ABSTRACT

YANIV, YIFAT RAHEL. Rheological Characterization of Alginate Microbead Gels and Suspensions. (Under the direction of Dr. Christopher R. Daubert.)

As the use of microbeads in food, pharmaceutical, and other industries becomes more prevalent, additional data is needed regarding the rheology of suspensions and gels composed of microbeads. The goal of this work was to evaluate the rheological properties of alginate microbead gels and suspensions.

The microbeads used in this research were produced by an air-assisted atomization process that was designed for this work. The process was based on disintegration of alginate solution jet by exposure to high-velocity air, and yielded alginate microbeads ranging in size from several microns to several hundred microns. The bead diameter was a function of solution viscosity and air velocity. Decreasing solution viscosity and increasing air velocity contributed to the disintegration of the atomized liquid jet and produced smaller beads. A correlation between the bead median diameter and the Weber and Reynolds numbers was obtained by dimensional analysis: \( D \propto (We \times Re)^{-0.25} \). The beads produced were used for construction of the “microbead gels” and suspensions.

The mechanical properties of the microbead gels were investigated as a function of bead mechanical properties and particle size distribution. Bulk gels were used to evaluate the mechanical properties of the beads, which depended on alginate type and concentration. The microbead gels were constructed from different bead types and the viscoelastic properties of the microbead gels were related to the viscoelastic properties of the bulk gels. While higher modulus beads contributed to the modulus of the microbead gel, they were also less deformable and therefore decreased interparticle contact. As smaller particles
were introduced into the system, the importance of particle deformability and interparticle interactions increased.

The rheology of suspensions composed of viscoelastic particles was investigated as a function of shear rate, volume fraction, particle size distributions, and mechanical properties of the beads. The viscoelastic properties of the beads proved to be very important in the analysis of the effects shear rate, particle volume fraction, and particle size distribution had on suspension viscosity. The diverse flow behavior could not be fully explained by the models presented in literature; therefore, several mechanisms were proposed to explain suspension rheology. The proposed mechanisms were based on the hydrodynamic forces, interactions between the particles, and the beads viscoelastic properties.
Rheological Characterization of Alginate Microbead Gels and Suspensions

by
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A dissertation submitted to the Graduate Faculty of North Carolina State University in partial fulfillment of the requirements for the degree of Doctor of Philosophy

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CHAPTER 1 INTRODUCTION

From the flow of liquids to deformation and fracture of solids, materials can be characterized by their response to stress. Rheology, as the study of flow and deformation of materials, is used to evaluate the type and extent of the microstructure of materials. This work focused on the rheological characterization of alginate microbead gels and suspension.

Alginate has been a source material for bead production in previous research. Literature cites alginate bead production to range in size from a few microns (microbeads) to a few millimeters utilizing various methods (Martinsen and others 1989; Velings and Mestdagh 1995; Ouwerx and others 1998; Simpson and others 2003; Herrero and others 2006a). However, air-assisted atomization has been reported to produce microbeads as small as several microns in diameter. In air-assisted atomization, the relatively slow-moving liquid is exposed to a high-velocity air stream to disrupt the alginate stream into droplets. Most practical spraying systems generate a range of droplet sizes. The droplet geometry is affected by the internal geometry of the atomizer, the properties of the gaseous medium into which the liquid stream is discharged, and the physical properties of the liquid (Lefebvre 1989). The first objective of this project was to engineer an air-assisted atomization-based apparatus to produce alginate microgel beads and analyze the particle size distribution of the beads produced as a function of alginate concentration and processing parameters.

While rheological properties of alginate bulk gels have been studied extensively (Smidsrod 1974; Mitchell and Blanshard 1976; Martinsen and other 1989; Ouwerx and other 1998;
Stokke and others 2000; Zhang and others 2005), the properties of a unique matrix such as
the microbead gel have not. Since rheology is a tool to gauge the type and extent of
microstructure, the objective was to evaluate the mechanical properties of microbead gels
as a function of bead mechanical properties and particle size distribution. These
relationships can then be applied to manipulate gel composition to adjust characteristics of
the matrix.

A suspension is a heterogeneous two-phase system, consisting of discrete particles
randomly distributed in a continuous fluid medium. Suspension rheology has been a topic
of interest for over a century. Starting with Einstein’s theory (1906) through models and
experimental results available in literature, most of the work done previously relied on
assumptions that are inappropriate for a large phase volume of viscoelastic particles. This
work evaluated the flow behavior of microbead suspensions as a function of the bead
mechanical properties, volume fraction, particle size distribution, and shear rate.

The objectives presented were addressed and are presented in separate chapters. The 3
objectives were:

1. Microbeads production and analysis;

2. Microbead and bulk gel preparation and analysis;

3. Evaluation of non-colloidal microbead suspensions
CHAPTER 2 MICROBEADS PRODUCTION AND ANALYSIS

2.1 Abstract

Alginate microbeads with a diameter ranging from several micrometers to several hundred micrometers were produced utilizing an air-assisted atomizer which was designed for this project. The diameter of the beads was measured by light scattering and was analyzed with respect to the viscosity of the alginate solution subject to atomization as well as the velocity of the pressurized air used for atomization. The bead diameter was found to increase with increasing solution viscosity and with decreasing air velocity. The factors influencing atomization were also analyzed by dimensional analysis. The correlation between the bead median diameter and the Weber and Reynolds numbers successfully predicted bead diameter.

2.2 Introduction

Alginate gel beads have been used in the past for various applications, primarily in the pharmaceutical industry as a drug carrier, but also in the food industry as flavor carriers and fat replacers (Aguilera and Stanley 1999; Smidsrod and Draget 1997). Alginate is a biocompatible, biodegradable water-soluble polysaccharide extracted from brown seaweed. Composed of alternating blocks of 1-4 linked α-L-guluronic and β-D-mannuronic acids (Figure 2.1), alginates form gels by reaction with divalent cations such as calcium (Figure 2.2) (Gacesa 1988).
Several technologies for alginate bead production are mentioned in literature, from dropwise addition of alginate solution into calcium chloride (Martinsen and others 1989; Velings and Mestdagh 1995; Ouwerx and others 1998) and electrostatic bead generation (Simpson and others 2003) to various air-assisted atomization techniques (Herrero and others 2006). Most methods cite beads ranging in size from hundreds of micrometers to several millimeters in diameter. However, air-assisted atomization has been reported to produce microbeads in the range desired for this research project (Herrero and others 2006).

Air-assisted atomization is based on disintegration of a liquid jet by exposure to high-velocity air or gas. Most practical atomization systems generate a range of droplet sizes affected by the properties of the gaseous medium into which the liquid stream is discharged, the physical properties of the liquid, and the internal geometry of the sprayer (full cone, flat sheet, etc) (Lefebvre 1989). The factors influencing atomization and the physical mechanism of liquid jet breakup have been addressed in numerous publications. However, there is no single mechanism or analysis that fully accounts for the erratic disintegration processes that occur during atomization. The work of Rayleigh (1879), Scheuble (1927), Haenlein (1931), and Weber (1931) was summarized by Schweitzer (1937) who showed the mechanisms of disintegration of liquid jets suggested by the authors, none of which accounted for all factors affecting the disintegration of the liquid jets. Scheuble (1927) identified several factors responsible for liquid droplet breakdown, including surface tension of the liquid, the velocity of the liquid and air, the density of the liquid and air, the nozzle geometry, liquid and air viscosities. Lefebvre (1989), Chigier and Reitz (1996), and Lasheras and Hopfinger (2000) provided more recent reviews of drop
and spray formation from a liquid jet and identified the same factors to affect the atomization process. Several authors (Reitz and Bracco 1982; Mansour and Chigier 1995) focused on the breakup of a liquid jet based on a development of surface waves on the stream, which governed the disintegration mechanism of a round liquid jet in a coaxial gas stream. Based on this theory, the breakup is a result of the unstable growth of short wavelength waves at the liquid-gas interface.

Atomization has been utilized for the production of alginate microbeads by Herrero and others (2006) who investigated the effect of solution viscosity and air pressure on bead size. Notably, the average diameter increased with an increase of alginate viscosity, and the average diameter decreased with an increase of air flow rate. Furthermore, Rehg and others (1986) also investigated the application of an atomizer in production of small alginate gel beads, concluding that a high gas flow rate produced a high shear rate at the droplet surface which helped to disengage the droplet escape from the needle. Mansour and Chigier (1995) also investigated the influence of fluid viscosity on particle size for non-Newtonian fluids during atomization, where increased viscosity led to increased particle size.

Since the important variables that affect atomization are known, dimensional analysis has been a very useful tool in exploring the effects that these variables have on the process (Mansour and Chigier 1995). The Weber and Reynolds numbers (Equation 2.1 and 2.2) are examples of dimensionless groupings which account for the various parameters influencing the atomization process and the resulting droplet size distribution. The Reynolds number relates inertial and viscous forces of the fluid or the air, considering velocities, viscosities, and densities of the fluid streams. The Weber number accounts for the inertial force of the air and the surface tension. These dimensionless numbers and their combinations are
frequently used in literature as a starting point for many liquid jet breakup models, including atomization.

\[ \text{Re}_{\text{liquid}} = \frac{\rho_{\text{liquid}} d v_{\text{liquid}}}{\mu_{\text{liquid}}} \quad \text{Equation 2.1} \]

and

\[ \text{We} = \frac{\rho_{\text{gas}} d v_{\text{air}}^2}{\sigma_{\text{liquid-air}}} \quad \text{Equation 2.2} \]

The objectives of this work were to design an apparatus to produce a large quantity of food grade alginate microbeads; and to analyze the particle size distribution of the beads produced as a function of alginate concentration and processing parameters.

### 2.3 Materials and Methods

#### 2.3.1 Solution preparation and properties

Alginate samples with an average molecular weight of 260,000 Da were provided by Danisco (Brabrand, Denmark). Alginate solutions of different concentrations (1%, 1.5%, 2%, 2.5%, and 3%) were prepared by blending alginate powder in de-ionized water, and hydrating for no less than 72 hours at 4°C. The viscosity of each solution was measured using a rheometer (StressTech Rheological Instruments AB, Lund, Sweden), performing a shear rate sweep from 1 to 1000 1/s over 500 s. Surface tension of the alginate solutions was measured with an automated contact angle goniometer (Rame-Hart Inc., Mountain
Lakes, NJ); and alginate density was measured using a Mettler-Toledo DE40 density meter (Mettler-Toledo, Columbus, OH).

### 2.3.2 Alginate microbeads production

An apparatus was designed for the production of alginate microbeads (Figure 2.3). An alginate solution was pumped through an atomization nozzle (Figure 2.4) (Spraying systems Inc. Wheaton, Illinois) with an outlet diameter of 500 μm at an average flow rate of 130 ml/min, allowing a constant flow through the nozzle. Atomization was assisted by an external compressed air stream at varying pressure ranges from 20 to 60 psi (138.9-413.7 kPa), correlating to air velocities of 166-498 m/s. The alginate solution was sprayed into a 1.5% w/w CaCl$_2$ (Dow Chemicals, Midland, MI) bath, which was sufficient to allow uniform gelation of the spheres. All experimental procedures were carried out under atmospheric pressure and at room temperature. The gelled alginate beads were then collected and filtered (Whatman, Piscataway, NJ) to remove excess liquid. Finally, the gel spheres were analyzed for particle size and distribution.

### 2.3.3 Particle size analysis

A Horiba LA-930 (HORIBA Instruments, Inc. Irvine, CA) was used for particle size analysis, measuring particle size distribution by angular light scattering techniques. The particles were also viewed under a Hoffman Modulation Contrast microscope (Modulation Optics, Inc. Greenvale, NY) to verify their spherical shape.
2.3.4 Dimensional analysis

Several factors are known to affect the process of atomization (Lefebvre, 1989): the gaseous medium, the internal geometry of the sprayer, and the liquid properties. The ratio between the median droplet diameter ($D$) and nozzle diameter ($d$) was selected as the dimensionless dependent variable:

$$\frac{D}{d} = f(d, \rho_{\text{air}}, \rho_{\text{liquid}}, \mu_{\text{liquid}}, \nu_{\text{air}}, \nu_{\text{liquid}}, \sigma_{\text{liquid-air}})$$  \hspace{1cm} \text{Equation 2.3}

Considering all the factors that affect the atomization process, 5-dimensionally independent variables are realized:

$$\frac{D}{d} = f(d, \rho, \mu, \nu, \sigma)$$  \hspace{1cm} \text{Equation 2.4}

The MLT (mass, length, time) system of units was applied to represent variable dimensions:

- $D$  Representative diameter of the droplet  \hspace{0.5cm} \text{L}
- $d$  Nozzle diameter  \hspace{0.5cm} \text{L}
- $\rho$  Density of the alginate solution or the air  \hspace{0.5cm} \text{M L}^{-3}
- $\mu$  Viscosity of the alginate solution  \hspace{0.5cm} \text{M L}^{-1} \text{T}^{-1}
- $\sigma$  Surface tension  \hspace{0.5cm} \text{M T}^{-2}
- $\nu$  Velocity of the air or the liquid  \hspace{0.5cm} \text{L T}^{-1}

Next, the dimensional variables were raised to an unknown order to insure dimensional homogeneity (Langhaar, 1951):

$$\frac{D}{d} = C_1 \; d^a \; \rho^b \; \mu^c \; \nu^d \; \sigma^e$$  \hspace{1cm} \text{Equation 2.5}
The variables were then replaced by the correlating MLT dimensions:

\[ [1] = [1][L]^a[ML^{-3}]^b[ML^{-1}T^{-1}]^c[LT^{-1}]^d[MT^{-2}]^e \quad \text{Equation 2.6} \]

Table 2.1 represents the matrix used to check the matrix rank and verify linear independence between the variables. Next, the exponents were determined, and Equation 2.5 was simplified. The 2 dimensionless groups of the system, known as \( \Pi \) groups, were determined:

\[
\frac{D}{d} = C_1 \left[ \frac{\mu}{\rho dv} \right]^c \left[ \frac{\sigma}{\rho dv^2} \right]^d \quad \text{Equation 2.7}
\]

\[
\frac{D}{d} = C_1 \left[ \Pi_1 \right]^c \left[ \Pi_2 \right]^d \quad \text{Equation 2.8}
\]

Where:

\[
\Pi_1 = \frac{\mu}{\rho dv} = \frac{1}{Re} \quad \text{Equation 2.9}
\]

and

\[
\Pi_2 = \frac{\sigma}{\rho dv^2} = \frac{1}{We} \quad \text{Equation 2.10}
\]

The exponents \( c \) and \( d \) (Equation 2.7), as well as the proportionality constant, \( C_1 \) were determined using multiple linear regressions based on 51 data points obtained from particle size analysis.

Equation 2.7 included several constants: air density and nozzle diameter were maintained as constants in this research; surface tension of the liquid and density of the liquid were
assumed constants as the alginate concentration effect was negligible. By grouping all the constants into one, $C_2$, Equation 2.7 was simplified:

$$\frac{D}{d} = C_2 \frac{\mu^c}{V^2d} \quad \text{Equation 2.11}$$

### 2.4 Results and Discussion

#### 2.4.1 Alginate solutions

Alginates solutions have pseudoplastic characteristics. (Herrero and others 2006a). Expectedly, the viscosity of an alginate solution depends on the concentration of alginate (Senuma and others 2000). As anticipated, an increase in alginate concentration led to an increase in solution viscosity and a pseudoplastic behavior was detected (Figure 2.5). While the addition of high molecular weight polymers to water is known to increase solution viscosity, some high molecular weight polymers had little or no influence on surface tension (Goldin and others, 1969). The surface tension of the solutions was not affected by the addition of alginate and was similar to that of pure water with an average of 0.071 N/m. The density of the alginate solution was affected by concentration, but given the low alginate concentrations the effect was not significant and was used in further calculations as a constant at 1,007 kg/m$^3$. Table 2.2 summarizes the physical and rheological properties of the alginate solutions used. Note that the only significant effect achieved by varying the concentration was solution viscosity.
2.4.2 Alginate microbeads production

The apparatus designed for the production of alginate microbeads (Figure 2.3) was an air-assisted atomization process. High gas velocities were generated by high-pressure gas flowing through annular orifices surrounding the alginate liquid jet (Figure 2.4). The high concurrent gas velocity transmits momentum to the liquid interface, causing destabilization of the liquid jet (Lin and Reitz, 1998). In the atomization regime of a round liquid jet, a diverging spray is observed immediately at the nozzle exit (Reitz and Bracco, 1982). The air pressures used in this work were high enough to initiate atomization at the nozzle exit. As drops of alginate solution were introduced into a CaCl$_2$ solution, alginate gelation starts. Some authors have considered the reaction to be instantaneous or nearly so (Somesh and others 1988; Herrero and others 2006a; Blandino and others 1999). The complete gelation of alginate is considered to be governed by diffusion of calcium through the gel. Given the size of the beads and the diffusion coefficient of calcium through an alginate gel, the maximum time required for diffusion of calcium into the center of the bead was calculated (Appendix B) to less than 20 s. The beads were maintained in the Calcium Chloride solution for no less than 60 s, therefore complete gelation was expected. The spherical shape of the beads was confirmed visually through a Hoffman Modulation Contrast microscope.

2.4.3 Particle size distribution and dimensional analysis

Particle size distribution was measured using a Horiba LA-930, utilizing angular light scattering techniques and assuming a spherical particle shape. Figure 2.6 shows the particle size distribution as a function of concentration at constants air velocities to demonstrate
the effect of solution viscosity; higher solution viscosity resulted in larger beads. Figure 2.7 shows the particle size distribution as a function of air velocity for a constant alginate concentration to demonstrate the effect of air velocity on bead diameter; higher air velocity resulted in smaller beads.

The solution viscosity and air velocity effects were supported by the dimensional analysis which was used to predict the particle size distribution produced by the apparatus designed for this research. The correlation between the median particle size, solution viscosity ($\mu$), and air velocity ($v$) was found to be:

$$\frac{D}{d} = 2.77 \left[ \frac{1}{Re \cdot We} \right]^{1/4}; R^2 = 0.91 \quad \text{Equation 2.12}$$

$$\frac{D}{d} = 3130 \left[ \frac{\mu}{v^2} \right]^{1/4} \quad \text{Equation 2.13}$$

The correlation was used to predict bead median diameter for the viscosities and air velocities that were investigated, and the results from the prediction were compared with the measured diameters (Figure 2.8).

The dimensional analysis was in agreement with the particle size distribution results, where the bead diameter increased with viscosity and decreased with air velocity. A correlation that did not consider liquid viscosity or air velocity was also considered, but the coefficients of determination, $R^2$, for both cases were lower than 0.5. A similar correlation was obtained by Herrero and others (2006), where the best correlation took into account
both air velocity and liquid viscosity. The median diameter was a function of $W_{e}^{-0.27}$ and $\mu^{0.27}$. Mansour and Chigier (1995) found that the median diameter depended on viscosity and air velocity as well. The median diameter was best described by equations involving the exponent of the liquid viscosity equal to the exponent of the Weber number.

The diameter of the beads depended on the breakup of the liquid jet, occurring when the magnitude of the disruptive force just exceeded the consolidating surface tension force. Larger beads are produced when the liquid jet disintegration is delayed (Lefebvre 1989). An increase in solution viscosity contributes to an increase in particle size, because liquid viscosity exerts a stabilizing influence by opposing any change in system geometry. Aerodynamic forces, on the other hand, act on the liquid surface and promote the disruption process by applying an external distorting force to the bulk liquid. Therefore, an increase in air velocity led to a decrease in particle size.

2.5 Conclusion

An apparatus was designed for the production of alginate microbeads utilizing air-assisted atomization. The process yielded microbeads ranging in size from several micrometers to several hundred micrometers. The particle median diameter was a function of solution viscosity and air velocity. Both higher air velocity and lower solution viscosity contributed to the disintegration of the atomized liquid jet into drops; therefore, producing smaller beads. The solution viscosity and air velocity effects were supported by the dimensional analysis which successfully predicted the median particle size produced by the apparatus designed for this research.
### Table 2.1

Matrix of the dependent variables and their MLT dimensions

<table>
<thead>
<tr>
<th></th>
<th>V</th>
<th>ρ</th>
<th>μ</th>
<th>σ</th>
<th>D</th>
</tr>
</thead>
<tbody>
<tr>
<td>Length</td>
<td>1</td>
<td>-3</td>
<td>-1</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>Mass</td>
<td>0</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>Time</td>
<td>-1</td>
<td>0</td>
<td>-1</td>
<td>-2</td>
<td>0</td>
</tr>
</tbody>
</table>

### Table 2.2

Alginate solution physical properties at 25°C as a function of concentration

<table>
<thead>
<tr>
<th>% Alginate</th>
<th>Viscosity at 500 1/s (Pa·s)</th>
<th>Surface tension (N/m)</th>
<th>Density (kg/m³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1%</td>
<td>0.0288±0.0005</td>
<td>0.071±0.00008</td>
<td>1001.9±0.0001</td>
</tr>
<tr>
<td>1.5%</td>
<td>0.0663±0.0002</td>
<td>0.071±0.00008</td>
<td>1004.3±0.0001</td>
</tr>
<tr>
<td>2%</td>
<td>0.1244±0.0004</td>
<td>0.072±0.00042</td>
<td>1007.0±0.0002</td>
</tr>
<tr>
<td>2.5%</td>
<td>0.1998±0.0021</td>
<td>0.071±0.00012</td>
<td>1009.4±0.0004</td>
</tr>
<tr>
<td>3%</td>
<td>0.2909±0.0010</td>
<td>0.072±0.00015</td>
<td>1012.1±0.0003</td>
</tr>
</tbody>
</table>
Figure 2.1 Blocks of 1-4 linked β-D-mannuronic acid (top) and α-L-guluronic acid (bottom) (Gacesa 1988)

Figure 2.2 Alginate gelation upon addition of Ca++ (●) (Gacesa 1988)
Figure 2.3 Beads production system
Figure 2.4 Air atomizing nozzle available with different spraying geometries and spray patterns (Spraying Systems co.)
Figure 2.5 Alginate (MW=260,000, Danisco, Europe) solution viscosities over a range of shear rates as a function of alginate concentration (%W/W)
Figure 2.6 (a) Particle size distribution as a function of alginate concentration at 20psi (166 m/s)
Figure 2.6 (b) Particle size distributions as a function of alginate concentration at 40psi (332 m/s)
Figure 2.6 (c) Particle size distributions as a function of alginate concentration at 60psi (498 m/s)
Figure 2.7 Particle size distributions as a function of air velocity (Alginate 1.5%)
Figure 2.8 Correlation between calculated diameters and measured diameters

\[ y = 0.9892x \]
\[ R^2 = 0.7967 \]
2.6 References


CHAPTER 3 MICROBEAD AND BULK GEL PREPARATION AND ANALYSIS

3.1 Abstract

Alginate microbeads were used for the construction of a unique gel matrix (the “microbead gel”). The mechanical properties of the microbead gels were investigated as a function of bead mechanical properties and particle size distribution. The microbead gels were also compared to bulk alginate gels to identify differences in microstructure. The mechanical properties of the beads were a function of alginate type and concentration yielding different viscoelastic properties, deformation, and fracture properties. Utilizing different bead types and sizes to construct the microbead gels affected the properties of the gels. Higher modulus beads contributed to a higher modulus of the microbead gel; however, because they were also less deformable, the contact surface and interaction between the beads was limited thus contributing to a weaker gel.

3.2 Introduction

Walstra (2003) defined structure as “the distribution over space of the component in a system.” This work focused on the effects of particle size distribution and particle mechanical properties on the rheology of a microbead gel matrix. The microbead gel was considered as a closely packed system of highly concentrated soft particles. When dealing with such a system, rheological properties of the particles are an important consideration affecting system behavior (Walstra 2003).
The viscoelastic properties of bulk alginate gels are a function of alginate composition and concentration. Martinsen and others (1989) showed that gel strength increased with increasing content of guluronic acid in the polymer chain and with increasing alginate content. High turbidity and low modulus was found to be typical for polymannuronic alginates, whereas polyguluronic was characterized by high stiffness and transparency (Smidsrod 1974). Ouwerx and others (1998) investigated the mechanical and structural properties of alginate gels made with different molecular weights and Mannuronic to Guluronic acid ratio. The Young's modulus (E) of alginate gels formed in the presence of calcium (0.1 M) increased with the square of the alginate concentration (C): \( E \propto C^2 \), demonstrating that alginate concentration is one of the parameters limiting bead elasticity.

Comparing alginate gels of different preparation methods, Mitchell and Blanshard (1976) showed that gels formed by dialysis had similar strength to those prepared by internal setting. Comparing alginate gels of different sizes and preparation methods, Amici and others (2007) investigated alginate gelation in microfluidic channels. The authors assumed that although the bulk gels and the gelled drops were prepared in different ways, if there is good and fast mixing of the reagents, then the final modulus would be the same. Loret and others (2006) assumed that the apparent elastic modulus of agarose microbeads was approximately the same as a bulk agarose gel at the same concentration.

Particle size distribution will affect the properties of gels that contain particles. The size and polydispersity of the particles determine the maximum volume fraction of particles in a confined space (Walstra, 2003). More polydisperse particles can lead to higher packing (higher volume fraction) because smaller particles can fill gaps and spaces between larger ones (Walstra 2003). Langley and Green (1989) investigate gels containing soft particles
and found that gels with small particles were ductile and those with large particles were brittle.

The rheology of the gel beads may help determine some of the system properties, such as viscoelastic and fracture properties. Langley and Green (1989) showed that surface chemistry of the particles has a large influence on the interactions between the particles and the matrix of a microbead. Velings and Mestdagh (1995) showed that the surface of an alginate bead (2% w/v alginate prepared with calcium ions) was smooth and uniform, this observation was supported by Ouwerx and others (1998). Surface properties of alginate gels are not readily available in literature. However, due to the structure of alginate and existence of numerous hydroxyl groups along the polymers, hydrogen bonding is considered to be the underlying mechanism in surface interactions (Caykara and others 2005).

The objective of this chapter was to evaluate the mechanical properties of microbead gels as a function of bead mechanical properties and particle size distribution.

### 3.3 Materials and Methods

#### 3.3.1 Alginate solution preparation

Alginate powders of different properties (Table 3.1) were provided by Danisco (Brabrand, Denmark). A 3% (w/w) alginate solution was prepared by blending the alginate powder in de-ionized water and allowing the dispersion to hydrate for no less than 72 hours.
### Table 3.1
Alginate powder properties (Provided by Danisco)

<table>
<thead>
<tr>
<th>Name</th>
<th>Guluronic Acid (%)</th>
<th>Mannuronic Acid (%)</th>
<th>Molecular weight (KDa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alginate De Sodium Flavicans</td>
<td>70</td>
<td>30</td>
<td>270</td>
</tr>
<tr>
<td>Alginate TS-A 6556</td>
<td>32</td>
<td>68</td>
<td>463</td>
</tr>
<tr>
<td>GRINDSTED Alginate FDG 125</td>
<td>50</td>
<td>50</td>
<td>500</td>
</tr>
</tbody>
</table>

#### 3.3.2 Bulk gel preparation

A homogeneous gel was prepared based on an internal-setting method described by Zhang and others (2005). A 3% alginate stock solution was prepared 3-4 days prior to bulk gel preparation. Next, 0.13 M CaHPO$_4$ and de-ionized water were added to the alginate solution, resulting in a 1.5% or 2.5% alginate dispersion. Then, D-glucono-δ-lactone (PMP Fermentation Products, Inc. Peoria, IL) at twice the molar amount of CaHPO$_4$, was added to decrease the solution pH and release calcium ions. To maintain a desired alginate concentration in the final gel, de-ionized water was added to the alginate stock solution based on the degree of syneresis (Velings and Mestdagh 1995) expected to achieve the desired alginate concentration. The final solution was immediately poured into plastic cups, covered, and held undisturbed at room temperature (23±2°C) for 48 hours. A total of 5 different bulk gel types were prepared from 3 different alginate solutions and 2 different concentrations as described in Table 3.2.
Table 3.2
Bead types produced and used as dispersed phase

<table>
<thead>
<tr>
<th>ID</th>
<th>Alginate</th>
<th>Guluronic Acid (%)</th>
<th>Mannuronic Acid (%)</th>
<th>Alginate (%, w/w)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Type I</td>
<td>Alginate TS-A 6556</td>
<td>32</td>
<td>68</td>
<td>1.5</td>
</tr>
<tr>
<td>Type II</td>
<td>Alginate TS-A 6556</td>
<td>32</td>
<td>68</td>
<td>2.5</td>
</tr>
<tr>
<td>Type III</td>
<td>Alginate De Sodium Flavicans</td>
<td>70</td>
<td>30</td>
<td>1.5</td>
</tr>
<tr>
<td>Type IV</td>
<td>Alginate De Sodium Flavicans</td>
<td>70</td>
<td>30</td>
<td>2.5</td>
</tr>
<tr>
<td>Type V</td>
<td>GRINDSTED Alginate FDG 125</td>
<td>50</td>
<td>50</td>
<td>1.5</td>
</tr>
</tbody>
</table>

3.3.3 Bulk gel rheological properties measurements

**Small-strain rheology**

Dynamic oscillatory testing was performed using a stress-controlled rheometer (StressTech Rheological Instruments AB, Lund, Sweden) equipped with a 20mm, smooth parallel plate configuration. The bulk gel samples (2 mm height and 20 mm in diameter) were glued (Loctite Corp, Rock Hill, CT) to the top and bottom plates to minimize slip. A stress sweep at a frequency of 1 Hz was done to determine the linear viscoelastic region limit, which was identified as the stress for which a 97% change in storage and loss modulus was measured. The dynamic frequency sweep tests were carried from 0.01 to 10 Hz with a stress of 40 Pa. All measurements were done at 25 °C and were replicated at least three times.

**Large-strain rheology**

Fracture properties were measured in compression using an Instron universal testing machine model 5524 (Norwood, MA) equipped with a 50 kg load cell. Mineral oil was applied to lubricate the Instron plates, thereby reducing friction between the sample and the plates. The bulk gel was cored and cut into cylindrical samples (15mm in diameter and 16mm length) which were compressed to the point of fracture at a constant crosshead...
speed of 50 mm/min. A total of 5 repetitions were tested for each bulk gel. The stress ($\sigma$, Pa) and strain ($\varepsilon$) were calculated from the load and compression data as described by Truong and Daubert (2000).

$$\sigma = \frac{F(L - \Delta L)}{\pi R^2 L} \quad \text{Equation 3.1}$$

$$\varepsilon = \ln \left(1 - \frac{\Delta L}{L}\right) \quad \text{Equation 3.2}$$

Where $F$ is the fracture force (N), $L$ is sample initial length (mm), $\Delta L$ is change in length (mm), and $R$ is sample radius (mm).

### 3.3.4 Bulk gel surface properties evaluation

#### Contact angle evaluation

The contact angle between the bulk alginate gels and water, mineral oil, glycerol, ethylene glycol, formamide, and dimethyl sulfoxide was visually evaluated. The gel surface was blotted to remove excess water and a drop of liquid was dispensed from a short distance onto the gel surface. Results from this preliminary measurement did not yield a system stable for contact angle measurements.

#### Adhesion

Alginate gel adhesiveness was measured using an Instron universal testing machine model 5565 (Norwood, MA) equipped with a 5 kg load cell. An alginate gel surface (diameter 1.5 cm) was glued (Loctite 401, Loctite Corp., Rock Hill, CT) to the bottom plate and to a 4 cm diameter stainless steel probe. The surfaces were brought to contact, followed by slight
compression to a loading force of 5 N. The surfaces were kept in contact for 60 sec at 5 N and then pulled apart at 0.5 mm/s. The tack force was the maximum force during separation, and the tack energy was calculated as the area under the force-distance curve similarly to Heddleson and other 1993.

3.3.5 Alginate microbead production

Five different bead types (Table 3.2) were produced using the apparatus and method described in chapter 2. The 3% alginate stock solution was diluted to 1.5% or 2.5%, and de-ionized water was added based on the degree of syneresis expected and the desired final alginate concentration. Larger alginate beads (D=0.5 cm) were used to measure syneresis. Alginate was measured and added drop wise to 1.5% w/w CaCl₂. The weight of the added alginate solution was considered as the initial weight. A final weight was measured after separation of the beads from the CaCl₂, and syneresis was calculated assuming that only water was lost from the gels (Velings and Mestdagh 1995):

\[ \% \text{ syneresis} = \frac{\text{initial weight} - \text{final weight}}{\text{initial weight}} \times 100\% \]  
Equation 3.3

Each alginate solution was then pumped through an atomization nozzle (Spraying systems Inc.) with an outlet diameter of 500 μm at an average flow rate of 130 mL/min, allowing constant flow through the nozzle. Atomization was assisted by an external compressed air stream at a pressure of 50 psi (343.7 kPa), correlating to an average air velocity of 415 m/s through the nozzle. The alginate solution was sprayed into a 1.5% w/w CaCl₂ (Dow Chemicals) bath under atmospheric pressure (101.325 KPa) and at room temperature (22±2°C). Next, the gelled alginate beads were separated according to size using a series of
standard US sieves resulting in two general populations: beads with diameter between 75 μm and 150 μm (population A) and beads whose diameter was below 75 μm (population B).

3.3.6 Microbead gel composition

Microbead gels were made from 5 different gel types (Table 3.2) at 5 different particle size distributions (Table 3.3). The two populations of beads were combined at different ratios to create the various particle size distributions. A total of 25 different combinations of gel type and particle size distribution were evaluated.

<table>
<thead>
<tr>
<th>Particle size distribution</th>
<th>Fraction of population A</th>
<th>Fraction of population B</th>
</tr>
</thead>
<tbody>
<tr>
<td>75 μm &lt; D &lt; 150 μm</td>
<td>100</td>
<td>0</td>
</tr>
<tr>
<td>75 μm &lt; D &lt; 150 μm</td>
<td>75</td>
<td>25</td>
</tr>
<tr>
<td>50/50</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>75/25</td>
<td>25</td>
<td>75</td>
</tr>
<tr>
<td>100/0</td>
<td>0</td>
<td>100</td>
</tr>
</tbody>
</table>

3.3.7 Microbead gel rheological properties measurements

Small-strain rheology

Dynamic oscillatory measurements were performed by the same method as the bulk gel. The main difference between the tests was sample loading. The microbead gel weight was measured, and a 0.48 g sample was carefully positioned on the bottom plate with a spatula. The top plate was lowered to a normal force of 1N to maintain uniform stress on the samples. The stress sweep was performed identically to the bulk gels, but the dynamic
frequency sweep tests were adjusted between 0.01 and 5 Hz at 40 Pa, unless otherwise noted. All measurements were done at 25 °C and were repeated at least three times.

**Yield stress**

A stress-controlled rheometer (StressTech Rheological Instruments AB, Lund, Sweden) equipped with a 4-bladed vane was used to measure the microbead gel yield stress at room temperature (23±2°C). The sample was loaded into the StressTech cup and preseheared for 30 s at 30 1/s. The sample was then allowed to achieve equilibrium for 240 s followed by a stress ramp starting at 1 Pa. Strain, shear rate, and viscosity were measured and the yield stress was determined as the stress for which the stain exceeded 1 and the shear rate was greater than 1 1/s. All measurements were repeated at least three times.

### 3.4 Results and Discussion

#### 3.4.1 Bulk gel preparation

A homogeneous gel was prepared based on an internal-setting method described by Zhang et al. (2005). The internal setting method of alginate gels have been studied extensively by (Smidsrod and Draget 1997; Draget and others 1991) and is characterized by the controlled release of calcium ions from an inert calcium salt (CaHPO$_4$ or CaCO$_3$) within the alginate solution. The ion release is controlled by lowering the pH of the solution through addition of organic acids or lactones (Smidsrod and Draget, 1997). One of the main advantages when using the internal setting method is the creation of a homogeneous gel which is especially important when making a large bulk gel for which calcium diffusion from an outside source may be too slow. However, gels made by the internal setting method may show higher
syneresis than those prepared by diffusion. This factor was taken into consideration by adding water to the solution to ensure the desired gel concentration was achieved. The 5 types of gels prepared showed different degrees of syneresis as a function of alginate type and concentration. Alginate with higher guluronic acid (G) content (types III and IV) showed less syneresis than the lower guluronic acid content alginates, where the alginate with the lowest guluronic acid content (types I and II) showed the highest syneresis. Also, a higher alginate percentage showed higher syneresis (Table 3.4). Draget and others 1991 showed that the ratio of excess calcium ions to G-residues affects syneresis: higher ratio led to higher syneresis. Since the Calcium salt concentration was constant, the ratio of excess calcium ions to G-residues increased as G-residue content decreased, causing greater syneresis in the lower-G alginate and at lower alginate concentrations.

3.4.2 Bulk gel rheological properties

Small-strain rheology

A stress sweep at 1 Hz determined the linear viscoelastic region and the limiting stress. Figure 3.1 shows the measured complex modulus ($G^*$) for the various gel types. The limiting stress was identified as the stress for which a 3% change in storage modulus ($G'$) was measured. The limiting stresses along with the corresponding strains are presented in Figure 3.2.

The gels made with highest G and alginate concentration (type IV) had the largest complex modulus, while the gel made with the lowest G and concentration (type I) had the lowest complex modulus. In the range between the highest and the lowest, the gels were distributed according to a G-content and alginate percent combination. The limiting
stresses were not statistically different between the gel types, but type IV did have a smaller limiting strain than types I and V. Gel types II and V showed a closer resemblance to one another than to the others and were the only gel types that were not statistically different with respect to $G^*$. All gels showed a linear viscoelastic region that extends beyond 100 Pa; therefore, the stress of 40 Pa chosen for the frequency sweep was appropriate.

A frequency sweep was performed to measure viscoelastic properties of different types of alginate gels. Figure 3.3 shows the dependence of the complex modulus on the different gel types. The complex modulus increased with increasing frequency, which is consistent with a viscoelastic gel (Ferry 1980). Type II and type V had the same complex modulus but type II had a higher phase angle at higher frequencies (Figure 3.3). At low frequencies (less than 0.1 Hz) there was no statistical difference between the phase angles of the various gel types.

The mechanical properties of alginate gels are a function of alginate composition and concentration (Martinsen 1989; Smidsrod 1974; Ouwerx and others 1998). These factors were combined to produce a new concept named "G-score". The G-score is a value calculated based on the guluronic acid content of the alginate used and alginate percentage in the final gel (Table 3.5). The $G$ score was calculated out of a base of 100 as the final gel; e.g. for type II:

$$\text{100} \times 0.025 = 2.5 \times 0.3 = 0.75$$

The G-score assumes that the G-residues are the primary residue responsible for gel formation. The higher the $G$ score, the more cross-links are formed. A comparison between the complex modulus and the G-scores reveals that higher G scores led to higher complex
modulus. Gel types II and V, for example, have the same G score and have the same complex modulus (they were not statistically different). However, while their G score is the same, they do not have the same phase angle. This observation may be explained by the components of the G score. Type II had a higher alginate concentration than type V, but both had the same degree of cross-linking (based on the G score). Therefore, type II had longer regions of unlinked alginate gels compared to type V (Figure 3.4) which contributed to a higher phase angle.

**Large-strain rheology**

The fracture stress and strain were a function of gel type. The highest G-content gels had the lowest strain and higher stress; the lowest G content gels had the higher deformation and lower fracture stress, and the mid G-content gels were in between. This observation and the strain hardening behavior seen in Figure 3.5 can be explained by the same mechanism that relates gel structure and deformation. Zhang and others 2006 addressed the strain-hardening mechanism for alginate gels, concluding that the rigid junction zone between the polymer chains (the linked parts of the chains) caused the strain hardening. As the gel is compressed, the junction zones oppose deformation and increase stress in the sample. The results displayed in Figure 3.5 and Figure 3.6 strengthen and add to this conclusion.

Gel types I and II were both made of the same alginate type which consisted of 30% Guluronic acid. Possibly, these gels had relatively short junction zones and longer fragments of unlinked chains. The unlinked fragments allowed the gel to deform easily with minimal resistance from the junction zones. Type II had a higher critical stress than type I because a higher percentage of alginate resulted in more junction zones.
Types III and IV were both made from the same alginate, consisting of 68% Guluronic acid, and probably had relatively long junction zones, which contributed to a rapid increase in stress upon deformation. The fragments of unlinked chains were shorter, inhibiting the deformation of the gels. Since type IV had a higher percentage of alginate, more force opposed deformation while the deformation range remained the same.

The results from the large-deformation rheology had the same trends as the limiting strains measured by stress sweep (Figure 3.2). The values, however, were different because Figure 3.2 presents the limit of the linear viscoelastic region as opposed to failure stress and strain shown in Figure 3.6.

3.4.3 Bulk gel surface properties evaluation

Contact angle evaluation

The contact angle between the bulk alginate gels and water, mineral oil, glycerol, ethylene glycol, formamide, and dimethyl sulfoxide was visually evaluated. Only mineral oil formed a stable drop on the bulk gel surfaces. There was no apparent difference between the gel type. In the absence of a second stable system, an accurate contact angle measurement and analysis was not performed. The main objective of contact angle analysis was to evaluate the polar and apolar components of the alginate gel surface (van Oss and Good 1992). Mineral oil was the only entirely apolar liquid used and was the only substance to form a drop on the gel surface, leading to the conclusion that the gel surface is polar. The same behavior was observed for all gel types. Given the high water content of the gels (greater than 95%), these results were not surprising.
**Adhesion**

Figure 3.7 presents the results of the tack test performed to assess adhesion. Types II and IV alginate gel systems had a statistically higher peak force than all other gels and higher tack energy than type I and type V. Since tack is measured as the energy required to break the intermolecular forces between the surfaces, types II and IV may be considered to have a “stickier” surface. Surface properties of alginate gels are not readily available in literature. However, due to the structure of alginate and existence of numerous hydroxyl groups along the polymers, the possibility of hydrogen bonding and electrostatic interaction between alginate gel surfaces is a likely explanation.

**3.4.4 Microbead gel preparation**

The microbead gel was a closely packed system of highly concentrated gel beads. The external setting alginate gelation which was used has limitations when making a large bulk gel for which calcium diffusion from an outside source may be too slow. However, given the small diameter of the alginate beads, this method was appropriate for the production of the microbeads (Appendix B). Following Amici and others (2007) and Loret and others (2006), it was assumed that the mechanical properties of the microbeads were the same as the bulk gel.

**3.4.5 Microbead gel rheological properties**

Dynamic oscillatory testing was done using a stress-controlled rheometer. Figure 3.8 shows the limiting stress and strain of the different gel types and their compositions (Bulk gel, microbead 0/100, and microbead 25/75). The limiting stress and strain of the 2 microbead
gels was the same for all gel types. The bulk gel limiting stress was higher than that of the
microbead gels for types II, IV, and V; and bulk gel type I had a larger limiting strain than
the corresponding microbead gels. The stress sweep results support the fact that unlike the
bulk gel, the microbead gel was not a continuous matrix but rather was divided into small
gel beads. The differences between the bulk gel and the microbead gels are further
demonstrated by the frequency sweeps.

Gel types I (Figure 3.9) and III (Figure 3.11) did not have a statistical difference between
the microbead gels and the bulk gel, and for type V (Figure 3.13) there was no statistical
difference between the bulk gel and the 0/100 microbead gel. For gel types II (Figure 3.10)
and IV (Figure 3.12) the storage and loss modulus of the bulk gel was not exceeded by the
microbead gels. This behavior was anticipated since the bulk gel was composed of an
uninterrupted cross-linked alginate network while the microbead gel was composed of
discrete particles.

The effect of gel type on the microbead gels is presented in Figure 3.14 and Figure 3.15 for
the 0/100 and 25/75 particle size distributions, respectively. The 50/50, 75/25, and 100/0
particle size distribution microbead gels could not be compared as a function of gel type or
based on gel composition. A stress sweep revealed that the 40 Pa stress chosen for the
frequency sweeps was well above the linear viscoelastic region of the 50/50, 75/25, and
100/0 microbead gels (Figure 3.16 (a)). A frequency sweep conducted for these samples at
a stress of 3 Pa showed that the storage and loss modulus were about 4 orders of
magnitude lower than the bulk gel, and had a high dependence on frequency (Figure 3.16
(b)).
Finally, since the microbead gel was too weak to be measured by compression, its strength was evaluated by yield stress measurements. Figure 3.17 (a) shows the gradual increase in strain and decrease in viscosity as the stress increased. At a stress of 60 Pa there is a sharp drop in viscosity and increase in strain; therefore, that stress was identified as the yield stress (Stokes and Telford 2004). Figure 3.17 (b) shows the measured yield stress for two gel types at the 5 different particle size distributions. For gel type III the 0/100 particle size distribution had the highest yield stress followed by the 25/75 and 50/50 particle size distributions. The 100/0 particle size distribution had the lowest yield stress. For type IV the 0/100 had the same yield stress as type IV 25/75 and as III 0/100. The 50/50, 75/25, and 100/0 particle size distributions for type IV were all lower than 2 Pa.

The comparison between the different gel types and compositions revealed the dependence of the microbead gels mechanical properties on the gel type of the beads and particle size distribution. Van Vliet and Walstra (1995) studied concentrated starch gels, considering the starch granules to be gel-like particles, and the thin layer of amylase gel between them as glue; and the modulus of the system was determined primarily by the modulus of the granules. If the modulus of the microbead gels was a function of the beads modulus alone, there would have been no difference between the results obtained for gel type II and V as they had the same bulk modulus (Figure 4.3). In addition, the modulus of microbead gels of type I would have been the lowest, and of type IV the highest. A comparison of the different gel types for the 0/100 microbead gels and the 25/75 microbead gels (Figure 3.14 and Figure 3.15) showed that was not the case: For the 25/75 particle size distribution, types III and IV had the highest storage modulus followed by type I and finally types II and V. The 0/100 microbead gels types I and II had a lower storage modulus than gel types III, IV, and
V. The loss modulus was not statistically different between any of the gel types for the 25/75 particle size distribution and the 0/100 particle size distribution. Therefore, other bulk gel properties should be considered.

Based on the literature available, it is reasonable to assume that deformable particles may accommodate each other when in close proximity (Barnes and others 1989; van Vliet and Walstra 1995; Macosko 1994). Figure 3.18 demonstrates the difference between packing elastic and deformable particles. The deformable particle packing is characterized by larger packing volume fraction and increased surface contact between the particles. As a result, the particles form a network that contains minimum continuous phase (in this case, water) and maximum surface interaction. The deformability of the gel beads was higher for gel types with a lower modulus. The increase in contact surface area and the more efficient packing would increase the microbead gel modulus. However, the lower modulus of the particles would decrease the modulus of the microbead gel (van Vliet and Walstra 1995), complicating the effect of particle modulus on the modulus of the microbead gel. This complex relationship is apparent at the 25/75 microbead gel, where the microbead gel made of type I beads had a higher modulus than those made of types II and V (Figure 3.16).

The modulus of the microbead gel could not have been a function of bead modulus alone. This response is evident by the difference between the 0/100 microbead gel type II and type V (Figure 3.15). Both had the same particle modulus, but the type V microbead gel had a higher modulus than type II. This observation may be attributed to the different surface properties of the two gels, since the two gels were statistically different with respect to tack energy and peak force (Figure 3.7).
The effect of particle size distribution was minimally noticeable when the larger particles (population B) composed 75% or more of the microbead gel. However, when the percentage of large particles was below 75%, the microbead gel linear viscoelastic region was shorter and at low frequencies, the viscous component was higher than the elastic component. This result was supported by the yield stress data. The weak structure of the 50/50, 75/25, and 100/0 microbead gels may be accounted for by the decrease of surface interactions between the particles. While the surface to volume ratio increased, the deformability decreased (Barnes 1994), resulting in less surface contact.

3.5 Conclusion

The objective of this chapter was to evaluate the mechanical properties of microbead gels as a function of bead mechanical properties and particle size distribution. The mechanical properties of the alginate beads were found to be a function of alginate type and concentration. As components of the microbead gels, the mechanical properties and particle size distribution of the beads determined the viscoelastic and fracture properties of the gel. The relationship between the properties of the beads and of the gel was complex; while a higher modulus beads contributed to a higher modulus of the microbead gel, they were also less deformable thus limiting contact surface and interaction. Limited surface interactions contribute to a weaker gel as observed for smaller beads gels. Future work should address the surface properties and interparticle interactions of the beads.
Table 3.4  
Syneresis as a function of gel composition and concentration

<table>
<thead>
<tr>
<th>Type</th>
<th>% Guluronic Acid</th>
<th>% Munuronic Acid</th>
<th>% alginate in final gel (w/w)</th>
<th>% syneresis</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>30</td>
<td>70</td>
<td>1.5</td>
<td>60</td>
</tr>
<tr>
<td>II</td>
<td>30</td>
<td>70</td>
<td>2.5</td>
<td>55</td>
</tr>
<tr>
<td>III</td>
<td>68</td>
<td>32</td>
<td>1.5</td>
<td>25</td>
</tr>
<tr>
<td>IV</td>
<td>68</td>
<td>32</td>
<td>2.5</td>
<td>20</td>
</tr>
<tr>
<td>V</td>
<td>50</td>
<td>50</td>
<td>1.5</td>
<td>45</td>
</tr>
</tbody>
</table>

Table 3.5  
G score as a function of guluronic acid content and alginate percentage

<table>
<thead>
<tr>
<th>Type</th>
<th>% alginate</th>
<th>% G</th>
<th>G Score</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>1.5</td>
<td>30</td>
<td>0.45</td>
</tr>
<tr>
<td>II</td>
<td>2.5</td>
<td>30</td>
<td>0.75</td>
</tr>
<tr>
<td>III</td>
<td>1.5</td>
<td>68</td>
<td>1.00</td>
</tr>
<tr>
<td>IV</td>
<td>2.5</td>
<td>68</td>
<td>1.68</td>
</tr>
<tr>
<td>V</td>
<td>1.5</td>
<td>50</td>
<td>0.75</td>
</tr>
</tbody>
</table>
Figure 3.1 Representative stress sweep data as a function of alginate type and concentration. The end of the linear viscoelastic region was identified as the stress for which a 3% change in storage modulus was measured (◊).
Figure 3.2 Linear viscoelastic region limiting stress and strain as a function of gel type
Figure 3.3 Bulk gel complex modulus and phase angle as a function of gel type
Figure 3.4 Schematic of alginate gel of type V (top) and type II (bottom); both have the same number of cross-links but at 2.5% alginate, type II had longer unlinked chain regions.
Figure 3.5 Bulk gel large deformation as a function of gel type
Figure 3.6 Fracture stress and strain as a function of gel type and concentration. The error bars represent a standard deviation.
Figure 3.7 Tack force-distance curve (a) used to calculate the tack force (b) as the maximum force during separation and the tack energy (c) as the area under the force-distance curve.
Figure 3.8 Limiting stress (a) and strain (b) measured by a stress sweep at a frequency of 1 Hz as a function of gel composition.
Figure 3.9 Storage ($G'$) and loss ($G''$) moduli obtained from frequency sweeps for different composition of gel type I.
Figure 3.10 Storage ($G'$) and loss ($G''$) moduli obtained from frequency sweeps for different composition of gel type II
Figure 3.11 Storage ($G'$) and loss ($G''$) moduli obtained from frequency sweeps for different composition of gel type III.
Figure 3.12 Storage ($G'$) and loss ($G''$) moduli obtained from frequency sweeps for different composition of gel type IV.
Figure 3.13 Storage (G') and loss (G'') moduli obtained from frequency sweeps for different composition of gel type V
Figure 3.14 Storage ($G'$) and loss ($G''$) moduli obtained from frequency sweeps for 0/100 microbead gels as a function of gel type.
Figure 3.15 Storage ($G'$) and loss ($G''$) moduli obtained from frequency sweeps for 25/75 microbead gels as a function of gel type.
Figure 3.16 (a) Storage ($G'$) and loss ($G''$) moduli obtained from a stress sweep for microbead gel type III 100/0; (b) Storage ($G'$) and loss ($G''$) moduli obtained from a frequency sweep for microbead gel type III 100/0 at 3 Pa
Figure 3.17 (a) Strain (●) and viscosity (○) measured as a function of stress for determination of yield stress; (b) yield stress measured as a function of gel type and particle size distribution (the error bars represent standard error)
Figure 3.18 Schematic of different particle packing (top) elastic particles; (bottom) deformable particles
3.6 References


Smidsrød O. 1974. Molecular Basis for some physical properties of alginate in Gel State. Faraday discussions 57:263.


CHAPTER 4 EVALUATION OF NON-COLLOIDAL MICROBEAD SUSPENSION

4.1 Abstract

Suspension rheology has been a subject for investigation for over a century. Various mechanisms have been offered to account for the effects of particle volume fraction and size distribution. However, the effects of the particles mechanical properties on suspension rheology have been neglected. The rheology of suspensions composed of viscoelastic particles was investigated and found to be a function of shear rate, volume fraction, particle size distributions, and mechanical properties of the beads. The diverse flow behaviors observed could not be explained by a single model or mechanism, and several mechanisms were proposed to explain suspension rheology.

4.2 Introduction

A suspension is a heterogeneous two-phase system, consisting of discrete particles randomly distributed in a continuous fluid medium (Mewis and Spaull 1976; Macosko 1994). This class of materials has many applications such as drugs, cosmetics, and food; and understanding suspension rheology is important when optimizing product design, processing conditions, and applicability.

The flow behavior of a suspension is complex and is a function of many factors, including the properties of the suspending medium, the dispersed phase, and the flow conditions (Macosko, 1994). Given their complexity and importance, suspensions have been
investigated for over a century. Over the years, many scientists developed models to
describe the dependence of suspension viscosity on volume fraction. Some authors
considered the effect of particle size and particle size distribution, while others focused on
the importance of flow conditions. The effect of particle rheology, specifically viscoelastic
behavior, has not been investigated to the same extent.

This chapter evaluates the flow of non-colloidal, viscoelastic microbead suspensions. The
importance of particle mechanical properties is addressed, and the effect of volume
fraction, particle size distribution, and shear rate are considered. Some of the models,
theories, and relationships established in literature will serve as a foundation for
understanding.

**Volume fraction**

One of the fundamental considerations when dealing with suspension rheology is the
volume fraction, \( \Phi \), of the dispersed phase. The original theory proposed by Albert Einstein
in 1906 introduced a relationship among the suspension viscosity \( \eta_s \), continuous phase
viscosity \( \eta_0 \), and volume fraction \( \Phi \):

\[
\eta_r = \frac{\eta_s}{\eta_0} \quad \text{Equation 4.1}
\]

\[
\eta_r = 1 + 2.5 \Phi \quad \text{Equation 4.2}
\]

\[
\Phi = \frac{\text{particle volume}}{\text{total volume}} \quad \text{Equation 4.3}
\]

This relationship was proposed for suspensions of rigid, uniform spheres at a very low
volume fraction \( \Phi < 10\% \). At this volume fraction, the effect of other particles and
interparticle interactions may be neglected. Mooney (1950) introduced another relationship that accounted for higher particle concentrations by introducing a “crowding effect” parameter, $k$:

$$\eta_r = \exp\left(\frac{2.5\phi}{1 - k\phi}\right) \quad \text{Equation 4.4}$$

The equations introduced by Maroon and Pierce (1956) and Krieger and Dougherty (1959) included a new concept: the volume fraction ($\Phi_m$) above which there will be no movement of particles, and the suspension viscosity increases rapidly. Theoretically, the $\Phi_m$ can be calculated for several cases where the shape, particle size distribution, and packing conformation of the particles are known (Barnes and others 1989).

$$\eta_r = \left(1 - \frac{\phi}{\Phi_m}\right)^{-2} \quad \text{Equation 4.5}$$

These relationships, established for uniform and rigid particles, represent one class of suspension behavior, where an increase in volume fraction leads to an increase in suspension viscosity.

**Particle size and distribution**

Particle size distribution may change the critical volume fraction because small spheres may fit into voids between packed large spheres (Stickel and Powell, 2005). Such an arrangement can reduce the resistance to flow, thereby lowering the viscosity of the suspension. This model is dependent on the type of particle size distribution (unimodal, bimodal, multimodal), the volume ratio of the different components, and the size ratio of the components. Farris (1968) demonstrated that lower viscosity could be obtained with a
variety of particle size combinations. He predicted the viscosity of multimodal suspensions from unimodal viscosity data, and proved that, in some cases, increasing total volume fraction by introducing smaller particles actually reduced the viscosity. The volume and size ratios of the particles were shown to play an important role in viscosity reduction by Chang and Powell (1994). The optimum viscosity reduction was achieved when 25% of the total volume fraction was comprised of small particles, which were 13.75 times smaller than the larger particles. The reduction in viscosity was directly related to the increase in maximum volume fraction.

The size of the particles also impacts suspension behavior. As the particle size decreases, the number of particles per volume increases while still maintaining the same volume fraction. The increase in number of particles per volume results in a smaller mean distance between the particles, thus increasing the potential for particle-particle interactions that can increase viscosity (Agarwala and others 1992). However, Metzner (1985) claimed that in dilute suspensions (φ ≤ 0.2), modest changes in particle size were of no consequence.

The size of the dispersed particles has an important effect on suspension behavior through the forces that govern flow: colloidal, Brownian, and hydrodynamic (Barnes and others 1989). Colloidal and Brownian forces are significant for smaller particles (usually D < 1 μm) but can be neglected for larger particles. Inertial forces may also exist for larger particles.

The Peclet (Pe) and Reynolds (Re) numbers are dimensionless groups that evaluate the forces governing flow:
Where \( D \) is particle diameter (m), \( \eta_0 \) is the viscosity of the continuous phase (Pa\( \cdot \)s), \( \rho_0 \) is the density of the continuous phase (Kg/m\(^3\)), \( \dot{\gamma} \) is shear rate (1/s), T is temperature (K), and K is the Boltzman constant (1.38 \times 10^{-23} \text{ J/K}). While neither the Peclet number nor the Reynolds numbers fully determine suspension rheology (Stickel and Powell 2005), as a rule, when \( \text{Pe} \ll 1 \), the colloidal and Brownian forces are dominant; when the \( \text{Pe} \gg 1 \), hydrodynamic forces dominate flow behavior; and inertial forces may be neglected when \( \text{Re} < 0.1 \) (Brady and Bossis 1984). The magnitude of the forces is not a function of particle size alone, but also of the flow conditions.

**Flow conditions**

Shear rate has an important role when describing suspension flow behavior. Higher shear rates increase the Peclet and Reynolds numbers and therefore the importance of hydrodynamic forces. Agarwala and others (1992) observed 3 shear regions (Figure 4.1): very low shear (non-hydrodynamic), mid shear (combination), and high shear (hydrodynamic). The hydrodynamic interaction forces are caused by relative motion of neighboring particles and are present in all flowing non-dilute suspensions (Macosko, 1994).
Suspension dependence on shear is a function of volume fraction and the structure of the suspension at rest. Flocculated systems are weak structures composed of discrete particles which may separate with applications of stress (Mewis and Spaull 1976). As such, flocculated systems have a higher viscosity at lower shear, exhibiting a shear thinning behavior (Metzner, 1985). Most suspensions exhibit mild shear thinning, but some concentrated systems can display shear thickening over a range of rates (Barnes et al., 1989). This behavior is more commonly associated with deflocculated systems at higher volume fraction as weak structures are formed under shear.

This purported thickening behavior has been attributed to hydrodynamic effects contributing to cluster formation (Brady and Bossis 1984; Barnes 1989). Clusters usually entrap a portion of the continuous phase within them, contributing to an apparent increase in phase volume (Metzner 1985; Barnes et al.; 1989). Inter-particle forces, friction, and closer packing achieved at higher volume fractions have also been introduced causes for the thickening behavior (Adams and others 2004; Mewis and Spaull 1976 Gadala-Maria and Acrivos, 1980; Hoffman, 1972).
Mechanical properties of the dispersed phase

One of the assumptions often made when dealing with suspension rheology is that the particles are elastic (Metzner 1985; Stickel and Powell 2005; Brady and Bossis 1984; Barnes 1994). The relationships and models presented were developed mostly for elastic particles. However, for most practical purposes, the particles are not of an elastic nature, because all polymeric materials have some degree of viscoelasticity (Macosko, 1994).

A viscoelastic material is a material with both viscous and elastic properties. Figure 4.2 displays dispersions on the viscoelastic spectra, with emulsions on one end and solid particle suspensions on the other end of the viscoelastic spectrum; a dispersion of viscoelastic particles (also referred to as a suspension) is within that range.

![Figure 4.2 Dispersions on the viscoelastic spectra](image)

Similar to suspension of elastic particles, emulsion rheology depends on volume fraction, particle size, and particle size distribution. Unlike an elastic particle suspension, emulsions have a deformable interface between the phases, and the viscosity of the dispersed phase must be taken into account (Pal, 2000). Barnes (1994) reviewed emulsion rheology and considered the deformability of the emulsion droplet. Compared to solid particle
suspensions, emulsions achieve complete phase filling resulting in lower viscosity. Barnes (2000) underscored that deformable particles (not just liquid droplets) could accommodate each other at rest and squeeze past each other during flow, increasing the maximum volume and resulting in a lower viscosity.

The importance of particle deformability was demonstrated by Adams and others (2004) who investigated the rheology of agar microbeads suspensions at very high volume fractions, showing that particle stiffness has a significant impact on relative viscosity, particularly under higher shear. The suspensions were shear thinning above a volume fraction of 55%, and the more rigid particles contributed to higher viscosity. The work by Frith and Lips (1995) investigated cornstarch suspensions and arrived at different conclusions. While significant difference between standard hard sphere data and starch suspension could only be accounted for by the deformability of starch granules, the deformability of starch granules did not play a significant role at high shear. A shear thickening behavior was observed and appeared to be strongly affected by the deformability of the particles.

Several models describing suspension behavior have been presented (Table 4.1). However, these models are not applicable for all systems especially in cases of viscoelastic particles, and some models may even contradict one another. It is the objective of this chapter to evaluate the flow behavior of microbead suspensions as a function of the bead mechanical properties, volume fraction, particle size distribution, and over a range of shear rates. These systems will be compared to the existing models to advance the discussion of different mechanisms governing suspension rheology.
<table>
<thead>
<tr>
<th>variable</th>
<th>viscosity</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Volume fraction</td>
<td>↑</td>
<td>Einstein 1906; Mooney 1950; Maroon and Pierce 1956; Krieger and Dougherty 1959</td>
</tr>
<tr>
<td>Particle size distribution</td>
<td>↓</td>
<td>Farris 1968; Chang and Powell 1994; Tsai and others 1994</td>
</tr>
<tr>
<td>Particle size</td>
<td>↑</td>
<td>Agarwala 1992; Yoo and Rao 1994</td>
</tr>
<tr>
<td>Shear rate</td>
<td>↓</td>
<td>Metzner 1985; Tsai and others 1994; Yoo and Rao 1994; Adams and others 2004</td>
</tr>
<tr>
<td>Shear rate</td>
<td>↑</td>
<td>Hoffman 1972; Gadala-Maria and Acrivos 1980; Barnes 1989; Frith and Lips 1995</td>
</tr>
<tr>
<td>Particle deformability</td>
<td>↓</td>
<td>Adams and others 2004; Barnes 1994</td>
</tr>
</tbody>
</table>
4.3 Materials and Methods

4.3.1 Alginate solution preparation

Alginate powders of different properties (Table 4.2) were provided by Danisco (Brabrand, Denmark). A 3% (w/w) alginate solution was prepared by blending the alginate powder in de-ionized water and allowing the dispersion to hydrate for no less than 72 hours.

4.3.2 Alginate microbeads production

Five different bead types (Table 4.3) were produced using the apparatus and method described in chapter 3. The 3% alginate stock solution was diluted to 1.5% or 2.5% and de-ionized water was added based on the degree of syneresis expected and the desired final alginate concentration. Larger alginate beads (D=0.5 cm) were used to measure syneresis. Alginate solution was measured and added drop wise to 1.5% w/w CaCl\(_2\). The weight of the added alginate was considered as the initial weight. The final weight was measured after separation of the beads from the CaCl\(_2\), and syneresis was calculated assuming that only water was lost from the gels beads (Velings and Mestdagh 1995):

\[
\% \text{ syneresis} = \frac{\text{initial weight} - \text{final weight}}{\text{initial weight}} \times 100\% \quad \text{Equation 4.8}
\]

Each alginate solution was then pumped through an atomization nozzle (Spraying systems Inc.) with an outlet diameter of 500 μm at an average flow rate of 130 mL/min, allowing constant flow through the nozzle. Atomization was assisted by an external compressed air
stream at a pressure of 50 psi (343.7 kPa), which correlated to an average air velocity of 415 m/s through the nozzle. The alginate solution was sprayed into a 1.5% w/w CaCl$_2$ (Dow Chemicals, Midland, IL) bath under atmospheric pressure (101.325 KPa) and at room temperature (22-24°C). Next, the gelled alginate beads were separated according to size using a series of standard US sieves that resulted in two populations: beads with diameter between 75 μm and 150 μm (population A) and beads with diameter below 75μm (population B).

### 4.3.3 Microbead suspension preparation

The suspensions were composed of a dispersed phase and a continuous phase. There were 6 dispersed phases: 5 alginate bead types (Table 4.3) and polystyrene beads (Fisher Scientific) to function as a control. The continuous phase was a 0.25% (w/w) xanthan solution which was prepared by dispersing xanthan powder (Tate and Lyle, Decatur, IL) in de-ionized water under agitation. At this concentration, the density and viscosity of the xanthan solution prevented settling of alginate beads. The viscosity of a week old suspension was measured and compared with a fresh sample to rule out alginate-xanthan interactions, which may result in reduction of particle size.

The 2 populations of beads were combined at different ratios to create the various particle size distributions; and the beads were weighed and mixed with the xanthan solution to create different volume fractions (30%, 45%, 60%, 75%, and 90%). A total of 140 different combinations of gel type, particle size distribution, and volume fraction were evaluated. Each system was prepared twice (replication) and measured twice for a total of 4 repetitions.
4.3.4 Viscosity measurements

The viscosity of the different suspensions was determined at room temperature (23±2°C) using a stress-controlled rheometer (StressTech Rheological Instruments AB, Lund, Sweden) with a smooth cup and bob attachment. The sample was pre-sheared for 30 sec at 250 1/s to ensure uniform strain history for all samples and then held for 30 s. The flow behavior of the suspension was measured as a function of shear rate from 5 to 650 1/s over 210 sec, using a step wise progression of rate to facilitate averaging of several data points per shear rate. Time dependence was also evaluated by a step wise decrease of shear rate from 650 1/s to 5 1/s over a period of 100 s.

4.3.5 Data representation and statistical analysis

The data collected can be presented in a variety of ways (Figure 4.3): shear stress as a function of shear rate, apparent viscosity as a function of shear rate, and relative viscosity ($\eta_r$) as a function of shear rate. Relative viscosity was selected to represent the data because it best captured the flow behavior of the suspension and its relation to the continuous phase.

Statistical analysis involved the averaging of repetitions and a two-sample t-test for equal means with $\alpha=0.05$, assuming equal variance. Furthermore, a t-test was performed to determine significant difference between sample means (Rao, 1998).
4.4 Results

Several factors affected the flow behavior of the systems used: shear rate, volume fraction, particle size distribution, and particle mechanical properties. In this section, the results were sorted by these factors, and several examples are presented to demonstrate the various flow behaviors and relationships observed. First, shear rate dependence was considered. Here, the flow behaviors observed among all suspension combinations were presented as flow patterns. Second, the data was sorted by gel type (Table 4.3) and analyzed with respect to flow pattern, volume fraction, and particle size distribution. Finally, to evaluate the effect of bead mechanical properties on the suspension, the results were compared by gel type. The discussion follows as a separate section.

4.4.1 Shear rate dependence and flow patterns

All systems where tested over a shear rate range of 5-650 1/s. Across this range, the suspensions had a higher, lower, or equal viscosity to the continuous phase viscosity. A higher suspension viscosity was referred to as a thickening effect, for which \( \eta_r > 1 \). A thinning effect was defined as a lower suspension viscosity relative to the viscosity of the continuous phase alone and \( \eta_r < 1 \). When \( \eta_r = 1 \) there was neutral effect, and the suspension viscosity was equal to the viscosity of the continuous phase. Any of the effects observed increased, decreased, or remained constant with shear.

The data collected was grouped by flow patterns. A flow pattern is a general trending of the suspension, describing the relative viscosity of each suspension combination and its
dependence on shear. The *flow patterns* observed are summarized in Table 4.5 and Figure 4.4.

**Flow pattern A** was characterized by a critical shear rate, $\dot{\gamma}_c$, below which the viscosity of the suspension was equal to the viscosity of the continuous phase ($\eta_r = 1$). A thickening effect began at the critical shear rate ($\eta_r > 1$) and increased with shear.

**Flow pattern B** was characterized by a critical shear rate, $\dot{\gamma}_c$, below which the viscosity of the suspension was higher than the viscosity of the continuous phase ($\eta_r > 1$), but the thickening effect was independent of shear rate. The thickening effect continued after the critical shear rate and increased with shear.

At lower shear rates for **Flow pattern C**, the viscosity of the suspension was lower than the viscosity of the continuous phase ($\eta_r < 1$). The thinning effect decreased with shear up to the critical shear rate, where a thickening effect started and continued to increase with shear.

With **Flow pattern D**, the viscosity of the suspension was higher than the viscosity of the continuous phase at all shear rates, and the thickening effect increased with shear.

At shear rates lower than the critical shear rate for **Flow pattern E**, there was a thickening effect, which decreased with shear. The thickening effect was followed by a region where $\eta_r = 1$ and was independent of shear. Above a second critical shear, the thickening effect increased with shear.

At shear rates lower than the critical shear rate for **Flow pattern F**, there was a thickening effect, which decreased with shear. The thickening effect was followed by a region where
$\eta_r > 1$ and was independent of shear. Above a second critical shear, the thickening effect increased with shear.

### 4.4.2 Type I suspensions

Type I suspensions were prepared with type I beads (section 4.3.3). Table 4.6 presents the flow patterns observed for type I suspensions. The diverse flow patterns and critical shear rates reveal the dependence of flow and relative viscosity on shear rate, particle size distribution, and volume fraction.

In most cases, the effect of volume fraction increased with shear rate, and an increase in volume fraction resulted in an increase in relative viscosity. This trend was consistent for all particle size distributions at shear rates above 30 $1/s$. At lower shear rates, there were several exceptions to this trend. For all of the particle size distributions but 0/100, at high volume fractions (90% and 75%), an opposite trend was observed (Figure 4.5 and Figure 4.6). The 90% volume fraction had a lower relative viscosity than the 75% volume fraction. The systems that obeyed this behavior showed flow pattern C, where the thinning effect observed at lower shear rates transitioned to a thickening effect at a critical shear rate. The critical shear rate for the 90% volume fraction was higher than that of the 75% volume fraction. This dependence of the critical shear rate on volume fraction was unique to the systems that had flow pattern C behavior. For all the other systems and flow patterns, the critical shear decreased with an increase in volume fraction.

The 0/100 particle size distribution combinations yielded the highest relative viscosity for all volume fractions and all shear rates (Figure 4.7). The 50/50 particle size distribution
combinations had the lowest relative viscosity. This particle size distribution was not statistically different from the 100/0 particle size distribution for the 60% and 45% volume fractions. Other similarities existed, including those between the 50/50 and 75/25 particle size distributions at 60% and 75% volume fractions; as well as 100/0 and 75/25 particle size distributions at the 60% and 90% volume fractions.

The effect of particle size distribution was dependent not only on the volume fraction, where the effect of particle size distribution was greater at higher volume fractions, but also on shear rate, where an increase in shear enhanced the effect of particle size distribution.

As mentioned in section 4.3.4, the shear rate analysis included a decreasing shear ramp. From all the systems investigated, the only system to show time dependence was type I at 90% volume fraction and 0/100 particle size distribution (Figure 4.8). The up and down-ramps were statistically different up to a shear rate of 500 1/s.

4.4.3 Type II suspensions

Type II suspensions were prepared with type II beads (section 5.2.3). Table 4.7 presents the flow patterns that were observed for type II suspensions. With an increase in volume fraction, the flow patterns changed and the critical shear for onset of a thickening effect decreased. With the exception of low shear rates, an increase in volume fraction led to a higher relative viscosity for all particle size distributions. At lower shear rates the volume fractions were statistically different only for the 0/100 particle size distribution (Figure 4.9). An increase in volume fraction also changed the particle size distribution effect on
flow. At low volume fractions, the 50/50, 75/25, and 100/0 particle size distributions were mostly equal and led to higher relative viscosity (Figure 4.10). At higher volume fractions, the 25/75 particle size distribution relative viscosity was higher. The particle size distribution effect was more pronounced at higher shear rates.

### 4.4.4 Type III suspensions

Type III suspensions were prepared with type III beads (section 5.2.3), and Table 4.8 presents the flow patterns that were observed for type III suspensions. Only 3 flow patterns were observed for these suspensions: E, B, and D; and with an increase in volume fraction there was a change in flow pattern and a decrease in the critical shear rate. A higher volume fraction led to a higher relative viscosity, and the dependence of flow on volume fraction increased with increasing shear rate (Figure 4.11). For lower shear rates there were cases where there was no statistical difference between volume fractions. At a particle size distribution of 50/50 the effect of volume fraction on flow was lower, and even at higher shear rates there was no statistical difference between the 45% and 60% volume fractions (Figure 4.12). Figure 4.13 demonstrates the dependence of particle size distribution on shear rate. At very low shear rates, the effect of the 0/100 was equal to that of the 100/0, and both had the highest relative viscosity, but at a shear rate of 600 1/s the 50/50 and 100/0 particle size distributions were equal and had the highest relative viscosity. At a volume fraction of 90% the rank of the particle size distribution was maintained across the entire range of shear rates. The term rank refers to the order of the results with respect to relative viscosity. For example, in Figure 4.13, the 0/100 and 100/0 particle size distributions were equal and had the highest relative viscosity, and therefore ranked
highest; while the 50/50 particle size distribution had the lowest particle size distribution and had the lowest rank.

4.4.5 Type IV suspensions

Suspensions made with type IV beads were prepared and measured at the same volume fractions and particle size distributions as the other suspension types. However, the data collected for these systems were not consistent and therefore is not presented in this unit. Reasons for this omission will be discussed further in the next section.

4.4.6 Type V suspensions

Type V suspensions were prepared with type V beads (section 4.3.3), and Table 4.9 presents the flow patterns observed for type V suspensions. The flow patterns changed with an increase in volume fraction, and the critical shear rate decreased. At lower shear rates, there was no significant difference between the volume fractions (Figure 4.14), but as the shear rate increased, so did the volume fraction effect, and an increase in volume fraction led to an increase in relative viscosity (Figure 4.14). An increase in volume fraction also changed the particle size distribution rank. At 30% volume fraction, most of the particle size distributions were not statistically different (Figure 4.15). As the volume fraction increased there was a difference between the particle size distributions, and the 50/50 and 75/25 particle size distributions had a higher relative viscosity. At a 90% volume fraction, the 0/100 and 25/75 particle size distributions yielded higher relative viscosity than the other particle size distributions (Figure 4.16).
4.4.7 Control suspensions

The polystyrene beads control was used to represent a perfectly elastic dispersed phase (Figure 4.17). With these systems, measurements were only taken up to a volume fraction of 20%. The control introduced the sixth flow pattern where an initial decrease in thickening effect was followed by constant thickening effect (Table 4.10). These systems showed some dependence on volume fraction and particle size distribution, where the particle size distribution 0/100 had the highest $\eta_r$ (the others were not statistically different). At very high shear rates ($\gamma > 5001/s$), the data collected was more discontinuous and unpredictable.

4.4.8 Gel type effect

Suspension rheology dependence on volume fraction, particle size distribution, and shear rate has been presented for each gel type. To assess the effect of gel mechanical properties on suspension rheology, the different particle size distribution and volume fraction combinations were analyzed as a function of gel type over the entire shear rate. For each of the 25 combinations (5 volume fractions X 5 particle size distributions) combination, the 4 types of suspensions were ranked from the gel type that yielded the highest relative viscosity, to the gel type that yielded the lowest relative viscosity. Table 4.11 presents the highest-ranking gel type at 4 different shear rates: 5, 32, 199, and 600 1/s. In some cases, a statistical difference did not exist between the top ranked gel types.

At low shear rates, the different gel types were not statistically different for all combinations. As the volume fraction increased, so too did the differentiation between the
gel types: at 90% volume fraction, a single type of alginate beads was identified to yield the highest relative viscosity.

At the low-mid shear rate range and for all volume fractions, the 0/100 particle size distribution, type I suspensions yielded the highest relative viscosity. For the 100/0 particle size distribution, gel type III was the highest. For the 25/75, 50/50, and 75/25 particle size distributions there was no single dominating gel type. At the mid-high shear rate range Type I dominated the 0/100 particle size distribution completely, most of the 25/75 particle size distribution and increased in dominance for the higher volume fraction for all other particle size distributions. At high shear rate the dominance of type I increased to be the highest ranked type for all volume fractions for the 0/100, 25/75 particle size distributions and for volume fractions higher than 60% for the other particle size distributions.

One observation made was the large dependence of type I on shear rate. Type III on the other hand, was the least shear sensitive. Also, while type I had diverse flow patterns, type III was characterized mostly by flow patterns B and E. Types II and V had intermediate shear dependence (less than I but more than III) and showed similar flow patterns, mostly B and D.

Figure 4.18 demonstrates the effect of particle size distribution at a volume fraction of 90% as a function of gel type. Inclusion of small particles in the system while maintaining the volume fraction decreased the rank of type I and increased the rank of type II. Even at low volume fractions, the particle size distribution effect may be a function of gel type (Figure 4.19).
Figure 4.20 demonstrates the effect of volume fraction at a particle size distribution of 50/50 as a function of gel type. An increase in volume fraction not only enhanced the differences between the gel types but also changed their rank.

4.5 Discussion

The objective of this work was to evaluate suspension rheology as a function of shear rate, volume fraction, particle size distributions, and rheological properties of the beads. Several models describing suspension behavior as a function of the above factors have been presented in the introduction (Table 4.1). While these models were applicable for some systems, many of the results presented did not fit the models existing in literature.

Shear rate had an important role when describing suspension flow behavior as a function of volume fraction. The magnitude of the hydrodynamic forces for the various systems was determined to identify the governing forces for the flow of the investigated systems. The Peclet number was calculated for the range of particle sizes used and shear rates tested. The minimum Peclet number calculated for the systems was $5 \times 10^5$ and the maximum was $8 \times 10^8$ which means that colloidal and Brownian forces may be neglected and hydrodynamic forces govern the flow. The hydrodynamic interaction forces are caused by relative motion of neighboring particles and are present in all flowing non-dilute suspensions (Macosko, 1994). It is not surprising then, that at higher volume fraction, the hydrodynamic forces had a larger effect on suspension viscosity, and the differences between the different volume fractions were visible and, for most parts, predictable. Suspension type I, however did yield unexpected behavior at high volume fractions. The
unexpected behavior was characterized by flow behavior C where at lower shear rates the relative viscosity was lower than 1. As the shear rate increased so did the relative viscosity. This type of behavior was not observed in previous work, and the mechanism responsible is unknown. However, considering the systems for which flow pattern C was observed, one plausible mechanism is proposed. Below a critical shear rate, some of the shear energy was dissipated, probably as heat. As the shear rate increased, more energy was applied to the system and the elasticity of the beads increased, thereby less of the applied energy could dissipate. This behavior was not observed for the 0/100 particle size distribution of type I suspensions. In the absence of smaller particles, the stress produced in the system was large even at lower shear rates.

This unique behavior of type I demonstrated the effect that the mechanical properties of the beads had on suspension viscosity. The different bead type behavior was a function of shear rate (as demonstrated by type I), but was also dependent on volume fraction and particle size distribution. The connection between gel type and volume fraction was displayed by the results for the control systems and type IV systems. As mentioned previously, the later could not be compared to the other gel types because the volume fractions achieved by types I, II, III, and V were too high for type IV. The control systems could only be measured up to a volume fraction of 20%. The elastic nature of the control and type IV beads prevented them from deforming and flowing past one another. This phenomenon may also explain the inconsistent flow seen for large volume fraction of the control systems.

The effect of particle size distributions was a function of volume fraction and bead type. It was anticipated that a less uniform particle size distribution would yield a lower
suspension viscosity (Farris 1968). However, the effect of particle size distribution was very diverse. This diverse behavior supported the possibility of a more complex mechanism or combination of mechanisms. The first mechanism supports the anticipated behavior where inclusion of smaller particles may lower the suspension viscosity by increasing the packing efficiency of the beads. This mechanism may account for the behavior observed for type III at a volume fraction of 90% (Figure 4.13) and type I at a volume fraction of 75% (Figure 4.7), but is not the case for type V at a volume fraction of 60% (Figure 4.15). A second mechanism which may explain the behavior observed for type V at 60% volume fraction is dependent on the interactions between the particles. As the smaller particles fill the voids between the larger particles, the contact between the beads increases giving rise to more friction and higher viscosity. A similar mechanism is presented by Agarwala and others (1992) who claimed that the increase in number of particles per volume results in a smaller mean distance between the particles, thus increasing the potential for particle-particle interactions that can increase viscosity. In any case, the particle size distribution effect for lower volume fractions was minimal. This observation was supported by Metzner (1985) who claimed that in dilute suspensions ($\Phi \leq 0.2$) modest changes in particle size were of no consequence. Another possible explanation for the dependence of suspension viscosity on particle size is based on Barnes (1994) work with emulsions. He observed that smaller emulsion droplets were less deformable hence increasing emulsion viscosity. In that case, inclusion of smaller beads may increase suspension viscosity.

Finally, another observation was the dependence of the gel type effect on shear rate, particle size distribution, and volume fraction (Table 4.11). Type I had a high dependence on shear rate and its rank increased as the shear rate increased. Type II and V had a very
similar behavior, and type III dominance was limited to a particle size distribution of 100/0. The viscoelastic nature of the beads may explain some of these observations, specifically the resemblance between II and V, which had similar viscoelastic properties (Table 4.3). It also appeared that the viscoelastic nature of the particles did not have the same impact at all particle size distributions, most likely because of packing efficiency and surface contact. Future work should focus on uniform particle size (as opposed to particle size distribution) to reduce some of the variability.

4.6 Conclusion

The rheology of suspensions composed of viscoelastic particles was a function of shear rate, volume fraction, particle size distributions, and mechanical properties of the beads. While the suspension viscosity dependence on volume fraction was predictable and well understood; the dependence on shear rate and particle size distribution was more complex, interrelated, and was strongly influenced by the viscoelastic properties of the beads. Several mechanisms were proposed to account for the flow behavior of the different systems investigate. The validity of the proposed mechanisms should be confirmed in future studies focusing on suspension rheology as a function of the viscoelastic properties of the dispersed phase
## Table 4.2
Alginate powder properties (Provided by Danisco)

<table>
<thead>
<tr>
<th>Name</th>
<th>Guluronic Acid (%)</th>
<th>Mannuronic Acid (%)</th>
<th>Molecular weight (KDa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alginate De Sodium Flavicans</td>
<td>70</td>
<td>30</td>
<td>270</td>
</tr>
<tr>
<td>Alginate TS-A 6556</td>
<td>32</td>
<td>68</td>
<td>463</td>
</tr>
<tr>
<td>GRINDSTED Alginate FDG 125</td>
<td>50</td>
<td>50</td>
<td>500</td>
</tr>
</tbody>
</table>

## Table 4.3
Bead types produced and used as dispersed phase

<table>
<thead>
<tr>
<th>ID</th>
<th>Guluronic Acid (%)</th>
<th>Mannuronic Acid (%)</th>
<th>Alginate (% w/w)</th>
<th>Storage modulus (Pa)</th>
<th>Loss modulus (Pa)</th>
<th>Tack energy (Nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Type I</td>
<td>32</td>
<td>68</td>
<td>1.5</td>
<td>5,500±800</td>
<td>850±150</td>
<td>3.1E-05±7.7E-06</td>
</tr>
<tr>
<td>Type II</td>
<td>32</td>
<td>68</td>
<td>2.5</td>
<td>13,000±1,500</td>
<td>1800±350</td>
<td>4.3E-05±5.2E-06</td>
</tr>
<tr>
<td>Type III</td>
<td>70</td>
<td>30</td>
<td>1.5</td>
<td>18,000±2,000</td>
<td>2200±400</td>
<td>3.6E-05±9.3E-06</td>
</tr>
<tr>
<td>Type IV</td>
<td>70</td>
<td>30</td>
<td>2.5</td>
<td>50,000±10,000</td>
<td>7100±1000</td>
<td>4.5E-05±8.7E-06</td>
</tr>
<tr>
<td>Type V</td>
<td>50</td>
<td>50</td>
<td>1.5</td>
<td>12,500±1,400</td>
<td>1400±200</td>
<td>2.1E-05±8.3E-06</td>
</tr>
</tbody>
</table>

## Table 4.4
Particle composition of the different particle size distributions

<table>
<thead>
<tr>
<th>Particle size distribution</th>
<th>Fraction of population A 75 µm &lt; D &lt; 150 µm</th>
<th>Fraction of population B D&lt; 75µm</th>
</tr>
</thead>
<tbody>
<tr>
<td>0/100</td>
<td>100</td>
<td>0</td>
</tr>
<tr>
<td>25/75</td>
<td>75</td>
<td>25</td>
</tr>
<tr>
<td>50/50</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>75/25</td>
<td>25</td>
<td>75</td>
</tr>
<tr>
<td>100/0</td>
<td>0</td>
<td>100</td>
</tr>
</tbody>
</table>
Table 4.5
Flow patterns observed and the systems comprising them

<table>
<thead>
<tr>
<th>Flow pattern</th>
<th>Description</th>
<th>Volume fraction</th>
<th>Particle size distribution</th>
<th>Gel type</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Below $\dot{\gamma}_c \cdot \eta_r = 1$ independent of shear rate Above $\dot{\gamma}_c \cdot \eta_r &gt; 1$ increasing with shear rate</td>
<td>Up to 60%</td>
<td>All but 0/100</td>
<td>Most often type I</td>
</tr>
<tr>
<td>B</td>
<td>Below $\dot{\gamma}_c \cdot \eta_r &gt; 1$ independent of shear rate Above $\dot{\gamma}_c \cdot \eta_r &gt; 1$ increasing with shear rate</td>
<td>All but 90%</td>
<td>All</td>
<td>All</td>
</tr>
<tr>
<td>C</td>
<td>Below $\dot{\gamma}_c \cdot \eta_r &lt; 1$ increasing of shear rate Above $\dot{\gamma}_c \cdot \eta_r &gt; 1$ increasing with shear rate</td>
<td>75% and 90%</td>
<td>All but 0/100</td>
<td>Only type I</td>
</tr>
<tr>
<td>D</td>
<td>$\eta_r &gt; 1$ increasing with shear rate No $\dot{\gamma}_c$</td>
<td>60%, 75%, and 90%</td>
<td>All</td>
<td>All</td>
</tr>
<tr>
<td>E</td>
<td>Below $\dot{\gamma}<em>c \cdot \eta_r &gt; 1$ deceasing of shear rate Above $\gamma</em>{c1}$ &amp; bellow $\gamma_{c2}, \eta_r = 1$ Above $\gamma_{c2} \cdot \eta_r &gt; 1$ increasing with shear rate</td>
<td>30%</td>
<td>All</td>
<td>All</td>
</tr>
<tr>
<td>F</td>
<td>Below $\dot{\gamma}<em>c \cdot \eta_r &gt; 1$ deceasing of shear rate Above $\gamma</em>{c1}$ &amp; bellow $\gamma_{c2}, \eta_r &gt; 1$ Above $\gamma_{c2} \cdot \eta_r &gt; 1$ increasing with shear rate</td>
<td>Mostly 15% and 20%</td>
<td>All</td>
<td>Polystyrene beads</td>
</tr>
</tbody>
</table>
Table 4.6
Flow patterns and critical shear rates for type I suspensions. Flow Pattern D did not have a critical shear rate (-)

<table>
<thead>
<tr>
<th>Particle size distribution</th>
<th>0/100</th>
<th>25/75</th>
<th>50/50</th>
<th>75/25</th>
<th>100/0</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flow pattern</td>
<td>( \gamma_c (1/s) )</td>
<td>Flow pattern</td>
<td>( \gamma_c (1/s) )</td>
<td>Flow pattern</td>
<td>( \gamma_c (1/s) )</td>
</tr>
<tr>
<td>30 B</td>
<td>150</td>
<td>A</td>
<td>80</td>
<td>A</td>
<td>500</td>
</tr>
<tr>
<td>45 B</td>
<td>32</td>
<td>B</td>
<td>43</td>
<td>A</td>
<td>60</td>
</tr>
<tr>
<td>60 D</td>
<td>-</td>
<td>D</td>
<td>-</td>
<td>A</td>
<td>13</td>
</tr>
<tr>
<td>75 D</td>
<td>-</td>
<td>C</td>
<td>8</td>
<td>C</td>
<td>13</td>
</tr>
<tr>
<td>90 D</td>
<td>-</td>
<td>C</td>
<td>13</td>
<td>C</td>
<td>23</td>
</tr>
</tbody>
</table>

Table 4.7
Flow patterns and critical shear rates for type II suspensions. Flow Pattern D did not have a critical shear rate (-)

<table>
<thead>
<tr>
<th>Particle size distribution</th>
<th>0/100</th>
<th>25/75</th>
<th>50/50</th>
<th>75/25</th>
<th>100/0</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flow pattern</td>
<td>( \gamma_c (1/s) )</td>
<td>Flow pattern</td>
<td>( \gamma_c (1/s) )</td>
<td>Flow pattern</td>
<td>( \gamma_c (1/s) )</td>
</tr>
<tr>
<td>30 E</td>
<td>17, 368</td>
<td>E</td>
<td>32, 270</td>
<td>B</td>
<td>370</td>
</tr>
<tr>
<td>45 B</td>
<td>368</td>
<td>B</td>
<td>200</td>
<td>B</td>
<td>270</td>
</tr>
<tr>
<td>60 B</td>
<td>200</td>
<td>B</td>
<td>200</td>
<td>B</td>
<td>150</td>
</tr>
<tr>
<td>75 B</td>
<td>13</td>
<td>D</td>
<td>-</td>
<td>D</td>
<td>-</td>
</tr>
<tr>
<td>90 D</td>
<td>-</td>
<td>D</td>
<td>-</td>
<td>D</td>
<td>-</td>
</tr>
</tbody>
</table>
Table 4.8
Flow patterns and critical shear rates for type III suspensions. Flow Pattern D did not have a critical shear rate (-)

<table>
<thead>
<tr>
<th>Particle size distribution</th>
<th>0/100</th>
<th>25/75</th>
<th>50/50</th>
<th>75/25</th>
<th>100/0</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flow pattern</td>
<td>γc (1/s)</td>
<td>Flow pattern</td>
<td>γc (1/s)</td>
<td>Flow pattern</td>
<td>γc (1/s)</td>
</tr>
<tr>
<td>30</td>
<td>E 32,</td>
<td>E 23,</td>
<td>B 271</td>
<td>B 271</td>
<td>B 271</td>
</tr>
<tr>
<td>45</td>
<td>B 200</td>
<td>B 200</td>
<td>B 108</td>
<td>B 271</td>
<td>B 150</td>
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<tr>
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<td>B 79</td>
<td>B 108</td>
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<td>B 197</td>
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<td>B 17</td>
<td>B 13</td>
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<td>B 23</td>
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</tr>
<tr>
<td>90</td>
<td>D -</td>
<td>D -</td>
<td>D -</td>
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Table 4.9
Flow patterns and critical shear rates for type V suspensions. Flow Pattern D did not have a critical shear rate (-)

<table>
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<th>Particle size distribution</th>
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<th>75/25</th>
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<tr>
<td>Flow pattern</td>
<td>γc (1/s)</td>
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<td>E 32,</td>
<td>E 43,</td>
<td>E 23,</td>
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<td>B 200</td>
<td>B 271</td>
<td>B 32</td>
</tr>
<tr>
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<td>B 200</td>
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<td>B 147</td>
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<tr>
<td>75</td>
<td>D -</td>
<td>D -</td>
<td>B 13</td>
<td>D -</td>
<td>D -</td>
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<tr>
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<td>D -</td>
<td>D -</td>
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### Table 4.10
Flow patterns and critical shear rates for control suspensions

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<th>$\gamma_c$ (1/s)</th>
<th>Flow pattern</th>
<th>$\gamma_c$ (1/s)</th>
<th>Flow pattern</th>
<th>$\gamma_c$ (1/s)</th>
<th>Flow pattern</th>
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<td>80, 110</td>
<td>F</td>
<td>80, 110</td>
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Table 4.11
The highest ranking gel type as a function of volume fraction and particle size distribution for 4 shear rates: (a) 5 1/s; (b) 32 1/s; (c) 199 1/s; (d) 600 1/s

(a) 5 1/s
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<th>75/25</th>
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<td>III V</td>
<td>I -</td>
<td>II III</td>
<td>V -</td>
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<tr>
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<td>I -</td>
<td>-</td>
<td>II - V</td>
<td>II -</td>
<td>-</td>
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<tr>
<td>60%</td>
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<td>III -</td>
<td>II III</td>
<td>II V</td>
<td>II III V</td>
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<tr>
<td>75%</td>
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<td>90%</td>
<td>-</td>
<td>III -</td>
<td>II -</td>
<td>- -</td>
<td>V -</td>
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(b) 32 1/s
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<th>50/50</th>
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<th>100/0</th>
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<tbody>
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<td>I -</td>
<td>-</td>
<td>I II</td>
<td>III V</td>
<td>II -</td>
</tr>
<tr>
<td>45%</td>
<td>I -</td>
<td>-</td>
<td>I -</td>
<td>II - V</td>
<td>II -</td>
</tr>
<tr>
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<td>-</td>
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<td>-</td>
<td>II -</td>
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<td>V -</td>
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<td>- -</td>
<td>V -</td>
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(c) 199 1/s
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<tbody>
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<td>-</td>
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<td>-</td>
<td>I -</td>
<td>I -</td>
<td>I -</td>
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<tr>
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<td>-</td>
<td>I -</td>
<td>I -</td>
<td>V -</td>
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<tr>
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(d) 600 1/s
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<th>75/25</th>
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</thead>
<tbody>
<tr>
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<td>I -</td>
<td>III V</td>
<td>II III</td>
</tr>
<tr>
<td>45%</td>
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<td>I -</td>
<td>-</td>
<td>II III</td>
</tr>
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<td>60%</td>
<td>I -</td>
<td>-</td>
<td>I -</td>
<td>I -</td>
<td>I -</td>
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<tr>
<td>75%</td>
<td>I -</td>
<td>-</td>
<td>I -</td>
<td>I -</td>
<td>V -</td>
</tr>
<tr>
<td>90%</td>
<td>I -</td>
<td>-</td>
<td>I -</td>
<td>I -</td>
<td>V -</td>
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Figure 4.3 (a) Shear stress as a function of shear rate for the continuous phase (0.25% xanthan), and a suspension composed of 30% type II beads with a particle size distribution of 100/0. (b) Relative viscosity and viscosity as a function of shear rate for the continuous phase (0.25% xanthan) and a suspension composed of 30% type II beads with a particle size distribution of 100/0.
Figure 4.4 Flow patterns observed. (a) The suspension and continuous phase viscosities as a function of shear rate; (b) relative viscosity as a function of shear rate
Figure 4.5 Relative viscosity as a function of shear rate for type I suspensions (a) 0/100 particle size distribution; (b) 75/25 particle size distribution.
Figure 4.6 Relative viscosity as a function of shear rate for higher volume fractions of type I
Figure 4.7 Relative viscosity as a function of shear rate for type I suspensions (a) 60% volume fraction; (b) 75% volume fraction
Figure 4.8 Relative viscosity as a function of shear rate: time dependence of Type I at 90% volume fraction and 0/100 particle size distribution
Figure 4.9 Relative viscosity as a function of shear rate for type II suspensions (a) 0/100 particle size distribution; (b) 75/25 particle size distribution
Figure 4.10 Relative viscosity as a function of shear rate for type II suspensions (a) 45% volume fraction; (b) 75% volume fraction
Figure 4.11 Relative viscosity as a function of shear rate for type III suspensions (a) 0/100 particle size distribution; (b) 100/0 particle size distribution
Figure 4.12 Relative viscosity as a function of shear rate for type III suspensions with a 50/50 particle size distribution
Figure 4.13 Relative viscosity as a function of shear rate for type III suspensions (a) 45% volume fraction; (b) 90% volume fraction
Figure 4.14 Relative viscosity as a function of shear rate for type V suspensions (a) 0/100 particle size distribution; (b) 75/25 particle size distribution
Figure 4.15 Relative viscosity as a function of shear rate for type V suspensions (a) 30% volume fraction; (b) 60% volume fraction.
Figure 4.16 Relative viscosity as a function of shear rate for type V suspensions with a 90% volume fraction
Figure 4.17 Relative viscosity as a function of shear rate for polystyrene bead suspensions (a) 10% volume fraction; (b) 15% volume fraction; (c) 20% volume fraction.
Figure 4.18 The effect of particle size distribution at a volume fraction of 90% as a function of gel type
Figure 4.19 The effect of particle size distribution at a volume fraction of 30% as a function of gel type
Figure 4.20 The effect of volume fraction at a particle size distribution of 50/50 as a function of gel type
4.7 References


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Mooney M. 1951. The viscosity of a concentrated suspension of spherical particles. J. Colloid Sci. 6:162–70


Tsai SC, Botts D, Plouff J. Effects of particle properties on the rheology of concentrated noncolloidal suspensions. J. Rheol. 36:1291


CHAPTER 5 CONCLUSION

The rheological properties of alginate microbead gels and suspension were investigated to evaluate the microstructure of gels and suspensions containing viscoelastic particles. This work was composed of 3 phases: beads production, microbead gel analysis, and suspension rheology.

First, an apparatus was designed for the production of alginate microbeads utilizing air-assisted atomization. The process yielded microbeads ranging in size from several microns to several hundred microns. The particle median diameter was a function of solution viscosity and air velocity. The Weber and Reynolds numbers were found to be of importance in the correlation between the diameters of the beads produced and processing parameters. Future work should include an evaluation of bead diameter as a function of apparatus geometry and over a wider range of air velocities.

Second, the mechanical properties of alginate bulk gels were evaluated as a function of alginate type and concentration. The content of guluronic acid and mannuronic acid as well as alginate concentration affected the mechanical properties of the gels. A higher guluronic acid content yielded a more elastic gel. The bulk gel properties were compared with the microbead gels properties. The viscoelastic properties of the microbead gels were related to the viscoelastic properties of the bulk gels. As smaller particles were introduced into the system, the importance of particle deformability and interparticle interactions increased. Future work should address the mechanical properties of microbead gels as a function of surface properties.
Finally, the viscosity of suspensions composed of viscoelastic particles was evaluated as a function of shear rate, volume fraction, particle size distributions, and mechanical properties of the beads. The mechanical properties of the dispersed phase proved to be very important in the analysis of shear rate effects, particle volume fraction, and particle size distribution. Future work should focus on suspension rheology as a function of the viscoelastic properties of the dispersed phase while isolating other variables such as particle size distribution and volume fraction.
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Tsai SC, Botts D, Plouff J. Effects of particle properties on the rheology of concentrated noncolloidal suspensions. J. Rheol. 36:1291


Vicente et al., 2005 Soft lubrication of model hydrocolloids and emulsions


APPENDICES
APPENDIX A

Rheology is the science of the flow and deformation of matter. Principles of rheology are commonly applied to understand and improve the flow behavior and mechanical properties of different materials, including foods. This section introduces basic terms in rheology including stress and strain, viscosity, and elasticity. Viscoelasticity and methods for determination of viscoelastic properties are presented, and gels are used as an example of a viscoelastic material.

Stress and strain

Stress (σ, Pa) is a ratio between force (F, N) and the surface upon which it is applied (A, m²) (Daubert and Foegeding 1998):

$$\sigma = \frac{F}{A}; \quad \text{[Pa]} = \frac{\text{[N]}}{\text{[m}^2\text{]}}$$  
Equation 1

The type of stress applied is a function of the direction of the force (Figure 5.1). If the force is perpendicular to the surface, a normal stress is applied. Shear stress is applied when the force is tangential to the surface. When a stress is applied, the material deforms. Strain is a dimensionless quantity that represents the relative deformation of the material. Normal strain (ε) is a result of normal stress (Figure 5.1 (a)):

$$\varepsilon = \ln \left(1 + \frac{\Delta L}{L_0}\right)$$  
Equation 2

When the force is applied parallel to the surface, the resulting strain is a shear strain (γ) (Figure 5.1 (b)):
\[ \tan(\gamma) = \frac{\Delta L}{h} \quad \text{Equation 3} \]

Where \( h \) is the sample height. For small strains: \( \tan(\gamma) = \gamma \).

When stress is applied to a liquid, it flows; therefore, deformation should be applied with respect to time. Figure 5.2 represents the application of shear force to a plate which, as a result, moves with a velocity, \( v \) (m/s). The shear strain rate, \( \dot{\gamma} \) (or simply, shear rate) can be calculated and has dimensions of 1/s.

\[ \dot{\gamma} = \frac{v}{h} \quad \text{Equation 4} \]

The mechanical properties of a solid are best characterized by the relationship between stress and strain and fluids are best characterized by relating shear stress and shear rate.

**Elasticity**

When ideal solids are subject to a load, they deform elastically, and upon removal of this force, return instantly to the original shape. The degree of deformation is proportional to the stress applied. In other words, Hooke's law, which states that a linear relationship exists between stress and strain, is obeyed. Figure 5.1 (a) illustrates the effect a normal force has on a surface, and Equation 5 displays the relationship between stress (\( \sigma \)) and strain (\( \varepsilon \)) for an ideal solid, where \( E \) is the Young's modulus (Pa):

\[ \sigma = E \times \varepsilon \quad \text{Equation 5} \]
Figure 5.1 (b) illustrates the effect a shear force has on a surface, and Equation 6 displays the relationship between a shear stress and shear strain, where $G$ is the shear modulus (Pa):

$$\sigma = G \times \gamma \quad \text{Equation 6}$$

The moduli (both $E$ and $G$) are inherent properties of an elastic material and may be measured by several methods, including compression, tension, and torsion. The compression method is presented later in this chapter.

**Viscosity**

Liquids flow when a sufficient force is applied. Figure 5.2 illustrates the velocity profile of a fluid contained between parallel plates. When a force is applied to the top plate, the layers of liquid between the plates are sheared, given the top layer of fluid is moving at the velocity of the plate, $v$. Equation 2.5 defines the term “shear rate” ($\dot{\gamma}$, 1/s) as the ratio between the velocity of the top plate ($v$, m/s) and the distance between the plates ($h$, m). An ideal relationship between shear stress and shear rate is then given in Equation 7, where $\mu$ is the Newtonian viscosity (Pa•s):

$$\sigma = \mu \times \dot{\gamma} \quad \text{Equation 7}$$

The viscosity is a measure of resistance to flow; therefore, it must be related to the structure of the fluid and the interactions among components (Aguilera and Stanley 1999). When the structure of the fluid changes with rate of deformation, the viscosity is dependent on shear rate, and a more complex relationship between shear stress and rate exists (Figure
5.3. For non-Newtonian liquids the ratio between stress and shear rate is called apparent viscosity, \( \eta \):

\[
\eta(\dot{\gamma}) = \frac{\sigma}{\dot{\gamma}} \quad \text{Equation 8}
\]

A shear thinning behavior is a result of structure change that leads to decreased resistance to flow as the rate is increased. Alignment of macromolecules, disaggregation of aggregates, and deformation of particles are some of the structure changes occurring with increasing shear that may lead to a pseudoplastic behavior (Steffe 1996; Barnes and others 1989; Aguilera and Stanley 1999). Shear thickening is characterized by an increase in viscosity with shear rate. Barnes and others (1989) explain shear thickening behavior by the rearrangement of the fluid microstructure increasing the resistance to flow. Entanglement of macromolecules, flocculation of particles, and deformation of particles are some of causes for shear thickening behavior (Macosko 1994; Barnes 2000; Kohdakov 2004).

**Viscoelasticity**

The ideal elastic behavior (Hooke’s Law) and the ideal viscous behavior (Newton’s postulate) represent two extremes of the mechanical spectrum (Figure 5.4). Between these two extremes, there exists a wide region of viscoelastic materials. These materials display simultaneous elastic-like and a viscous-like behavior. The deformation time scale determines the magnitude of the viscous and elastic components of the material (Kavanagh and Ross Murphy 1998).

For viscoelastic materials, the shear modulus has two components: storage modulus (\(G'\), Pa) and loss modulus (\(G''\), Pa) (Equation 5). Notably, \(G'\) is the measure of the energy stored
and recovered, and \( G'' \) is a measure of the energy dissipated or lost as heat. The ratio of energy lost to energy stored, \( \tan \delta \), is an indication of the material elasticity (Ferry 1980).

\[
G^* = \sqrt{G'^2 + G''^2} \quad \text{Equation 9}
\]

\[
\tan \delta = \frac{G''}{G'} \quad \text{Equation 10}
\]

The storage and loss moduli are measured within the linear viscoelastic region, where Hooke’s Law applies. In other words, the stress and strain are linearly related. Within that region, the viscoelastic properties are only a function of the deformation time scale, and the material is characterized without disrupting sensitive sample structure. The concept of viscoelasticity is best explained by an oscillatory technique for determination of viscoelastic properties.

**Small amplitude oscillatory tests**

Small-amplitude oscillatory tests allow the quantitative determination of viscoelastic characteristics of a material. Generally, samples are subjected to harmonically varying stresses or strains. The material response (strain or stress, respectively) is used to construct a mechanical spectrum that can provide information about the viscous and elastic nature of the sample behavior.

Figure 5.5 illustrates strain applied in sinusoidal oscillation. The maximum strain applied is the amplitude of the sinusoidal wave \((\gamma_0)\), and the time scale of deformation is determined by the frequency \((\omega)\) of the oscillation (measured in rad/sec or Hz). The strain \((\gamma)\) may be calculated at any given time \((t)\) as:
\[ \gamma = \gamma_0 \sin(\omega t) \quad \text{Equation 11} \]

The stress response is measured:

\[ \sigma = \sigma_0 \sin(\omega t - \delta) \quad \text{Equation 12} \]

Where \( \delta \) is the phase angle. If the material tested is perfectly elastic, the stress response follows the strain applied (it is “in-phase”) and the phase angle is 0°. For Newtonian fluids, the phase angle is 90°, and the stress and strain, in this case, are “out-of-phase. A viscoelastic material exhibit both elastic and viscous behavior and therefore has an “in-phase” component which is the storage modulus (\( G' \)), and an “out-of-phase” component which is the loss modulus (\( G'' \)).

\[ G' = \frac{\gamma_0}{\sigma_0} \cos(\delta) \quad \text{Equation 13} \]

\[ G'' = \frac{\gamma_0}{\sigma_0} \sin(\delta) \quad \text{Equation 14} \]

The viscoelastic properties are a function of time, where an increase in frequency generally results in a more solid-like behavior (Daubert and Foegeding 1998). It is useful to determine the rheological properties of a gel over a range of frequencies. The dependence of \( G', G'' \), and \( \tan(\delta) \) on frequency (also called “mechanical spectra”) is often used when comparing different materials (Steffe 1996). For dilute solutions, the loss modulus is larger than the storage modulus over the entire frequency range; cross-linked gels exhibit a higher storage modulus over the entire frequency range; and concentrated solutions typically display a “cross-over” frequency, where the loss modulus and storage modulus are equal (Figure 5.6).
Large strain rheology

While small strain rheology measurements are conducted in the linear viscoelastic region to maintain the structure of the sample, large strain rheology extends beyond the linear viscoelastic region up to sample fracture. Large deformation rheology can be performed in compression, where a normal stress is applied to a sample (Figure 5.1 (a)) and can potentially be compressed to fracture. The force and deformation (Equation 2) are measured and converted to stress and strain (Truong and Daubert 2000). Equation 15 provides a corrected equation for stress that effectively corrects for excessive shape change of the specimen during the test.

\[
\sigma = \frac{F(L_0 - \Delta L)}{\pi R^2 L_0} \quad \text{Equation 15}
\]

Where \( F \) is the fracture force (N), \( L_0 \) is sample initial length (mm), \( \Delta L \) is change in length (mm), and \( R \) is sample radius (mm). The stress and strain curve is presented in Figure 5.7 and demonstrates not only the different yield points but also a different curve shape. The yield point of the gel correlates with the strength and deformability of the gel. The shape of the curve is related to the strain hardening or strain weakening behavior of the gel (Zhang and others 2006).

The large strain rheology compliments the small strain rheology in the ability to distinguish between strong and soft gels. Both respond as solids at small deformation but whereas strong gels are also responding as solids under large strains, the weak gels flow under large deformation (Kavanagh and Ross-Murphy 1998).
Figure 5.1 Normal (a) and shear (b) forces applied to a solid and causing elastic deformation
Figure 5.2 Velocity profile between parallel plates. The bottom plate (B) is fixed and the top plate (A) is moving at a velocity $\nu$. 
Figure 5.3 Shear stress vs shear rate for Newtonian and non-Newtonian fluids
Figure 5.4 Rheological behavior spectrum
Figure 5.5 Stress response to a sinusoidal strain
Figure 5.6 Mechanical spectra (a) dilute solution; (b) gel; (c) concentrated solution
Figure 5.7 stress-strain curve and the correlation to material properties
APPENDIX B

The development of bead production method relied on the fast and complete gelation of the alginate beads. The binding of calcium ions to the sodium alginate chains is considered instantaneous or nearly so (Somesh and others 1988; Herrero and others 2006a; Blandino and others 1999), and the time required for the diffusion of calcium to the center of the bead was calculated to ensure gelation.

![Diagram showing calcium ions (Ca++) diffusing through a bead structure.](image-url)
According to Fick’s law for diffusion (Singh and Heldman 2003) the flux (Jr) of Ca++ into the center of the bead is calculated:

\[ J_r = D \frac{dc}{dr} \]

Where:

\[ dc = c_\infty - c_0 = 15 \text{ kg/m}^3 \]

\[ dr = R = 75 \text{ \mu m} = 7.5 \times 10^{-5} \text{ m} \]

The volume of the bead:

\[ V = \frac{4}{3} \pi r^3 = 1.8 \times 10^{-12} \text{ m}^3 \]

If 1.5% Calcium is needed to gel the entire volume of the bead, then the mass of calcium is:

\[ m = V \times c = 1.8 \times 10^{-12} \text{ m}^3 \times 15 \text{ kg/m}^3 = 2.7 \times 10^{-11} \text{ kg} \]

The diffusion coefficient of calcium through the alginate gel is:

\[ D = 10^{-9} \text{ m}^2/\text{s} \quad \text{(Skjåk-Bræk and others 1989)} \]

Therefore, the calculated flux is:

\[ J_r = \frac{\dot{m}}{A} = 10^{-9} \text{ m}^2/\text{s} \times \frac{15 \text{ kg/m}^3}{7.5 \times 10^{-5} \text{ m}} = 2 \times 10^{-4} \text{ kg/m}^2 \cdot \text{s} \]
The surface area of the bead is:

\[ A = 4\pi r^2 = 7.065 \times 10^{-8} \text{ m}^2 \]

Therefore, the mass flow of calcium is calculated to be:

\[ \dot{m} = J \times A = 7.065 \times 10^{-8} \text{ m}^2 \times 2 \times 10^{-4} \text{ kg/m}^2 \cdot \text{s} = 1.413 \times 10^{-11} \text{ kg/s} \]

Finally, given the mass of calcium required and the mass flow rate, the time is:

\[ t = \frac{m}{\dot{m}} = \frac{2.7 \times 10^{-11} \text{ kg}}{1.413 \times 10^{-11} \text{ kg/s}} = 1.9 \text{ s} \]