CHARACTERIZATION AND RHEOLOGICAL PROPERTIES OF CAMELINA SATIVA GUM: INTERACTIONS WITH XANTHAN GUM, GUAR GUM, AND LOCUST BEAN GUM

by

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Abstract

Gums are water-soluble polysaccharides used in many industrial and food applications because of their functions such as thickening, gelling, emulsification, adhesion, and encapsulation. Interactions between gums are conducted to enhance functional properties of finished products and reduce processing costs. In this study, camelina gum, from the oil-seed plant Camelina sativa, is characterized by carbohydrate composition and morphological, thermal, and rheological properties. Interactions with xanthan gum, galactomannans guar gum, and locust bean gum (LBG) are also studied. Camelina gum is composed of arabinose, rhamnose, galactose, glucose, xylose and mannose; according to high-performance anion exchange chromatography analysis. Scanning electron microscopy and transmission electron microscopy images showed camelina gum with fibrillar structure and intermeshed network. Camelina gum solutions exhibited a shear thinning flow behavior in a range of concentrations (0.1% to 2.0% w/w) and shear rate (0.001 s⁻¹ to 3000 s⁻¹). Camelina gum is temperature independent at temperature ranges from 4 °C to 90 °C. The apparent viscosity increased as gum concentration increased. Mechanical properties of camelina gum demonstrated viscoelastic behavior with entangled molecular chains. Interaction of camelina gum with monovalent salt NaCl significantly reduced the viscosity of camelina gum solution at 1% when NaCl concentration increased. Camelina gum is soluble in water up to 60% ethanol content, in which the rheological properties do not significantly differ from camelina gum in water solution only. A synergy with xanthan and galactomannans was determined. All mixtures exhibited shearthinning flow behavior, solid-like behavior at low frequencies, and liquid-like behavior at high frequencies. For camelina-galactomannans mixtures, synergistic interactions occurred in LBGcamelina mixtures at ratios of 1:1 and 3:1. For xanthan-camelina mixture, maximum synergy was observed at the ratio 1:1. Synergistic effects of gum mixtures suggest dependency on the ratios and chemical structures of the gums. The effect of temperature on apparent viscosity of mixtures is not significant. Results showed that camelina gum can be used for commercial applications.

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Chapter 1 - Introduction

Carbohydrates such as starch and inulin in plants, and glycogen in animals, are natural compounds which are energy reserves and structure building materials in animal and vegetal tissues. Cellulose, hemicellulose, and pectin are carbohydrates commonly found in plants. Carbohydrates are typically referred to as saccharides (from the Greek word, sakchar, meaning sugar or sweetness), because isolated compounds were sweet. However, only a limited group of saccharides are sweet, while other compounds taste sweet but do not structurally correspond to saccharides (Tomasik 2004).

Natural carbohydrates are primarily polysaccharides. More than 90% of plant dry matter is carbohydrates, and polysaccharides comprise up to 80% of total plant material. Polysaccharides are monosaccharide residues connected by O-glycosidic linkages; the number of monosaccharides which form a polysaccharide is called the degree of polymerization (DP). DPs vary between 200 and 300, and just a limited number of natural polysaccharides have DPs less than 100. Polysaccharides, such as cellulose, have DPs between 7000 and 15000, and amylopectin, a component of starch, has a DP greater than 90000 (BeMiller 2007).

Structural characteristics, such as monosaccharide composition, chain length and shape, linkage pattern, and DP, control physical properties of polysaccharides comprising solubility, flow, and gelling behavior. A majority of polysaccharides exhibit diverse physical properties and chemical structures, thus enabling multiple applications, such as controlled drug release, tissue engineering, and viscosupplementation (Izydorezyk et al 2005; Rinaudo 2008).

Water-soluble polysaccharides are known as hydrocolloids, but these polymers are also referred to as gums because they are glue-like and mucilaginous when mixed with water. Functional properties of gums include adhesion, crystal growth inhibition, binding, encapsulation, coating, emulsification, foam stabilization, thickening, film forming, suspending, whipping, structure and texture stabilization and gelling. Gums are used in food and non-food industries, including adhesives, biotechnology, biomedical, agriculture, oil, cosmetics, explosives, paper, and textiles (Chenlo et al 2010; Gaonkar 1995; Moreira et al 2012; Nussinovitch 1997; Sri et al 2012; Verbeken et al 2003).

In aqueous solutions, gums may adopt a spherical, rod-like or random coil conformation related to their monosaccharides composition, linkage pattern and anomeric configuration, and capacity to establish intra and intermolecular interactions. These interactions occur with water and other molecules (e.g., proteins, sugars, salts) present in the solution and influence the conformation, which is also affected by the amount of water in the solution and system temperature. Conformation significantly influences functional properties, such as hydrodynamic volume and viscosity of the gum solution. Polysaccharides with linear conformation tend to maximize polymer-water contact in solutions of solvent (water) free of other substances. If a polysaccharide is dissolved in water containing other dissolved substances, the polysaccharide molecules may create intramolecular hydrogen bonds which lower polymer-solvent contact and viscosity, coil back on themselves, or form aggregates via intermolecular bonding, consequently decreasing polymer-solvent contact but increasing viscosity. Therefore, polysaccharides typically do not hydrate completely when dissolved in solutions of salt, sugars, or other water soluble ingredients. In general, ionic hydrocolloids have higher solubility, faster dissolving rate, and stronger interaction with water molecules than neutral hydrocolloids of identical shape and size. However, the presence of electrolytes (salts) in solution can decrease the solubility of ionic gums compared to the solubility of neutral gums (Al-Assaf and Phillips 2009; BeMiller 2007; Tomasik 2004).

Composition and concentration are fundamental factors affecting rheological properties and industrial applications of gums. Rheology is the study of mechanical characteristics of liquid flow and solid deformation as a function of stress, strain, and time. Stress (σ = applied force/area) corresponds to the magnitude of force components applied to a material object, and strain (γ = deformation/original size) is the difference in size or shape of a material object due to an applied force, expressed as a ratio or a percent change in regards to original size and shape. Therefore, strain is a nondimensional factor denoting movement. Time is a variable that determines the rate of strain or stress, behavior of materials under constant strain or stress, and elasticity rate of a material once a stress is removed. The magnitude of deformation for ideal elastic materials is directly proportional to the applied stress which ceases as soon as the stress is removed. Conversely, an ideal viscous material does not recover its original shape or size when applied stress is removed; the deformation is proportional to the rate of strain. Therefore, the rate of flow of a viscous material is proportional to the applied stress (BeMiller 2007). Polysaccharides, such as gums, can modify the rheology of aqueous systems at low concentrations; this is due to viscoelastic properties and hydration ability of the large polysaccharide molecular chains that consequently increase solution viscosity. Rheological behavior of gum solutions is frequently pseudoplastic since viscosity decreases at high shear rates. A limited number of gums exhibit Newtonian behavior, where viscosity is independent of shear rate and time (Tomasik 2004). Properties of gum solution can be modified by mixing different gums, thereby creating interactions between the gums and altering the rheology, gelling capacity, stability, and solubility of the gum solution. Gum mixtures are often used for industrial applications to improve process, reduce costs of production, and design novel products (Gaonkar 1995; Igoe 1982).

Currently, the demand for hydrocolloids has notably increased. For example, the food hydrocolloid market is predicted to reach \$7 billion by 2018, demonstrating a compound annual growth rate of 5%. North America dominated the global food hydrocolloid market during 2012, and Asia-Pacific is the fastest growing market for gums (Research and Markets 2013).

Camelina gum is extracted from *Camelina sativa* oil-seed plant. This plant is cultivated in Europe since the nineteenth century and sold as an animal feed supplement in the United States (U.S.) market (Keske et al 2013). Camelina can be cultured as rotational crop and grown under extremely resistant, adverse environmental conditions, such as drought or winter with low-input of water, fertilizer, and pesticides. Its growing season is approximately 110 days, and the crop can be cultivated on fallowed land without interrupting the prevailing crop rotation. As a commodity and a fuel, camelina offers farmers and communities a profitable source of economic diversification. Recent breeding techniques have developed new varieties of camelina with higher yield, enhanced seed quality, and resistance to shattering and lodging (Zubr 2003). The outcrossing rate of camelina is significantly low (less than 1%), so the chance of transgenic pollen impacting other species is little. In addition, camelina production costs are considerably lower than production costs for other oilseed crops, including soybean and canola, and projections have indicated that as a grain crop, camelina could potentially be as profitable as wheat (Small 2013).

Biofuel research has shown that camelina is a biofuel oilseed crop and camelina oil is suitable for high-energy density fuels, such as biodiesel and jet fuel. However, research on utilization of camelina co-products, such as protein, carbohydrates, and fibers, is limited. After oil extraction, approximately 50% of camelina seed mass is recovered as byproduct (Moloney et al 1998). Camelina gum is a co-product with suitable rheological properties with potential for food and industrial applications (Eynck 2013; Fernando Rodriguez-Rodriguez et al 2013; Keske et al 2013; Peng et al 2014; Taasevigen 2010; Zanetti et al 2013).

This work is proposed to increase understanding of camelina gum by studying its monosaccharide composition and morphological, thermal, and rheological properties. A second objective is to evaluate rheological behavior of camelina gum solutions interacting with various ratios of substances such as sodium chloride and ethanol and other gums such as xanthan gum, guar gum, and locust bean gum.

Chapter 2 - Literature Review

2.1 Polysaccharide Gums

Polysaccharides are typically polyuronides composed of monosaccharide units linked through glycoside bonds by the removal of water. Gums are naturally occurring polysaccharides that have multiple industrial applications because of their ability to form a gel, make a viscous solution, or stabilize emulsion systems. Hydrocolloids are water-soluble gums with a high molecular weight and many hydroxyl groups. Hydrocolloids may also be polyelectrolytes. Their sugars composition can be derived from one monosaccharide unit (e.g., cellulose contains only glucose), two distinct monomers (e.g., alginate contains mannuronic acid and gluluronic acid) or many distinct monosaccharides (e.g. gum arabic contains galactose, arabinose, rhamnose, and uronic acid) (Al-Assaf and Phillips 2009; Burey et al 2008; Jahanbin et al 2012).

The presence of hydroxyl (-OH) groups significantly increases gums' affinity to bind water molecules and produce a dispersion between a true solution and a suspension, thus exhibiting colloid properties. Therefore, the term "hydrophilic colloid" or "hydrocolloid" refers to a system in which colloid particles are spread throughout water; according to the amount of available water, this system can be a gel or a sol (liquid) (Mirhosseini and Amid 2012; Saha and Bhattacharya 2010).

Gums are soluble or dispersible in water and can increase system viscosity. Certain gums form gels under specific conditions while other gums act only as thickeners. Gums can be extracted from botanical, algal, microbial, and animal sources and from chemical or enzymatic treatment of cellulose and chitin. Gums naturally act as energy reserves, exudates, cell wall components, and extracellular substances from plants or microorganisms. The food industry has incorporated gums into a range of diverse food formulations because of the ability of gums to resist unwanted physical processes such as mechanical disaggregation, crystallization, and gravitational sedimentation (Casadei and Chikamai 2010; Dickinson 2003; Ibanez and Ferrero 2003; Izydorezyk et al 2005; Jahanbin et al 2012; Marcotte et al 2001; Nishinari et al 2000; Nussinovitch 1997; Saha and Bhattacharya 2010; Sri et al 2012).

2.2 Xanthan Gum

Xanthan gum is an extracellular polysaccharide obtained by a complex enzymatic process, from *Xanthomonas campestris* bacterium secretions at its cell wall surface. The bacteria are found on leaves of vegetables from the genus Brassica, such as cabbage. Xanthan gum is a high molecular weight heteropolysaccharide with a primary structure of repeated pentasaccharide units of two glucose units, two mannose units, and one glucuronic acid unit.

Xanthan backbone is a linear $(1 \rightarrow 4)$ -linked β -D- glucose chain, attached to a charged trisaccharide side chain on every other glucose at C-3, containing a glucuronic acid unit $(1 \rightarrow 4)$ -linked to a terminal mannose unit and $(1 \rightarrow 2)$ -linked to a second mannose unit that connects to the backbone (Garcia-Ochoa et al 2000; Izydorezyk et al 2005; Lopez-Franco et al 2008; Pinheiro et al 2011; Rinaudo 2008; Sworn 2009).

Xanthan is commercially produced by an aerobic fermentation process, recovered by precipitation with ethanol or isopropyl alcohol, dried, milled, and packaged.

Xanthan gum is resistant to enzymatic degradation and highly soluble in cold and hot water due to its polyelectrolyte nature. Xanthan solutions are pseudoplastic, or shear thinning, because of a resultant ordered network of molecules that form intermolecular aggregates by hydrogen bridges. This network reveals high viscosity at low shear rates, thus demonstrating the exceptional suspension properties of xanthan gum in solution. The aggregates are gradually disrupted at high shear rates, so the pseudoplastic flow characteristics (Garcia-Ochoa et al 2000).

Xanthan gum viscosity is stable over a wide temperature and pH range. Synergistic interactions of xanthan gum and galactomannans, such as guar gum and locust bean gum (LBG), result in enhanced viscosity with guar, and in formation of thermo reversible, soft, and elastic gels with LBG. Optimum functionality of xanthan gum in solution depends on complete hydration; dispersion, composition, and agitation of the solvent are relevant factors that affect gum functionality (Igoe 1982).

Because of its unique shear thinning flow behavior and weak gel structures, xanthan gum is the most frequently used gum in the food industry for food applications such as beverages, dairy products, and baked and frozen foods. Xanthan gum is also used in the manufacturing of paints, cosmetics, foams, textiles, coatings, and adhesives. It is also applied as an emulsion and foam stabilizer and as suspension thickener and stabilizer (Al-Assaf and Phillips 2009; Garcia-Ochoa et al 2000; Izydorezyk et al 2005; Nussinovitch 1997; Rinaudo 2008; Sworn 2009).

2.3 Galactomannans

Neutral polysaccharide gums are extracted from endosperm of leguminous plant seeds, in which the gums serve as energy reserves. Their structure is a linear β - $(1 \rightarrow 4)$ - mannose (M) backbone attached to side chains with a single galactose (G) unit by α -(1 \rightarrow 6) linkages. Depending on botanical origin, galactomannans differ in mannose/galactose (M/G) ratio, distribution of galactose residues along the mannan backbone, molecular weight, and molecular weight distribution. These features influence their distinct physicochemical and rheological properties. Higher M/G ratio results in higher thickening properties and larger galactose content results in higher solubility in water. Flow behavior of galactomannans depends on gum concentration and shear-rate: At low concentrations and low shear rate, the flow exhibits Newtonian behavior; at higher concentrations and higher shear rate, the flow behavior is pseudoplastic. Galactomannans have many applications in food, cosmetic, and pharmaceutical products in which they have been used as thickeners, stabilizers, emulsifiers, and gelling agents. Synergistic interaction with other gums, such as xanthan, results in increased viscosity and/or gel strength, enhanced product quality, and reduced production costs. The most commercially used galactomannans are guar gum, Locust Bean Gum (LBG), tara gum, and fenugreek gum (Dea and Morrison 1975; Dickinson 2003; Mirhosseini and Amid 2012; Pinheiro et al 2011; Rinaudo 2008; Schorsch et al 1997; Wielinga 2009).

2.3.1. Guar Gum

Guar gum is ground endosperm halves, called guar splits, recovered from seeds of the guar plant, *Cyamopsis tetragonolobus (L,) Taub.* (Leguminosae). This annual summer legume, grown primarily in arid and semi-arid zones, is used as human and animal food. Guar gum plantings are found in Malawi, Australia, Brazil, Argentina and Colombia. In the United States, guar grows mainly in parts of Texas, Oklahoma, and Arizona (Wielinga 2009).

Guar gum is a nonionic galactomannan polysaccharide with a linear chain of $(1 \rightarrow 4)$ linked β -D-mannopyranosyl units and side chains of $(1\rightarrow 6)$ -linked α -D-galactopyranosyl residues. Mannose: galactose ratio is approximately 2:1.

Guar gum contains higher galactose content than LBG and swells and disperses in cold and hot water. Even at low concentrations, guar gum produces highly viscous, pseudoplastic solutions attributable to its high molecular weight and the presence of hydrogen bonds (Iqbal 2010; Saha and Bhattacharya 2010). Guar gum is used in many food and non-food industries, such as textile, pharmaceutical, paper, oil, explosives, and chemical. Guar gum is also used in frozen foods, beverages, bakery products, confectionery, and canned foods as an emulsifier, stabilizer suspending agent, thickener, and mouth-feel improver (Castillo Garcia et al 2005; Izydorezyk et al 2005). Guar derivatives, such as hydroxyl-propyl-, hydroxyl-ethyl-guar, and carboxy-methyl guar, are produced for food and non-food applications (Wielinga 2009).

2.3.2. Locust Bean Gum

The carob gum, Locust Bean Gum (LBG), is a powder obtained from endosperm of carob tree seeds (*Ceratonia siliqua L*.) grown in the Mediterranean region. LBG is a linear polysaccharide containing a β -(1 \rightarrow 4)-mannane backbone chain and a single D-galactopyranosyl residue connected via α -(1 \rightarrow 6) linkage as side chain, with an average M/G ratio of approximately 3.5. Since water solubility is affected by the degree of substitution, LBG exhibits low solubility at ambient temperature and requires heat treatment in order to maximize solubility.

LBG was the first galactomannan used in food and non-food industries, including pharmaceutics, paper, cosmetics and textiles. Its primary properties are its ability to form very viscous solutions at low concentration, to stabilize dispersions and emulsions, and to form gels at high concentrations under specific conditions such as low temperature or upon aging. LBG is resistant to pH, salts, or heat processing because it is a non-ionic polysaccharide. It has an enhanced synergy with other gums such as xanthan and carrageenan to form more elastic and stronger gels (Dakia et al 2008; Damasio et al 1994; Izydorezyk et al 2005; Mirhosseini and Amid 2012; Schorsch et al 1997).

2.5 Camelina sativa

Camelina sativa (L.) Crantz (or camelina, gold of pleasure, false flax, Dutch flax, linseed dodder, German sesame, Siberian oilseed, or wild flax), an oilseed crop belonging to the Cruciferae (Brassicaceae) plant family (mustard family) was initially found in southeastern Europe and southwestern Asia during the Bronze Age (1500 - 400 BCE). It is currently produced in Europe and Asia, a majority of the U.S., Canada, Mexico, Ireland, Japan, Chile, Australia, and New Zealand. Figure 2-1 shows a camelina sativa plant (Davis et al 2013; Imbrea et al 2011; Ludeke-Freund et al 2012; Small 2013; Waraich et al 2013).

Camelina species are well-adapted to cool, temperate, semi-arid climates and, because they are short-growing season plants (approximately 110 days), they can survive in conditions with low rainfall, dry, nutrient-poor soils, and frost. Camelina is a low input crop that does not require much irrigation and tillage, neither periodic applications of fertilizers and pesticides and it has a low response to phosphorous (P), potassium (K), and nitrogen (N) (Davis et al 2013; Keske et al 2013; Small 2013; Waraich et al 2013; Zanetti et al 2013).



Figure 2.1 Painting of Camelina sativa. Flower (left), fruit (right), long section of fruit (bottom right) (Adopted from Small 2013).

2.5.1 Uses and Applications

The genus *Camelina* includes eight species, but only two species are used for oil production: *Camelina sativa* and *Camelina silvestris*. Camelina sativa is one of the most cost-effective oilseed crops to produce, therefore making it a potential source of low-cost vegetable oil for biodiesel, natural antioxidants, and essential fatty acids, specifically (omega-3) fatty acids (Davis et al 2013; Small 2013; Waraich et al 2013). Biodiesel produced from camelina oil is particularly used on commercial flights and military fuel consumption.

2.5.1.1 Biofuel

In 2012, the U.S. Environmental Protection Agency (EPA) reported that 20,000 ha of camelina are currently cultivated. The EPA also reported that 379 million L of biofuel could be produced without land use change if camelina is grown in rotation with other crops such as wheat, corn, and sorghum (Keske et al 2013; Small 2013). Camelina oil has a longer shelf life than other oils high in omega-3 fatty acids, but it has a similar cetane number to those oils. Camelina oil reduces greenhouse gas emissions 40 - 60% more than petroleum-diesel fuel (Keske et al 2013; Ludeke-Freund et al 2012; Waraich et al 2013).

2.5.1.2 Human Food

Camelina seeds were used as gruel and in bread in the Iron Age (400 BC-500 AD) (Fan and Eskin 2013). Currently, camelina oil is particularly valuable to the human diet because of its high ratio of omega-3 to omega-6 fatty acids which are essential for brain and nervous system development. Because of the presence of phytosterols that lower the Low-Density Lipoprotein (LDL) cholesterol ("bad cholesterol"), camelina oil is used for baking and frying and in products such as dressings, ice cream, dietary supplements, and nutritionally fortified foods (Keske et al 2013). Natural antioxidants, such as vitamin E, make the oil highly stable and tolerant to heat and rancidity (Imbrea et al 2011; Keske et al 2013; Small 2013; Waraich et al 2013).

2.5.1.3 Various Uses and Products

Because camelina is used as animal feed, various trials have been conducted to establish the optimum percentage of camelina necessary to enhance the diets of poultry, rabbits, cows, swine, chicken, fish and ewes (Waraich et al 2013). Camelina meal is used as an energy and protein source that increases fatty acid composition of animal meat, consequently benefitting human nutrition (Moloney et al 1998; Small 2013; Waraich et al 2013). Industrial applications of camelina include use in the manufacturing of paints, coatings, cosmetics, pet food, pharmaceuticals, and plastic additives (Small 2013; Zanetti et al 2013).

2.5.2 Seed Composition

Camelina seed is approximately 2 - 3 mm or approximately 0.1 inch long. One thousand seeds weigh approximately one gram. Camelina seed is pale yellow-brown, turning to dark brown upon ripening and in storage (Small 2013). Oil content in the seed is approximately 43%, and 90% of this oil content comes from unsaturated fatty acids, consisting of a 30–40% fraction of α -linolenic acid, 15–25% linoleic acid, approximately 15% oleic acid, and approximately 15% eicosenoic acid (Waraich et al 2013). The protein content of camelina seed is between 39.2 and 47.4%, the fiber content is about 12.5 to 16.8%, and the carbohydrate content is approximately 10% (Waraich et al 2013; Zubr 2010).

2.6 Rheology

Rheology studies flow and deformation of materials under conditions such as shear rate, composition, time, and temperature. Rheological properties are crucial in the design, modeling, and evaluation of processes, and rheological data are necessary to determine process characteristics involving fluid flow, such as extraction, filtration, pump sizing, and purification (Marcotte et al 2001).

Strain and stress are primary factors of rheological studies. Stress and strain constants of proportionality are known as moduli. Materials can range from ideal solids to ideal fluids. Ideal solid-like-behavior materials obey Hooke's Law in which stress and strain are directly related, and materials with ideal fluid behavior follow Newtonian principles. The constant of proportionality is called viscosity. Stress (σ) is designated as force per unit area. According to the direction of force with respect to the material surface, two types of stress exist: normal stress occurs when applied force is perpendicular to the material surface, and shear stress occurs when applied force is parallel to the material surface. Strain corresponds to the relative deformation of materials when a stress is applied. Similar to stress, strain types depend on the direction of applied stress to the material surface. Normal strain (ϵ) occurs when the stress is perpendicular to the material surface, and shear stress is perpendicular to the material surface, stress is perpendicular to the material surface. Strain types depend on the direction of applied stress to the material surface. Normal strain (ϵ) occurs when the stress is perpendicular to the material surface, and shear stress is perpendicular to the material surface.

Shear (strain) rate is the degree of deformation per time used to determine strain during fluid flow (Yaseen 2002).

Rheological properties of hydrocolloids provide data for determining attributes in order to modify texture of food products. The design of food processing equipment, storage stability, quality control, food structure, sensory evaluation, and food product development can be achieved by studying rheological properties of food (Garcia-Abuin et al 2011; Marcotte et al 2001; Yaseen 2002).

2.6.1 Viscosity

Fluids can be classified as Newtonian and non-Newtonian. Viscosity, "the resistance to flow," applies to Newtonian fluids, and apparent viscosity applies to non-Newtonian fluids. Rheological properties of a Newtonian fluid depend on composition and temperature; whereas, non-Newtonian fluids are shear rate-dependent and can be divided into two categories: time dependent and time independent. Time dependent fluids are known as thixotropic and rheopectic fluids. When viscosity decreases with time at a constant shear rate and temperature, the fluid is called thixotropic. The fluid is rheopectic if viscosity increases as a function of time. Time independent fluids are classified into pseudoplastic, dilatant, and Bingham plastic fluids. Pseudoplastic, or shear thinning fluids are fluids in which viscosity decreases when shear rate increases. Pseudoplastic fluids include gum solutions, emulsions, and dispersions. Dilatant or shear thickening fluids are fluids in which viscosity increases when shear rate increases. Bingham plastic fluids do not flow below a specific shear stress value due to internal forces. This minimum shear stress value required to initiate the flow of this type of fluids is called yield stress.

Viscosity is a property to consider in processes that comprise polymer solutions in which rheological behavior is complex. Polymer solution viscosity is more difficult to predict and correlate than the viscosity of systems containing low molecular weight compounds. Hydrocolloids viscosity is affected by variables such as temperature, shear rate, pressure and time of shearing (Garcia-Abuin et al 2011; Marcotte et al 2001; Yaseen 2002).

2.6.2 Viscoelasticity

Materials with viscosity and elasticity properties are known as viscoelastic. Most materials can be considered viscoelastic. Long-chain polymer solutions, gels, and colloids

demonstrate viscoelastic flow behavior. The proportion of viscous (fluid) to elastic (solid) properties is determined by the timescale of the deformation (Ross-Murphy 1984). Viscoelastic behavior is studied using oscillatory shear measurements. Elasticity can be determined by studying a sine (deformation or stress) wave through the tested material; a shear stress wave that leaves the material corresponds to the degree of elasticity. The phase shift allows establishment of the degree of viscous and elastic behavior: If a material is ideally elastic, the resultant stress wave is completely in phase with the strain wave; conversely, if the material is purely viscous, the resultant stress wave is 90° out of phase with the applied deformation. Elastic (in- phase) and viscous (out- of- phase) components of the stress wave can be represented by measurements of in-phase shear storage modulus (G') and out-of-phase shear loss modulus (G'') respectively. The ratio of G'' to G' is the tangent of the loss angle (δ), which is a measure of the viscous/elastic ratio for a material at certain frequency ω . (Ross-Murphy 1984; Yaseen 2002).

2.6.3 Rheology of Synergistic Gum Interactions

Rheological properties of hydrocolloids in solution depend on several factors, including shear rate, previous shear history, duration of the shear rate, concentration, degree of dispersion, temperature, electrical charge, dissolution, presence or absence of other hydrocolloids, thermal and mechanical pretreatment, age of the hydrocolloid solution, and presence of electrolytes and non-electrolytes (Marcotte et al 2001; Moorhouse 2003). The phenomenon where certain gum combinations yield a disperse system that has a higher viscosity than the addition of viscosities of constituent gum dispersions prepared separately is known as viscous synergism. The type of gum to be used and ideal proportions required are crucial in the resulting viscous synergism of the system (Hernandez et al 2001). Therefore, apparent viscosity and gelation strength are variables to analyze in order to evaluate synergistic interactions in mixed hydrocolloid systems (Liang et al 2011). Synergistic interactions between polysaccharides are important for dispersion systems preparations with industrial applications, including food, pharmaceutical, and biomedical fields. In the food industry, synergistic polysaccharide-polysaccharide interactions favor the creation of new textures and rheology manipulation of the products. Many hydrocolloid blends are intended to attain a functionality that cannot be achieved by individual gum dispersions, as well as to reduce overall gum concentration and processing costs (Khouryieh 2006; Moorhouse 2003).

Galactomannans, such as LBG can interact synergistically with biopolymers, such as xanthan gum, resulting in reduced production costs and improved product quality. The LBG/xanthan system, which forms a gel, has been analyzed in pharmaceutical applications for controlled release purposes (Pinheiro et al 2011; Sandolo et al 2010).

The study of interactions between hydrocolloids in aqueous solutions is relevant for food formulation development, stabilization and thickening, as well as fluid flow. Synergy of viscosity of the mixture can demonstrate distinct behaviors depending on the polymers employed, resulting in (a) positive deviation blends, (b) negative deviation blends, and (c) positive and negative deviation blends. Blends with positive deviation behavior show strong interactions between phases; negative deviation blends form weak interactions between polymers.

A mixed hydrocolloid system can exhibit one of the following phase behaviors: (i) complete miscibility and formation of a single homogenous phase, (ii) formation of two layers with different concentrations of polymers in each layer in which interactions between polymers are repulsive in nature, and (iii) polymer-polymer interactions are attractive, so the system shows a two-phase region with polymers concentrated in one phase (Khouryieh 2006).

Chapter 3 - Composition and Physicochemical Properties of Camelina Gum

3.1 Materials and Methods

3.1.1 Materials

Camelina gum powder was provided by Sunhai Bioadhesive Technologies (Manhattan, Kan.). All the standards sugars used were of analytical reagent quality; the standard sugars glucose (Glc), galactose (Gal), rhamnose (Rha), glucuronic acid (GlcA), and galacturonic acid (GalA) were purchased from Fisher Scientific (Pittsburg, Pa.); mannose (Man), arabinose (Ara) and xylose (Xyl), were purchased from Acros Organics (New Jersey, USA).

3.1.2 Chemical Composition Analysis

Moisture content was measured according to Association of Official Agricultural Chemists standard methods (AOAC. 2005). Carbon (C), hydrogen (H), nitrogen (N), and sulfur (S) content were determined with a PerkinElmer 2400 Series II CHNS/O Elemental Analyzer (Shelton, Conn.). Protein content was converted from nitrogen content (N×6.25). Tests were performed in duplicate.

3.1.3 Monosaccharide Analysis

Camelina gum was hydrolyzed by using modified Saeman method (Saeman et al 1963). 0.3 g of camelina gum was mixed with 12 M H₂SO₄ and incubated at 37 °C for 1 hr, and then 15 ml of distilled water was added to dilute the H₂SO₄ to 2 M. The mixture was heated at 120 °C for 3 h. After cooling, the hydrolysate was diluted 1:50 with distilled water, neutralized with calcium carbonate, and filtered through a 0.45 μ m filter. A standard containing all aforementioned sugars was also filtered through a 0.45 μ m filter. The hydrolysate and standard samples were stored at 4 °C until they were analyzed. Subsequently, the samples were analyzed in a high performance anion exchange chromatograph with pulsed amperometric detection (HPAEC-PAD) (Dionex ICS-3000). The test was carried on using isocratic eluent (15 mM NaOH), with a Carbopac PA1 column (250×4 mm) and a guard column (50×4 mm) at an eluent flow rate of 1.0 ml/min. A second test was carried on using isocratic eluent (150 mM NaOH and 0.5 M NaOAc). The temperature of the chromatograph column was maintained at 25 °C.

3.1.4 Fourier Transform Infrared Spectroscopy

The chemical structure and functional groups of camelina gum were determined using a PerkinElmer Spectrum 400 FT-IR/FT-NIR spectrophotometer (Shelton, Conn.). Spectra were recorded in the absorbance mode from 400 - 4000 cm⁻¹ (mid-infrared region) at a resolution of 1 cm⁻¹, and 32 scans were collected. Duplicate spectra readings were obtained.

3.1.5 Thermal Properties

3.1.5.1 Thermal Gravimetric Analysis

In order to establish thermal gravimetric analysis of camelina gum, a thermal gravimetric analysis (TGA) instrument (TGA 7, Perkin-Elmer, Norwalk, Conn.) was used under a nitrogen atmosphere. Approximately 8 mg of camelina gum was placed into a platinum cup and scanned at a temperature range of 25 °C to 600 °C at a heating rate of 20 °C/min. The maximum degradation rate was determined as the ratio of mass (%) at peak temperature to peak temperature.

3.1.5.2 Differential Scanning Calorimetry

Before beginning measurements, thermal transition properties of camelina gum were determined using a differential scanning calorimetry (DSC) instrument (DSC Q200 V24.4, TA Instruments, New Castle, Del.) calibrated with indium and zinc. Approximately 5 mg of camelina gum was placed in a hermetic aluminum pan in a nitrogen atmosphere with a gas flow rate of 50ml/min. The sample was heated in an inert environment from 25 $^{\circ}$ C to 300 $^{\circ}$ C at a heating rate of 20 $^{\circ}$ C/min.

3.1.6 Morphological Properties

3.1.6.1 Scanning Electron Microscopy (SEM)

Camelina gum powder was affixed to an aluminum stub using two-sided adhesive tape and the gum powder was coated with an alloy of 60% gold and 40% palladium with a sputter coater. A Hitachi S-3500N (Hitachi Science System, Ibaraki, Japan) scanning electron microscope was used at an accelerating voltage of 5 kV.

3.1.6.2 Transmission Electron Microscopy (TEM)

TEM photographs were captured with a transmission electron microscope model CM 100 (FEI Company, Hillsboro, Ore.) operated at 100 kV. A solution of camelina gum at 0.01% in distilled water containing sodium azide (0.02 g/L) to prevent bacterial contamination was prepared. Formvar/carbon-coated 200-mesh copper grids were submerged into the sample for approximately 30 s at room temperature, and then copper grids were stained with 2% (w/v) uranyl acetate for 60 s at room temperature before TEM imaging.

3.2 Results and Discussion

3.2.1 Chemical and Monosaccharide Composition

According to the chemical composition analysis, camelina gum contains 9.4% of moisture (wet basis) and 29.2% of crude protein (dry basis). Regarding the monosaccharide composition, chromatograms of camelina gum and a standard sugar solution containing six neutral sugars (arabinose, rhamnose, galactose, glucose, mannose and xylose) and two acidic sugars (glucuronic acid and galacturonic acid) are shown in Figure 3.1. These chromatograms were obtained by using 15 mM NaOH as eluent. Five peaks appeared in the chromatogram of the standard solution, and the retention times coincided with the retention times of five peaks in camelina gum chromatograph. Therefore, these peaks may correspond to arabinose, rhamnose, galactose, glucose, xylose and mannose. The separation of arabinose and rhamnose, and xylose and mannose sometimes can be hard to achieve (Lebet et al 1997). Sugars differentiation is difficult under isocratic conditions, although it is possible by using the adequate eluent gradients (Lebet et al 1997; Wunschel et al 1997).

The acidic hydrolysis using H_2SO_4 is a frequent method for the composition analysis of neutral sugars in plant-based substrates; however this hydrolytic agent can interfere with the eluents during neutral-sugar separation on the analytical column. The elution of acidic sugars from the CarboPac PA1 column requires a stronger eluent than the eluent used for neutral sugars. Sodium acetate (NaOAc) is usually added to the sodium hydroxide eluent to accomplish this goal (Lebet et al 1997). The second test performed using a concentration of 150 mM NaOH and 0.5 M NaOAc did not show a good separation of neutral and acidic sugars. The concentration of NaOAc was excessively high.



No.	Possible compound	Ret.Time	Area	Height	Rel.Area
		min	nC*min	Nc	%
22	Rhamnose	7.151	2.4129	6.675	1.47
23	Arabinose	8.076	2.3245	6.658	1.42
25	Galactose	10.359	16.6718	37.449	10.16
26	Glucose	11.392	15.8279	32.424	9.65
27	Xylose-Mannose	12.351	2.2625	2.979	1.38



Figure 3.1 Chromatogram of a) camelina gum, and b) standard sugar solution containing arabinose, rhamnose, galactose, glucose, mannose, xylose, glucuronic acid and galacturonic acid.

3.2.2Fourier Transform Infrared Spectroscopy

Vibrational spectra can be used for sugars identification and analysis. Carbohydrates show high absorbencies in the region 1200–800 cm⁻¹, known as the fingerprint region, in which every polysaccharide can be identified by specific band position and intensity. However, overlapping of ring vibrations with stretching vibrations of (C-OH) side groups and (C-O-C) glycosidic bond vibration in this region causes difficulty when assigning absorbencies at certain wavenumbers to specific bonds or functional groups. (Cerna et al 2003; Kacurakova et al 2000). FT-IR spectra for camelina gum are shown in Figure 3.2.



Figure 3.2 FTIR analysis of camelina gum.

Absorptions at 2927 cm⁻¹ and 1469 cm⁻¹ represent C–H stretching and bending vibrational bands. Absorption at 1570 cm⁻¹ is primarily associated to C=O stretching vibration of the carboxylate anion in acidic sugars (glucuronic acid) (Hu et al 2010). The peak at 1151 cm⁻¹ corresponds to glycosidic linkages (C-O-C). Galactose residues with any linkage pattern and position can be found at frequencies at 1155 cm⁻¹, xyloglucan can be found at 1153 cm⁻¹, and polysaccharides containing mannose, arabinose, and rhamnose are found at frequencies in the range 1051 cm⁻¹ - 1039 cm⁻¹ (Kacurakova et al 2000).

In carbohydrates, distinctive absorption bands for α -linkage at 834 cm⁻¹ and β -linkage at 898 cm⁻¹ discriminate satisfactorily between the two glycosidic linkage types of aldopyranoses at 879 cm⁻¹ and furanoid compounds at 858 cm⁻¹ respectively. The absorption band of camelina

gum at 858 cm⁻¹ is stronger than the absorption band at 879 cm⁻¹, indicating predominance of β glycosidic linkages (Kacurakova et al 2000).

The peak at 1550 cm⁻¹ indicates the presence of protein (amide II). This type of protein absorption contains contributions from N-H bending (60%) and C-N stretching (40%) vibrations (Jackson and Mantsch 1995).

3.2.3Thermal Properties

3.2.3.1 Thermal Gravimetric Analysis

TGA data analysis allows for the study of the decomposition pattern and thermal stability of polymers. TGA and derivative termogravimetric analysis (DTG) curves of camelina gum as a function of temperature are shown in Figure 3.3. Thermal behavior and thermal stability of camelina gum show three distinct stages of weight losses in the temperature range from 25 °C to 600 °C with heating rate of 20 °C/min. Early weight loss (less than 12%) from 25 to 200 °C is attributed to desorption of moisture as hydrogen bound water to the saccharide structure. The second and third weight loss stages overlap; decomposition of camelina gum occurs in the range of 250 - 400 °C. Initial decomposition temperature (IDT) corresponds to 264 °C (onset, second stage), at which point the sample begins to decompose, the maximum peak, approximately 292 °C, relates to the temperature at which maximum polysaccharide decomposition occurs. Other gums, including xanthan and guar, exhibit decomposition temperatures at 300 °C (Bothara and Singh 2012; Zohuriaan and Shokrolahi 2004). A slight peak at 350 °C may be attributed to protein decomposition in camelina gum (Li 2013).



Figure 3.3 Thermograms of camelina gum: a) TGA and b) DTG.

3.2.3.2 Differential Scanning Calorimetry

DSC is a technique used to study physicochemical changes in polysaccharides during thermal processing. Figure 3.4 shows the DSC curve for camelina gum. The baseline shift, observed at approximately 65.53 $^{\circ}$ C, may be interpreted as the glass transition region in which amorphous polymers are converted from a glasslike form to a rubbery, flexible form and therefore mechanical properties of those polymers change (Altay and Gunasekaran 2012). The endothermic peak shows a melting temperature of 228.87 $^{\circ}$ C, an extrapolated onset temperature of 206.69 $^{\circ}$ C, and an enthalpy of fusion of 244.7 J/g. Since most polysaccharides are constituted by carboxylate or carboxylic acid functional groups, thermal transitions may follow the mechanism of scission of carboxylate groups and CO₂ production from the corresponding carbohydrate backbone; dehydration, depolymerization, and pyrolysis can also be involved during these high temperatures, resulting in H₂O, CH₄, and CO formation (Zohuriaan and Shokrolahi 2004).



Figure 3.4 DSC thermogram of camelina gum.

3.2.4 Morphological Properties

Morphological features of camelina gum can be related to its physicochemical and functional properties. SEM and TEM analysis are described in the following sections.

3.2.4.1 Scanning Electron Microscopy (SEM)

SEM images of the surface morphology of camelina gum are shown in Figure 3.5 at $20,000 \times (A), 25,000 \times (B)$, and 2 µm scale. As illustrated, camelina gum exhibits strands that link together to form a particulate network structure; these fibrils are intermeshed, forming a wide-meshed network of long fibrils. This net-like, fibrillar structure may significantly impact rheological properties of gum in solution since a porous and loosened gum structure facilitates water absorption, water holding, and swelling capacity. Because of this structure, camelina gum may form a gelling network in interaction with other gums.



Figure 3.5 SEM images of camelina gum at different magnifications: A (20,000×); B (25,000×).

3.2.4.2 Transmission Electron Microscopy (TEM)

A prominent feature of camelina gum solution noticed on TEM images is a singlestranded fibril structure (Figure 3.6). These strings have an inside diameter between 4-6 nm and are connected with each other, forming a network. The dark aggregates may correspond to protein; the long strings comprise polysaccharides.

Camelina gum in aqueous solution at room temperature and neutral pH exhibits linear string entanglement; this type of structure affects the rheological properties of the gum in solution. The protein adheres to linear polysaccharide fibers and may restrict the motion of these fibers; therefore, viscosity of the solution may increase. This cohesion between protein and gum in camelina may hinder the camelina gum purification process (Li 2013).



Figure 3.6 TEM Images of camelina gum solution (0.01%) at various magnifications: A (130,000×); B (245,000×); C (64,000×); D (130,000×).

Chapter 4 - Rheological Characteristics of Camelina Gum, and Mixtures of Camelina Gum with Selected Hydrocolloids (Xanthan Gum, Locust Bean Gum, and Guar Gum)

4.1 Materials and Methods

4.1.1 Materials

Ground camelina gum powder grade #2 was provided by Sunhai Bioadhesive Technologies (Manhattan, KS). Xanthan gum, galactomannans, locust bean gum (LBG), and guar gum were purchased from Sigma-Aldrich (St Louis, Mo.).

4.1.2 Preparation of Individual Gum Solutions and Gum Mixtures

4.1.2.1 Individual Gum Solutions

In order to study the effect of concentration on rheological properties of camelina gum, camelina gum solutions with 0.1%, 0.5%, 1.0%, 1.5%, and 2.0% camelina gum contents (w/w) were prepared by mixing camelina gum powder with distilled water containing sodium azide (0.02 g/L) to prevent bacterial growth.

In order to study the interaction of camelina gum with other substances, camelina gum solutions with 0.5% and 1.0% camelina gum (w/w) were mixed with 2%, 5%, and 10% monovalent salt, sodium chloride (NaCl). A total of six gum solutions was prepared. In addition, camelina gum solutions with 0.5% and 1.0% gum concentration (w/w) containing 40% water and 60 % ethanol were prepared. All dispersions were stirred for 10 hours at room temperature and then allowed to stand by storing them for 12 h at 4 $^{\circ}$ C prior to performing rheological measurements.

Xanthan, LBG, and guar solutions were prepared at 0.5% and 1.0% w/w following the described procedure. LBG was stirred for 1 h at room temperature, heated to 80 °C in a water bath, and kept at this temperature for 30 min with continuous stirring. After cooling, the solution was stirred for 10 hours at room temperature as Xanthan and guar solutions.

4.1.2.2 Gum Mixtures

Gum mixtures with 1% total gum concentration were prepared by mixing camelina gum and commercial gums (xanthan, LBG and guar) at ratios of 1:3, 1:1, and 3:1, respectively. Distilled water containing 0.02 g/L of sodium azide was used as solvent. For mixtures containing LBG, this gum was dissolved, stirred for 1 h and then heated to 80 °C for 30 min under constant stirring, to ensure LBG solubility. After heating, LBG solution was cooled to room temperature and the required amount of camelina gum was added to form the mixture. All gum mixtures were stirred for 10 hours at room temperature and stored at 4 °C for 12 hours prior to rheological measurements.

4.1.3 Rheological Measurements

Elastic and viscous components of each gum solution were determined as a function of shear rate using a Bohlin CVOR 150-900 rheometer (Malvern Instruments, Southborough, Mass.), with a parallel plate head. The cone diameter was 8 mm and the distance between cone and plate was set to 0.5 mm for all measurements. All experiments were conducted in duplicate with average values reported.

4.1.3.1 Apparent Viscosity Measurement

The continuous shear test was conducted at a shear rate range of 0.005 to 2 s⁻¹ and 0.001 to 3000 s⁻¹ at 25 °C. Temperature effect on apparent viscosity of camelina gum solutions was determined at constant shear rate by varying temperature from 4 °C to 90 °C.

The interaction of camelina gum with other substances such as ethanol and sodium chloride was also studied.

4.1.3.2 Dynamic Viscoelastic Measurement

Frequency sweep tests were performed at 25 $^{\circ}$ C in a strain-controlled mode with an amplitude of shear strain of 0.05%, which was within the linear viscoelastic region. Frequency range was from 0.01 Hz to 10 Hz and from 0.01 Hz to 100 Hz. Storage modulus (G') and loss modulus (G') were continuously measured.

4.2 Results and Discussion

4.2.1 Effect of Concentration on Apparent Viscosity of Camelina Gum Solutions

Shear rate dependency of the apparent viscosity of 0.1–2.0% (w/w) camelina gum solutions at 25 °C is presented in Figures 4.1 and 4.2. All gum solutions exhibited a shear thinning (pseudoplastic) behavior over the entire range of shear rates tested. The shear thinning behavior of camelina gum may be due to macromolecular organization change in the solution caused by shear rate changes. The disruption of chain entanglements by the applied shear force produced a molecular disentanglement, and the molecules aligned themselves with the flow direction. Consequently, the dynamic viscosity decreased as shear rate increased (Cui 2005; Dakia et al 2008). No Newtonian region was identified at low shear rates, suggesting a zero-shear viscosity that could exist at very low shear rates.

A stiff molecular conformation in polysaccharides typically contributes to high zeroshear rate viscosity; these polysaccharides in solution exhibit strong shear thinning features. A high shear thinning behavior of gum solutions enables processing operations, such as mixing and pumping, and thinner consistency during swallowing. High viscosity values at low shear rates account for consistency in mouth-feel of a product and contribute to long-term stability of gum dispersions, whereas low viscosity values at high shear rates facilitate pouring properties of these gum dispersions (Hosseini-Parvar et al 2010; Williams and Phillips 2000). Camelina gum solutions at a concentration of 0.5% and 1.0% exhibited a tendency to form a viscosity plateau at high shear rates (Figure 4.2), A typical steady shear flow curve for pseudoplastic fluids in a bilogarithmic plane comprises a constant viscosity at very low shear rates (zero-shear viscosity, η_0), followed by a shear thinning region in which viscosity decreases as shear rate increases, and a high shear rates viscosity shows a constant behavior (infinite shear viscosity, η_{∞}) (Cui 2005).

Gum solution viscosity can be significantly influenced by molecular weight and structure; generally linear, rigid molecules have a larger hydrodynamic size compared to highly branched, flexible polymers of the same molecular weight. Therefore, linear molecules can exhibit higher viscosity. In addition, ionic gum viscosity is higher than the viscosity of neutral gums of similar molecular weight to ionic gums, since the molecular chains of ionic gums expand because of intramolecular charge repulsions. The degree of pseudoplasticity increases with the concentration and molecular weight of the polysaccharides (Williams and Phillips 2000).



Figure 4.1 Apparent viscosities of camelina gum solutions with varying concentrations (0.1-2%) at low shear rate.



Figure 4.2 Apparent viscosities for solutions of camelina gum at 0.5% and 1.0% concentrations and shear rate of 0.001 s⁻¹ – 3000 s⁻¹.

4.2.2. Effect of Temperature on Apparent Viscosity of Camelina Gum Solutions

The apparent viscosities of 0.1-2.0% (w/w) camelina gum solutions at various temperatures were determined (Figure 4.3). Camelina gum solutions exhibited a constant flow behavior at various temperatures; viscosity remained constant over the studied temperature range (4 °C - 90 °C) at a shear rate of 0.1 s^{-1} . In most cases, the increase of temperature fosters disentanglement of molecular chains in polysaccharides; therefore, viscosity of polysaccharide solutions decreases. Temperature changes may influence changes in molecular conformations of polysaccharides in solution (Cui 2001). However, certain gums, such as xanthan, have shown solution viscosity stability over temperature ranges of 0 °C to greater than 100 °C (BeMiller 2007); xanthan gum solutions retain viscosity until a specific melting temperature is reached. At melting temperature, a reversible molecular conformation change occurs and viscosity decreases (Sworn 2009). The viscosity-temperature relationship depends on the shear rate at which viscosity is measured and is usually reversible for the tested gum solution.



Figure 4.3 Apparent viscosities of camelina gum solutions at different temperatures at constant shear rate of 0.1 s⁻¹.

4.2.3 Effect of Salt on Apparent Viscosity of Camelina Gum Solutions

The effect of adding monovalent salt (NaCl) on apparent viscosity of camelina gum solutions is shown in Figure 4.4. The solutions exhibited a shear thinning behavior with a trend

to reach lower constant viscosity at very high shear rates (infinite shear viscosity, η_{∞}). No significant difference in viscosity was noted for camelina gum solution with 0.5% gum and NaCl concentrations (Figure 4.4 a). However, camelina gum solution at 1.0% showed decreased viscosity when NaCl concentration increased (Figure 4.4 b).

NaCl is commonly used in food industry as flavoring, preservative, leavening agent, and texturizing agent. The addition of salt to gum solutions can improve the efficiency of ohmic heating, which is a thermal process in which electricity is conducted through a food product that behaves as an electrical resistor, releasing heat. However, the presence of salts affects positively or negatively the rheological properties of gum solutions (Marcotte et al 2001). Gums such as yellow mustard, increase solution viscosity when salt concentration increases; other gums such as flaxseed gum, decrease viscosity because of increased intramolecular interactions that produce increased molecular coiling (BeMiller 2007). Previous studies reported that the viscosity of gums such as xanthan and galactomannans is not affected when salt is added to their solutions. If the addition of solutes such as salts decrease viscosity; this may be associated to suppression of intermolecular charge-charge repulsion that allows closer association of chains (Koocheki et al 2011; Rochefort and Middleman 1987; Vardhanabhuti and Ikeda 2006).





Figure 4.4 Effect of NaCl on apparent viscosities of camelina gum: a) 0.5% camelina gum with 2%, 5%, and 10% NaCl and b) 1.0% camelina gum with 2%, 5%, and 10% NaCl.

4.2.4 Viscoelastic Properties of Camelina Gum Solutions

Camelina gum solutions exhibited viscoelastic characteristics similar to polysaccharide solutions. The viscoelastic behavior of camelina gum solutions (0.5% and 1% w/w) at 25 °C was analyzed, and mechanical properties obtained at a constant strain (γ) of 0.05 are shown in Figure 4.5 (frequency 0-10 Hz), and Figure 4.6 (frequency 0-100 Hz). The elastic modulus (G') that relates to elastic response of the system, remained higher than the viscous modulus G" related to viscous response. The system demonstrated a solid-like behavior at low frequencies (Figure 4.5) characteristic of weak gels in which G'>G" and both moduli have a reduced frequency dependence (Williams and Phillips 2000). Polymer molecules are presumably entangled and bound to one another by weak and short associations (BeMiller 2007). The mechanical spectrum of gels exhibited G'>G" during tested frequencies. G' is frequency independent and G" slightly increases with an increase of frequency. The loss tangent (tan δ , where $\delta = G$ "/G') is the ratio of the loss and storage moduli and describes energy lost compared to energy stored in a cyclic deformation. The loss tangent is approximately 10⁻¹ for weak gels and 10⁻² for gels (Cui 2005;

Gaonkar 1995). Camelina gum solution at 0.5% (Figure 4.5 a) shows an elastic response independent of frequency from 0 to 2 Hz and a slightly increased viscous response. The frequency independent elastic modulus for camelina gum solutions at 1.0% (Figure 4.5 b) is clearly visible for the frequency range of 0.01 to 3 Hz. The viscous modulus also increased slightly. Loss tangent (tan δ) is in the order of 10⁻¹ for both gum solutions, confirming their weak gel-like behavior. G' and G" are visibly higher in camelina gum solutions at 1% than at 0.5% (Figure 4.5 c) for this frequency range. An increase in concentration results in an increase of G' and G" moduli (Cui 2005).





Figure 4.5 Oscillatory shear data for camelina gum solutions: a) 0.5% camelina gum concentration; b) 1.0% camelina gum concentration; and c) both 0.5% and 1.0% concentrations.

Regarding the frequency range 0-100 Hz, no difference between G" and G' values was observed for camelina gum solution at 0.5% gum concentration at low frequency from 0 to 0.4 Hz (Figure 4.6 a). G' was higher than G" for the frequency from 0.4 to 27 Hz, and, after 27 Hz, viscous and elastic moduli combined again to slightly overlap. For camelina gum solution at 1.0% (Figure 4.6 b), G' was higher than G" until a frequency of 10 Hz, at which point a cross-over of G" and G' occurred; G" was higher than G' at the subsequent frequency range. The cross-over frequency shifted to lower values, 27 Hz to 10 Hz compared with 0.5% gum concentration, indicating that gum concentration affects viscoelastic behavior of gum solutions (Ibanez and Ferrero 2003). Viscoelastic gum solutions typically are composed of a three-dimensional network of molecules with an elastic component emerging from elastic deformation of large molecules. In an oscillatory deformation test of viscoelastic gum solutions, after a partial recovery of applied energy, some extent of deformation is typically observed, since regions of the three-dimensional network tend to flow under stress. If the network is very resistant to loss

its structure, then the elastic component is greater. Conversely, if the network readily flows (breaks down its structure), then the viscous component is greater (Gaonkar 1995).





Figure 4.6 Oscillatory shear data of camelina gum solutions: a) 0.5% gum concentration;b) 1.0% gum concentration; and c) both 0.5% and 1.0% gum concentrations.

4.2.5 Apparent viscosity and viscoelastic properties of camelina gum in ethanol-water solutions

Camelina gum solutions at 0.5% and 1.0% w/w gum concentrations were prepared by dissolving camelina gum in an ethanol (60%)-water (40%) solution. The gum solutions exhibited pseudoplastic behavior with tendency to reach a lower constant viscosity at high shear rates (infinite shear viscosity, η_{∞}) (Figure 4.7 a). No significant changes in viscosity of both solutions were observed. For 0.5% camelina gum solution (Figure 4.7 b), G" was slightly higher than G' until a cross-over point at 0.4 Hz; thereafter, G' remained significantly higher than G" until another cross-over point at 27 Hz, where G" superimposed slightly again. For 1.0% camelina gum solution (Figure 4.7 c), G' was higher than G" until a cross-over point at 27 Hz, where G" until a cross-over point at 22 Hz; thereafter, G" superimposed slightly. A comparison of these results with oscillatory shear data obtained for camelina gum in water solutions (Figure 4.4 c) reveals that the rheological behavior of gum is affected by the presence of organic solvent. Solutions tend to show a liquid-like behavior at low and very high frequencies for 0.5% camelina gum and only at very high frequencies for 1.0% camelina gum.

Certain gums such as LBG and guar gum do not dissolve directly in alcohol, but gums such as xanthan, modified guar gum, and gum arabic can be dissolved in water-miscible solvents such as ethanol with a maximum concentration of 60% of the organic solvent (Sworn 2009). Products such as alcoholic beverages may be formulated with gums that dissolve in alcohol.





Figure 4.7 Effect of ethanol on rheological properties of camelina gum: a) apparent viscosities of camelina gum solution and camelina gum solution with 60% ethanol; b) oscillatory shear data for 0.5% camelina gum solution with 60% ethanol; and c) 1.0% camelina gum solution with ethanol (60%).

4.2.6 Rheological Properties of Camelina Gum Mixed with Xanthan, Guar, and LBG

Comparative flow curves for camelina gum and selected gums, includig xanthan, guar, and LBG, at 0.5% and 1.0% (w/w) are shown in Figure 4.8. All four gums exhibited pseudoplastic behavior. Camelina gum solution at 0.5% concentration showed higher viscosity than selected commercial gums at very low shear rates (Figure 4.8). Xanthan had the highest viscosity, followed by guar and camelina. All the gum solutions exhibited a tendency to reach an infinite shear viscosity, η_{∞} .

Viscosity of xanthan gum solution at 1.0% (Figure 4.8 b) is much higher than viscosities of other gums until a shear rate of 0.8 s⁻¹, at which point guar exhibits the highest viscosity, followed by LBG. A trend to reach a low constant viscosity at high shear rates (η_{∞}) can be noted in the figure.



Figure 4.8 Apparent viscosities of the gum solutions: a) at 0.5% gum concentration and b) at 1.0% gum concentration.

4.2.6.1 Rheological Properties of the Mixtures of Camelina Gum with Selected Commercial Gums

Apparent viscosity of mixtures of camelina gum with xanthan, guar, and LBG gums are shown in Figure 4.9. Gum concentration was kept constant at 1.0% (w/w) for all mixtures. The mixtures showed pseudoplastic behavior with tendency to reach a low constant viscosity (η_{∞}) and similar viscosity values at high shear rates. Camelina gum exhibited increased viscosity as a result of interaction with the three selected gums. Synergy was reached by xanthan-camelina mixture at a ratio of 3:1 at low shear rate (Figure 4.9 a), which demonstrated higher viscosity than other dispersions. The interaction of guar-camelina showed the highest viscosity for the mixture at a ratio of 1:3 at low shear rate (Figure 4.9 b).

LBG-camelina mixture at a ratio of 1:1 exhibited a higher viscosity performance than other tested ratios at low shear rate (Figure 4.9 c). The mixture at a ratio of 3:1 showed a similar viscosity performance than LBG-camelina mixture at ratio 1:1 after passing the low shear rate. A marked gap on viscosity behavior was evident between the mixture LBG-camelina at a ratio of 1:1 and camelina gum solution.







Figure 4.9 Apparent viscosities of 1.0% gum mixtures: a) xanthan (X):camelina (C); b) guar (G):camelina (C); and c) LBG:camelina (C) at ratios of 1:1, 1:3, and 3:1.

4.2.6.1 Effect of Temperature on Rheological Properties of Gum Mixtures

Apparent viscosity of mixtures of camelina gum and the gums xanthan, guar and LBG at various ratios, as a function of temperature and at constant shear rate of 0.1 s⁻¹, is shown in Figure 4.10. Similarly, interactions of camelina gum and the aforementioned gums showed an enhanced viscosity than camelina gum solution alone. The effect of temperature on apparent viscosity of the gum mixtures was small, the mixtures xanthan-camelina at ratio of 3:1 and LBG-camelina at ratio of 1:1 showed significant decreases (Figure 4.10 a and c). LBG-camelina at ratio of 1:1 displayed the highest viscosity of all mixtures. Xanthan-camelina mixtures at ratio of 3:1 showed the highest viscosity of all the xanthan-camelina mixtures at ratio of 1:1. Guar-camelina mixture at ratio of 1:1 exhibited the highest viscosity of all the other guar-camelina mixtures (Figure 4.10 b), although the three guar-camelina mixtures showed similar viscosity performances. A large gap exists between viscosity performance of camelina gum solution and camelina gum-guar mixtures. LBG-camelina mixtures at ratios of 3:1 and 1:3 showed similar viscosity performances to each other over the temperature range, although the mixture at ratio of 1:3 displayed increased viscosity at higher temperatures.





Figure 4.10 Effect of temperature on apparent viscosities of the gum mixtures: a) 1.0% gum mixtures of xanthan (X):camelina (C); b) guar (G):camelina (C); and c) LBG:camelina (C) at ratios of 1:1, 1:3, and 3:1.

4.2.6.1 Viscoelastic Properties of the Gum Mixtures

Mechanical properties of xanthan-camelina mixtures are exhibited in Figure 4.11. Interactions of camelina gum with xanthan resulted in enhanced viscoelastic properties compared to camelina gum solution; however, the viscous component of camelina gum solution was higher than the viscous component of the xanthan-camelina mixtures at high frequencies. G' modulus of xanthan-camelina mixture at ratio 1:1 was over G" until a cross-over frequency of 27 Hz, at which point G" was slightly over G' (Figure 4.11 a). Xanthan-camelina mixtures at ratios 1:3 and 3:1 showed similar viscoelastic behavior as the mixture at ratio 1:1 (Figure 4.11 b and c). G' modulus of the xanthan-camelina mixture at ratio of 3:1 was above the G' modulus of other dispersions at low frequencies (Figure 4.11 d), followed by G' modulus of the xanthan-camelina mixture at ratio of 1:1.

Guar-camelina mixtures also showed enhanced viscoelastic properties compared to viscoelastic properties of camelina gum solution alone (Figure 4.12). The viscous component of camelina gum solution was also higher than the viscous component of guar-camelina mixtures at high frequencies except for guar-camelina mixture at ratio of 3:1 which showed similar data to camelina gum solution at this frequency region (Figure 4.12 c). G' modulus of all mixtures was slightly over G" until a cross-over frequency of 27 Hz. Guar-camelina mixtures at ratios 1:1 and 3:1 showed the highest elastic modulus of all guar-camelina mixtures (Figure 4.12 d), although there is a cross- over at a frequency of 18 Hz, at which point G" of camelina gum solution and guar-camelina mixture at ratio 3:1 are over G' of the aforementioned guar-camelina mixtures.

G' modulus of LBG-camelina mixtures at all ratios was higher than G" until a cross-over at 27 Hz (Figure 4.13 a, b and c). LBG-camelina mixture at ratio of 3:1 exhibited the most enhanced viscoelastic properties of all mixtures (Figure 4.13 d). The viscous component of camelina gum solution surpassed the viscoelastic moduli of mixtures at high frequencies.

A comparison of camelina gum mixtures with xanthan, guar and LBG gums reveals that LBG-camelina mixtures have the highest moduli of all mixtures at all ratios. At high frequencies, LBG-camelina mixtures viscous moduli surpassed all mixtures and viscous modulus of camelina gum solution. Viscous moduli of camelina gum solution and LBG-camelina mixtures overlapped at ratios 1:3 and 3:1.



Figure 4.11 Oscillatory shear data for 1.0% gum mixtures of xanthan (X):camelina (C) at ratios of a) 1:1, b) 1:3, and c) 3:1; and d) comparison of all the data.



Figure 4.12 Oscillatory shear data for 1.0% gum mixtures of guar (G):camelina (C) at ratios of a) 1:1, b) 1:3, and c) 3:1; and c) comparison of all the data.



Figure 4.13 Oscillatory shear data for 1.0% gum mixtures of LBG:camelina (C) at ratios of a) 1:1, b) 1:3, and c) 3:1; and d) comparison of all the data.

Mechanical spectra of the mixtures showed a solid-like response throughout the frequency range and a slight liquid-like response at high frequencies. Gum interactions may produce a continuous network of polymer molecules or bundles of molecules primarily connected by noncovalent weak or short bonds (BeMiller 2007; Sandolo et al 2010). Xanthan, guar, and LBG are used as viscosity enhancing agents in different applications such as food products, and oil drilling. These gums are known as nongelling agents, but they can enhance the properties of gelling polysaccharides or cause gel-formation when interacting with gums that do not gel alone. For example, LBG can increase the firmness and elasticity of carrageenan and agar gels, also LBG can form a gel by interacting with xanthan (Dea and Morrison 1975). It has been proposed that all plant polysaccharides have a 1-4-diequatorial linkage geometry, so during interactions involving galactomannans or xanthan, the gum polysaccharides adopt ordered structures of extended ribbons and their associates experience thermoreversible disorder-order transitions under hydrated conditions (Liang et al 2011). Xanthan undergoes a temperatureinduced conformational transition from an ordered helical structure at low dissolution temperatures to a disordered helical structure at high temperatures. When xanthan is in a disordered state and interacting with plant polysaccharides, the plant polysaccharides attach to the xanthan backbone, forming a 6-fold helix (Liang et al 2011; Mao et al 2012).

LBG-camelina mixtures showed the highest elastic modulus of other mixtures at the same ratios (3:1, 1:1, 1:3), followed by guar-camelina mixtures. This behavior may be explained by the galactomannans chemical structure because guar gum has a galactose content of approximately 33% and LBG has a galactose content of approximately 20%. If the galactose content is higher, then the synergism is lower (Pinheiro et al 2011; Schorsch et al 1997). Many studies have validated the increase in viscosity when xanthan interacts with guar, and the gel formation when xanthan interacts with LBG. Guar gum has a higher molecular weight than LBG; therefore, guar solutions may exhibit higher viscosity than LBG solutions. Xanthan-guar gum mixtures can show higher viscosity than xanthan-LBG mixtures at the same experimental conditions (Casas et al 2000).

Gum interaction depends considerably on the dissolution temperature of each gum and the gum ratio. Dissolution of guar and LBG at high temperatures affects their mannose/galactose ratio and viscosity. The portion of guar gum dissolved at low temperatures (25 °C) is 88%, and at high temperatures (80 °C) the portion increases to 91% (Casas et al 2000). Temperature may also

influence apparent viscosity of the mixtures. Apparent viscosity decreases when mixtures are heated, probably because of thermal degradation of molecules in solution and weaker or broken molecular interactions (Casas et al 2000; Gomez-Diaz et al 2008). However, this behavior is reversible.

The viscous modulus of all camelina gum solutions and mixtures exhibited a similar pattern at the small strain tested (0.05) (Figure 4.14). At low frequencies, G' and G" were slightly frequency dependent, with G' > G" which implies that the gum solutions behaved as weak gels. The slope of a trend line crossing G" was small. At higher frequencies, G" crossed over G', a fluid-like behavior of the gum solutions was observed. A trend line crossing G" exhibited a large slope. An intersection point of the trend lines crossing G' and G" indicates the frequency at which the gum solution experiences a transition from a weak gel-behavior to a fluid-like behavior.



Figure 4.14 Viscous modulus pattern for camelina gum solutions and camelina gum mixtures.

The observed transition frequencies for camelina gum solution and mixtures were as follows:

- 4.09 Hz -- Camelina gum solution alone (1.0% w/w);
- 5.96 Hz -- X-C mixture at ratio 3:1, G-C mixture at ratios 1:1 and 3:1;
- 6.58 Hz -- LBG-C mixture at ratio 1:3;
- 6.89 Hz -- X-C mixture at ratio 1:3;
- 7.20 Hz -- X-C mixture at ratio 1:1, G-C mixture at ratio 1:3, LBG-C mixtures at ratios 1:1 and 3:1

Transition frequencies for camelina gum mixtures are higher than the transition frequency for camelina gum solution alone. This response can be explained by the intermolecular associations between the mixed gums; intermolecular aggregation between the gums produces significant effects on the rheological properties of the gum mixture, intermolecular gum interactions can involve associations of chain segments of the mixed gums forming junction zones or chain-chain associations by charge-charge attractions. The nature of the gums and the mechanism of molecular interactions are factors influencing the mechanical and rheological properties of camelina gum mixtures. Camelina gum mixed with other gums, can undergo self-association and intermolecular associations with the mixed gum molecules. The disruption of the entanglements formed by mixing gums occurs at higher frequencies for the mixtures than for camelina gum solution alone. The ratio of the gum mixture and structure of the gums influence this transition frequency. LBG-camelina mixtures exhibited the highest elastic components in the frequency sweep test (Figure 4.13), and a transition frequency of 7.20 Hz was observed for LBG-C mixtures at ratios 1:1 and 3:1, which stands for a distinctive solid-like behavior for these mixtures in comparison with the other camelina-gum mixtures (Lapasin and Pricl, 1999).

Chapter 5 - Conclusions and Recommendations for Further Research

5.1 Conclusions

In this study, physicochemical and rheological properties of camelina gum and camelina gum mixture with selected commercial gums were analyzed. Proximate analysis composition showed a protein content of 29.2% and a moisture content of 9.4%. Monosaccharides present in the sample are arabinose, rhamnose, galactose, glucose, xylose and mannose; the acidic sugars glucuronic acid and galacturonic acid could not be identified by the eluents concentration used. The analysis of neutral and acidic sugars using high performance anion-exchange chromatography requires specific NaOH and NaOAc eluent gradients in order to obtain a complete separation of the sugars and avoid peak overlapping.

The primary functional groups determined by FTIR spectrum included 2927 cm⁻¹ and 1469 cm⁻¹ (C-H), 1570 cm⁻¹ (C=O), and 1151 cm⁻¹ (C-O-C). Peaks between 1153 cm⁻¹ and 1039 cm⁻¹ related to polysaccharides containing mannose, arabinose, and rhamnose were also observed.

Thermal gravimetric analysis showed three distinct stages of weight losses, with overlapping by the second and third stages. The weight loss is primarily due to desorption of moisture and thermal decomposition of the gum. Differential scanning calorimetry showed an endothermic peak at 228.87 °C, which is related to melting temperature.

The structure of camelina gum is fibrillar, consisting of single strands with diameters between 4 and 6 nm, connected to each other and forming a network. This type of structure is highly associated to rheological properties of the gum, favoring characteristics such as water absorption and swelling capacity.

Camelina gum solution exhibited a shear thinning behavior with tendency to low constant viscosity at very high frequencies. This behavior was observed for camelina gum solution and camelina gum mixtures with other components (NaCl, ethanol, and other gums). The effect of camelina gum concentration was noted in increased viscosity. The temperature did not significantly influence rheological properties of the gum solutions. This response has also been reported for xanthan gum solutions. Camelina gum solutions exhibited gel-like behavior at a frequency range of 0 - 10 Hz; the elastic component was higher than the viscous component over

the frequency range tested. At 1.0% concentration, the gel-like behavior is clearly visible. Polysaccharides that form weak gels exhibit a G' higher than G" and a reduced frequency dependence; the molecules are entangled and bound to one another by weak and possibly short associations, forming a three-dimensional network structure. At a frequency range of 0 - 100 Hz, camelina gum solutions exhibited solid-like behavior (G'>G") at low frequencies and a cross-over to liquid-like behavior at high frequencies.

Dissolution of camelina gum in ethanol-water did not show a distinctive difference in apparent viscosity and rheological behavior compared to camelina gum in water solution, thus inferring that the gum can be formulated in products containing alcohol, such as alcoholic beverages. The interaction of sodium chloride (NaCl) with camelina gum at 1.0% gum concentration decreased viscosity when salt concentration increased. Camelina gum solution at 0.5% concentration did not show relevant viscosity differences related to salt concentration. Interactions of camelina gum with two galactomannans (guar and LBG) and xanthan were studied. Since one gum cannot deliver a complete range of properties, price, and functionality, the use of gum mixtures in industry has been a relevant alternative. All gum mixtures exhibited viscosity increase compared to camelina gum solution alone. Synergies of apparent viscosity were exhibited by xanthan-camelina at ratio of 3:1, LBG-camelina at ratio of 1:1, and guar-camelina at ratio of 1:3 at low shear rate. The effect of temperature on apparent viscosity of the mixtures was insignificant. Solid-like behavior was predominant over a broad frequency range with a cross-over to liquid behavior at high frequencies. LBG-camelina at ratios of 1:1 and 3:1 exhibited the highest elastic components of mixtures at those ratios.

5.2 Recommendations

Camelina gum is a plant polysaccharide with rheological characteristics to be used in various industrial and food applications. Future studies may focus on detailed structural analysis of camelina gum polysaccharides to determine linkage pattern, anomeric configuration, ring size, sequences of monosaccharides, molecular weight, and molecular weight distribution. The relationship between apparent viscosity and temperature needs to be described by mathematical equations such as the Arrhenius equation in order to more fully understand the dependency of camelina gum rheological behavior to temperature. In addition, various mathematical models suggested to determine rheological patterns of solutions must be applied in order to describe

camelina gum rheological patterns. The performance of a complete rheological characterization that allows consideration of a long-time scale, small and large deformations, and the entire viscoelastic spectrum must be undertaken. The synergy of camelina gum with tested gums needs to be analyzed considering additional ratios and various dissolution gum temperatures since xanthan and the galactomannans exhibit higher or lower viscosities according to the dissolution temperature. The continued study of the interactions of camelina gum with other components such as divalent salts, low-molecular-weight sugars, protein, starch, and other commercial gums comprising gelling and non-gelling agents is relevant. These interactions must consider parameters such as different ratios and temperature of dissolution. The conformation that camelina gum adopts in solution when interacting with other components may be considered in order to predict rheological and morphological properties of these interactions. Consideration of properties such as surface tension, foaming, emulsion capacity and stability, and water and oil absorption capacity may allow a complete characterization of camelina gum.

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