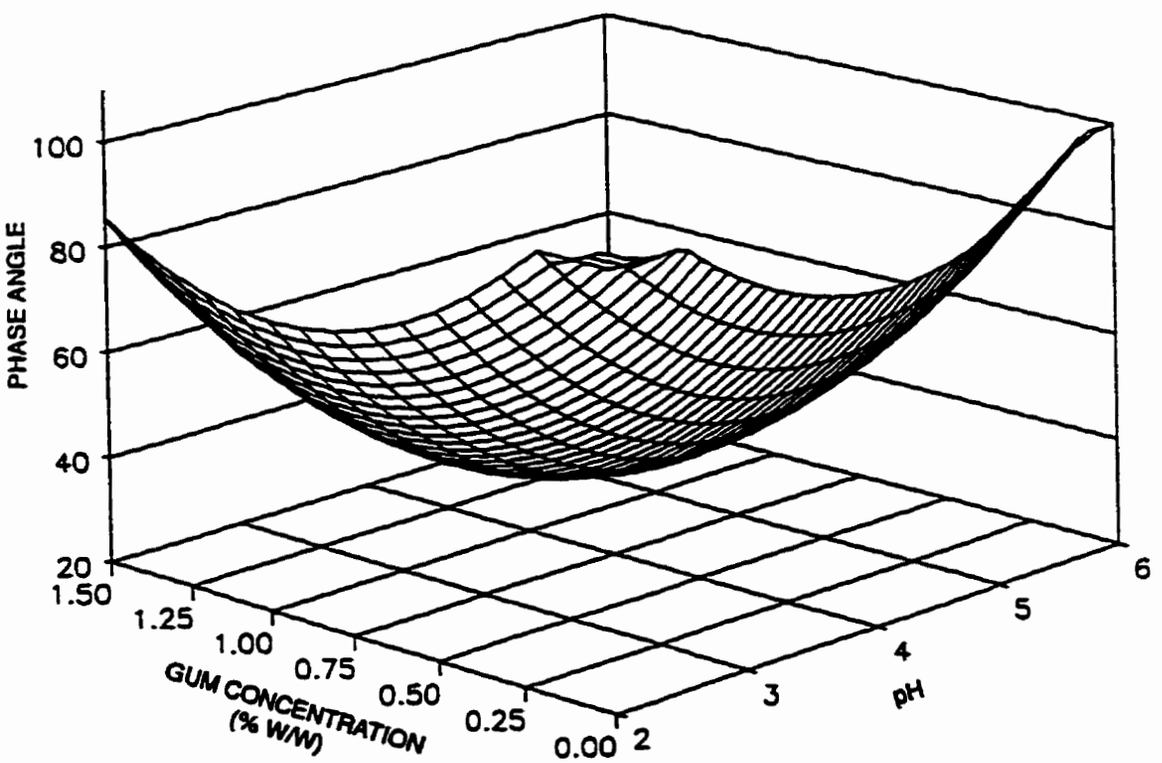


Figure 5.07. Response surface plot for the effect of gum and pH on phase angle at a salt concentration of 2.5%. Day one of aging.

Table 5.07. Effect of aging on frequency (ω) in model salad dressings.

Day	0% gum; 2.5% salt; pH 4 (run 9)	0.75% gum; 2.5% salt; pH 4 (run 17)	1.5% gum; 2.5% salt; pH 4 (run 10)
	ω	ω	ω
1	G">G'	2.51*	G'>G"
5	G">G'	1.29	G'>G"
10	G">G'	0.93	G'>G"
20	G">G'	0.76	G'>G"
30	G">G'	0.34	G'>G"
40	G">G'	0.20	G'>G"

*frequency value (Hz) at which G" crosses over to become greater than G'

In contrast, the high gum concentration samples exhibited typical 'weak gel' properties where the storage modulus (G') is greater than that of loss modulus (G") over the entire frequency investigated (Table 5.07). Typical rheological profiles for samples in the mid-range viscosity is shown in Figure 5.08. The storage modulus is higher than the loss modulus at lower frequencies with a crossover occurring that has the G" greater than G' at higher frequencies. The reverse is true in typical viscoelastic fluids; however, due to the complexity of the model salad dressing, one should not compare it to the simple aqueous rheological profile. Pettitt *et al.*, (1995) suggested the possibility that the elasticity of the oil droplets suspended in the aqueous phase dominates the measured viscoelasticity thereby masking the viscoelastic effects of the hydrocolloid. As the emulsion ages, G' and G" decrease as well, the crossover frequency shifts to the left (Figure 5.08).

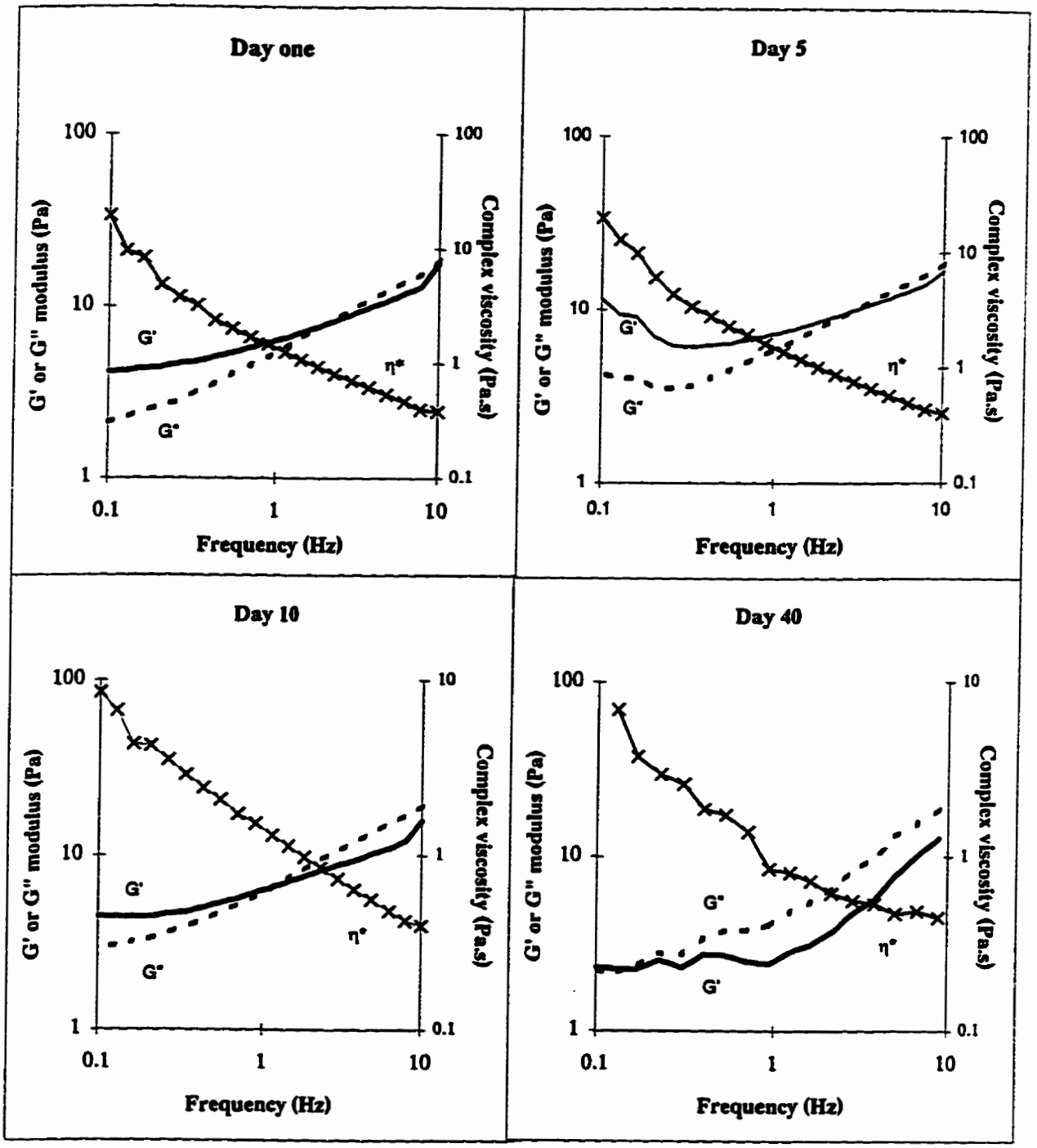


Figure 5.08. Frequency sweep of 0.75% flaxseed gum; 2.5% salt model oil in water salad dressing emulsion at pH 4 as a function of aging (25 °C)

Moving towards a lower frequency signified a reduced degree of entanglement. The reduced degree of entanglement is confirmed by the increasing phase angle (Table 5.04). For 0.75% gum concentration, 2.5% salt concentration and pH 4 (run 17), the frequency crossover moved from 2.5 Hz to 0.2 Hz with a corresponding shift in phase angle from a semi-elastic value of 36.1 to a more viscous phase angle of 55.1 after 40 days.

5.4.6. Creep Parameters

In Figure 5.09, a typical creep compliance curve of a low viscosity and a high viscosity model salad dressing is shown. A levelling off is observed with the high viscosity sample indicating that a higher stress would be required for this sample to reach viscous flow (Figure 5.09B). The predictive models designed for the creep parameters: Newtonian viscosity (η_N) and the instantaneous elastic modulus (Eo), were considered less predictive even though they possessed a significant model value. These parameters possessed a significant lack of fit ($p<.01$), a moderate R^2 (0.79 and 0.77, respectively) and a relatively high CV (79.9 and 84.4 respectively). The significant lack-of-fit suggests that the second-order model was not adequate. That is, there was variation due to a possible missing component (eg. cubic effects) observed other than due to random effects. Overlaying the predicted and the residual data values showed a significant difference at the outer limits of the experimental design (Appendix C3). The predicted values were significantly higher than the experimental values at values of gum concentration 0.3% or lower. Response surface plots were generated for both of these parameters; even though, a significant lack of fit was found for both models. Consequently, firm statements can not be made. Nevertheless, because of the moderate R^2 value and significant model F-ratios, the model developed still offered a reasonable and meaningful starting point in determining emulsion stability.

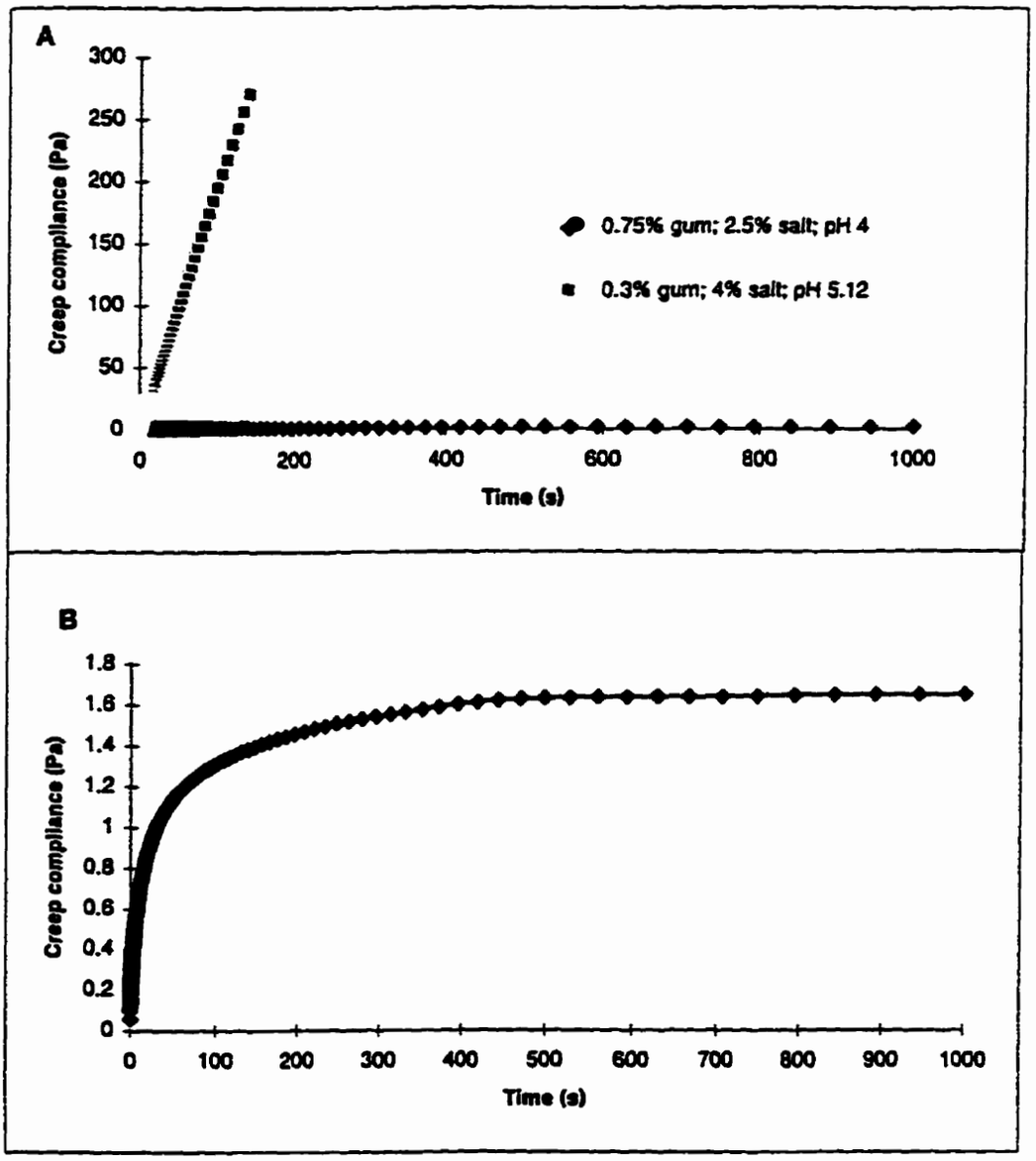


Figure 5.09. A) Typical creep compliance curve of a low viscosity and a high viscosity oil in water emulsion on day one (25°C). B) the same high viscosity sample illustrating the levelling off of the curve.

Creep/recovery measurements are indicative of breaking and reformation of secondary bond network (Zosel, 1982). Figure 5.10 details the influence of salt and gum concentration at constant pH on the viscoelastic parameter, η_N. As would be expected, parameter values increase significantly when flaxseed gum was incorporated into the emulsion formulation. Because the model does not accurately predict at low gum concentration, firm statements can not be made. Table 5.08 shows the effect of gum concentration and aging on the creep parameters: Newtonian viscosity (η_N) and instantaneous elastic modulus (Eo). As expected, Newtonian viscosity (η_N) increased from 0.14 Pa.s for 0% gum concentration to 1.3 x10^5 Pa.s for 1.5% flaxseed gum containing emulsion. The larger mean droplet size for 0% flaxseed gum (1.31μm) compared to the treatments containing flaxseed gum was likely a contributing factor to the lower η_N (Table 5.03). The independent variable, gum concentration, was significant ($p<0.05$) (Table 5.02).

Table 5.08. Effect of flaxseed gum concentration at pH 4 and 2.5% (w/w) salt concentration on creep parameters Newtonian viscosity (η_N) and instantaneous modulus (Eo) with respect to aging of the emulsions (stored at 25°C).

day	Treatment					
	0% (w/w) gum		0.75% (w/w) gum		1.5% (w/w) gum	
	η_N (Pa.s)	Eo (Pa)	η_N (Pa.s)	Eo (Pa)	η_N (Pa.s)	Eo (Pa)
1	0.14	0	2.9×10^4	31.4	1.3×10^5	167.0
5	0.10	0	3.1×10^4	18.8	6.9×10^4	480.8
10	0.08	0	2.5×10^4	17.9	5.3×10^4	52.9
20	0.03	0	2.6×10^4	18.2	4.3×10^4	49.4
30	0.03	0	2.5×10^4	17.9	3.2×10^4	37.0
40	0.03	0	2.5×10^4	17.6	3.0×10^4	34.3

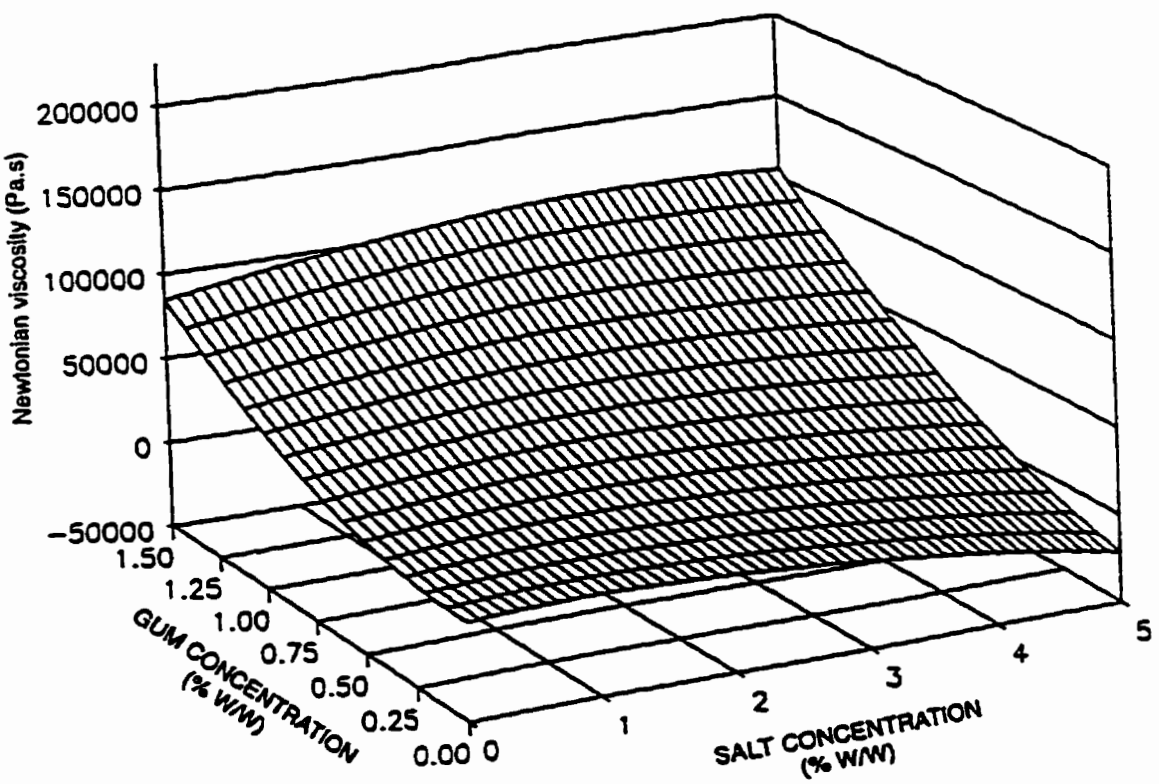


Figure 5.10. Response surface plot for the effect of gum concentration and salt concentration at pH 4 on Newtonian viscosity (Day one).

The influence of adding salt to the creep parameters in the presence of 0.75% (w/w) flaxseed gum at pH 4 is shown in Table 5.09 with the response surface plot shown in Figure 5.10. The absence of salt influenced the rheological properties of the flaxseed gum as shown by a higher η_N (4.8×10^4 Pa.s) compared to 2.5% (w/w) salt ($\eta_N = 2.9 \times 10^4$ Pa.s). This was also confirmed by the results from the dynamic rheological analysis (Table 5.06). There was little difference in η_N for 2.5% and 5% (w/w) salt. This was to be expected due to their similar initial mean droplet size (0.90μm) (Table 5.03). As the emulsion aged, η_N increased in the first 5 days then progressively decreased. Again, this can be assumed to be due to configurational adjustment. Flaxseed gum was hydrated overnight to ensure maximum hydration (and viscosity) prior to the salt addition. In this case, salt addition would effect the cross linking network (Eo) more so than the viscosity. After 40 days of aging, 5% (w/w) salt recorded a lower η_N which can be explained on account of the larger mean droplet size (Table 5.03).

Table 5.10 summarizes the influence of pH on the viscoelastic parameters of emulsions containing 0.75% (w/w) flaxseed gum and 2.5% (w/w) salt. The values of the creep parameters were influenced significantly by pH. Emulsions at pH 6 had a higher η_N and a smaller initial mean droplet size (Table 5.03). The order of increasing η_N independent of time was:

$$2<4<6$$

The creep parameters for pH 2 and 4 reached their maximum values soon after preparation (Table 5.10). At pH 6, maximum η_N was reached at day 5. This was to be expected as it has been reported that flaxseed gum is at its most expanded form at pH 6-7 (Mazza and Biliaderis, 1989). The polymer will therefore, adsorbed more slowly then when it is in a compact form. In the extended form, a finite time would be required for configuration readjustments after adsorption at the oil interface. Similar observations were seen for mesquite gum stabilized

Table 5.09. Effect of salt concentration and aging on creep parameters : Newtonian viscosity (η_N) and instantaneous elastic modulus (Eo) on 0.75% (w/w) flaxseed gum containing model oil in water emulsions at pH 4 stored at 25°C.

Day	Treatment					
	0% (w/w) salt		2.5% (w/w) salt		5% (w/w) salt	
	η_N (Pa.s)	Eo (Pa)	η_N (Pa.s)	Eo (Pa)	η_N (Pa.s)	Eo (Pa)
1	4.8×10^4	87.3	2.9×10^4	31.4	2.1×10^4	27.9
5	5.0×10^4	40.5	3.1×10^4	18.8	5.4×10^4	32.1
10	2.4×10^4	38.5	2.5×10^4	17.9	5.0×10^4	26.1
20	2.2×10^4	37.7	2.6×10^4	18.2	3.4×10^4	25.0
40	1.9×10^4	38.2	2.5×10^4	17.6	4.4×10^3	21.0

emulsions after 5 days of aging (Vernon-Carter and Sherman, 1980). The more compact polysaccharide form at pH 2 or pH 4 would be unable to readjust to any degree following adsorption hence progressively lower values as the emulsion ages.

It is also feasible, especially in the case of pH 2, that the hydration of flaxseed gum in the acidic medium cleaved the polymer reducing the overall viscosity and the potential for crosslinking between adjacent polymers (as would be reflected by a very low elastic modulus). Hydration of gums in low pH media has been known to reduce the viscosity of other polysaccharides due to acid hydrolysis (Paredes *et al.*, 1989).

The response surface plot for gum concentration and pH at a constant salt concentration (2.5% w/w) for Newtonian viscosity is shown in Figure 5.11. The range in η_N from low to high gum concentration increases as the pH increases. At 0% gum concentration, egg yolk contributes to the stability and viscosity of the oil in water emulsion. The rheological behaviour of this sample is predominantly due to the oil fraction and the egg yolk protein. When salt levels increase in

Table 5.10. Effect of pH and aging on creep parameters: Newtonian viscosity (η_N) and instantaneous elastic modulus (Eo) on 0.75% (w/w) flaxseed gum and 2.5% (w/w) salt containing model oil in water emulsions stored at 25°C.

Day	Treatment					
	pH 2		pH 4		pH 6	
	η_N (Pa.s)	Eo (Pa)	η_N (Pa.s)	Eo (Pa)	η_N (Pa.s)	Eo (Pa)
1	1.1	0.83	2.9×10^4	31.4	4.8×10^4	30.0
5	0.9	0.81	3.1×10^4	18.8	9.4×10^4	37.0
10	0.8	0.82	2.5×10^4	17.9	8.1×10^4	33.3
20	0.7	0.81	2.6×10^4	18.2	6.4×10^4	32.3
30	0.3	0.79	2.5×10^4	17.9	6.3×10^4	29.1
40	0.3	0.75	2.5×10^4	17.6	6.3×10^4	17.9

the 0% gum treatment, η_N also increases (Figure 5.10). This is to be expected on account of in the absence of salt, the egg yolk granules remain intact with fewer protein segments available for adsorption and/or crosslinking between adjacent proteins adsorbed on other droplets (Kiosseoglou and Sherman, 1983). In Figure 5.11, a slight increase in η_N for the 0% flaxseed gum treatment is seen at pH ca. 4.6, the isoelectric point for egg yolk proteins. This is consistent with Kiosseoglou and Sherman's (1983) findings for egg protein stabilized o/w emulsions. These researchers reported that the independent variable pH exerted a greater effect on the emulsion's viscoelastic parameters than salt concentration which is consistent with our results. The maximum film strength of pure protein has been oberved at or near the protein's pI (Walstra, 1988). It is the primary reason for optimum stability of pure protein stabilized foams (Ahmed and Dickinson, 1991). Although many proteins (eg. β-casein, β-lactoglobulin, gelatin) give stable emulsions near their isoelectric pH, others (eg. soybean) lose their stabilizing property (Ahmed and Dickinson, 1991; Kiosseoglou and Doxastakis, 1988).

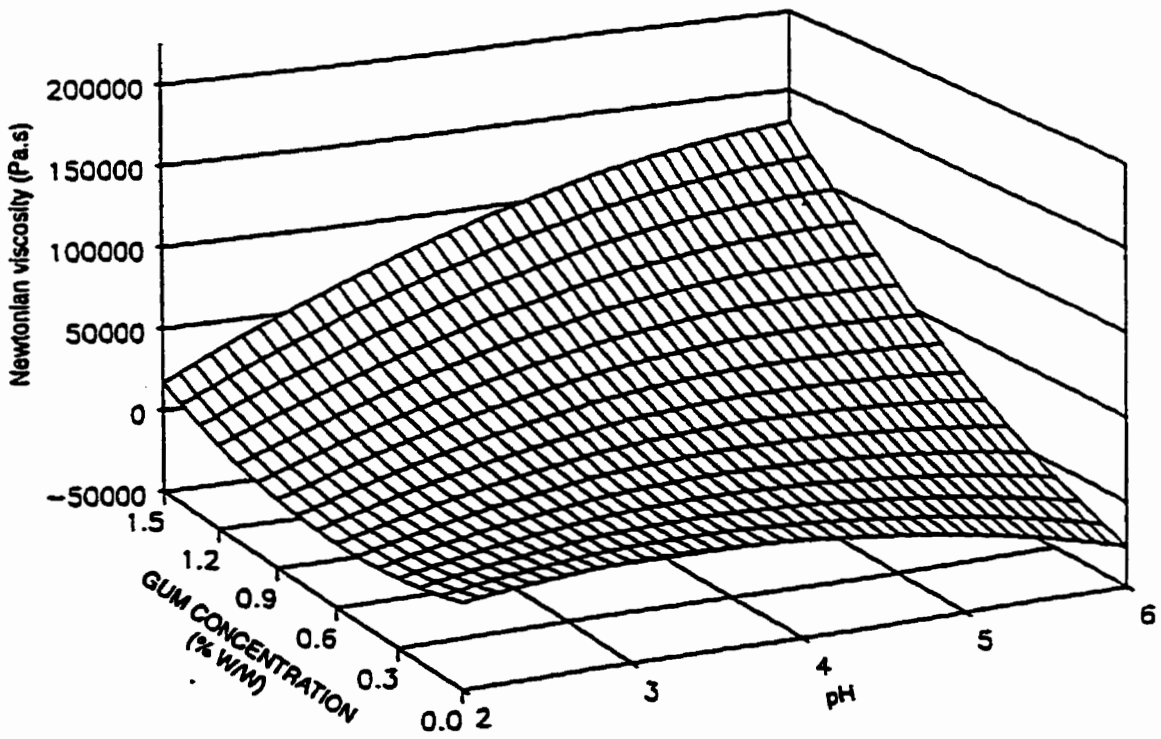


Figure 5.11. Response surface plot for the effect of flaxseed gum concentration and pH on Newtonian viscosity at 2.5% (w/w) salt concentrations. Day one of testing.

A high elastic modulus (Eo) will stabilize the salad dressing and suspend any spices in the emulsion (Paredes *et al.*, 1989). Eo reflects the strength of the network before cross links begin to rupture (Vernon-Carter and Sherman, 1980). Therefore, the elasticity and not the viscosity of the model salad dressing is what imparts stability by holding the dispersed phase "in place" and creating an increased yield stress for the emulsion (Paredes *et al.*, 1989). It is well understood from the non-Newtonian flow behaviour and the viscoelastic data, that flaxseed gum can establish cross linked structures in aqueous solutions (Cui *et al.*, 1994ab). It has already been shown for gum acacia and mesquite tree gum, that the films at the water-oil interface result from cross linking of adsorbed polymer molecules by hydrogen bonds (Shotton and White, 1963; Vernon-Carter and Sherman, 1980). Interpenetration between polymer molecules physically prevents oil droplets from coming together.

The crosslinks formed by flaxseed gum adsorbed on adjacent oil droplets within a flocculate will influence Eo. It was therefore expected that increasing the flaxseed gum concentration would increase Eo. Figure 5.12 shows the response surface plot for the effect of gum concentration and salt concentration at a constant pH on instantaneous elastic modulus. As is the case for Newtonian viscosity, the elastic modulus increases significantly when flaxseed is incorporated into the emulsion formulation. The independent variable, gum concentration is significant ($p<0.5$) (Table 5.02). Even though the model was significant ($p<0.10$), the instantaneous elastic modulus showed a significant lack-of-fit error which suggests the possibility of a missing component. Firm statements on the overall process, therefore, can not be made on just the above analysis. Table 5.08 summarizes the effect of gum concentration on the instantaneous elastic modulus. As gum concentration increased from 0% to 0.75% to 1.5% (w/w), the corresponding Eo value shifted from 0 Pa to 31.4 Pa to finally 167 Pa (Table 5.08). Without flaxseed gum, network formation is reduced. The Newtonian viscosity constitutes the main contribution to the overall creep compliance (Sherman, 1966). Consequently, no substantial

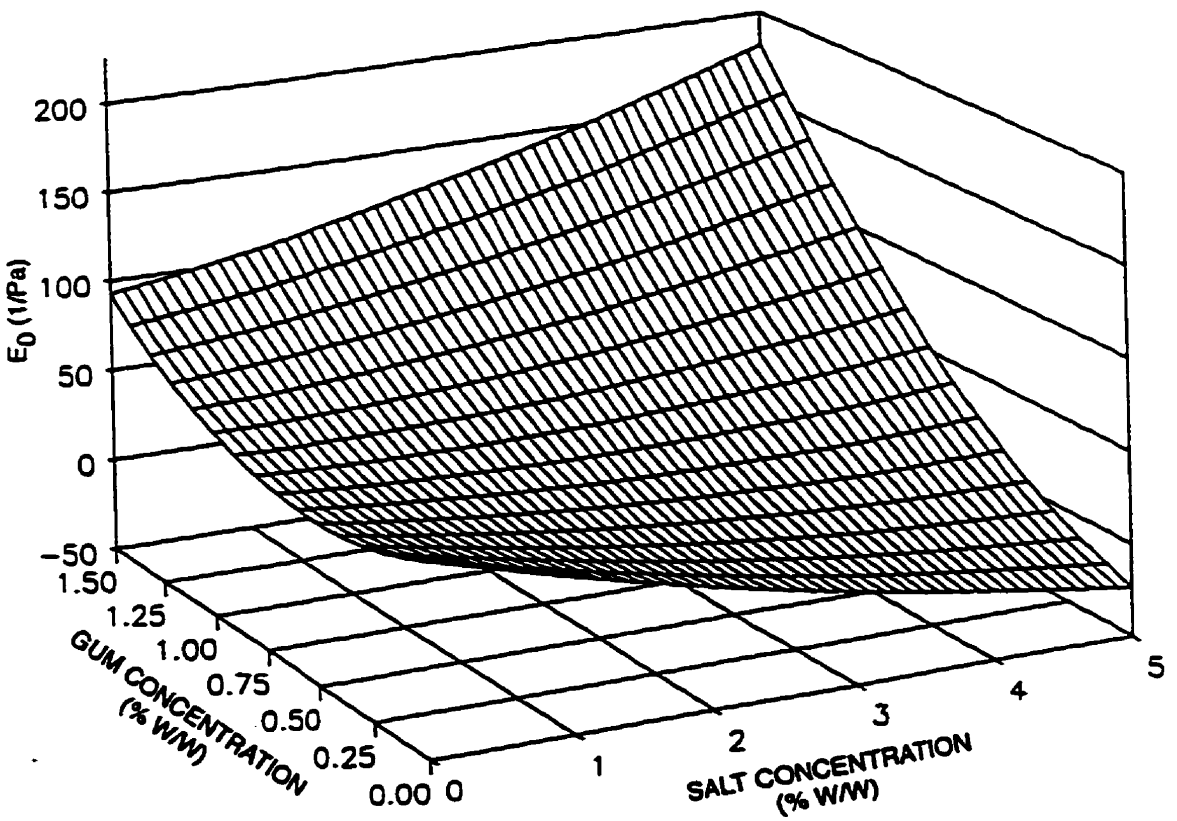


Figure 5.12. Response surface plot on the effect of flaxseed gum and salt concentration on the Instantaneous elastic modulus (Eo) at a pH 4. Day one of testing.

recovery is noticed (Table 5.08). Confirming the Newtonian viscosity data, Eo increased significantly at day 5 for 1.5% (w/w) flaxseed gum. As the emulsion aged, the protruding segments of the flaxseed gum projecting outwards into the aqueous phase, can overlap and form crosslinks. The most dramatic changes in creep compliance of model salad dressings occur during the first week of storage. This trend was consistent with other reports (Vernon-Carter and Sherman, 1980; Paredes *et al.*, 1989; Yilmazer *et al.*, 1991). Once the emulsion is prepared, oil droplets begin to flocculate and form a three dimensional network with viscoelastic behaviour (Kisseoglou and Sherman, 1983). The distance separating the droplets is dependent on three components: van der Waal's attraction, electrostatic repulsion and steric repulsion (Walstra, 1987). The rate of flocculation will therefore be influenced by the rate at which the proteins will adsorb at the oil/water interface, unfold and interact with other proteins on adjacent droplets to form a network (Kisseoglou and Sherman, 1983). If the hydrocolloid is in an expanded form either attributed to a low salt or neutral pH environment, the polymer will adsorb more slowly to the oil/water interface compared to a more compact configuration due to configurational readjustments (Vernon-Carter and Sherman, 1980). Because the viscoelastic parameters for some of the samples reached their maximum values soon after preparation on account of a more compact polymer configuration, it is suggested that flocculation proceeds rapidly and coalescence is the dominant process (Kisseoglou and Sherman, 1983). Overall, the process leads to a further decrease in the viscoelastic parameters. Paredes *et al.* (1989) reported smaller sized oil droplets coalesce into larger ones during the initial two to three days aging to correspond to the significant changes in the viscoelastic parameters. The change in rheological properties during storage, therefore, is dependent on the balance between the rate of droplet coalescence and the stabilizing ability of the gum layers in adjacent oil droplets to interpenetrate and form new networks.

The probability of entanglements will be higher when the adsorbed polymer is in the expanded

form (Vernon-Carter and Sherman, 1980). Flaxseed gum is at it's most expanded form at the pH range between 5 and 8 (Mazza and Biliaderis, 1989). Consequently, the increase in the strength of the polysaccharide network and in the viscoelastic response is observed in this pH explaining why Eo is highest at pH 6 (Table 5.10) and at 0% (w/w) salt concentration (Table 5.09). The Eo of emulsions at pH 6 therefore increased as the emulsion aged to a larger extent than for emulsions at other pH's (which would favour a more compact polymer thereby retarding potential crosslinkages). At pH 2, the potential for acid hydrolysis of the polysaccharide is increased (Paredes *et al.*, 1989). Acid hydrolysis would cleave the polysaccharide reducing the potential for crosslinking as reflected by a low instantaneous elastic modulus (Table 5.10).

When a treatment did not reach viscous flow under a 0.45 Pa stress, a higher stress (6.25 Pa) was applied. The samples that reached viscous flow within the specified time were runs 1 through 5, run 9 and run 11. These treatments did not receive the higher stress and coincidently, were also the ones that creamed (Figure 5.02). Employing Stokes' Law (eq. 2) the rate of individual particle velocity (ie. creaming) is dependent on the viscosity of the aqueous phase (Walstra, 1987). The lower the viscosity of the sample, the greater potential for creaming. The one exception was the sample containing 1.2% (w/w) flaxseed gum, 4% (w/w) salt at a pH 2.81. Table 5.11 summarized the effect of the two different stresses on this treatment.

Using the 6.25 Pa shear stress, the first obvious difference is the decreased creep parameters. On day one of aging, η_N had a value of 1.8×10^4 Pa.s at 0.45 Pa shear stress compared to 1.62 Pa.s using 6.25 Pa.s. The fact that this sample and the others like it that could not reach viscous flow suggests that there was a measurable yield stress for these samples and that the

Table 5.11. Effect of shear stress on the creep parameters (Newtonian viscosity , η_N, and Instantaneous elastic modulus, Eo) for the emulsion containing 1.2% (w/w) flaxseed gum, 4% (w/w) salt and pH 2.81.

Day	Shear stress (0.45 Pa)		Shear Stress (6.25 Pa)	
	η_N (Pa.s)	Eo (Pa)	η_N (Pa.s)	Eo (Pa)
1	1.8×10^4	63.7	1.6	6.54
5	1.4×10^5	225.7	1.3	8.07
10	3.8×10^4	184.5	1.2	8.13
20	2.2×10^4	84.0	1.2	8.33
30	1.6×10^4	75.3	1.2	0
40	1.1×10^4	73.8	1.1	0

stress used (0.45 Pa) was well below this point. Pettitt *et al.*, (1995) believe the observance of a significant yield stress provides emulsion stability. Interestingly, for run 6 (1.2% w/w flaxseed gum; 4% w/w salt; pH 2.81) with the higher shear stress (6.25 Pa) on day 30 (ca. 720 h), the observed Eo is zero. It was around this time frame when this sample started to cream (Figure 5.02). This supports the hypothesis of acid hydrolysis of the polymer chain.

Emulsion samples containing low gum concentrations showed Newtonian viscosities comparable to complex viscosities at the low shear plateau (Table 5.01). For run 3 (0.3% flaxseed gum, pH 5.12 and 1% salt concentration), low shear viscosity was 0.436 Pa.s and Newtonian viscosity was 0.484 Pa.s. The model salad dressings that contained moderate to high gum concentrations displayed behaviour similar to that of a viscoelastic solid at the low shear creep study. This is shown by an observed compliance approaching a limiting or equilibrium value (Zosel, 1982). The stress-strain relationship of a typical elastic liquid that has a viscosity of up to ten powers

of ten higher than the value observed at higher shear stresses, indicates that the coagulated structure does not behave like a rigid gel but as an elastic liquid (Zosel, 1982). For these plastic-like systems, discrepancies between viscosities at low shear rates (as is the case for creep measurements taken for these moderate to high flaxseed gum treatments at 0.45 Pa) and dynamic viscosities at low frequencies were observed. For example, run 8 (1.2% flaxseed gum, 4% salt concentration at a pH 5.12) had a low shear viscosity of 24 Pa.s but a Newtonian viscosity of 64 000 Pa.s. Discrepancies between viscosities are attributed to the different ways in which the flocculated particle network breaks down and reforms under the influence of oscillatory shear. The dependence of viscosity on the rate of shear is connected to the structural changes of the network caused by shearing forces (Sherman, 1968). When liquids have a yield stress below a certain stress, no flow (ie. no structural changes due to a dynamic equilibrium of bond breaking and reforming) takes place and viscosity is very large because the shear rate is very small (Zosel, 1982). Frequency dependence of dynamic viscosity originates from the relaxation of the network structure (Sherman, 1968). When the high viscosity samples were tested at 6.25 Pa, the Newtonian viscosities were more comparable to the low shear viscosities in oscillation mode.

5.4.7. Model Verification

For verification purposes, two emulsions were prepared. Sample 1 contained 0.45% flaxseed gum and 2% salt with an emulsion pH of 3.8. The second sample contained 1% flaxseed gum and 2% salt with an emulsion pH of 4.54. Both emulsions maintained a constant 0.4 (oil volume/emulsion volume) ratio. Surface tension and low shear viscosity were not tested in the confirmation since both models recorded low R^2, were insignificant ($p>0.15$) and had significant

Table 5.12. Verification test for the observed and the predicted reponse variables using the second order polynomial equation.

Variable	Treatment			
	0.45% gum; 2% salt; pH 3.8		1% gum; 2% salt; pH 4.54	
	expected	observed	expected	observed
phase angle	49.4	44.3	28.1	31.7
Newtonian viscosity (Pa.s)	13 868	56.5*	42 168	47 736*
Eo (Pa)	18.1	3.85*	57.3	69.2
ΔE	10.2	9.7	9.5	10.3
mean droplet diameter (μm)	0.98	1.09	0.75	0.88

* comparisons that are statistically different at the 0.05 level as determined by a Chi Square Test.

lack-of-fit error. Observed and predicted values of the second order polynomial equations are compared (Table 5.12). Results show that observed and predicted values for phase angle, colour difference and mean volume diameter were not significantly different indicating that the equations (Table 5.02) could be used to predict the actual relationship. Both confirmation tests observed a significant difference for creep viscosity. This was to be expected on account of the low R^2 value (0.79) for this parameter (Table 5.02). For the 0.45% (w/w) gum concentration confirmation sample, there was a significant difference between observed and expected values for the instantaneous elastic modulus. It was speculated that the 0.45% flaxseed gum was still not sufficient to cover the entire oil droplet hence bridging flocculation occurred. There was a significant lack-of-fit for this parameter and this sample may have fallen outside the limits of the model. This hypothesis was confirmed with a second sample tested whose gum concentration was 1% (w/w). There was no significant difference between observed and expected values for the Eo parameter for the 1% flaxseed gum formulation.

5.4.8. Effect of other Hydrocolloids and Fresh Egg Yolk as an Emulsifier

A higher stress (6.25 Pa) was used for the following emulsions to allow them to reach viscous flow in the required time. All of the emulsions that required a higher stress to reach viscous flow were stable with regards to no observed creaming and low droplet coalescence rate. Results of colour difference, phase angle, complex viscosity (η^*) at the low shear plateau, Newtonian viscosity (η_N), Instantaneous elastic modulus (Eo), mean droplet diameter and creaming rate for the emulsions prepared by different gums or by using fresh egg as the emulsifier are shown in Table 5.13.

There were no significant difference in colour difference, phase angle, complex viscosity, Newtonian viscosity, Eo and inital or final mean droplet size for flaxseed gum cv. Norman and Linola™. This was expected on account of the two gums are said to be rheologically similar (Mazza *et al.*, 1994).

The 0.75% (w/w) xanthan gum treatment was the only sample that still showed the compliance levelling off to a horizontal curve. The formulations containing 0.75% xanthan gum registered the lowest phase angle as well as the highest complex viscosity, Newtonian viscosity, instantaneous modulus and the lowest mean droplet diameter. At equal solids concentration, xanthan gum had significantly higher viscosity compared to flaxseed gum therefore, it would be expected to have higher viscoelastic parameters and behave as a predominantly elastic material (Mazza and Biliaderis, 1989). Our results confirm the findings of Coia and Stauffer (1987).

The model emulsion that contained 0.3% xanthan gum recorded a lower phase angle (ie. a more elastic material) which corresponded to a higher complex viscosity (21.4 Pa.s) compared to the

flaxseed gum cv. Norman sample (Table 5.13). Evidently, the replacement ratio of 2.5 flaxseed gum to 1 xanthan gum was not sufficient and a higher ratio should have been used. Even though there was an observed difference in Newtonian viscosity, 0.3% (w/w) xanthan gum and 0.75% (w/w) flaxseed gum stabilized emulsions had similar Eo, mean droplet size and coalescence rate. It was assumed that due to the similar mean droplet size the samples should have had similar Newtonian viscosities. No explanation for this difference in η_N is readily apparent. It is possible that the xanthan gum formulated emulsion had larger flocculated aggreates which would relate to a larger viscosity. Parker and coworkers (1995) suggested that depletion flocculation induced by xanthan gum leads to the formation of a particle network.

For colour difference, only the fresh egg treatment was significantly different from the other samples with a value of 9.01. This would be expected since all gums have relatively similar colour hues. To account for moisture difference between the fresh and dried egg yolk, 4% (w/w) of the fresh yolk replaced 2% (w/w) dried egg yolk. The bright yellow protein would make a significant difference to the colour. Fresh egg yolk recorded similar dynamic tests (ie. η^* and phase angle) compared to the cv. Norman flaxseed gum emulsion contain 2% (w/w) dried egg yolk (Table 5.13). In contrast, a significant lower Newtonian viscosity but similar Eo was observed for the fresh egg yolk sample. No obvious explanation for the difference in η_N is apparent. The fresh egg yolk emulsion did have a smaller initial (0.56 μm) and final (0.61μm) mean droplet size although the rates of droplet coalescence was the same for both treatments

Table 5.13. Tukey's Standardized test for the dependent response variables between treatments of different hydrocolloids and fresh egg emulsifier.

Response Variable	Treatment				
	0.75% Norman	0.75% Linola™	0.75% Xanthan	0.3% Xanthan	Fresh Egg
colour difference	11.1^{b}	11.3^{b}	11.6^{b}	11.6^{b}	9.01^{a}
phase angle	36.0^{c}	35.2^{c}	16.1^{a}	33.5^{b}	36.3^{c}
Complex viscosity, η^* (Pa.s)	7.08^{c}	7.49^{c}	177.5^{a}	21.4^{b}	10.1^{c}
Newtonian viscosity, η_N (Pa.s)	2.73^{c}	1.55^{c}	$52\ 500^{a}$	8.9^{b}	0.37^{d}
Instantaneous elastic modulus, Eo (Pa)	21.3^{b}	25.3^{b}	102.3^{a}	20.6^{b}	21.3^{b}
Initial Mean droplet size (μm)	0.92^{bc}	0.94^{bc}	0.77^{ab}	1.12^{c}	0.56^{a}
Mean droplet size (day 40)(μm)	0.97^{bc}	1.01^{bc}	0.81^{abc}	1.14^{c}	0.61^{a}
Rate of drop coalescence ($s^{-1} \times 10^{-7}$)	0.43^{a}	0.47^{a}	0.25^{a}	0.13^{a}	0.75^{a}

$^{a-d}$ values in the same row bearing the same superscipt are not significantly different at the $p < 0.05$ level

5.5. Conclusions

The predicted response for seven variables were produced with a combination of flaxseed gum concentration, salt concentration and pH. The degree of emulsion stabilization appears to be more of a function of gum concentration and pH than for salt concentration. Flaxseed gum significantly contributed to the stability and viscosity of model oil in water salad dressings. The independent variable, pH, affected the stability of the emulsion by affecting the configuration of the egg yolk protein and the flaxseed gum. The most stable emulsion occurred at pH 6 and

the least stable at pH 2. At pH 2, the potential for polymer cleavage resulting in increased emulsion instability, increases. Salt contributed to the destabilizing of the flaxseed gum as shown by salt concentrations not significantly altering the solution rheology except at the 0% (w/w) salt level. The addition of salt did improve the functionality of the egg yolk protein.

Due to the presence of the protein fraction, flaxseed gum appears to act as a steric stabilizer by adsorbing at the surface of the egg yolk and coating the emulsion droplets. It is assumed that flocculation which leads to instability occurs via polymer bridging between adjacent emulsion droplets. For stabilization, flaxseed gum must be in sufficient amounts for complete coverage of the droplet. Even with sufficient coverage, the salad dressing can be destabilized if the solvent quality is reduced to the point where the polysaccharide becomes compact. The change in viscosity and elasticity appear to be due to either kinetics of aggregate formation and breakdown or coalescence as demonstrated by whether the mean oil droplet diameter size alters over the 40 day storage. The most stable emulsion was at 0.75% (w/w) flaxseed gum, 2.5% (w/w) salt at pH 4. This emulsion had a low droplet size, low droplet coalescence rate and did not show obvious signs of creaming.

There was no significant difference when Linola™ replaced cv. Norman flaxseed gum. Both emulsions were stable with regards to creaming and coalescence. The 0.75% (w/w) xanthan gum treatment displayed significantly higher viscosities and networking structure compared to flaxseed gum at similar gum concentrations. At lower levels of xanthan gum, slightly higher values were observed possibly due to particle network formation.

As expected, fresh egg yolk stabilized emulsions recorded a greater deviation from the white tile compared to the dried egg yolk stabilized flaxseed gum emulsion. Both fresh and dried egg yolk stabilized emulsion had similar dynamic parameters but differed in Newtonian viscosity. No

apparent explanation could be surmised. Fresh egg yolk emulsion did have smaller inital and final mean droplet size.

6. SUMMARY AND RECOMMENDATIONS

Results of the extraction of flaxseed gum have indicated that it can be used as a potential food gum due to its favourable rheological behaviour, ease of extraction and low cyanogenic glucoside content. This data supports flaxseed's gum shear thinning behaviour. The 2% (w/w) flaxseed gum dispersions did not exhibit typical "weak gel" properties as reported by Cui et al., (1994ab). The loss of this behaviour is likely due to the concentration step. Extraction of the gum under optimum conditions produces a material containing high carbohydrate and low contaminants.

Results of flaxseed gum added to muffin formulations indicate that the gum could easily replace both guar gum and xanthan gums in the formulation. Flaxseed gum improved muffin height and volume without noticeable changes in texture measured by instrumental and sensory test methods. Moisture content and water activity values of muffins stored in plastic bags at room temperature for a seven day period revealed that neither composition of batter nor storage time significantly affected the shelf life of the muffins. There was no evidence of a polysaccharide/ovalubumin complex via electrostatic interaction from the DSC results. There was evidence of the flaxseed gum destabilizing the protein at pH's around that of a muffin formulation. How this in turn might affect muffin quality is not clear. It appears that the primary effect of hydrocolloids is to maintain higher minimum batter viscosities while baking which results in increased muffin volume. The hydrocolloids are able to maintain the foam structure thereby slowing the migration of air bubbles to allow for a uniform texture. The primary impact of this research is that flaxseed gum can be used to replace xanthan gum in muffin formulations at a 5 to 1 ratio to produce muffins of good volume and texture.

Results of the model salad dressing study, indicates that RSM was successfully used to identify the effects of gum concentration, pH and salt concentration on the dependent response

variables: colour difference, phase angle and dispersed particles' mean volume diameter. These models did not meet all the criteria but were a good starting point for understanding the interaction between the independent variables. Additional work will be required to verify and extend the response variables. Models developed for surface tension and low shear viscosity had low predictability. All rheological parameters decreased as the emulsion aged except for phase angle which increased. This indicates a weakening of the structure which may be attributed to the coalescence of small oil droplets into larger ones (Paredes *et al.*, 1989). The degree of emulsion stabilization appears to be a function of gum concentration and pH with salt concentration having a minor role in emulsion stabilization. There is an advantageous stabilizing effect at high gum concentrations with unfavourable destabilization at low polymer concentrations. Flaxseed gum appears to act as a steric stabilizer in model salad dressing emulsions. For stabilization, sufficient adsorbing flaxseed gum is required to cover the particle surface completely or else bridging flocculation will occur. Bridging flocculation is most likely to occur when the polymer concentration is approximately half that required for saturation coverage (Dickinson, 1988). Flocculation may occur in a sterically stabilized system (ie. sufficient polymer load) if the solvent quality of the continuous phase is reduced such as in the case of low pH or high salt concentrations. The flaxseed gum film layer must be sufficient enough to prevent two particles from approaching one another.

As expected, there was no significant difference between cv. Norman and Linola™. Both emulsions were considered stable. Xanthan gum stabilized emulsions displayed higher viscosites and a possible greater degree of network structures. Fresh egg yolk stabilized emulsions deviated from the white colour tile to a greater extent than the dried egg yolk containing emulsion. As well, there was no difference observed with fresh versus dried egg yolk in dynamic parameters or in instantaneous elastic modulus. There was a significant differece in Newtonian viscosity; however, no obvious explanation is apparent. Any potential interaction

may have been electrostatic in nature. The samples compared contained 2.5% salt and perhaps a better experiment to ensure possible interactions would have been to test the emulsifiers under a much lower salt environment.

From the results of the overall study, further investigations might include:

1. documenting possible synergistic effects of flaxseed gum in combination with other commercial gums such as guar or xanthan gum. Most food applications use a combination of gums for cost efficiency, textural considerations, and to expand on the physical and chemical range that additional complementary hydrocolloids can provide. Understanding how flaxseed gum interacts with other hydrocolloids would provide increased options for use in food systems.

2. studying the effect of hydrocolloids on the mixing properties of batters since this application has marketable quality. Expanding on other bakery products such as cakes and breads that have different sugar:flour:liquid ratios as well as using typical dough analytical techniques such as a farinograph or mixograph would provide information more directed to the baking industry.

3. examining the effect of temperature on emulsion stability. Using a refrigeration system to closely monitor a more typical salad dressing environment during aging.

4. studying whether flaxseed gum can stabilize an oil in water emulsion without the aid of egg yolk protein on account of the gums' ability to adhere to the oil/water interface. As well, it would be interesting to see if there was a sufficient amount of egg yolk protein to stabilize the emulsion, how flaxseed gum could compete with the protein for the oil/water interface (and how this would be reflected in the emulsion stability and rheology).

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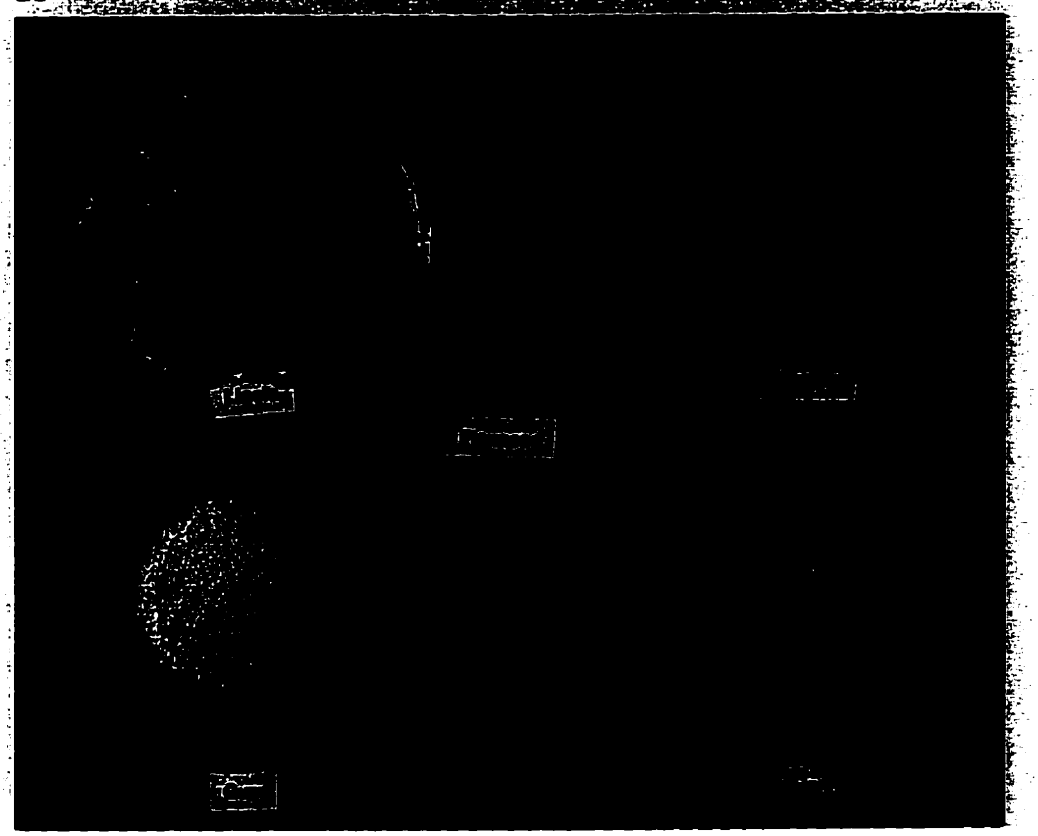
APPENDICES

Appendix A: Flaxseed, C. Norman and Linola with their respective gums



Appendix B 1: Baking order

A = Control (0% hydrocolloid)
B = 0.5% Flaxseed gum formulated muffins
C = 0.1% Xanthan gum formulated muffins
D = 0.1% Guar gum formulated muffins
E = 0.1% Flaxseed gum formulated mufffins

	Conventional Oven	
	Left Hand Side	Right Hand Side
Run 1	A	B
Run 2	C	D
Run 3	E	C
Run 4	C	A
Run 5	B	E
Run 6	D	E
Run 7	A	D
Run 8	B	C
Run 9	E	A
Run 10	D	B

Appendix B 2: Ballot used for sensory evaluation of muffins

Name:

Sample codes:

--------- --------- --------- --------- ---------

Evaluate the samples in the order presented. Place a vertical line across the horizontal line at the point that best describes that property in the sample. Identify the scores by writing the sample code near the vertical line. Compare all samples to the reference (R), which has been positioned on the line.

1. Exterior Colour (muffin top only)

R

----------x----------

light golden dark golden

2. Extent of Browning (muffin top only)

R

----------X----------

low high

3. Surface Roughness (visually assess the degree of abrasiveness of the products surface)

R

----------X----------

low high

4. Degree of Tunnelling air pockets (> 2 mm in dia) that may or may not be circular in shape.

R

----------X----------

low (< 5%) high (> 25%)

5. Sponginess place muffin between thumb and fore finger. Assess the force with which the sample returns to its original size/shape after partial compression.

R

----------X----------

low sponginess high sponginess

6. Degree of Chewing length of time and the amount of force required to prepare the sample for swallowing.

R

----------X----------

low degree high degree

Appendix B 2. Continued.

7. Gumminess the denseness that persists throughout mastication; energy required to prepare the sample for swallowing.

R

----------X----------

low high

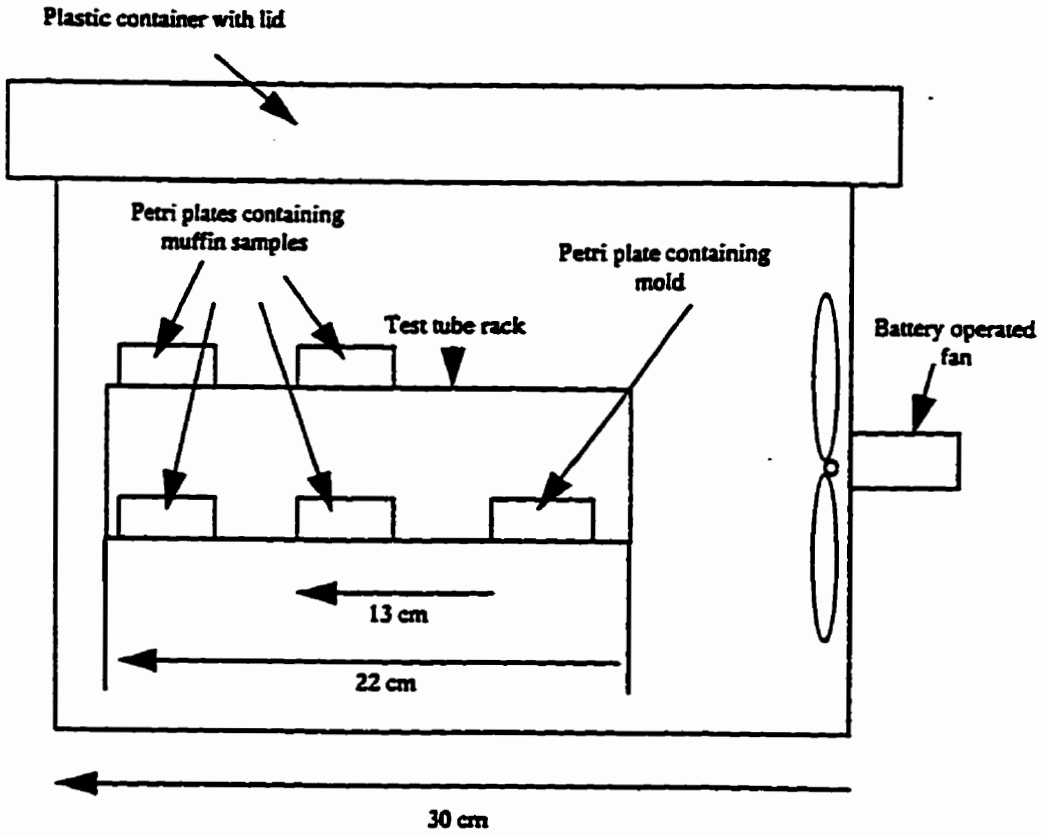
Comments:

Appendix B 3. Potato Dextrose Agar

Recommended for detection and enumeration of yeasts and molds.

Potato extract	**4 g/L**
Glucose	**20 g/L**
Agar	**15 g/L**
pH	**5.6 ± 0.2**

Appendix B 4: Diagram of Muffin molding apparatus



Appendix C 1: Model salad dressing formulation

Dried egg yolk	2 g
Sodium Azide	0.1 g
Gum	A g
Salt	B g
oil/aqueous (C)	100 - (A + B) g
soybean oil (density 0.927 g/mL)	C - E g
aqueous phase	C - D g
Total	100 g

Run	Gum (A)	Salt (B)	oil/aqueous (C)	oil (D)	aqueous (E)	dd H_2O	HAc
1	0.3 g	1g	96.6 g	36.74 g	59.86 g	51.47 g	8.39 g*
2	0.3 g	4 g	95.6 g	35.13 g	58.47 g	54.27 g	4.20 g*
3	0.3 g	1 g	96.6 g	36.74 g	59.86 g	59.26 g	0.6 mL
4	0.3 g	4 g	94.65 g	35.76 g	58.89 g	58.48 g	0.4 mL
5	1.2 g	1 g	95.7 g	36.39 g	59.31 g	58.61 g	0.7 mL
6	1.2 g	4 g	92.7 g	34.79 g	57.91 g	57.31 g	0.6 mL
7	1.2 g	1 g	95.7 g	36.39 g	59.31 g	59.23 g	0.08 mL
8	1.2 g	4 g	92.7 g	34.79 g	57.91 g	57.83 g	0.08 mL
9	0 g	2.5 g	95.4 g	36.04 g	59.36 g	58.96 g	0.4 mL
10	1.5 g	2.5 g	93.9 g	35.48 g	58.42 g	58.02 g	0.4 mL
11	0.75 g	2.5 g	94.65 g	35.76 g	58.89 g	34 g	24.89 g*
12	0.75 g	2.5 g	94.65 g	35.76 g	58.89 g	58.88 g	0.01 mL
13	0.75 g	0 g	97.15 g	37.07 g	60.08 g	59.4 g	0.68 mL
14	0.75 g	5 g	92.15 g	34.43 g	57.72 g	56.94 g	0.78 mL
15	0.75 g	2.5 g	94.65 g	35.76 g	58.89 g	58.49 g	0.4 mL
Linola	0.75 g	2.5 g	94.65 g	35.76 g	58.89 g	58.49 g	0.4 mL
Xanthan	0.75 g	2.5 g	94.65 g	35.76 g	58.89 g	58.29 g	0.6 mL
Xanthan	0.3 g	2.5 g	95.1 g	35.93 g	59.17 g	58.67 g	0.5 mL
Fresh egg	0.75 g	2.5 g	92.65 g	35 g	57.65 g	57.28 g	0.37 mL

*Assumption: less than 1% Acetic acid (HAc) in formulation: 1 gram = 1 mL
Maintain phase ratio = volume of oil/volume of emulsion = 0.400

Density of salt at 20 C (CRC Handbook, 1970-71, 51st ed. pp. D-207)

!% (w/w)	1.0071
2.5% (w/w)	1.0178
4% (w/w)	1.0286
5% (w/w)	1.0359

Maintain phase ratio = volume of oil/volume of emulsion = 0.4

Sample calculations: For run #3 with 1% salt concentration (density = 1.0071)

$$\frac{volume\ of\ oil}{volume\ of\ oil + volume\ of\ HAc + volume\ of\ water}$$

$$\frac{36.74g/0.927\ gL^{-1}}{39.63\ mL + 0.6\ mL + 59.26\ g/1.007gL^{-1}} = 0.399 \approx 0.4$$

Sample calculation 2: run #11 (density of HAc = 1.049gmL^{-1}) with 2.5% salt concentration

$$\frac{35.76\ g/0.927\ gL^{-1}}{38.576\ mL + 24.89g/\ 1.049\ gL^{-1} + 34\ g/1.0178gL^{-1}} = \frac{38.576}{95.708} \approx 0.4$$

Appendix C2: ΔE, L, a, b values for salad dressing emulsions.

Treatment	ΔE	L	a	b
0.3 % gum/ 1% salt/ pH 2.81	13.83	84.77	-0.44	10.24
0.3 % gum/ 4% salt/ pH 2.81	11.23	89.10	-0.42	8.50
0.3 % gum/ 1% salt/ pH 5.12	9.36	91.12	0.13	6.48
0.3 % gum/ 4% salt/ pH 5.12	8.67	90.25	-0.51	5.97
1.2 % gum/ 1% salt/ pH 2.81	32.26	63.65	2.70	15.80
1.2 % gum/ 4% salt/ pH 2.81	28.86	67.65	3.10	15.31
1.2 % gum/ 1% salt/ pH 5.12	11.43	84.79	0.89	7.36
1.2 % gum/ 4% salt/ pH 5.12	12.14	84.07	-0.51	8.01
0 % gum/ 2.5 % salt/ pH 4	9.85	93.77	-2.27	6.96
1.5 % gum/ 2.5 % salt/ pH 4	12.84	88.51	0.34	7.20
0.75 % gum/ 2.5 % salt/ pH 2	41.55	53.31	2.10	16.61
0.75 % gum/ 2.5 % salt/ pH 6	10.17	86.62	-0.11	6.93
0.75 % gum/ 0 % salt/ pH 4	10.36	87.49	0.33	7.30
0.75 % gum/ 5 % salt/ pH 4	11.76	85.91	0.44	8.31
0.75 % gum/ 2.5 % salt/ pH 4	11.56	86.19	-0.02	8.25
0.75 % gum/ 2.5 % salt/ pH 4	10.04	93.24	-1.22	6.63
0.75 % gum/ 2.5 % salt/ pH 4	10.66	87.41	0.13	7.63
0.75 % gum/ 2.5 % salt/ pH 4	11.04	87.44	-0.08	8.07
4% fresh egg	8.89	88.48	0.14	6.00
4% fresh egg	9.13	87.57	-0.05	6.10
0.75 % Linola	10.72	93.95	-1.56	7.26
0.75 % Linola	11.83	95.12	-2.57	7.92
0.75 % xanthan/ 2.5 % salt/ pH 4	11.77	95.22	-2.22	7.81
0.75 % xanthan/ 2.5 % salt/ pH 4	11.27	95.17	-2.69	7.23
0.3 % xanthan/ 2.5 % salt/ pH 4	11.60/ 11.62	94.52/ 94.49	-1.70/ -1.69	7.98/ 8.00

Appendix C3: Actual versus predicted dependent values for response surface plot

Gum	pH	Salt	type	phase angle	ΔE	Size	η_N	Eo	Complex viscosity
0	4	2.5	predict	81.7	5.8	.92	7101.3	7.1	-3.6
0	4	2.5	residual	-13.3	4.1	.49	-7101.2	-8.2	3.8
0.3	2.81	1	predict	73.4	15.5	1.83	4923.8	14.4	12.7
0.3	2.81	1	residual	10.7	-2.1	-0.08	-4923.7	-14.6	-12.6
0.3	2.81	4	predict	71.3	15.1	1.54	-4596.3	-9.6	-2.3
0.3	2.81	4	residual	7.3	-2.5	-0.20	4596.7	10.9	2.5
0.3	5.12	1	predict	60.4	9.6	1.40	7462.7	15.8	11.1
0.3	5.12	1	residual	11.5	-0.5	-0.11	-7465.2	-14.0	-10.7
0.3	5.12	4	predict	63.9	9.6	0.83	-3204.7	-12.7	-4.7
0.3	5.12	4	residual	1.8	-0.9	-0.04	3205.3	14.8	5.4
0.75	2	2.5	predict	76.5	37.8	3.49	-11411	-15.7	-9.7
0.75	2	2.5	residual	-11.0	2.1	0.03	11412	16.5	10.7
0.75	4	0	predict	35.4	11.7	1.05	20785.5	39.8	41.1
0.75	4	0	residual	-16.1	-0.3	-0.07	26894.5	47.5	26.9
0.75	4	2.5	predict	35.3	11.2	0.92	30172.5	34.9	7.7
0.75	4	2.5	residual	1.1	0.3	0.09	-4926.5	-6.2	-1.0
0.75	4	2.5	predict	35.3	11.1	0.92	30172.5	34.9	7.7
0.75	4	2.5	residual	0.0	-0.1	-0.03	2829.5	14.5	1.9
0.75	4	2.5	predict	35.3	11.1	0.92	30172.5	34.9	7.7
0.75	4	2.5	residual	1.6	-0.2	-0.02	-735.5	-3.5	-1.1
0.75	4	2.5	predict	35.3	11.1	0.92	30172.5	34.9	7.7
0.75	4	2.5	residual	0	-0.1	-0.04	-1382	-9.4	-2.4
0.75	4	5	predict	35.3	10.6	1.00	18212.7	45.6	16.0
0.75	4	5	residual	-0.4	0.5	-0.10	2665	-17.7	-10.5
0.75	6	2.5	predict	51.2	13.6	1.34	32207	18.8	3.7
0.75	6	2.5	residual	-4.6	-2.4	-0.55	15793	11.2	4.6
1.2	2.81	1	predict	52.5	31.1	2.50	22897.9	34.9	18.8
1.2	2.81	1	residual	9.1	0.6	0.09	-22874.5	-34.0	-16.2
1.2	2.81	4	predict	48.7	29.7	3.03	30515.9	70.6	4.5
1.2	2.81	4	residual	0.3	0.2	0.17	-12815.9	-6.9	-1.0
1.2	5.12	1	predict	28.3	7.5	0.62	73482.9	80.6	37.6
1.2	5.12	1	residual	2.4	2.2	0.27	-25982.9	-32.9	-14.4
1.2	5.12	4	predict	30.1	8.5	0.86	79950	111.8	22.4
1.2	5.12	4	residual	0.5	2.3	0.15	-15850.5	-5.8	1.6
1.5	4	2.5	predict	36.0	15.7	1.46	92589.0	129.1	24.6
1.5	4	2.5	residual	-3.1	-3.9	-0.58	36661	37.9	12.6

• Actual value - predicted value = residual

Appendix C4: Regression coefficient and analysis of variance of the second order polynomial for the response variables:phase angle (δ), complex viscosity (η*), Newtonian viscosity (η_N) and instantaneous elastic modulus (Eo) on day five of testing.

	Dependent Response Variables			
	Y_1 (δ)	Y_2 (η*)	Y_3 (η_N)	Y_4 (Eo)
β_0	214.8****	16.117	750345*	-251.578
Linear				
β_1	-52.024	-37.089	-728881**	-422.458
β_2	-63.230****	10.123	-197464	109.592
β_3	-2.388	-20.630	-185911*	82.947
Quadratic				
β_{11}	41.078***	10.944	63720	343.153***
β_{22}	7.214***	-1.773	11093	-6.608
β_{33}	.009	2.907	8534.8	1.572
Interaction				
β_{12}	-8.374	9.176	127863**	18.173
β_{13}	-3.963	1.105	111108**	20.748
β_{23}	1.607	0.281	22552	-24.688*
R^2	0.857	0.612	0.760	0.840
CV	22.14	141.33	138.5	104.1
F-Ratio (model)	5.305***	1.402	2.809**	4.663***
F-Ratio (Lack of Fit)	16.826***	180.0****	2378.2****	10733****

Model in which X1 = gum concentration, X2 = pH, X3 = salt concentration

**** Significant at 0.01 level

*** Significant at 0.05 level

** Significant at 0.10 level

* Significant at 0.15 level