

**LIBRARY
Michigan State
University**

This is to certify that the

thesis entitled

Effect of Formulation and Particle Size on the
Rheological Properties of Salad Dressing

presented by

Julie Krista Branch

has been accepted towards fulfillment
of the requirements for

M.S. degree in Food Science

James F. Steffe

Major professor

Date June 22, 2001

PLACE IN RETURN BOX to remove this checkout from your record.
TO AVOID FINES return on or before date due.
MAY BE RECALLED with earlier due date if requested.

DATE DUE	DATE DUE	DATE DUE

**EFFECT OF FORMULATION AND PARTICLE SIZE ON THE
RHEOLOGICAL PROPERTIES OF SALAD DRESSING**

By

Julie Krista Branch

A THESIS

**Submitted to
Michigan State University
in partial fulfillment of the requirements
for the degree of**

MASTER OF SCIENCE

Department of Food Science and Human Nutrition

2001

por

dep

vis

Op

and

of

pro

pro

vis

6.5

par

the

ABSTRACT

EFFECT OF FORMULATION AND PARTICLE SIZE ON THE RHEOLOGICAL PROPERTIES OF SALAD DRESSING

By

Julie Krista Branch

The effect of formulation and particle size on the rheological properties of pourable salad dressing was studied utilizing rotational viscometry. Slightly time-dependent and strong shear-thinning behavior was observed. The apparent viscosity at a shear rate of 25 s^{-1} was strongly affected by xanthan gum. Optimum viscosity was achieved with a formulation having 0.45% xanthan gum and 1.5% egg yolks. Egg yolks provided emulsion stability, and increasing levels of egg yolk had a minor influence on viscosity. Temperature was also shown to produce minor changes in the viscosity at 25°C and 5°C. Increases in the processing rate (differential pressure over a hydroshear) did not strongly affect viscosity, but had a strong effect on the particle sizes ranging from 5.17 μm to 6.50 μm . Xanthan gum and egg yolks were shown to only slightly influence the particle size compared to the process rate. No correlation was found between the particle size and the viscosity.

DEDICATION

To my ryan.

ACKNOWLEDGEMENTS

**Thank you Dr. Steffe for all of your guidance and patience.
Special thanks to my committee Dr. Ustunol and Dr. Uebersax,
to Suzanne Case and Raju Borwankar from Kraft Foods,
my POST family, my 'coach' Jeff Feneley,
my family and friends and to Ryan for his continued support.**

LIS

LIS

KE

Ch

1.1

1.2

1.3

Ch

2.1

2.2

2.3

2.4

2.5

TABLE OF CONTENTS

LIST OF TABLES	vii
LIST OF FIGURES	viii
KEY TO SYMBOLS OR ABBREVIATIONS	x
 Chapter 1 –INTRODUCTION	
1.1 Salad Dressings	1
1.2 Consumer Market	2
1.3 Objectives	4
 Chapter 2 –LITERATURE REVIEW	
2.1 Emulsion Systems and Stability	5
2.2 Ingredients	8
2.2.1 Fat / Oil	9
2.2.2 Emulsifiers and Stabilizers	11
2.2.3 Egg Yolks	14
2.2.4 Proteins	17
2.2.5 Xanthan gum	18
2.3 Manufacturing of Dressings	22
2.4 Rheology of Salad Dressings and Methodology of Fluids	28
2.4.1 Time/Temperature Dependence	31
2.4.2 Steady State Shear Measurements	37
2.4.3 Unsteady State Shear Measurements	40
2.4.4 Yield Stress	43
2.5 Particle Size Analysis	46
2.5.1 Measurement	48
2.5.2 Control of Particle Size	51
2.5.3 Size and Composition	52

Cha

3.1

3.2

3.3

3.4

3.5

Ch

4.1

4.2

Ch

Ch

Bit

TABLE OF CONTENTS (cont'd)

Chapter – 3 MATERIALS AND METHODS

3.1 Formulas / Samples.....	54
3.2 Processing.....	56
3.3 Rheology.....	61
3.4 Particle Size.....	61
3.5 Statistical Design and Analysis.....	67

Chapter 4 - RESULTS AND DISCUSSION

4.1 Influence of Formula and Processing on Rheological Behavior.....	68
4.1.1 Time dependent behavior.....	72
4.1.2 Xanthan Gum / Egg Yolks.....	80
4.1.3 Processing Rate.....	88
4.1.4 Temperature.....	92
4.2 Particle Size Influence.....	94
4.2.1 Influence of pressure drop.....	100
4.2.2 Influence of particle size on viscosity.....	101

Chapter 5 - SUMMARY AND CONCLUSIONS.....

104

Chapter 6 – FUTURE RESEARCH.....

106

Bibliography.....

108

TAB

TAB

TAB

TAE

TAE

TAE
wei

TA

TA
mo

TA

TA

LIST OF TABLES

TABLE 1 Ingredients typically found in food emulsions.

TABLE 2 Typical fat content of dressings and sauces.

TABLE 3 Sources of emulsifiers.

TABLE 4 Xanthan gum functionality.

TABLE 5 Comparison of different types of emulsifying devices.

TABLE 6 Model salad dressing samples formulation by percentage of total weight

TABLE 7 HAAKE Viscotester © 550 MVI Specifications

TABLE 8 Initial Brookfield viscosity, pH, titratable acidity and salt analysis of the model salad dressing samples

TABLE 9 Rheological analysis of model salad dressing formulations at 5°C

TABLE 10 Rheological analysis of model salad dressing formulations at 25°C

FIGU

FIGU

FIGU
fine

FIGU

FIGU

FIGU

FIGU

FIGU
sam

FIGU
in p

FIGU
top

FIGU

FIGU
det

FIGU
form
1.5
yoll

FIGU
diff

Fig
pro

FIGU
pro

LIST OF FIGURES

FIGURE 1 Emulsion instability

FIGURE 2 Breakage of cylinders of liquid into small droplets caused by shear

FIGURE 3 High pressure valve homogenizer, used to produce emulsions with fine droplet size

FIGURE 4 Time-dependent behavior of fluids

FIGURE 5 Typical curves for time-independent behavior fluids

FIGURE 6 Apparent viscosity of time independent fluids

FIGURE 7 Static and dynamic yield stress

FIGURE 8 Overview of pilot plant salad dressing process used to manufacture samples

FIGURE 9 Cross section of in-line emulsification system hydroshear unit utilized in pilot plant salad dressing system

FIGURE 10 MVI concentric cylinder testing apparatus showing to bob recessed top and bottom to minimize end effects

FIGURE 11 Horiba principle laser measurement flow diagram

FIGURE 12 Configuration of the Horiba LA-500 benchtop system utilized to determine lipid particle size

FIGURE 13 Rheological behavior of commercial samples in comparison to formula 1, containing 0% egg yolk and 0.15% xanthan gum; formula 5, containing 1.5% egg yolk and 0.30% xanthan gum; and formula 9, containing 3.0% egg yolks and 0.45% xanthan gum. (All at 140 psi and 25°C)

FIGURE 14 Time-dependent fluid behavior at 25°C before shear sweep at different processing levels

Figure 15 Time dependent fluid behavior at 25°C after shear sweep at different processing levels.

FIGURE 16 Effects of aging: comparison of measurements of fresh and aged product at two processing levels.

LIS

FIG

25°

FIG

xan

FIG

inc

FIG

inc

FIG

xa

FIG

an

FIG

siz

FIG

at

FIG

of

FIG

LIST OF FIGURES (Cont'd)

FIGURE 17 Effects of increasing xanthan gum at 1.5% egg yolks and 220 psi at 25°C.

FIGURE 18 Effects of Increasing egg yolk at 0%, 1.5% and 3.0% and increasing xanthan gum at 220 psi at 25°C.

FIGURE 19 Effect of processing rate increase 140, 180 and 220 psi with increasing egg yolk and xanthan gum level of 0.30% at 25°C.

FIGURE 20 Effect of increasing processing rate 140, 180 and 220 psi with increasing xanthan gum 0.15%, 0.30% and 0.45% and egg yolk level at 3.0%.

FIGURE 21 Effects of increasing process rate with 0% egg yolks and increasing xanthan gum 0.15%, 0.30% and 0.45% at 5°C.

FIGURE 22 Influences of temperature at 0.15% and 0.45% xanthan gum and 0% and 3.0% egg yolk levels.

FIGURE 23 Effect of increased differential pressure in the hydroshear on particle size.

Figure 24 Effects of increasing egg yolk and xanthan gum levels on particle size at 180 psi.

Figure 25 Effect of increased levels of egg yolk, at a constant xanthan gum level of 0.15% on particle size.

Figure 26 Viscosity versus particle size effects with processing rate increases.

σ

K

.

γ

n

η

t

σ_0

η^*

J

J_0

J_1

λ_n

μ

G

KEY TO SYMBOLS OR ABBREVIATIONS

σ = shear stress (Pa)

K = consistency coefficient (Pa sⁿ)

$\dot{\gamma}$ = shear rate (1/s)

n = flow behavior index (dimensionless)

η = apparent viscosity (Pa s)

t = time (s)

σ_0 = yield stress (Pa)

η^* = complex viscosity (Pa s)

J = shear creep compliance (Pa⁻¹)

J_0 = instantaneous compliance (Pa⁻¹)

J_1 = retarded compliance (Pa⁻¹)

λ_{ret} = retardation time (s)

μ = Newtonian viscosity (Pa s)

G' = shear storage modulus (Pa)

1.1

can

force

beh

in t

sala

ing

thic

own

sys

of f

aqu

of

bet

effe

cha

con

CHAPTER 1

INTRODUCTION

1.1 Salad Dressings

A pourable emulsion salad dressing is defined as a fluid system, which can be made to stream or flow continuously or profusely due to gravitational forces acting upon the system. The influence of particle size on the rheological behavior of a pourable model system impacts consumer acceptance.

The standard of identity for pourable emulsion salad dressings, as stated in the code of federal regulations, 21 CFR 161 (1999) provides a definition of salad dressing: Oil in water emulsion manufactured from oil, egg yolks, acidified ingredient and optional ingredients (salt, nutritive sweetener, stabilizer and thickener, acid). Mayonnaise, salad dressing and French dressing all have their own standard of identity.

Salad dressing is a thermodynamically unstable two-phase emulsion system. It contains two immiscible liquids, one dispersed in the other in the form of fine droplets. The surrounding liquid called the continuous or external phase, is aqueous. Oil is the dispersed or internal phase. Oil in water emulsions consists of fine droplets dispersed in an aqueous phase. The droplet size averages between 0.1 and 100 μ m. Size and aggregation of these oil droplets have an effect on the flow behavior and rheological characteristics. Knowledge of these characteristics assists in product development, production, packaging, and consumer acceptability.

conten

fully e

agitat

layers

applic

mode

emu

inter

type

cont

may

is c

to e

res

1.2

Th

As

ho

On

Pourable dressings include a variety of compositions, flavors and oil content. They are manufactured and formulated into two basic types. The first is fully emulsified which provides long-term stability, and requires little mechanical agitation. The second type is an emulsion that separates into oil and aqueous layers and has short-term stability, upon which mechanical agitation must be applied to suspend the particles in solution. The current study focused on a model system exhibiting long-term stability.

Lipid droplets are the main particle component of a salad dressing emulsion system. These droplets vary in size and are covered with an interfacial film. The width of this film ranges from 100 – 200Å, and varies with the type of dressing (Ford and others 1997). The aqueous or continuous phase contains spices and other plant materials, which provide flavor.

The continuous phase of some dressings contains starches and gums. In mayonnaise, the continuous phase is composed of egg granules. In dressing it is composed of hydrocolloids. These particles adhere to the interfacial film and to each other, forming a protein network. The formation of a protein network results in an increase in viscosity and stability of the emulsion.

1.2 Consumer Market

Salad dressings have been part of food history for thousands of years. The Babylonians used oil and vinegar for dressing greens over 2,000 years ago. As early as the 1920s many of the popular brand names of today became household names. In 1896 – Joe Marzetti opened a restaurant in Columbus, Ohio and served his customers a variety of bottled dressings. In 1912 – Richard

Hell

Che

the

(Ass

Rand

follow

(Ass

the

pou

she

Sau

to 6

Lar

bas

its

pro

and

the

co

Hellman, deli owner in New York sold “blue ribbon” mayonnaise. In 1925 – Kraft Cheese Company purchased several regional mayonnaise manufacturers and the Milani Company. This initiated Kraft’s pourable dressing business (Association for Dressing and Sauces 2000).

Ranch dressing was introduced in the mid 1970s by Hidden Valley Ranch© as a dry mix. Ranch style dressing holds reign as America’s favorite followed by Italian, creamy Italian, Thousand Island, French and Caesar (Association for Dressing and Sauces 2000).

As a consumer peruses down the grocery market aisle and travels through the produce section, they can find an overwhelming number of choices of pourable salad dressings. These include composition, flavor, size, brand, texture, shelf stability and packaging. According to the Association for Dressings and Sauces the amount of salad dressing sold grew from 6.3 million gallons in 1950 to 60 million gallons in 1997.

The consumer demand for product variety is a real issue in food stores. Large food stores provide the consumer with over twenty brand names and ten basic flavors in various types, including shelf stable to refrigerated dressings in its pourable dressings selection. This emphasizes the importance of competitive products in the market place and drives the food industry forward to develop new and improved products.

Reduced fat products and new flavors continue to be developed to satisfy the nutrient, textural, sensory and flow characteristics of a pourable dressing that consumers accept. Average consumers judge and purchase products based on

brand

Flow

depen

These

to pro

partic

proper

rheolo

1.3 C

The c
dress

1) As

2) E

th

3) E

th

4) E

brand loyalty, flavor, taste, price, composition and appearance of the product. Flow characteristics, emulsion stability, particle size, shelf life, temperature dependency and textural attributes all contribute to consumer acceptance. These product characteristics can be measured using rheological methodologies to produce a consumer accepted pourable dressing. In this study, the impact of particle size, due to formulation and production conditions, on the physical properties of a pourable emulsion model, was evaluated using various rheological methodologies.

1.3 Objectives

The objectives of this research were to do the following for a pourable salad dressing:

- 1) Assess the effects of temperature on the rheological properties.
- 2) Evaluate the influence of different formulations and processing conditions on the rheological properties.
- 3) Evaluate the influence of different formulations and processing conditions on the lipid particle size.
- 4) Evaluate the relationship between particle size and rheological properties.

2.1

foo

imr

imr

var

eg

cre

tim

a t

are

mi

th

ac

fre

pr

ag

th

in

CHAPTER 2

LITERATURE REVIEW

2.1 Emulsion Systems and Stability

Today's food supply is filled with natural and manufactured emulsions. A food emulsion is defined as: "A homogeneous dispersion of two dissimilar immiscible liquid phases (Stauffer 1996)". Dressings consist of the two immiscible liquids of oil and water. Typical food emulsions display of a wide variety of appearances, textures, taste and shelf life. Examples include milk and eggs, which exist in nature. Manufactured emulsions include ice cream, coffee creams, soups, sauces, mayonnaise, butter, margarine, and salad dressing.

Dressing emulsions are thermodynamically unstable and, given enough time, these emulsions will separate. Emulsion stability ranges from seconds, for a Caesar dressing to years for mayonnaise. Emulsions can be produced which are stable for a reasonable period of time to make the product acceptable: for minutes, hours, days, weeks, months or years. The introduction of emulsifiers to the emulsion formula prior to homogenization allows for kinetic stability to be achieved.

Emulsifiers are surface active molecules, which absorb to the surface of freshly formed droplets during the homogenization process. Emulsifiers form a protective membrane around the oil droplet and stabilize the emulsion against aggregation. Surface active compounds, emulsifier surfactants, position themselves in the oil / water interface where they act to lower surface or interfacial tension.

enc

cha

ma

res

flow

ph

the

ins

(M

Go

arr

(D

flo

co

de

su

dr

Fl

de

Emulsions, due to their instability, will undergo phase separation given enough time. Loss of emulsion stability results in an undesirable product due to changes in the physical and rheological characteristics. Emulsions can be manufactured to hold stability over a specified shelf life. This forced stability results in a product that maintains acceptable appearance, texture, flavor, and flow characteristics and flavor desired and accepted by the consumer.

An emulsion can become unstable due to a number of different types of physical and chemical processes. Physical instability results in an alteration in the spatial distribution or structural organization of molecules. Chemical instability results in an alteration in the chemical structure of molecules (McClements 1999), and is the result of oxidation or hydrolysis (Nawar 1996). Good stability implies that there is no change in the size distribution or the spatial arrangement of droplets over the designated stability time of the emulsion (Dickinson 1994).

Physical or kinetic emulsion instability includes, sedimentation, flocculation, coalescence or Ostwald ripening of lipid droplets within the continuous phase, (Figure 1). Creaming (rise of droplets) is a result of the density difference, i.e., and the droplets having a lower density than the surrounding liquid. Sedimentation is the result of density difference in which the droplets move downward.

Flocculation and coalescence both involve the aggregation of droplets. Flocculation occurs as droplets close to each other form a floc as a result of van der Waal's and ionic forces. Flocculation occurs without the rupture of the



Fig

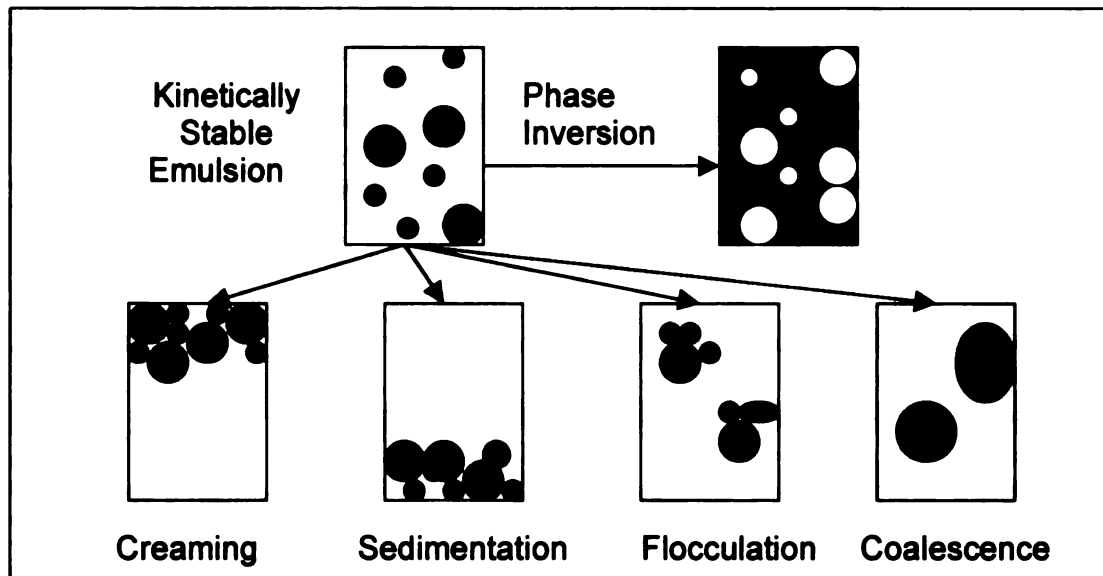


Figure 1 - Emulsion instability (McClements 1999)

pro

Flo

bu

oth

infi

film

dro

exp

ma

(Dr

ten

will

2.2

saf

for

oil,

whi

protective stabilization layer at the oil / water interface (Dickenson 1994). Flocculation results in aggregation, which typically is considered kinetic instability but, can be beneficial to an emulsion due to its effects on flow behavior (Ford and others 1997). The size and structure of the flocs within an emulsion have a large influence on the rate at which the droplets cream.

Coalescence involves the combination of two droplets into one. The thin film of the continuous phase between the two droplets breaks and forms a large droplet. Ostwald ripening is a process whereby large droplets grow at the expense of smaller ones. This physical change occurs due to the solubility of the material in a spherical droplet increasing as the size of the droplet decreases (Dickenson 1994).

Understanding the factors effecting stability including formulation, time, temperature, processing conditions, mechanical agitation and storage conditions will result in better control of emulsion stability and product integrity.

2.2 Ingredients

Ingredients play a key role in the flow behavior, shelf stability, product safety, product identity and consumer acceptance of a product. The main formulation ingredients, which make up a salad dressing emulsion system, are oil, emulsifiers and stabilizers. All of these ingredients play a functional role, which dictates the structural and textural properties of the dressing system.

Understanding the role of each ingredient and how it effects the structure, stability, particle size and rheology of the system is very important as formulas are changing in today's competitive market to met consumer and industry pricing needs while maintaining a texturally similar and consumer acceptable product. Food emulsions are compositionally complex materials that contain a wide variety of different chemical constituents (Table 1).

A wide variety of natural and synthetic or modified ingredients are available as ingredients for the formulation of a dressing system. Each ingredient will provide unique benefits and functional properties to create a desired system. Ingredients need to be selected to create the desired appearance, rheological characteristics, mouthfeel and product stability. This selection is continuous through the product storage, shipping shelf life and consumption. The appropriate selection of ingredients is critical to successful creation the desired finished product (Mc Clements 1999).

2.2.1 Fat / Oil

Fats and oils or lipid compounds play an influential role on the organoleptic and textural characteristics of an emulsion system. To form the desired emulsion, we must understand the functionality of a lipid during processing, manufacturing and storage. The consumer, during use and consumption, ultimately judges this functionality relationship.

Table 1 – Ingredients typically found in food emulsions (McClements 1999)

Macrocomponents	Microcomponents
Water	Emulsifiers
Lipids	Minerals
Proteins	Gums
Carbohydrates	Flavors Colors Preservatives Vitamins

Sala

dres

typ

rang

2).

2.2.2

stab

1994

prod

deve

phys

qua

aera

she

emu

des

ten

inte

Salad dressing oil is a refined, bleached, deodorized and winterized oil. Salad oil has a cloud point of a minimum of 5.5 hours, with typical good quality dressings being 15 hours (Stauffer 1996). Salad dressing formulations are typically at a pH of 2.8–4.0. The typical fat content of dressings and sauces ranges from 0.1% for ketchup up to a maximum of 84% for mayonnaise (Table 2).

2.2.2 Emulsifiers and Stabilizers

Emulsifiers also called surfactants are molecules that promote and/or stabilize an emulsification or dispersion of one liquid in another liquid (Stauffer 1996). They have been used in the food industry for nearly 70 years and have produced solutions to many problems encountered during food product development. Emulsifiers can provide many key functions by controlling the physical nature of the interfaces in the emulsion. This is crucial to produce high quality and stable systems. Structurally they promote emulsion stability, stabilize aerated systems, control aggregation of fat globules, modify texture, promote shelf life, and create desirable rheological characteristics. The role of the emulsifier is to promote the long-term stability of an emulsion system or to control destabilization under shear.

Emulsifiers are surface-active substances. They reduce the surface tension of two normally immiscible liquids (phases) by absorbing at the liquid interface. Control of this interface, through formulation with emulsifiers,

Tab

199

May

Italia

Sala

Blue

Fren

Russ

Thos

Italia

Bart

Keto

Table 2 -Typical fat contents of dressings and sauces (Ford and others 1997)

Sample	Percentage (%)
Mayonnaise	75-84
Italian	50-60
Salad Dressing (Spoonable)	30-60
Blue Cheese	30-40
French	36-40
Russian	30-40
Thousand Island	30-45
Italian (low calorie)	0-3
Barbecue Sauce	1-2
Ketchup	0.1-0.2

is critical in making a high quality food product. Insufficient emulsifier covered droplets result in a higher tendency of the droplets to coalesce (Stang and others 1996). Emulsifiers maybe components of an ingredient, such as egg yolks or additives including monoglycerides and polysaccharides. Since emulsions are inherently unstable, emulsifiers are added during manufacturing. The proper formation and stability of the emulsion is needed for stabilization at the time of formation and for long term product stability and increased shelf life.

Emulsion systems possess minimal stability characteristics, which can be improved by surface active agents such as finely divided solids, lipoproteins, mono- and di-glycerides and polysaccharides. Each works in different ways to maintain the oil in small droplets. Some gums, for example, actually absorb to the oil-water interface forming a film with good droplet coalescence (Stauffer 1996).

Emulsifiers are used throughout the food industry to contribute to both long and short-term stability. Those added to the dressing system are amphiphilic molecules. Surface active compounds (emulsifiers) operate through a hydrophilic head group that is attached to the aqueous phase, and a lipophilic tail attracted to the oil phase (Hasenhuettl and Hartel 1997). These hydrophilic, or water loving, and lipophilic, fat loving groups are made up of hydrocarbons that are branched, straight –chained or cyclic. The lipophilic part of an emulsifier is usually a long chain fatty acid. This causes formation of a threadlike network within the intermolecular structure of the emulsion causing increases in viscosity. These groups play a major role in the type of emulsifier selected for a particular

application. An emulsifier should be chosen based on the food system. It is common to utilize two or three emulsifiers in one system to achieve multiple functions (Hasenhuettl and Hartel 1997).

According to the FDA standards of identity, salad dressings must contain a minimum of 30% vegetable oil and up to 0.75% by weight of emulsifying agents. Food emulsifiers are esters of edible fatty acids with the most commonly used in salad dressings including polysorbates, citric acid esters of monoglycerides and diacyl tartaric acid esters of monoglycerides. These common emulsifiers come from various sources (Table 3).

Polysorbates, polyoxyethylene sorbitan esters, are a product of the reaction of sorbitan esters with ethylene oxide. There are three types of polysorbates permitted by the FDA for use in food systems at limited amounts: polysorbate 60, polysorbate 65, and polysorbate 80. Each emulsifier is permitted for use in specific foods. Polysorbate 60 can also be applied to sugar type confection coatings, shortenings, and edible oils for baking and frying applications. In this study liquid egg yolks and polysorbate 60 were used.

2.2.3 Egg Yolks

Egg yolks have long been recognized as providing functional emulsifying properties in dressing systems. Egg yolks are the most functional compounds of the egg for emulsifying functionality in dressings. Emulsifying activity is a result of the lecithin protein complex, lipoproteins (Ford and others 1997). Emulsifying properties of egg yolk are a result of the lipoprotein fractions, which attach to the

Table 3 – Sources of emulsifiers (Ford and others 1997)

Emulsifier Type	Ingredients
Protein	Buttermilk, sourcream, skim milk, nonfat dry milk, whole milk, sodium caseinate, whey, whole eggs (fresh, salted, frozen), egg whites (fresh, salted, dried), egg yolks (fresh, salted, sugared, dried)
Phospholipids	Egg yolks, whole milk, sour cream
Particle	Mustard Flour
Synthetic	Polysorbate
Chemically modified	Propylene glycol alginate

oil droplets at the salad dressing oil interface. Egg yolks provide a protective barrier on the droplets due to steric stabilization.

Egg yolks contribute to emulsion stability by both steric and particle mechanisms. The particle mechanism is evident from the discovery of protein particles at the interfaces between oil droplets (Ford and others 1997). Egg yolks have an isoelectric point of 5.3. At a neutral pH, egg yolks are negatively charged, but since most salad dressings have a pH level of 2.8 – 4.0 they are positively charged.

Egg yolk, a rich source of phospholipid, significantly contributes to the stability and viscosity of salad dressing emulsions. Carrillo and Kokini, 1988, determined through creep analysis, steady shear and particle size analysis that emulsions are most stable in the presence of 2% egg yolk with 0% salt, or 3% egg yolk with 2% salt.

Carrillo and Kokini (1988) determined that under steady shear measurement both egg yolks and salt increased viscosity and showed shear-thinning behavior. Emulsions containing egg yolk and no salt, a decrease in apparent viscosity was observed at higher shear rates. Higher levels of egg yolk in an emulsion lead to larger aggregates formed. These aggregates disperse under the applied shear rate. As the continuous phase, which was entrapped between aggregates, is released due to shear, the viscosity decreased. Salt enhances the stability of oil / water emulsions by disrupted the egg yolk granules, leaving more active sites exposed at the interface and lowering the interfacial tension.

During the same study, Carillo and Kokini, in 1988 showed that particle size distributions changed very little, as emulsion age increased, 0 – 60 days. This suggests that for emulsions with egg yolks, and egg yolk and salt, the viscosity change is caused by the build up and break down of aggregates. In samples with egg yolk concentrations greater than 2%, they did see an increase in apparent viscosity. These results cannot be explained through coalescence since the droplet size distribution did not change significantly for all egg yolk concentrations. Therefore, rheological properties are controlled by the kinetics of aggregate formation and breakdown.

2.2.4 Proteins

Many formulations of salad dressing contain proteins that act as an emulsifier and stabilizer. Polysaccharides are also added to a majority of emulsion systems. This protein-polysaccharides interaction at the droplet interface influences the stability and rheology of the emulsion aqueous phase.

To be an effective emulsifier the protein being adsorbed, such as egg yolks, must protect the oil droplets against spontaneous flocculation or coalescence. The protein forms a film around the surface of the oil droplets resulting in stable oil / water emulsions. The physicochemical properties of the protein, emulsion characteristics and processing parameters all affect the emulsification stability. The interfacial activity of a protein molecule in an emulsion system involves: 1) the protein molecule diffusing to the interface, 2) the protein penetrating to the interface, 3) molecules rearranging to achieve minimum energy in the system (Ford and others 1997).

salts

be a

emuls

drop

funct

are p

can b

prote

side

oil, to

phas

phas

2.2.5

salin

a fo

grow

stab

textu

gum

Other factors influencing protein functionality include temperature, pH, and salts or the presence of other ions. The viscosity of the external solution or can be altered by adjusting the net charge on the proteins which increase the emulsifying ability of the protein. In an oil in water emulsion, the protein coated droplets are kept apart as a result of charged and steric stabilization. A functional protein must be soluble; therefore proteins near their isoelectric point are poor emulsifiers due to low solubility.

Surfactants, molecules that contain hydrophilic and hydrophobic regions, can be used to decrease interfacial tension and stabilize the emulsion. When proteins are used as surfactants, they must migrate to the interface, orientates side chain groups to polar or nonpolar areas and form a stable film around the oil, to function properly. This formation of a stable film around the oil droplet phase, is the primary key to forming a stable emulsion that exhibits minimal phase separation.

2.2.5 Xanthan Gum

Hydrocolloids, often referred to as gums, are widely used in production of salad dressings. The functional properties provided by hydrated hydrocolloids in a food system include: adhesion, binding, enhancing body, inhibition of crystal growth, emulsification, encapsulation, coating, flocculation, film forming, foam stabilization, gelling, thickening, suspension, stabilization for structure and texture, whipping and fat replacement (Phillips and Williams 1995). Xanthan gum is a commonly utilized hydrocolloid in dressing systems. Its functional

bene

biote

ferme

gum.

been

since

gluco

gluco

units

side

to hy

in co

pseu

At ve

of its

This

solut

(Urla

benefits can be seen in (Table 4).

Xanthan gum was the first of a new generation of polysaccharides biotechnologically produced. First made in the early 1960s, through the fermentation of the bacterium *Xanthomonas campestris*, this biosynthesised gum, was able to functionally compete with natural gums. Xanthan gum has been an approved food additive in the United States since 1969 and in Europe since 1974 (Urlacher and Noble 1997).

The primary structure of xanthan contains a backbone of 1,4-linked β -D-glucose with side chains. These side chains contain mannose and one glucuronic acid and represent 60% of the total molecule. Half of these mannose units carry a pyruvic acid residue. When hydrated in solution the xanthan gum side chains wrap around the backbone thereby protecting the β -1, 4 linkages due to hydrolysis. These side chains allow the polymer to completely hydrate, even in cold water (Urlacher and Noble 1997).

Aqueous solutions of xanthan exhibit a very high viscosity, very strong pseudoplasticity, with no evidence of thixotropy, even at very low concentrations. At very low concentrations, xanthan forms reversible entanglements, as a result of its rod like conformation of xanthan in solution and its high molecular weight. This behavior can be advantageous by decreasing the viscosity of a xanthan solution with increasing shear rate, resulting in easy pouring, pumping or mixing (Urlacher and Noble 1997). Xanthan gum is also a very resilient molecule.

Table

Prop

Yield

Pseud

Stabil

Table 4 - Xanthan Gum Functionality (Phillips and Williams 1995)

Property	Function of benefit
Yield Value	Emulsion stability Prevents runoff Suspension of particles
Pseudoplasticity	Improve pourability Clean mouthfeel
Stability	Uniform viscosity after high shear or temperature variations Stable in low-pH or high-salt dressings

The secondary structure of the molecule, in which the side chains are wrapped around the cellulose backbone, provides degradation resistance of this hydrocolloid in the presence of high temperatures, enzymes, mixing, and changes in pH. Under high temperatures xanthan, in the presence of salt, remains stable and maintains viscosity. Emulsions stabilized with xanthan gum exhibit very high viscosity at rest and are exceptionally stable under the low shear conditions encountered during transport, storage and subsequent use. Xanthan is therefore a very useful ingredient in salad dressings.

Xanthan, being very hydrophilic, requires special care for proper dispersion and hydration when incorporated into a salad dressing system. Time of hydration is a result of the effectiveness of dispersion, or separation of the gum particles at introduction to the solution, size of the gum particles and the other components in the solution. In 1989, Paredes and others showed that a minimum storage or aging period is required to complete xanthan gum solubilization and reach the desired product viscosity.

In preparation of a dressing, the main objective is to stabilize the oil / water emulsion. Good hydration is obtained by mixing the xanthan with other dry ingredients or by dispersion in oil. Xanthan gum dissolves readily at an ambient temperature (20°C) and over a range of pH values and salt concentrations. Hennock and others in 1984, proposed that xanthan gum provides emulsion stability through two mechanisms. First, xanthan gum is absorbed at the oil / water interface, which lowers the surface tension and

reduc

by p

the x

Unde

brou

occu

stab

stron

such

body

in the

thick

of the

2.3 M

/man

ingre

toget

excel

emuls

reduces the droplet size. Second, the remaining xanthan stabilizes the emulsion by physically trapping the emulsion droplets.

In industrial production, a dispersion funnel can be utilized, which draws the xanthan from a funnel through a venturi tube with water under a vacuum. Under a continuous process, the xanthan powder and liquid phases can be brought together in a cyclone chamber where dispersion and hydration can occur.

In dressing manufacturing, the objective of using xanthan is to produce a stabilized oil / water emulsion, for up to one year. Strong pseudoplasticity and strong stabilizing properties of xanthan give dressings which suspend particles, such as spice, herbs and vegetable and give the dressing its overall appearance, body, ease of pouring, cling to salad, and textural attributes. Texture is revealed in the flow of the dressing system. Over application of xanthan can result in a thick appearance, resulting in an unacceptable flow behavior, due to the elasticity of the xanthan gum.

2.3 Manufacturing of Dressings

Formation of a stable emulsion is the ultimate goal during the production /manufacturing of a dressing. The manufacturing of a dressing is where the ingredient functionality, processing equipment and production conditions come together. Oil / water emulsions which contain a high oil content must have excellent stabilizers due to the tendency of the system to be a water / oil emulsion.

Not only the ingredient functionality of the emulsifiers, including the egg yolks is important in maintaining a stable emulsion, but numerous processing conditions need to be avoided to increase stability. Holding emulsion premixes for extended periods of time, over shearing and multiple restarts of the process can break the emulsion. Making a stable pre-emulsion is critical to creating stable unbroken emulsions with minimal process down time.

Formation of emulsions can be accomplished with a variety of unit operations, which range from high-energy short time systems (homogenizer), to long-time low energy processes (mixer). The choice of the homogenizer is dependent on the volume of batch, throughput, formulation and desired droplet size. Various types of homogenizers can be used to achieve acceptable products under a given set of conditions, (Table 5).

The emulsification of a dressing system occurs under turbulent flow conditions as a result of the energy distributed by the droplets density, interfacial tension and mass density. Input of mechanical energy, during the homogenization process, causes an increase in the amount of interface in the emulsion system as a result of energy input. This energy causes subdivision of oil droplets, resulting in a greater amount of interfacial area between two phases. Application of shear forces subdivides droplets in an emulsion, (Figure 2).

During homogenization, new droplet interfaces are formed. Emulsifiers diffuse to the interfaces and lower the interfacial tension as the droplets are formed. The emulsifier acts as a protectant for the newly formed droplets. A colloid mill, agitating vessel, homogenizer and hydroshear are the most popular

Table 5 - Comparison of different types of emulsifying devices (Mc Clements 1999).

	Throughput	Relative energy efficiency	Minimum droplet size	Sample viscosity
High speed blender	Batch	Low	2 μ m	Low to medium
Colloid mill	Continuous	Intermediate	1 μ m	Medium to high
High pressure homogenizer	Continuous	High	0.1 μ m	Low to medium
Ultrasonic probe	Batch	Low	0.1 μ m	Low to medium
Ultrasonic jet homogenizer	Continuous	High	1 μ m	Low to medium
Microfluidization	Continuous	High	<0.1 μ m	Low to medium

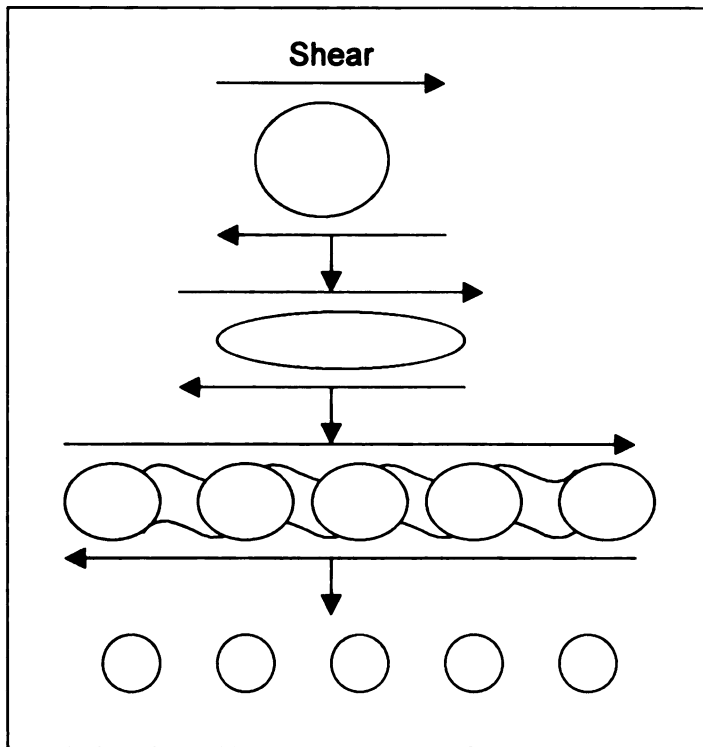


Figure 2- Breakage of cylinders of liquid into small droplets caused by shear (Stauffer 1996).

emulsification devices used in the dressing industry (Ford and others 1997). Colloid mills are commonly used for mayonnaise and spoonable dressings. The hydroshear and high-pressure homogenizers are used for pourable salad dressings. Other homogenizer types are used for sauces and ketchup.

The high-pressure homogenizer, also called the hydroshear, is the most commonly used method to produce fine emulsions in the food industry. This homogenizer pumps the coarse emulsion into a chamber and then forces it through a narrow valve at the end of the chamber, (Figure 3). High-pressure valve homogenizers can be used for a variety of different foods. Processing parameters and conditions influence the interactions among food components within a system. The interactions of proteins, color, flavor and ingredient functionality can all be manipulated and altered with changes applied to the processing parameters.

Ingredient interactions have an effect on all stages of the product life, from processing conditions, heat transfer, flow properties, packaging, and storage through the final handling of the product by the consumer. Understanding the interaction of the ingredients and manufacturing parameters, such as shear rate, can result in comprehending the relationship between the food system and processing conditions. In this study the relationship of three processing variables were compared to the physical properties of particle size, and flow behavior of the fluid system.

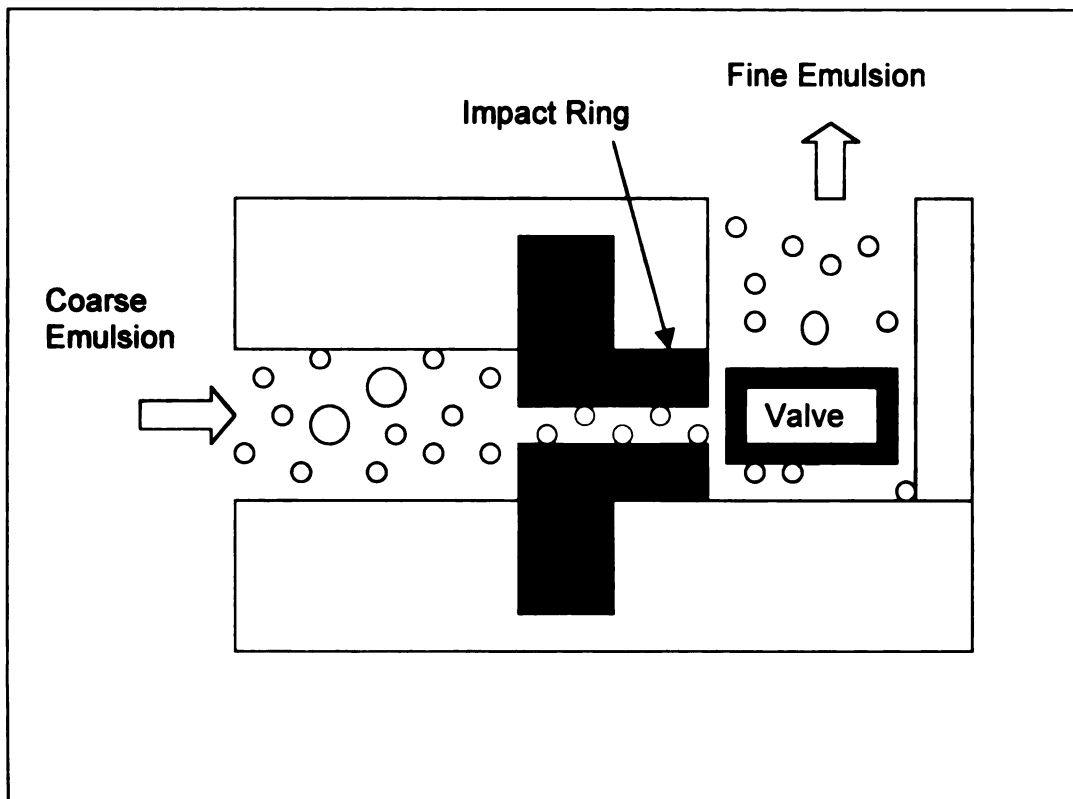


Figure 3 - High pressure valve homogenizer, used to produce emulsions with fine droplet sizes (Mc Clements 1999).

2.4

of th

App

deve

know

des

flow

1982

prop

cont

varia

appr

(For

invol

appli

cons

visco

thick

bottle

of ma

2.4 Rheology of Salad Dressings and Methodology of Fluids

Rheology is the study of the deformation and flow of matter. It is the study of the response to an applied stress or strain, and is the material science of food. Applications of rheological data are numerous: process engineering, product development, quality control, shelf life and sensory evaluation (Steffe 1996). The knowledge of the rheological properties of fluid foods is essential for the proper design and operation of product production equipment, and for understanding the flow and transport of the product during production (Rao and Anantheswaran 1982). Studying the relationship between particle size and the rheological properties of a pourable model system, salad dressing, will provide a quantitative contribution of the control of flow behavior for different formulations and process variables. The flow behavior of salad dressings is very complex and consumer approval of product “flow” is an overall affect of all relevant textural attributes (Ford and others 1997).

In this study, the rheological approach to characterizing salad dressing involves a large deformation issue as a result of the consumer, gravity driven application of pouring. The application of pouring from a bottle gives the consumer a visual assessment of the product thickness (textural attribute) and viscosity of flow (rheological attribute). The consumer perception of the thickness and viscosity of a salad dressing begins from the pouring out of the bottle, the clinging of the dressing to the salad, and the final sensory perception of mouthfeel.

The typical shear rate range of pouring from a bottle is 10^1 to 10^2 (Steffe

199

In 1

and

perd

judg

pou

cont

the s

effec

that

and

visco

syrup

at the

neck

pane

inside

This

result

aggre

1996). Pourability and spreadability are important attributes of salad dressings. In 1983, Kiosseoglou and Sherman conducted a study in which the shear stress and shear rates of two salad dressings were associated with the sensory perception of pourability and spreadability of the dressings, based on human judgement. The sensory panel noted that they based their judgement of pourability on the rate at which the samples flowed down the inside of the container, and spreadability on the area of a plate that was eventually covered by the sample. This suggests that yield stress and shear-thinning characteristics effect panelist judgement. Kiosseoglou and Sherman concluded from their study that shear force and shear stress are dependent on the thickness of the sample and the container degree of tilt by the panelist.

In 1992, Elejalde and Kokini performed a study on the psychophysics of viscosity in which they evaluated the sensory viscosity of the unsteady flow of syrup from a bottle. It was concluded that the "degree of fill" or stream thickness at the neck of the bottle can be represented by the cross sectional area of the neck of the bottle filled by the product stream. They also determined that the panelists based their judgments on the rate at which the sample flowed down the inside of the bottle.

The viscosity of salad dressings is the most widely used characterization. This study focuses on the rheological response of the emulsion system as a result of the particle size and aggregation of the droplets. It has been shown that aggregation of oil droplets increases emulsion viscosity. The interaction of the

droplets determines whether the aggregates form compact or open systems. Open aggregates pull along large amounts of continuous phase, resulting in a higher viscosity than compact systems (Ford and others 1997). Open aggregates occur when there is a strong attractive interaction between the droplets and compact aggregation occurs during weak interaction. The state of aggregation is a result of shear history. As shear rates increase, the aggregates are broken into smaller sizes and the emulsion viscosity decreases.

Fluids and their rheological properties can be classified and characterized under various types of rheological behavior: Newtonian, non-newtonian, power law, pseudoplastic, shear-thinning, shear-thickening, rheopectic, thixotropic, time-dependent, time-independent. A large number of fluid foods are non-Newtonian. The most common characterization of fluid foods is achieved by constructing a flow curve in which the relationship of shear stress and shear rate is established. Rheological behaviors of many fluid food emulsions and suspensions, including the measurement of flow properties, factors influencing the rheological behavior in relation to sensory and viscosity, were characterized by Rao (1977).

A common instrument used for the study of the flow behavior properties of fluids and semi-solid foods is the rotational viscometer. Rotational instruments may be operated in the steady shear or oscillatory mode. Rotational type instruments include concentric cylinder, mixer, parallel plate and cone and plate systems. A concentric cylinder viscometer was used in the current study.

2.4.1 Time/Temperature Dependence

Different temperatures and time parameters are often encountered during processing, storage, distribution, and consumption of liquid foods (Rao 1977). The determination of the time and temperature effects on the apparent viscosity, for Newtonian fluids (1), and power law fluids (2), at a determined shear rate are described by the following model equations:

$$\eta = f(\dot{\gamma}) = \sigma / \dot{\gamma} \quad (1)$$

$$\eta = f(\dot{\gamma}) = K (\dot{\gamma})^n / \dot{\gamma} = K (\dot{\gamma})^{n-1} \quad (2)$$

The power law fluid model, also known as the Ostwald-de Waele model, is the simplest and most popular model applied to non-Newtonian fluid flow. The power law model has two parameters, n and K , which are the flow behavior index and consistency coefficient, respectively. The flow behavior index, n , provides a convenient way to identify the shear-thinning ($n < 1$) or shear thickening ($n > 1$) behavior.

Thixotropic behavior (Figure 4) is seen when a system experiences a reversible decrease in shear stress or apparent viscosity at a constant shear rate. These fluids are thought to consist of asymmetrical molecules or particles, which form a network or aggregated structure at rest. When a continuous shear rate is applied to the system, weak bonds are broken, which results in the fluid exhibiting time-dependent thinning characteristics. A rheopectic fluid, the opposite of thixotropic, is a material, which exhibits a reversible increase in shear

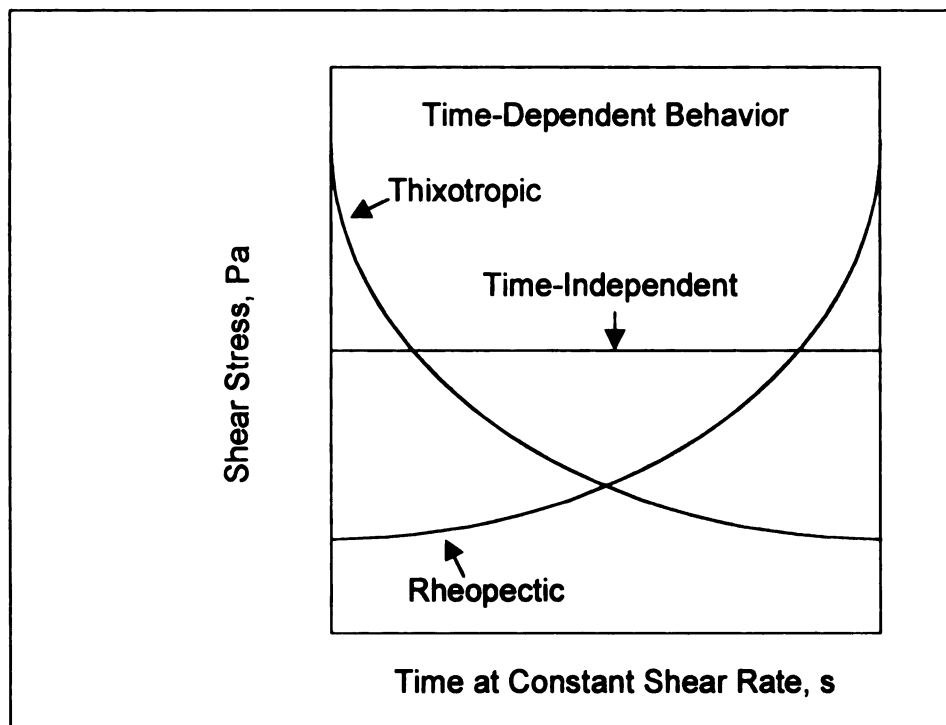


Figure 4 - Time – dependent behavior of fluids (Steffe 1996).

stress or apparent viscosity when sheared at a constant rate.

The viscoelasticity and/or structural changes of liquid food depend on temperature, composition, the application of an applied shear rate or shear stress, and the duration of shear (Rao 1977). Ideal time-dependent behavior of a material is considered to be inelastic with a viscosity function, which depends on time (Steffe 1996). It is important to study the rheological properties as a function of temperature and time due to varying processing conditions, duration of shear and temperatures faced during production of the material, and use by the consumer during shaking and mixing the product.

Fluids may exhibit time-dependent flow in which there are decreasing or increasing effects on the shear stress or apparent viscosity with time during a constant shear rate and temperature. Salad dressing, a non-Newtonian fluid, would have time-dependent behavior as a result of the weak interaction among the components in the emulsion system resulting in easy disruption during the shaking of the product prior to use (Tung and Paulson 1995).

In characterizing time-independent flow behavior, the Herschel-Buckley model can be used to describe the general relationship:

$$\sigma = K (\dot{\gamma})^n + \sigma_0 \quad (3)$$

This model is appropriate for many fluid foods and can be utilized for Newtonian, power law and Bingham plastic fluids, figure 5 and 6 (Steffe 1996).

Figure

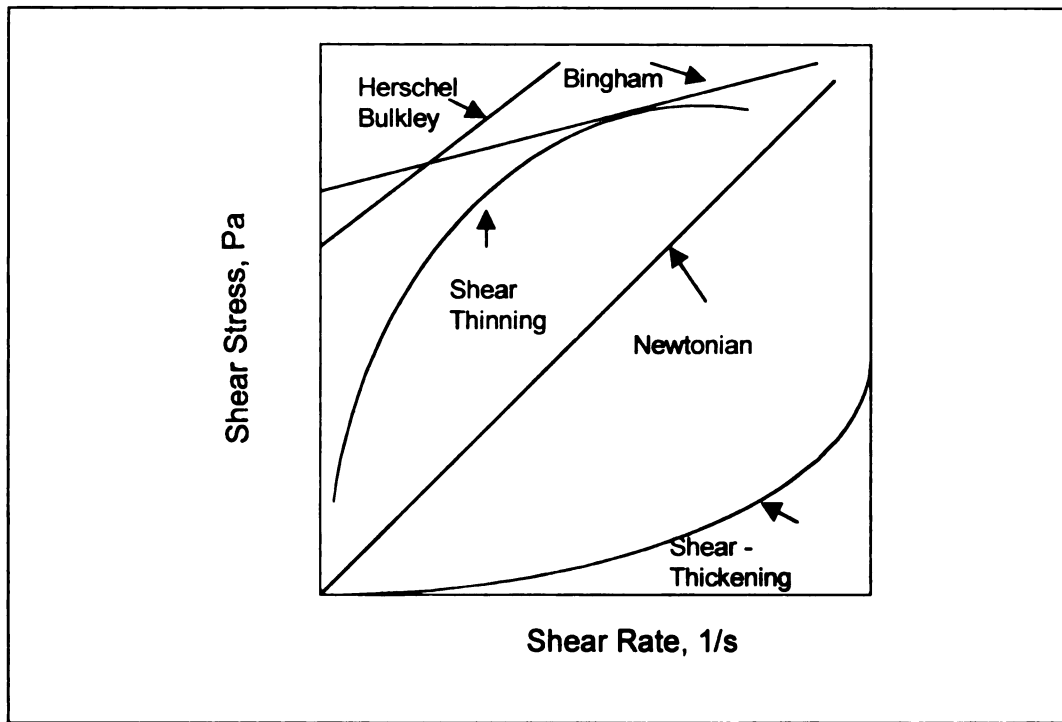


Figure 5 Typical curves for time-independent behavior fluids (Steffe 1996)

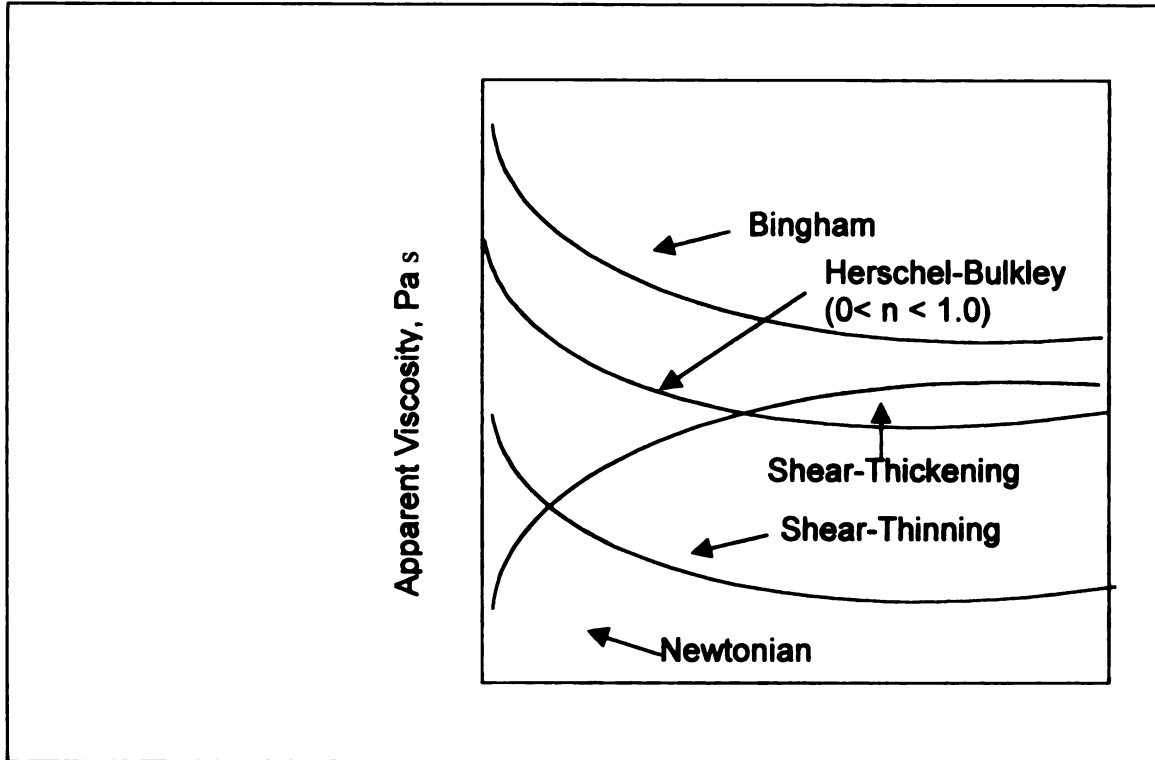


Figure 6 – Apparent viscosity of time-independent fluids (Steffe 1996)

Fluids

(Steff)

proper

break

0.016

rate

final

determ

be a

exhib

shear

allow

shear

chara

system

deca

shea

the

appa

Bog

Fluids can be studied by subjecting them to continuous shear at a constant rate (Steffe 1996).

In 1983, Figoni and Shoemaker studied the time-dependent flow properties of commercial mayonnaise to investigate the stress decay or structural breakdown of the mayonnaise at shear rates of 0.530, 0.169, 0.052 and 0.0169^{sec}. They found that the initial and final stress values increased with shear rate, while the initial stress values were not significantly different. Values for the final stress did discriminate between the different shear rates, but were not determined to not be significantly different. The insignificance was determined to be a result of the thixotropic nature of the mayonnaise, with the lipid droplets exhibiting pseudoplastic behavior due to the flocculation-deflocculation, at high shear rates, of the lipid droplets. Overall they found that steady shear studies allow for reproducible calculations of rates of structural breakdown as well as shear stress-shear rate data, to study time-dependency.

Tiu and Boger (1974) and Figoni and Shoemaker (1983) performed a characterization of the time-dependent flow properties of the non-Newtonian fluid system mayonnaise. Using a cone and plate viscometer to measure the stress decay, Figoni and Shoemaker measured the time dependent flow properties at shear rates of 0.530, 0.169, 0.052 and 0.0169 s⁻¹. The shear stress increased as the shear rate increased, indicating pseudoplastic flow. This decrease in apparent viscosity as the shear rate increases was also reported by Tiu and Boger (1974), Elliott and Ganz (1977) and Figoni and Shoemaker (1983). This

flow d

and d

flow d

flow

deflod

shifte

Shoe

large

proc

2.4.

sub

and

rate

vis

Ro

cyl

de

sh

flow behavior of mayonnaise can be explained by the following:

“Since the oil droplets in mayonnaise are stabilized by egg yolk (Chang and others 1972), and droplet deformation is unimportant when considering the flow behavior of a stabilized emulsion (Van den Temple 1963), the pseudoplastic flow behavior of mayonnaise probably is due principally to the flocculation-deflocculation of the oil droplet. As the shear rate increases, the reaction is shifted towards deflocculation, thus lowering the apparent viscosity. (Figoni and Shoemaker 1983).” Figoni and Shoemaker also concluded the breakdown of larger aggregates continually generates smaller aggregates during the shearing process.

2.4.2 Steady State Shear Measurements

The measurement of a fluid under steady state conditions classifies a substance according to type of fluid. A specific shear rate can then be selected and once conditions in the rheometer have stabilized, the viscosity at that shear rate is determined. The shear rate can also be examined in a sweep test in which viscosity data is collected over a wide shear rate range resulting in a flow curve. Rotational viscometers including cone and plate, parallel plate and concentric cylinder, can all operate under steady shear conditions.

The apparent viscosity - shear rate relationship of shear-thinning foods is described by Rao, 1999 as: “At sufficiently high polymer concentrations, most shear-thinning biopolymer (also called a gum or hydrocolloid) dispersions, exhibit

a sin

desc

prop

by (2

with

and

result

to sh

assur

const

veloc

rate a

is im

use.

and

stead

degre

a se

dress

tempe

a similar three stage viscoelastic response over a wide shear rate range." Rao describes these three stages as (1) at low shear rates, they show Newtonian properties with a constant zero-shear viscosity (η_0) over a shear range, followed by (2) a shear-thinning range where solution viscosity decreases in accordance with the power law relationship. At (3) high shear rates the fluid shows a limiting and constant infinite shear viscosity (η_∞). These regions are thought to be a result of the rearrangement in the conformation of the molecules in the fluid, due to shearing (Rao 1999).

The relationship used to describe a concentric cylinder viscometer assumes: flow is laminar and steady, end effects are negligible, temperature is constant, there is no slip at the walls of the instrument and radial and axial velocity components are zero (Steffe 1996). Understanding the steady shear rate and its relationship during the typical application of pouring a salad dressing is important to understand the flow behavior exhibited during actual consumer use.

Rheological characterization of salad dressing began in the 1970s. Elliott and Ganz in 1977 performed a preliminary rheological characterization, under steady shear measurements to determine the flow properties and estimate the degree of structure breakdown. Paredes and others in 1988 and 1989 performed a series of rheological characterization studies of bottled and dry salad dressings. They evaluated the steady shear, thixotropic behavior and effect of temperature in their first study (1988) and the effect of storage in the second

stud

rang

bottl

prod

are p

The

Hahr

appa

equa

flow

natu

18.3

dres

incre

study (1989).

Paredes and others (1988) collected shear stress data over a shear rate range of 30 to 1000 s⁻¹. The power law equation described the data and that bottled dressings showed a greater decrease in viscosity with an increase in product temperature than dry dressing mix. They also found that the dressings are pseudoplastic fluids, with a flow behavior index (n) between 0.43 to 0.93. The thixotropic behavior, the rate of structural breakdown, was described by the Hahn (4) and the Weltman (5) equations:

$$\sigma = A_1 - B_1 \log t \quad (4)$$

$$\text{Log } (\sigma - \sigma_c) = A_2 - B_2 t \quad (5)$$

The rate of structural breakdown was faster at 2°C than at 10°C. The apparent viscosity was also described by Paredes and others, with the Arrhenius equation (6):

$$\eta_a = B \exp (E_a / Rt) \quad (6)$$

Paredes and others (1989) showed that the consistency index (K) and the flow behavior of the power law model were able to describe the viscoelastic nature of salad dressing as a function of storage time and temperatures of 1.7, 18.3, 29.4 and 37.8°C. They determined that the magnitude of K of a model dressing, which decreased after 24 hour storage at 2.8°C, showed a great increase during the first seven days after production at the designated

tempe

of the

were

Their

least

solub

2.4.3

viscoe

ampli

small

foods

gap b

can be

the ch

a shea

steady

of stea

and s

temperatures of 18.3, 29.4 and 37.8°C. They also saw that after seven days all of the viscosities increased except the one stored at 37.8°C. Similar results were seen in samples pulled out of storage conditions 24 hours prior to testing. Their study showed that a minimal storage temperature, 18.3°C to 29.4°C for at least 24 hours maybe required, prior to a cold test at 2.8°C, for complete solubilization of xanthan gum and to obtain the desired viscosity for the dressing.

2.4.3 Unsteady State Shear Measurements

Unsteady state shear measurements or dynamic evaluation of viscoelasticity, can be defined in either transient or oscillatory flow. Small amplitude oscillatory shear, where a sample is exposed to harmonically varying small amplitude deformations, is used to determine viscoelastic properties of foods. Uniform shear can be achieved during measurements through a small gap being achieved in a cone and plate geometry. Many viscoelastic properties can be determined (Rao 1999).

Transient shear testing involves numerous measurements under which the characteristics of a viscoelastic food under a sudden shear rate. As a result a shear stress is exhibited which displays an overshoot before reaching a final steady state. Transient shear flow experiments include: start-up flow, cessation of steady shear flow, step strain, creep and recoil (Steffe 1996).

Bistany and Kokini (1982) performed a comparison study of steady shear and small amplitude dynamic viscoelastic properties of fluid foods, including

mayo

the s

law b

utiliz

angle

stress

know

dress

data

dress

typic

varie

cree

writ

the

Pa

m

mayonnaise. The dynamic viscosity (η^*) was determined to be much larger than the steady shear viscosities (η). Both viscosities could be described by power law behavior. Their study focused on a shear rate range of $0.1 - 100 \text{ sec}^{-1}$, utilizing a cone and plate geometry with a plate radius of 1.25cm and a cone angle of 0.04 radians for their dynamic measurements.

Another type of transient shear flow experiment, where an instantaneous stress is applied to a sample and the change in strain is observed over time is known as creep compliance. Paredes and others in 1989 characterized salad dressings, bottled varieties and dry mixes, at $2.8^\circ\text{C} \pm 0.3^\circ\text{C}$. Creep compliance data for the bottled dressings were collected at $55.2 \text{ dyne cm}^{-2}$ and dry salad dressings at $22.8 \text{ dyne cm}^{-2}$. These shear stress rates were chosen to develop typical creep compliance-time response curves for each type / brand of dressing variety: bottled creamy, reduced calorie and dry mixes. They determined that the creep compliance model response can be described using the Burgers model, written in terms for shear creep compliance (7) (Steffe 1996):

$$J = f(t) = J_o + J_1 \left[1 - \exp \left[\frac{-t}{\lambda_{ret}} \right] \right] + \frac{t}{\mu_o} \quad (7)$$

Paredes, 1989, also compared creep compliance analysis in relation to the effects of storage. Xanthan gum was utilized in the dressing formulations. Paredes determined that the solubilization of the xanthan gum is important in maintaining the emulsion stability during storage. The greatest changes were

seen in the creep compliance time plots during the first week of storage.

Munoz and Sherman, 1990, performed controlled stress rheometer measurements on commercial salad dressings. Oscillatory tests were conducted at a frequency of 1 Hz with an amplitude of applied stress of 14.93, for full fat mayonnaise or 8.96 Pa, for reduced calorie mayonnaise and salad cream, over a frequency sweep of 600s, at 25°C. Upon evaluation of the G' values, the full fat and reduced caloric mayonnaise produced at the same manufacturer had significantly similar G' values. This may be due to the formula of the reduced caloric dressing which contains modified starches and gums and the substitution of egg whites for egg yolks. In comparing the G' values of two dressings which both contain xanthan gum, the dressing with which contained sugar and lemon juice, instead of lactic acid, had a lower G' value. It is thought that the sugar molecules may effect the proteins which interact and form a network formation among the oil droplets.

Overall, Munoz and Sherman, 1990, found in high fat mayonnaise that the droplets are tightly packed together, forming a three dimensional network between the egg protein molecules around the lipid droplets. This is responsible for the viscoelastic properties of the high fat mayonnaise. These highly flocculated structures of lipid droplets are not formed in the salad creams measured, due to the lower oil content, resulting in different flow behavior.

Peressini and others in 1998, performed an extensive rheological characterization of traditional and light mayonnaise. It was shown that under the

measurement of the oscillatory and creep recovery tests, the storage modulus (G'), compliance and yield stress increased as the fat level increased in the mayonnaise. These measurements were performed at 25°C, with each sample resting for 5 minutes after being loaded to allow sample-induced stress on sample to relax and temperature to equilibrate.

As can be seen most of the rheological testing on dressing and mayonnaise systems involves dynamic rheological testing methods. Measurement and evaluation of the flow behavior as a consumer would use it, needs to be further evaluated. Pouring in relationship to a variety of formulation and processing parameters, as would be seen by a consumer, can be evaluated through rheological steady state rotational viscometry testing.

2.4.4 Yield Stress

Yield stress (σ_0) can be defined as the minimum shear stress required to initiate flow. The yield stress of a fluid is important in the engineering of systems, quality control measurement for reproducibility of product, and comparison of products. Yield stress is also important for dispersion food systems such as emulsions, in order to keep the particles in suspension.

Fluids which exhibit yield stress can be described as structurally having a network of bonds that are breaking and deforming as a result of the applied stress (Rao and Steffe 1997). Yield stress can be characterized from this structural breakdown as two types. An undisturbed sample is known as static

and in a completely broken down sample is known as dynamic yield stress, figure 7 (Steffe 1996).

Using a rotational viscometer and the Casson equation, Paredes and others, 1989 described the yield stress flow properties of bottled and dry mix and prepared salad dressings. The yield stress, at 2.8°C, of the model system increased after seven days of storage. The yield stress of salad dressing at 18.3°C, 29.4°C and 37.8°C remained stable over the same period of time. All of the salad dressings stored at 21°C exhibited similar yield stresses, showing an increase for seven days and then remaining relatively stable. Results indicated that salad dressings need to be held for at least seven days prior to quality control testing and sensory evaluation.

Peressini and others in 1998 examined the yield stress of mayonnaise was measured utilizing a plate-plate geometry, diameter 40mm and gap of 1.5mm. The yield stress was shown to increase with increasing fat content in mayonnaise. Mayonnaise with 76% fat, exhibited a yield stress of 40.6 Pa, while the samples with 68.6% fat exhibited a yield stress of 25.4% and mayonnaise at 63.4% fat exhibited a yield stress of 19.4 Pa. The higher yield stress values in the high fat mayonnaise is a result of the higher level of egg lipoproteins which create a stable network at the water / oil interface, resulting in increased equilibrium, over the lower fat mayonnaise samples.

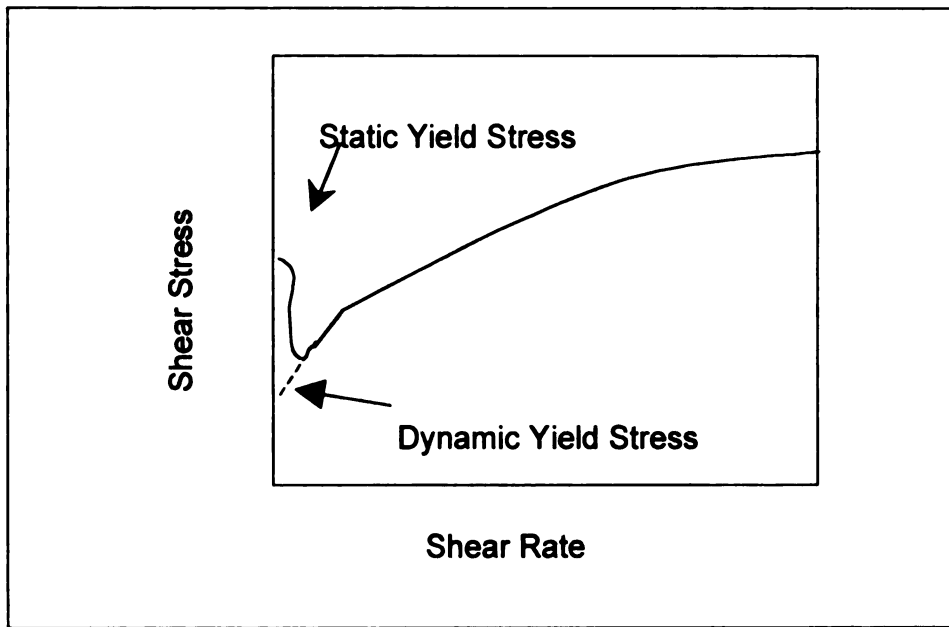


Figure 7 Static and dynamic yield stress (Steffe 1996).

No evidence of the utilization of the vane method to determine the yield stress of salad dressings can be found. This controlled-shear-rate and controlled-shear-stress mode methods measure the yield stress of a fluid system through the immersion of a vane directly into a product. This method can be a great advantage due to possible immersion of the vane directly into a packaged product and reduction of disruption of the sample during loading for static measurements (Steffe 1996). This method is advantageous for allowing for quality control work to be performed directly in the packaged food, resulting in measurements which result in yield stress measurements as would be seen by the consumer.

2.5 Particle Size Analysis

A “particle” can be described as any object having definite physical boundaries in all directions, without any limit with respect to size. The concept that all matter is made up of particles is fundamental to science (Cadle, 1965). It has also been shown that smaller particles may not be uniformly distributed through out a material. The size of particles found in the atmosphere, or in other gases range in diameter from about 0.001 to 100 μm . These particles can possess different shapes chemical compositions refractive indexes electric properties and densities. Fine particles are defined as particles in which the diameters are less than 1.0 μm .

Particle shape and size in emulsions are an important characteristic because, they influence many other characteristics and behaviors of the

emulsion. The flow properties as a result of the particle size and shape can play a major role in the pouring and pumping of food systems through pipes, during manufacturing, and during customer application of a dressing.

Most colloidal suspensions exhibit a wide range of particle sizes. A complete knowledge, in addition to the maximum, minimum and average size may be needed to completely understanding the material being analyzed. Particle shapes can vary greatly unless special processes, to form uniform shapes throughout the product are applied during processing. Shapes can include oblate and prolate spheroid or disc shapes, which can be, either an oblate spheroid, cylinder or a flat plane.

Many foods can be classified as colloidal systems, containing particles or macromolecules (polymers) of various kinds (Walstra, 1992). Aggregation of these particles can be defined as the staying close together for a much longer time than would be the case in the absence of attractive forces between them. The particle size of the droplets within an emulsion system generally exceeds 0.1μ (Coia and Stauffer, 1987).

According to colloidal science theory, aggregation occurring within the emulsion / colloidal system depends upon the interaction forces between the particles. Food systems contradict the theories of interactions of classical emulsion / colloidal systems, which involve the interaction between two identical homogeneous spheres. But, as we know food systems are very complex systems and contain many types of particles, varying in size, shape and

homogeneity. Hence, it is essential to know the food system, the particles it contains, size, shape and how they aggregate.

During flocculation part of the continuous phase becomes immobilized due to the formation of aggregates, therefore increasing viscosity. Upon aging of the product, globule aggregation continues due to flocculation of the remaining globules as well as the joining of small aggregates into larger ones. A high yield stress can be seen in the emulsion if the continuous phase becomes trapped within the linking up of aggregates which form a loose continuous network (Sherman, 1967).

According to studies performed by Sherman, 1964, "fine" emulsions are known to give higher viscosities than "coarse" emulsions of the same formulation. Also, emulsions with a broad distribution of globule sizes will have a lower viscosity than comparable emulsions with a narrow distribution of particle size.

2.5.1 Measurement

Particle size analysis measurement has begun to evolve as the modern developments in computers, electronics, lasers and chromatography have all continued to improve the measurement of small size emulsion droplets. According to Orr, 1988, the phenomena traditionally used to characterize submicroscopic entities has begun to reveal new size information. These phenomena include, hydrodynamics, light scattering and diffraction and Browning diffusion.

The methodologies used to determine emulsion systems particle size may involve various techniques. The hydrodynamic chromatography method involves the separation of the emulsion based on size through a porous packed column, thus related the molecular weight and micelle size. Photon correlation spectroscopy involves the intensity of light scattered from dispersions of particles and macromolecules. Particles can also be measured through the analysis of the intensity pattern created when light is diffracted from a beam, which passes through the emulsion. This type of method is non-destructive and very rapid.

Two types of measurement that are non-destructive and rapid include Magnetic resonance imaging and Spectroscopy. Magnetic resonance imaging involves the measurement in the variations in signal intensity in relation to the relaxation times of the oil and aqueous phases and the proportionality of the projected frequencies to the spatial distribution of the sample constituents. In spectroscopy, the percentage of oil is determined from standard curves which relate the integrals of oil for the total spectra are correlated to the known amounts of oil in standard preparations (Heil, 1990).

Optical microscopy is also a traditional type methodology, which can be utilized to directly measure individual particle sizes. This type of methodology is viewed as being reliable, but results in difficulty in the reproducibility and accuracy for the measurement of emulsion systems. Other methodologies include the measuring of particle size and count as they flow past a sensor and a sedimentation technique, based on gravitational separation of phases and

fractional creaming based on the relationship between the creaming agent and creamed particle size.

The mechanism of light scattering measurement occurs as light strikes particles causing (diffraction) scattering to occur. This principle is based on the Fraunhofer diffraction and Mie scattering theories (Horiba, 1998). The laser light beam irradiates the particles and then measures the pattern of light scattering by the particles.

Munoz and Sherman, 1990, performed droplet size distribution analysis of mayonnaise using a Coulter-counter. For the full fat mayonnaise the mean size (μm) ranged between 2.53 – 3.81 μm , with a standard deviation of 1.43 – 1.78. Reduced calorie mayonnaise had a mean diameter of 1.71 – 1.82 μm and a standard deviation of 1.35 – 1.38.

Early measurement of mayonnaise with electron microscopy began with the work of Chang and others in 1972. The electron microscope observed that the oil droplet in all of the mayonnaise samples to possess a continuous layer. This layer is thought to contain coalesced low-density egg yolk lipoproteins and microparticles of egg yolk granules. Heil and others, 1990 utilized magnetic resonance imaging and spectroscopy to determine the percent of oil in a French style dressing. Both of these methodologies allow for rapid measurement and nondestructive analysis.

In an emulsion system, the size and shape of the lipid droplets and the

connecting networks between them have an impact on the textural properties, as well as appearance of the emulsion. Langton and others, 1999, studied the relationship of the microstructure of an undiluted mayonnaise sample, in relationship to its textural properties. The mayonnaise variables included variable emulsification cylinder speed, speed of viscorotor, exit temperatures and egg yolk content. The mayonnaise microscopy was studied through the use of confocal laser scanning microscopy and transmission electron microscopy. It was concluded that the oil droplets form a network which has an impact on texture. They also detected aggregates of egg yolk particles, which ranged in diameter size of 1.5 – 7 μm . The emulsification cylinder speed and the exit temperature were shown to have a strong effect on the size of the egg yolk particles.

2.5.2 Control of Particle Size

The use of macromolecules or polymers within a continuous phase may result in the absorption of the polymers onto the particles. This would result in a change in viscosity or the colloidal system and manipulating the formation of aggregates. Absorption of polymers may either prevent aggregation or cause it. This depends on the solubility of the polymer. Xanthan gum is a prime example of a polymer used in salad dressings.

Carrillo and Kokini, 1988, conducted a study measuring the effect of egg yolk and egg yolk + salt on the rheological properties and particle size distribution of model oil in water salad dressing emulsions. They found that the egg yolk

significantly contributed to the stability and viscosity of the model system. Salt also contributed to the stabilization action of the egg yolk. Creep and steady shear analysis, along with particle size determinations showed that the emulsions were most stable in the presence of 2% egg yolk of 3% egg yolk. These formulas were pre-stabilized with xanthan gum and propylene glycol alginate. The steady shear measurements showed that both the egg yolk and salt increased viscosity radically. Also, particle size distribution changed with both the addition of egg yolk and salt to the model system.

The effects of formulation, including pH and NaCl have been shown to affect the mean droplet size of a mayonnaise system (Kiosseoglou and Sherman 1983). Droplet size was determined with a Joyce-Loebel disc photosedimentometer. Kiosseoglou and Sherman determined that the oil drops flocculated and form a three dimensional network structure that exhibited viscoelastic behavior, which is effected by pH, NaCl and temperature. The mean particle size increased as the sample aged from 4 – 150 hours. As the pH degreased the mean particle size increased: at 24 hours, pH 6.2, mean particle diameter size 0.378 μ m, while at pH 3.5, mean particle diameter size 0.875 μ m.

2.5.3 Size and Composition

There are a limited number of publications dealing with the microstructure of dressings. In 1972, Chang used electron microscopy and determined the stability of mayonnaise was attributed to the film membrane surrounding the droplets. It was concluded that the film consisted of low-density lipoprotein 9

(LDL) micelles from the plasma and granules of egg yolk. It was then postulated that the stability of the droplets and plasticity of the droplets could be attributed to the LDL and this barrier should obstruct coalescence. Heil, in 1990, used magnetic resonance imaging and spectroscopy to determine the percentage of edible oils in French style salad dressings.

Carrillo and Kokini, in 1988, measured and studied the particle size distribution of a model oil-in-water emulsion dressing in relation to the effects of egg yolk and egg yolk and salt on the rheological properties. Particle size was measured using a Modified Coulter Counter Particle Size Analyzer with a 128 μm orifice. A shift in particle size distribution toward small values was noted upon addition of both egg yolk and salt, and a shift to larger values was found when egg yolk and salt were not present.

CHAPTER 3

MATERIALS AND METHODS

3.1. Formulas / Samples

Salad dressings are an emulsion-based system usually containing oil, buttermilk, water, sugar, egg yolks, salt, vinegar, sorbic acid, phosphoric acid, gum and emulsifiers. This research involves the evaluation of nine different model-dressing formulas. These formulas are comprised of 59% oil which gives the emulsion flavor and texture. Formulations vary in percentage of xanthan gum and egg yolks used for the production of each individual batch. Xanthan is added to provide emulsion stability, prevent runoff, suspend particles, improve pourability, mouthfeel, and create uniform viscosity under shear and temperature variations and stability with variable pH and salt contents. Egg yolks also provide emulsifying functionality, due to the lecithin protein complex (lipoproteins). Use of two emulsifiers, egg yolk and polysorbate 60, is common to achieve multiple functions in the emulsion system (Hasenhuettl and Hartel 1997).

A wide range of textures have been developed with the nine formulas tested. The amount of sugar and oil varied slightly to make up for the reduction or addition of the xanthan gum and egg yolks. The percentage by weight of each ingredient used in the nine formulas is given in Table 6. Four major competitive brands of basic Ranch Dressing, (Kraft Ranch®, Hellmann's Ranch®, Wishbone Ranch® and Hidden Valley Ranch®), purchased from Meijer™ grocery store, where also tested for comparison. Total weight of each batch was 13.67 kg (30.12 lbm).

Table 6 – Model salad dressing samples formulation by percentage of total weight

Ingredients	Formula #1	Formula #2	Formula #3	Formula #4	Formula #5	Formula #6	Formula #7	Formula #8	Formula #9
Water	15.99%	15.99%	15.99%	15.99%	15.99%	15.99%	15.99%	15.99%	15.99%
Salt	1.99%	1.99%	1.99%	1.99%	1.99%	1.99%	1.99%	1.99%	1.99%
Sugar	6.30 %	4.80 %	3.3 %	6.15%	4.65%	3.15%	6.00%	4.50%	3.00%
Xanthan Gum	0.15%	0.15%	0.15%	0.30%	0.30%	0.30%	0.45%	0.45%	0.45%
Buttermilk	14.99%	14.99%	14.99%	14.99%	14.99%	14.99%	14.99%	14.99%	14.99%
Sorbic Acid	0.20%	0.20%	0.20%	0.20%	0.20%	0.20%	0.20%	0.20%	0.20%
Egg Yolks	0%	1.50%	3.00%	0%	1.50%	3.00%	0%	1.50%	3.00%
Polysorbate 60	0.20%	0.20%	0.20%	0.20%	0.20%	0.20%	0.20%	0.20%	0.20%
Soybean Oil	58.96%	58.96%	58.96%	58.96%	58.96%	58.96%	58.96%	58.96%	58.96%
Phosphoric Acid, 80%	0.12%	0.12%	0.12%	0.12%	0.12%	0.12%	0.12%	0.12%	0.12%
Vinegar, 120 gr	1.10%	1.10%	1.10%	1.10%	1.10%	1.10%	1.10%	1.10%	1.10%
Total Batch Weight, kg	13.67	13.67	13.67	13.67	13.67	13.67	13.67	13.67	13.67

3.2 Processing

Experimental dressings were prepared at a pilot plant scale in a batch system. Three processing variables, (low, medium and high shear) were applied to one-third of each 13.67kg batch resulting in twenty-seven different manufacturing variables. Production of the formulas began with the initial weighing out of all of materials needed for each batch. Next, the phosphoric acid was mixed in with the buttermilk using a Hobart mixer while the buttermilk was being heat to 175°F with a steam jacketed mixing bowl. Buttermilk heating keeps the protein from precipitating due to the alteration of the pH below the isoelectric point (4.3 pH).

A large portion of the water is then placed into a regular Hobart mixer. The dry ingredients sugar and salt, are added to the water. Flavor and spices would be added at this time during normal production; however, this research does not utilize spices or flavorings. Sorbic acid is then added to the mixture to maintain microbiological stability of the final product. Potassium sorbate and sodium benzoate are also utilized for microbiological stability in some commercial formulas. The solution is mixed for three minutes allowing the dry ingredients to completely hydrated. The buttermilk and phosphoric acid mixture is then added under continuous agitation.

The xanthan gum was mixed with a small portion of the soybean oil to allow the xanthan gum to completely hydrate. The egg yolks, polysorbate 60 and xanthan gum / oil mixture are then added forming a structure around the oil

droplets which stabilizes the emulsion. After the emulsifiers are added and mixed, the soybean oil is added slowly. One Hobart® A200 Mixer was used to form the emulsion model system, at Kraft Foods™ pilot plant, Glenview, Illinois. The mixer was set up with a 20 quart stainless steel bowl and wire loop whip, and ran at 113 RPMs to form the emulsion (Hobart 2000). The agitation speed at which the oil is incorporated into the emulsion is very important because excessive speeds will break the emulsion.

After the ingredients are blended together, the emulsion system is placed into a small vat and pumped through a positive displacement pump, and a homogenization hydroshear (designed at Kraft) at 140, 180 and 220 psi (pounds per square inch) (Figure 8). Hydroshear is an in-line pipe homogenization shear system through which the product is pumped (Krishnamurthy and others 1998). The hydroshear has a knife edge homogenization element located within a closely surrounded impact ring. The product enters the hydroshear through an orifice located in the valve and seat. Product then proceeds through the in-line pipe and orifices and is impacted on the edge of the valve and seat. The collision with the in-line stream impact ring causes a change in the direction of flow. The product is under pressure as it is forced through this homogenization unit and is released at atmospheric pressure (Figure 9). One third of each batch was processed at each pressure variable. Each sample was then packaged into glass quart jars and labeled with a batch number, production date and pressure variable.

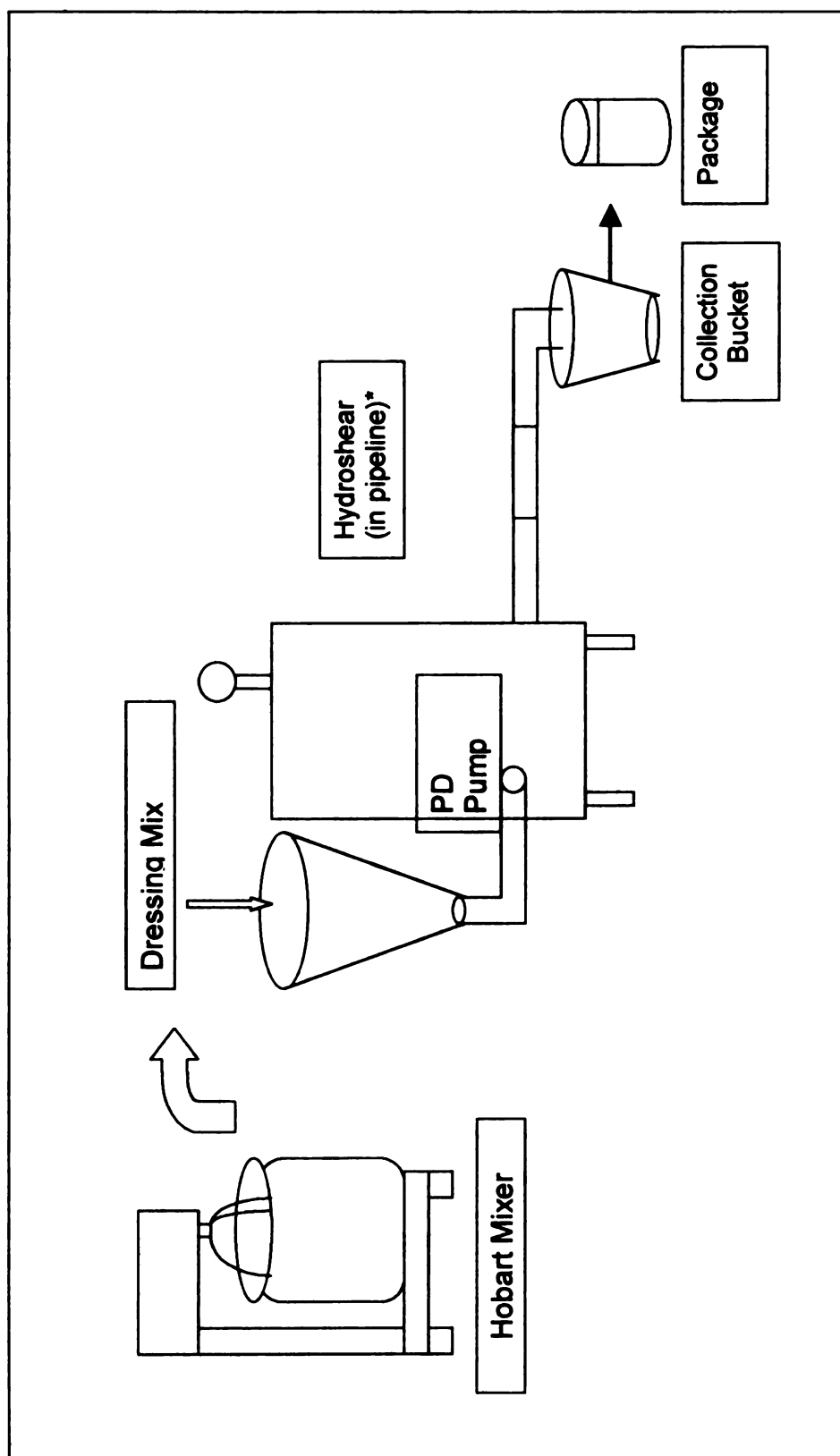


Figure 8 – Overview of pilot plant salad dressing process used to manufacture samples.

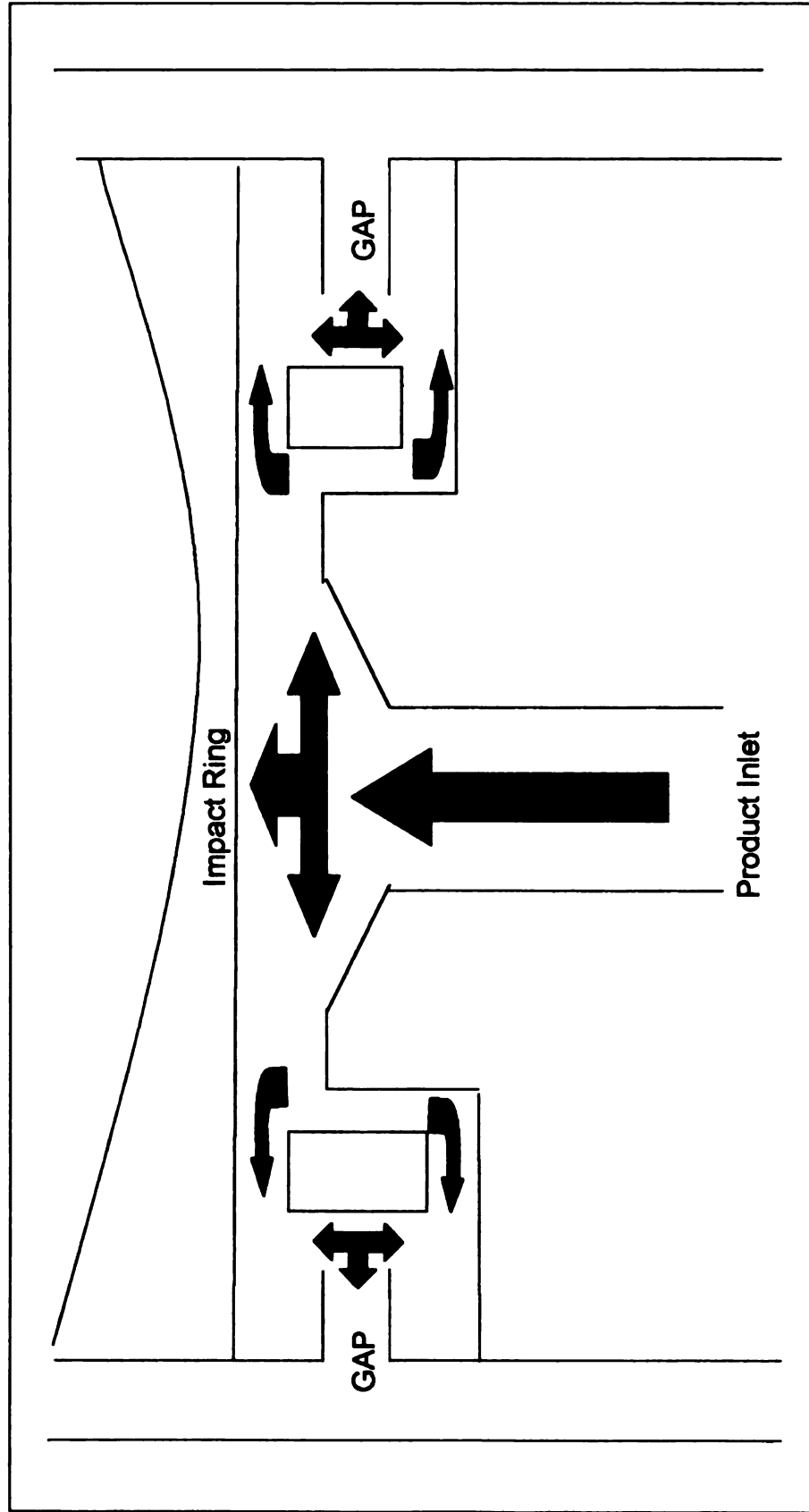


Figure 9 – Cross section of in-line emulsification system hydroshear unit utilized in pilot plant salad dressing system (Krishnamurthy and others 1998).

After packaging, the viscosity, pH, titratable acidity and salt levels were measured for the nine formulations. A standard pH meter was utilized. Also a Brookfield Viscometer was used to determine the initial viscosity. This preliminary data was used to identify variances in initial processing formulation variables.

The viscosity measurement, was done immediately after packaging of the product. A Brookfield Viscometer, with a #4 rotating disk or spindle, was used to measure viscosity at 20 rpm under ambient temperatures. The torque required to maintain constant rotation was recorded as viscosity in centipoise, cP. This empirical information provides a quick viscosity check of the model dressing systems prepared in relationship to a standard ranch dressing which has a standard viscosity of 8000cP.

Titration with a standard base, also known as titratable acidity, was performed to determine the percent acid in a sample. A 0.1 N NaOH solution of the stock alkaline solution was used. The pH was also measured using a standard pH meter to determine the logarithm of the reciprocal of the hydrogen ion concentration.

3.3 Rheology

The HAAKE Viscotester© 550 (HAAKE, 1996), equipped with the MV1 concentric cylinder sensor system was utilized for this research, (Table 7). The VT-550 is a rotational viscometer used to examine the rheological properties of

fluid substances. The MV1 system (Figure 10) includes a rotating cylinder, which has a recessed top and bottom to minimize end effects that may adversely influence the torque. This system was temperature controlled with the HAAKE C2 water bath system. Samples were stored in ambient and refrigerated conditions prior to rheological testing. The testing protocol was applied using the RheoWin© software program provided by HAAKE. A series of three independent tests were performed sequentially on each dressing system: 1) steady shear at 10 s^{-1} for 60 s, 2) ramp up and down from a shear rate range of 1 to 50 s^{-1} over a period of 6 min., 3) steady shear at 10 s^{-1} for 120s. Shear stress, σ (Pa) and apparent viscosity, η (Pa s) were determined from experimental data. All tests were conducted at 5°C and 25°C , and replicated five times.

The five replications were performed after the product aged 0 – 3 months from the date of manufacture. Two additional replications were performed once the product aged a total of 6 months. This was performed to determine if the emulsion viscosity was changing at the product aged.

3.4 Particle Size

The Horiba LA-500© laser scattering particle size distribution analyzer and LA-500© software were utilized for the measurement of oil lipid particles in the base dressings. Measurement of the particles, suspended in a liquid, is possible with this instrument over a diameter range of $0.1 \mu\text{m}$ - $200\mu\text{m}$. This analyzer

Table 7 HAAKE Viscotester© 550 MV I Specifications (HAAKE, 1996)

Sensor System		MV1
Inner Cylinder (Rotor)		
Radius R_b	(mm)	20.04
Height L	(mm)	60.0
Outer Cylinder (Cup)		
Radius R_c	(mm)	21.0
Radii Ratio	R_a / R_i	1.05
Gap Width	(mm)	0.96
Sample Volume V	(cm ³)	34.0

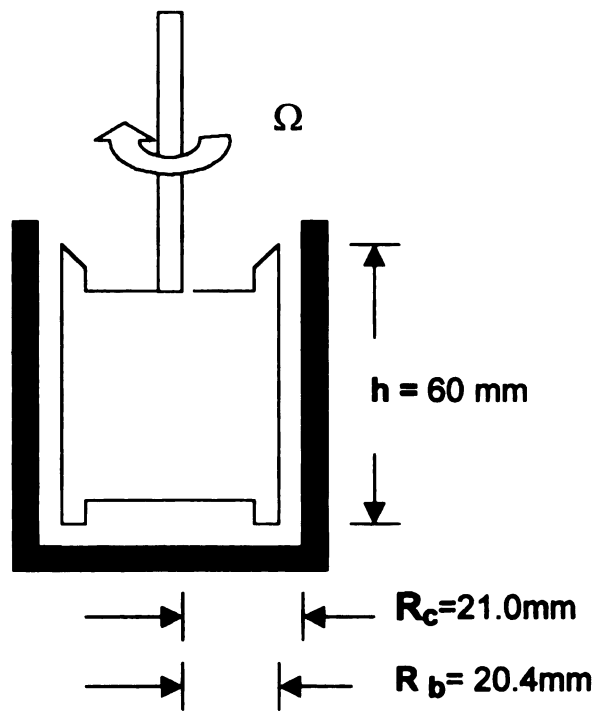


Figure 10 - MVI concentric cylinder testing apparatus showing the bob recessed top and bottom to minimize end effects.

measures the particle size distribution through the application of laser diffraction. The light intensity of the laser at the photoelectric detector and the diffracted light pattern of particles is related to the particle radius (Figure 11). Light diffraction is based on the various sizes of particles in a sample and the light diffraction patterns that occur as a result of their size.

In the LA-500 system, the sample travels past the laser by a circulating pump while being dispersed and stirred in an ultrasonic chamber, (Figure 12). The sample is then pumped in front of a Helium – Neon laser. The diameter of the laser beam emitted is increased by a beam expander and radiated upon the particles suspended in the liquid. Once the light has been dispersed and diffracted by the particles in the flow cell, the laser beam passes through a condenser lens and an image is formed on the photoelectric detector. The intensity of the diffracted light is converted to an electrical signal which is used to calculate the particle size distribution (Horiba Ltd. 1999). This instrument is very easy to use on emulsion systems.

To start the particle size analysis, samples are prepared in two solutions, a 0.2% SDS (Sodium Dodecyl Sulfate) and a 2% NaCl solutions and are placed in the ultrasonic chamber. A 1gm sample of the base emulsion dressing system is placed in a glass vial. To this is added 9gm of either the 0.2% SDS or 2% NaCl solution. The sample is mixed until the emulsion is dispersed.

An aliquot of each sample is added to the analyzer with a disposable pipette until the required concentration level has been met for the analyzer to

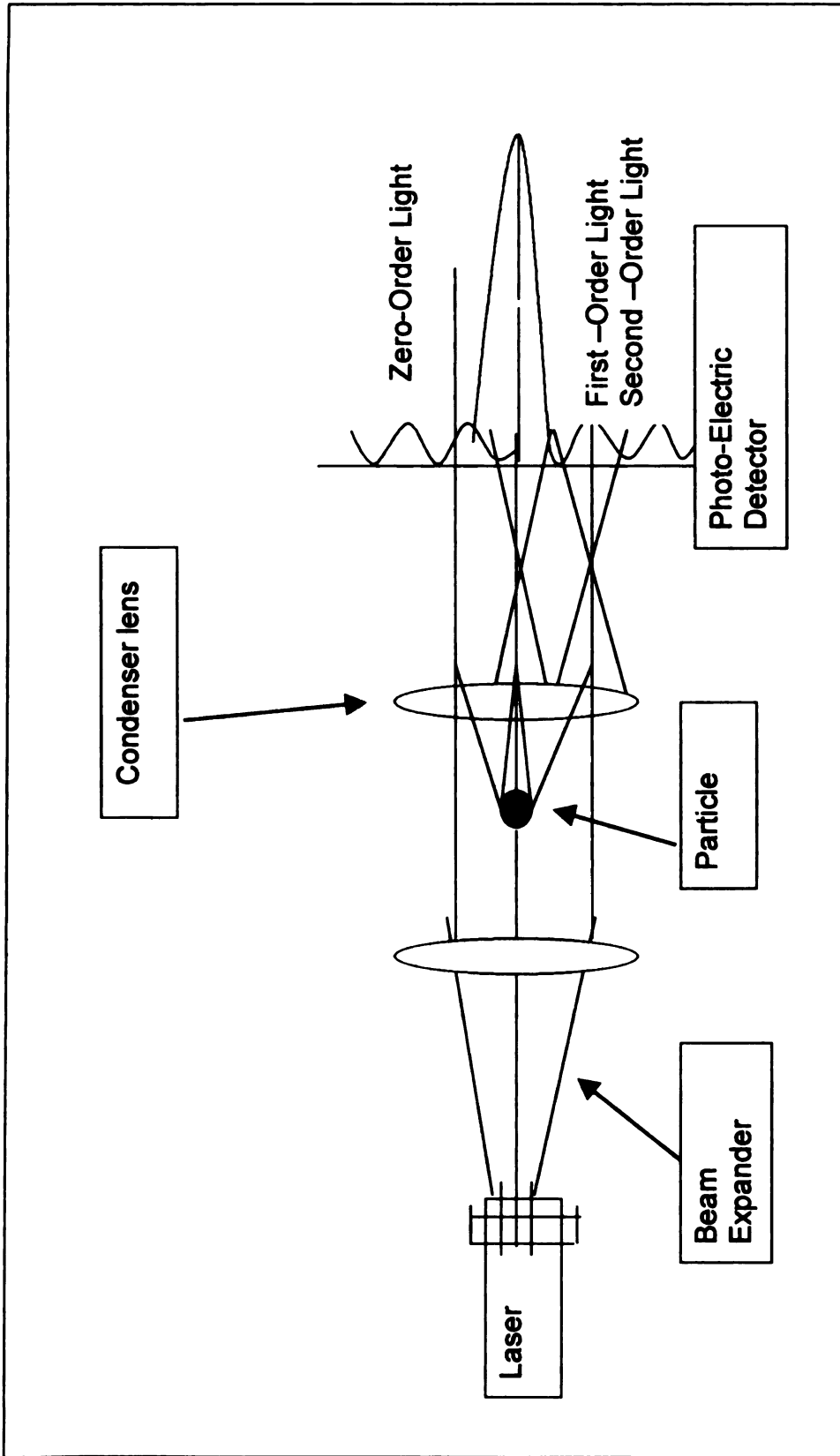


Figure 11 – Horiba principle laser measurement flow diagram

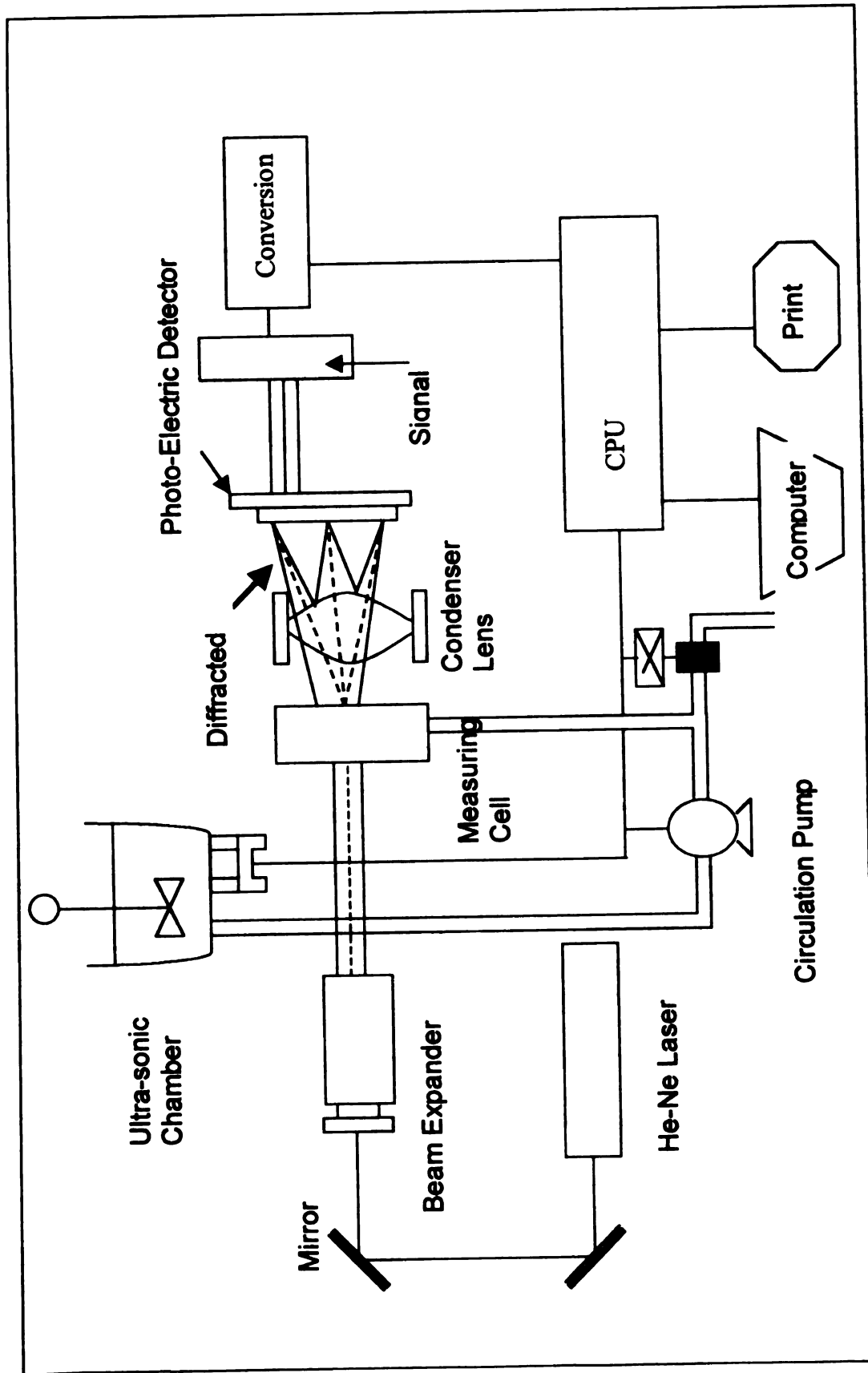


Figure 12 – Configuration of the Horiba LA-500 benchtop system utilized to determine lipid particle size (Horiba, 1999).

begin the analysis. Samples were circulated through the LA-500 system at two circulation levels, high and low speed. These speeds allow for measurements at two different circulation rates. The sample is then held at the recommended concentration level for one minute. At this time a particle size reading is taken.

After two minutes another reading is taken. Comparison of these to time variable readings allows for analysis of particle size changes over time. A read out of the analysis is displayed on the main screen of the instrument. Data are then sent to a remote computer, through the LA-500 Horiba software program, where graphs and charts of the actual data points can be displayed, printed and saved for future reference.

3.5 Statistical Design and Analysis

The effects of the variables, xanthan gum at 0.15%, 0.30% and 0.45%, egg yolk at 0%, 1.5% and 3.0% and applied processing rate at 140, 180 and 220 psi and the interactions at the three shear rates on the rheological properties and particle size analysis was analyzed with a response surface analysis factorial design. This analysis was performed using the JMP statistical software 2.0 at Kraft Foods, Glenview IL. The design determined the significant effects of the mean values of apparent viscosity and the mean particle size.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Effect of Formula and Processing on Rheological Behavior

Analysis of the influence of the formulation and processing rate on the rheological properties of a model salad dressing system were determined through viscosity testing upon production of the samples, and latter rotational viscometry at 25°C and 5°C. The rheological data were analyzed using response surface analysis, to identify the main ingredients or combination of ingredients that influenced viscosity.

Nine formulations, with varying levels of xanthan (0.15%, 0.30% and 0.45%) and egg yolk (0%, 1.5% and 3.0%) were produced, under three processing shear rates through the hydro shear unit using differential pressures of 140, 180 and 200 psi. Initial observations showed that samples varied in color from very white in formula 1 to pale yellow in formula 9. This results from the xanthan gum level affecting the emulsification of the oil droplets. As the samples were removed and loaded into the rheometer, the texture appeared thicker as the level of xanthan gum increased to 0.45%. No visual differences were detected from increased levels of egg yolk or differential pressures.

Empirical rheological testing performed at the time of production showed that the Brookfield viscosity of the model systems ranged from 2240 cP – 20100 cP. This compared well to standard Ranch dressing that has an initial viscosity

of 8000 cP. These initial measurements indicate an increase in viscosity and creaminess as the xanthan level increased from 0.15% to 0.45% (Table 8). There is also a slight increase in viscosity due to the increase in egg yolks. No pattern could be seen as the processing rate (differential pressure) increased. The pH of the model dressing system samples ranged from 3.18 – 3.55 for the various formulas. These samples have a pH in the typical range for salad dressing formulations (Stauffer 1996).

The samples produced exhibit a wide range of textures. The rheological behavior of these samples was compared to four competitive brands of basic Ranch dressing, (Kraft Ranch ©, Hellman's Ranch©, Wishbone Ranch ©, Hidden Valley Ranch ©). The decreasing apparent viscosity with increasing shear rate was shown to be very similar for all four commercial samples. When compared to three of the model dressing systems processed at a processing rate of 140 psi, all measured at 25°C, it can be seen that the viscosity of the commercial dressings is similar to formula 5, which contained 0.30% xanthan gum and 1.5% egg yolks. When compared to formula 1 containing 0.15% xanthan gum and 0% egg yolk, the commercial dressings have a much higher apparent viscosity at low shear rates. The opposite is true for formula 9 at the highest xanthan gum level of 0.45% and highest egg yolk level of 3.0%, where the apparent viscosity is lower for the commercial samples at shear rates of less than 20 s^{-1} , Figure 13.

Table 8 – Initial Brookfield viscosity, pH, titratable acidity and salt analysis of the model salad dressing samples.

Formula	Processing Rate	Viscosity* [cP]	PH	Titratable Acidity	Salt
1	140	2240	3.3	0.36%	2.13%
1	180	2960			
1	220	3360			
2	140	5120	3.32	0.36%	2.28%
2	180	5040			
2	220	4880			
3	140	6160	3.49	0.37%	2.46%
3	180	6080			
3	220	6080			
4	140	6400	3.18	0.39%	2.16%
4	180	7040			
4	220	8000			
5	140	7760	3.36	0.37%	2.27%
5	180	7760			
5	220	14000			
6	140	14400	3.5	0.38%	2.47%
6	180	12400			
6	220	10700			
7	140	11840	3.2	0.39%	2.13%
7	180	11600			
7	220	1170			
8	140	15300	3.37	0.38%	2.31%
8	180	19500			
8	220	16700			
9	140	15400	3.55	0.36%	2.40%
9	180	20100			
9	220	17800			

*Viscosity – measured with a Brookfield at 20 rpm, base ranch = 8000cP

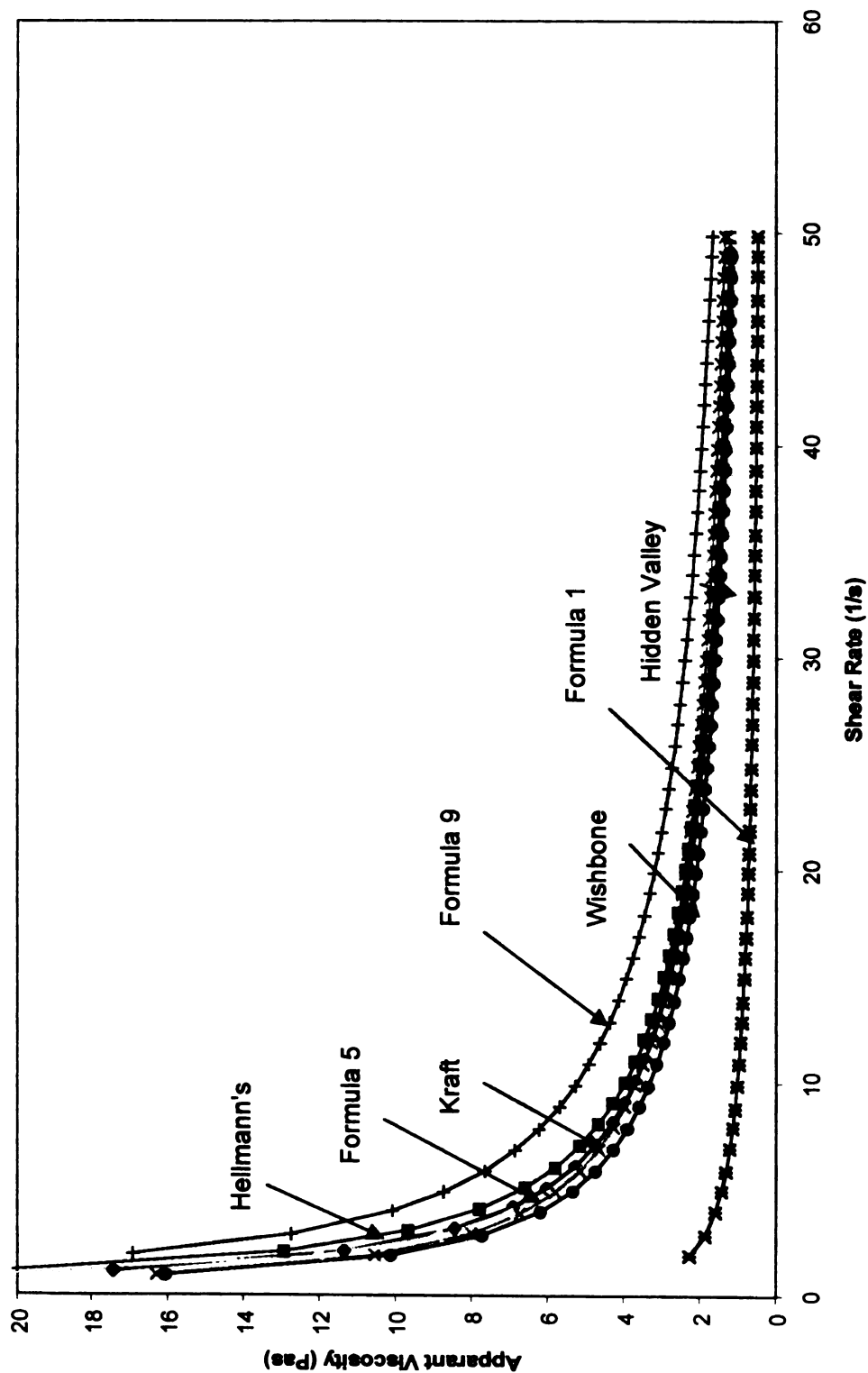


FIGURE 13 Rheological behavior of commercial samples in comparison to formula 1, containing 0% egg yolk and 0.15% xanthan gum; formula 5, containing 1.5% egg yolk and 0.30% xanthan gum; and formula 9, containing 3.0% egg yolks and 0.45% xanthan gum. (All at 140 psi and 25°C).

4.1.1 Time Dependent Behavior

Prior to the shear sweep performed on all twenty-seven samples at both 25°C and 5°C, the time-dependent behavior of the dressing was analyzed using a controlled shear rate of 10 s^{-1} for 60 seconds at each temperature. This test showed the samples became time-independent after 60 s of preshear, Figure 14. Formulas 1, 5 and 9 were chosen to represent the increasing level of xanthan gum and egg yolk levels of the samples while all formulas exhibited the same flow behavior.

The time-dependent behavior was small and diminished after 30 s. As the amount of xanthan gum increased from 0.15% (formula 1) to 0.30% (formula 5) and then to 0.45% (formula 9) the shear stress increased from 10-12 Pa (at 0.15% xanthan gum), to 35-40 Pa (0.30% xanthan gum) and 57-62 Pa (0.45% xanthan). This increasing level of xanthan gum resulted in smaller particles and more pronounced time-dependent behavior. Preshear eliminated the time-dependent effects from the subsequent sweep tests, allowing for all samples to be evaluated as time-independent fluids.

A shear rate sweep was performed, from 1 s^{-1} to 50 s^{-1} for 180 seconds at each temperature, 25°C and 5°C. The power law fluid model was utilized to determine the consistency coefficient (K) and the flow behavior index (n) from resulting rheograms. Apparent viscosity was calculated at: 10 s^{-1} , 25 s^{-1} and

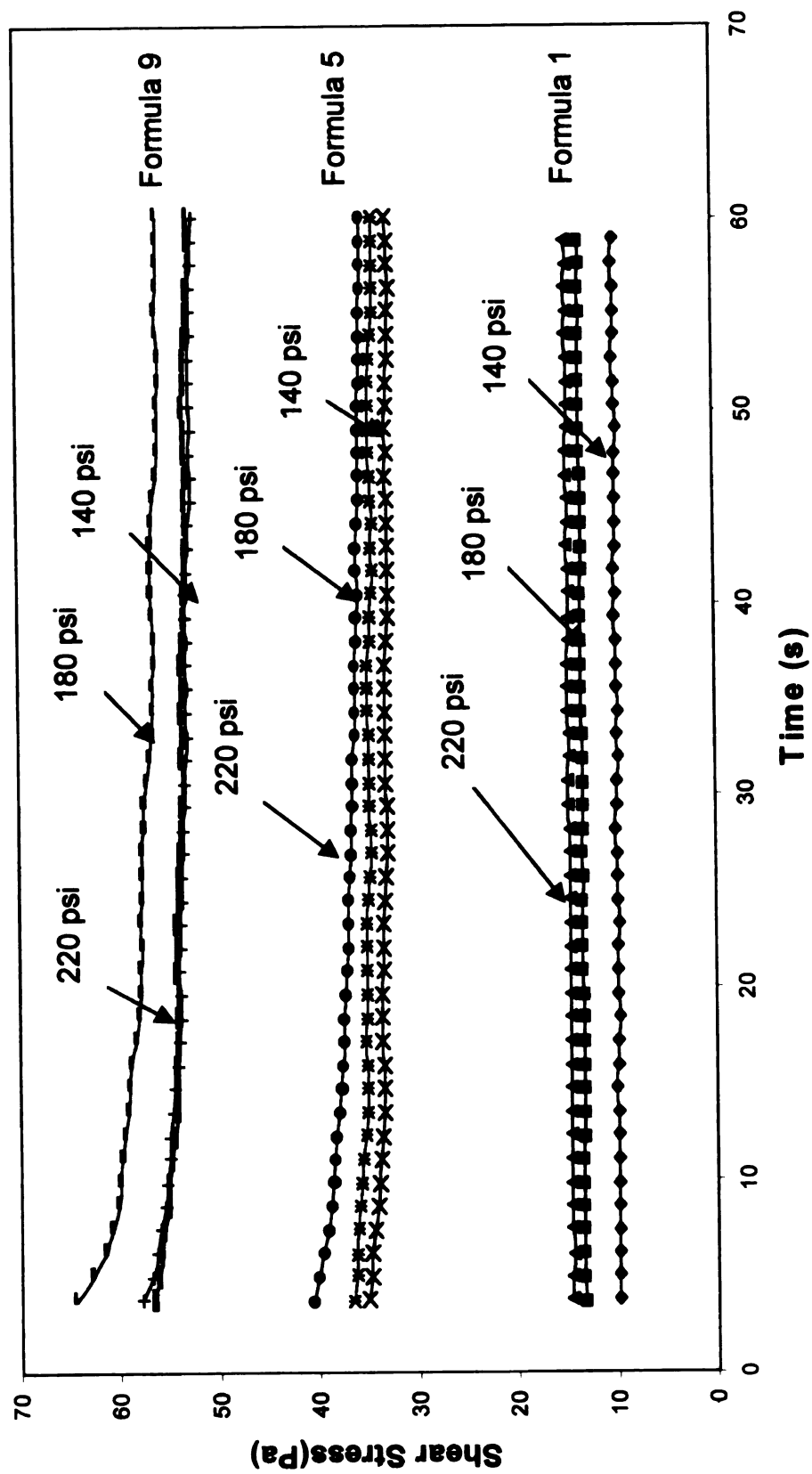


Figure 14 – Time-dependent fluid behavior at 25°C before shear sweep at different processing levels.

40 s⁻¹, with 25 s⁻¹ being reported in Table 8 and 9.

After the shear sweep, a final time-dependency sweep was performed at a controlled shear rate of 10 s⁻¹ for 60 seconds at each temperature. This test showed that all of the samples did not exhibit residual time-dependent behavior (Figure 15). Formulas 1, 5 and 9 can be compared to Figure 14, where it can be seen that the samples exhibited some degree of permanent structural breakdown. Formula 9, prior to the shear sweep, exhibited a shear stress of 57-62 Pa s, while after the sweep the shear stress was 48-50 Pa s. The time-independent behavior of this fluid after minimal shear is a prime product characteristic. If these samples were highly time-dependent fluids, it would propose a larger operations challenge due to breakdown issues associated with pumping, packaging, and use by the consumer.

The rheograms, the apparent viscosity versus shear rate, showed that the flow behavior followed the power law fluid model given in equation (8):

$$\eta = f(\dot{\gamma}) = K (\dot{\gamma})^n / \dot{\gamma} = K (\dot{\gamma})^{n-1} \quad (8)$$

The apparent viscosity at 25 s⁻¹, the consistency coefficient (K) and the flow behavior index (n) at 25°C and 5°C, calculated from the shear rates and apparent viscosity are listed in Tables 9 and 10. It can be seen that all n values are less than 1 indicating shear-thinning behavior. The consistency coefficient increased as the level of xanthan gum increased: at 0.15% xanthan gum and 0% egg yolks,

Table 9 - Rheological analysis of model salad dressing formulations at 5°C

Egg Yolks %	Xanthan Gum %	Formula	Δp (psi)	K (Pa s ⁿ)	n (-)	R ²	$\dot{\eta}$ at $\dot{\gamma} = 25 \text{ s}^{-1}$ (Pa s)
0	0.15	1	140	4.07	0.53	0.993	0.891
0	0.15	1	180	5.37	0.51	0.997	1.10
0	0.15	1	220	6.47	0.49	0.996	1.24
1.5	0.15	2	140	7.21	0.48	0.996	1.36
1.5	0.15	2	180	7.82	0.47	0.997	1.44
1.5	0.15	2	220	7.12	0.48	0.996	1.35
3.0	0.15	3	140	8.52	0.46	0.997	1.49
3.0	0.15	3	180	9.72	0.44	0.997	1.61
3.0	0.15	3	220	9.07	0.45	0.997	1.53
0	0.3	4	140	15.2	0.40	0.997	2.21
0	0.3	4	180	14.9	0.40	0.996	2.20
0	0.3	4	220	17.5	0.40	0.997	2.52
1.5	0.3	5	140	17.2	0.39	0.998	2.45
1.5	0.3	5	180	17.9	0.39	0.998	2.57
1.5	0.3	5	220	19.2	0.38	0.997	2.59
3.0	0.3	6	140	22.3	0.35	0.998	2.74
3.0	0.3	6	180	23.2	0.35	0.998	2.91
3.0	0.3	6	220	22.9	0.36	0.998	2.87

Table 9 – (Cont'd)

Egg Yolks %	Xanthan Gum %	Formula	Δp (psi)	K (Pa s ⁿ)	n (-)	R ²	$\dot{\eta}$ at $\dot{\gamma} = 25 \text{ s}^{-1}$ (Pa s)
0	0.45	7	140	28.4	0.33	0.998	3.28
0	0.45	7	180	27.4	0.34	0.998	3.25
0	0.45	7	220	34.0	0.31	0.998	3.76
1.5	0.45	8	140	28.2	0.34	0.998	3.38
1.5	0.45	8	180	32.7	0.32	0.998	3.70
1.5	0.45	8	220	26.1	0.36	0.998	3.34
3.0	0.45	9	140	33.4	0.31	0.999	3.68
3.0	0.45	9	180	35.5	0.31	0.999	3.84
3.0	0.45	9	220	33.7	0.32	0.998	3.77

Table 10 - Rheological analysis of model salad dressing formulations at 25°C

Egg Yolks %	Xanthan Gum %	Formula	Δp (psi)	K (Pa s ⁿ)	n (-)	R ²	$\dot{\eta}$ at $\dot{\gamma} = 25 \text{ s}^{-1}$ (Pa s) ^{a,b,c}	Particle Size μm^d	Particle Size Std. Dev.
0	0.15	1	140	3.08	0.52	0.996	0.656	5.432	0.6660
0	0.15	1	180	4.32	0.49	0.997	0.847	5.019	0.6050
0	0.15	1	220	4.90	0.48	0.998	0.914	4.877	0.5960
1.5	0.15	2	140	6.91	0.43	0.998	1.09	4.954	0.6820
1.5	0.15	2	180	6.91	0.43	0.998	1.09	4.842	0.7450
1.5	0.15	2	220	7.14	0.43	0.998	1.14	4.690	0.7450
3.0	0.15	3	140	8.28	0.40	0.999	1.12	4.087	0.5020
3.0	0.15	3	180	9.10	0.38	0.999	1.24	4.204	0.5830
3.0	0.15	3	220	8.60	0.39	0.999	1.23	3.809	0.5130
0	0.3	4	140	12.8	0.38	0.998	1.73	5.679	0.7180
0	0.3	4	180	14.2	0.38	0.998	1.42	5.550	0.6920
0	0.3	4	220	19.3	0.32	0.991	2.15	4.983	0.5940
1.5	0.3	5	140	15.4	0.33	0.992	1.81	6.442	1.198
1.5	0.3	5	180	15.0	0.35	0.998	1.87	5.639	1.004
1.5	0.3	5	220	15.9	0.34	0.998	1.87	4.550	0.6980
3.0	0.3	6	140	18.6	0.31	0.999	2.01	4.526	0.6540
3.0	0.3	6	180	19.2	0.31	0.999	2.15	3.918	0.5270
3.0	0.3	6	220	18.8	0.31	0.998	2.07	3.656	0.4910

a – egg yolk significantly effects viscosity, f value of 0.005; b – xanthan gum significantly effects viscosity, f value <0.001;

c – differential pressure significantly effects viscosity, f value 0.0093, all f values <0.05;

d – particle size measured in SDS: egg yolk, f value = 0.0002, xanthan gum, f value = 0.0015, processing rate, f value = 0.0003, all significantly effecting particle size.

Table 10 – (Cont'd)

Egg Yolks %	Xanthan Gum %	Formula	Δp (psi)	K (Pa s ⁿ)	n (-)	R ²	$\dot{\eta}$ at $\dot{\gamma} = 25 \text{ s}^{-1}$ (Pa s) ^{a,b,c}	Particle Size μm^d	Particle Size Std. Dev.
0	0.45	7	140	23.2	0.30	0.998	2.46	5.403	0.6600
0	0.45	7	180	23.7	0.31	0.997	2.61	5.075	0.6130
0	0.45	7	220	27.9	0.29	0.998	2.84	4.796	0.5760
1.5	0.45	8	140	22.9	0.31	0.998	2.50	6.534	1.167
1.5	0.45	8	180	27.7	0.30	0.998	2.96	6.388	1.155
1.5	0.45	8	220	30.4	0.28	0.998	3.05	5.172	0.8150
3.0	0.45	9	140	26.5	0.29	0.998	2.74	5.463	0.9170
3.0	0.45	9	180	28.3	0.29	0.999	2.93	4.584	0.7070
3.0	0.45	9	220	27.1	0.29	0.998	2.72	4.699	0.7990

a – egg yolk significantly effects viscosity, f value of 0.005; b – xanthan gum significantly effects viscosity, f value <0.001; c – differential pressure significantly effects viscosity, f value 0.0093, all f values <0.05;

d – particle size measured in SDS: egg yolk, f value = 0.0002, xanthan gum, f value = 0.0015, processing rate, f value = 0.0003, all significantly effecting particle size.

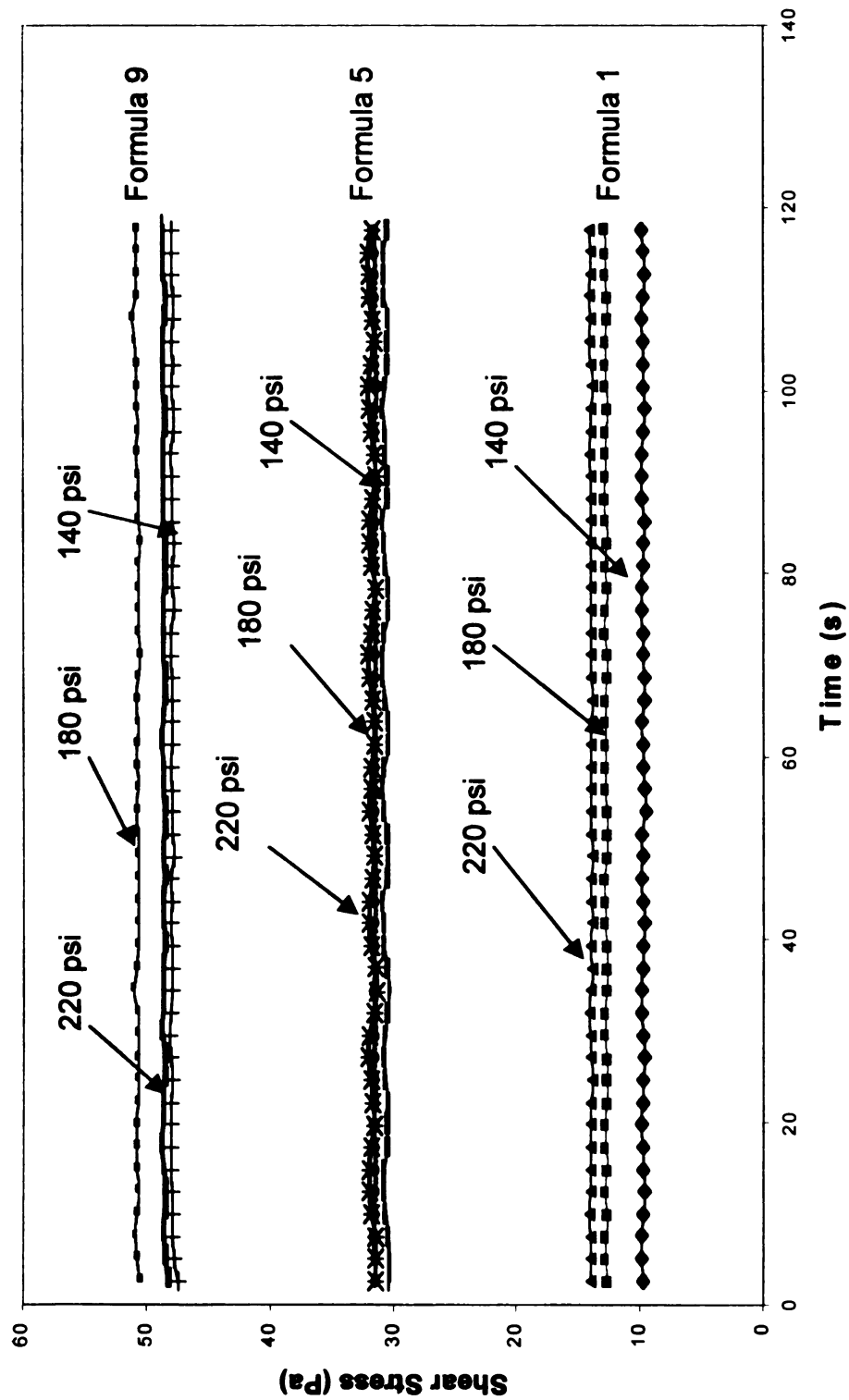


Figure 15 – Time dependent fluid behavior at 25°C after shear sweep at different processing levels.

is 4.072 – 6.467, over the range of differential pressures, 0.45% xanthan gum and 3.0% egg yolks, K is 33.427 – 33.719, over the range of differential pressures.

To determine if the viscosity of the dressing systems was changing over time, additional rheological testing was performed after aging. Five replications of the shear sweep were conducted when the product was 1 to 3 months old. Two more replications were performed to determine if the emulsion was changing over time. These replications were performed when the product was 6 months old. In Figure 16, at 25°C it can be seen that for formula 1 and 9 at 140 psi and 220 psi there is little change between the pooled data of the five replications and the pooled data of the two replications with aging. The rheogram shows that the effect on apparent viscosity for the first five replications is very close to the two completed after the product aged. This was also seen for formulas 2-8 at all three differential pressures. Formula 1 and 9 were chosen, and are represented in Figure 16, because they represent the two extremes of xanthan gum levels of 0.15% and 0.45% and egg yolk levels of 0% and 3.0%. Paredes (1989) also showed, through measurements of creep compliance, that salad dressing emulsions utilizing xanthan gum as a stabilizer, maintained emulsion stability during storage.

4.1.2 Xanthan Gum / Egg Yolks

The ingredient producing greatest effect on the viscosity is xanthan gum. Egg yolks only have a slight effect on the viscosity compared to xanthan gum.

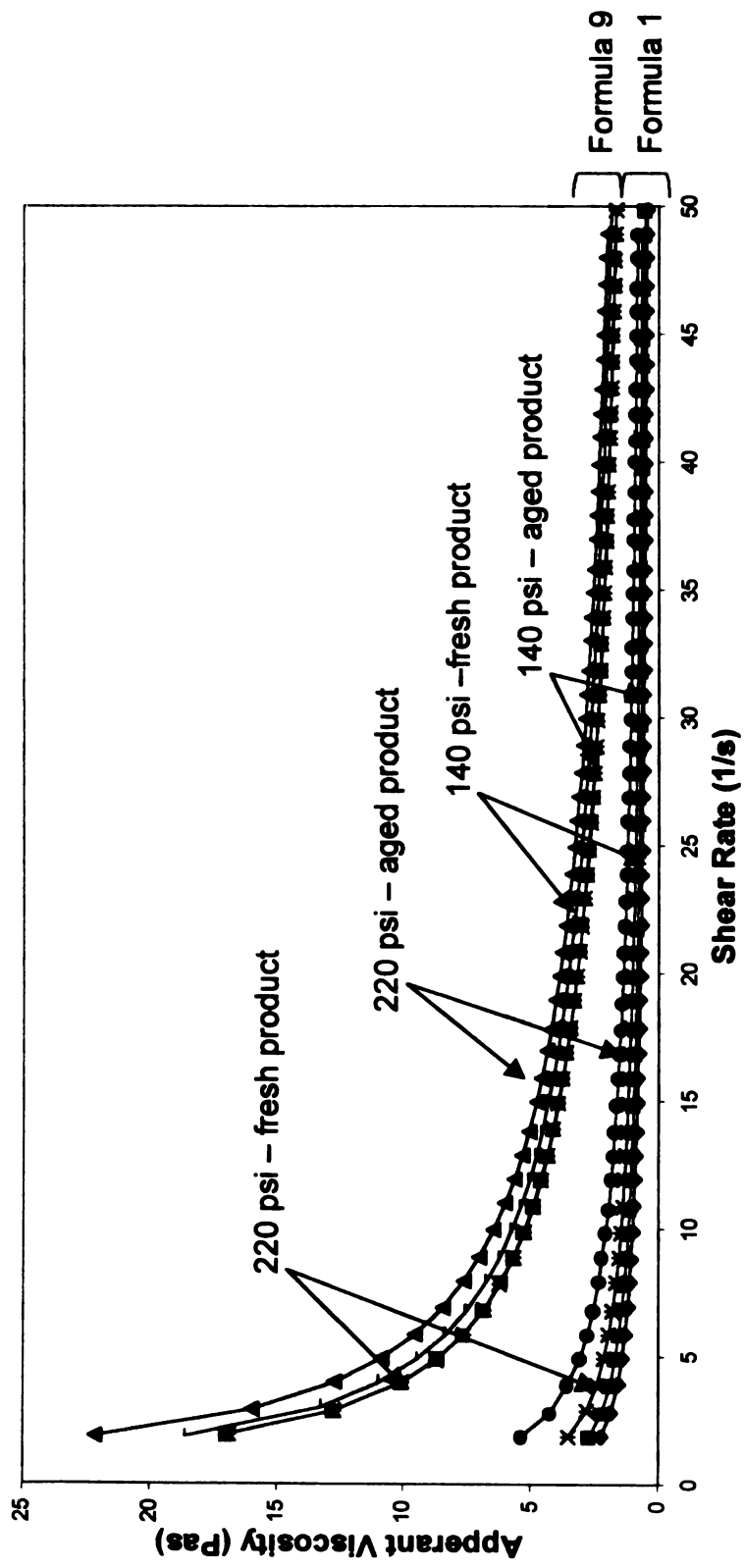


Figure 16 – Effects of aging: comparison of measurements of fresh and aged product at two processing levels.

As the xanthan gum level is increased from 0.15% to 0.30% and 0.45%, with the egg yolk level held at 1.5%, the apparent viscosity increases an average of 0.70 Pa s at a shear rate of 25 s^{-1} .

Xanthan gum, which affects the creaminess, is a viscosity builder and provides emulsion stability (Phillips and Williams 1995). It has the greatest impact on the viscosity due to its rod like conformation forming entanglements (Figure 17). In 25°C temperature conditions, the apparent viscosity increases, as the xanthan level increased from 0.15% (formula 1), to 0.30% (formula 5) and finally 0.45% (formula 8).

The greatest apparent viscosity difference is seen at shear rates less than 20 s^{-1} . This is a result of the xanthan gum polymers forming reversible entanglements. As stated by Urlacher and Noble in 1997, this behavior can be advantageous, where increasing the shear rate can decrease the viscosity of a xanthan gum solution.

This is especially important during the production of dressings which have formulas with higher xanthan levels or if over application occurred. During pumping and mixing a higher shear rate could be applied if too much xanthan gum was added to the product in order to move and package the product. But upon used by the consumer issues could arise, where a higher shear rate would be needed to use the product, due to high levels of xanthan gum. The amount of shear needing to be applied by the consumer would increase where the typical shear rate during pouring is in a range of $10 - 100 \text{ s}^{-1}$. The product would

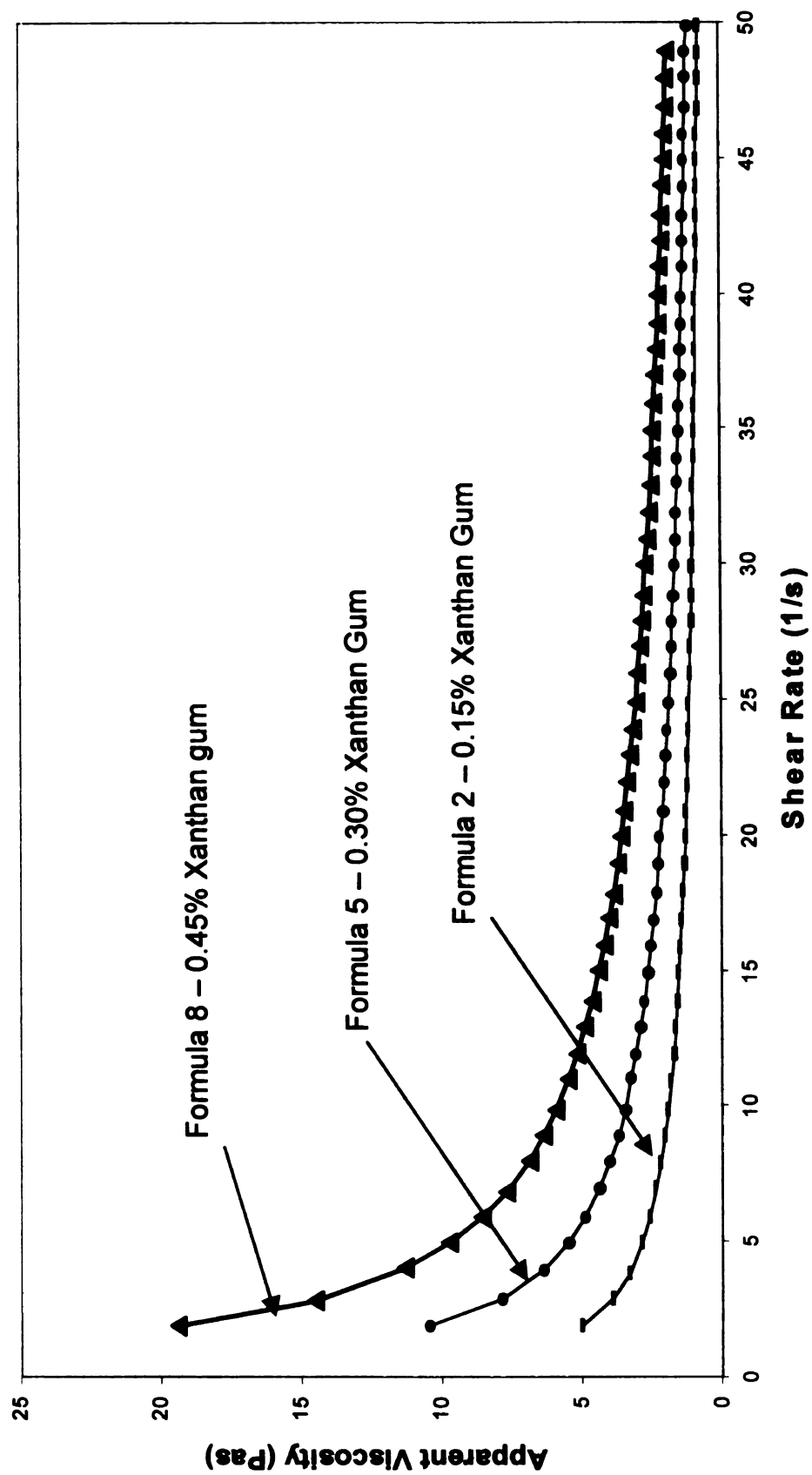


Figure 17 – Effects of increasing xanthan gum at 1.5% egg yolks and 220 psi at 25°C

essentially become spoonable, not pourable giving it a whole new flow behavior profile and product identity.

Xanthan gum has a strong effect on the K and n values, table 9 and 10. The K value increases as the xanthan level increases. It can also be seen in these tables that egg yolk also affects K, although not as significantly as xanthan gum.

Xanthan gum was shown to significantly affect apparent viscosity as the levels increased from 0.15% to 0.30% and 0.45%. This effect is independent of egg yolk or processing rates increasing. It is the result of the xanthan gum being dispersed in oil and then mixed in the sample to achieve hydration during production. The increase in xanthan gum level resulted in a stable emulsion with increased apparent viscosity. This is due to the mechanism described by Hennock and others 1984, where it was proposed that xanthan gum is absorbed at the oil / water interface, lowering surface tension, with the remaining xanthan gum stabilizing the emulsion by physically trapping the emulsion droplets. As the xanthan gum level increased in each formula, the level surrounding each droplet increased and therefore increased the viscosity. The level of xanthan gum in a dressing formula needs to be carefully controlled due to the rheological impact and subsequent effect on production and consumption.

Egg yolks have only a slight effect on the viscosity of xanthan gum. In addition to slightly affecting the viscosity, they provide emulsion stability due to

the emulsifying activity of the lecithin protein complex, lipoproteins attaching to the oil droplets at the oil interface (Ford and others 1997). Egg yolks also provide a protective barrier around the droplets due to steric stabilization and add color and flavor attributes to the product. Insufficient egg yolk emulsifier covering droplets results in droplets having a higher tendency to coalesce (Stang and others 1996). Therefore, an emulsifier like egg yolk is necessary to properly form a stable emulsion for long term product stability and increased shelf life.

While egg yolks were shown to statistically have a significant effect on apparent viscosity through response surface analysis, f value = 0.0005, in a rheogram the increasing level of egg yolk appears to have only a slight effect on apparent viscosity, Figure 18 and 19. In Figure 18 as the egg yolk levels increase from 0% to 1.5% and to 3.0%, egg yolk has very little influence on apparent viscosity at all three levels of xanthan gum, while all three formulas exhibit shear-thinning behavior. In contrast, Carillo and Kokini (1988) found that egg yolk and egg yolk plus salt had an effect on the rheological properties of a model oil in water salad dressing emulsion. They found that the egg yolk significantly contributed to the stability and viscosity of the model system. While in this study egg yolk provided stability but did not greatly affect viscosity.

In Figure 19, as the egg yolk level increases from 0% to 1.5% and 3.0% and the xanthan level is held at 0.30%, there is a slight increase in apparent viscosity. This was also seen at 0.15% and 0.45% xanthan gum. There is no effect seen as the processing rate increases. This shows that some egg yolk is

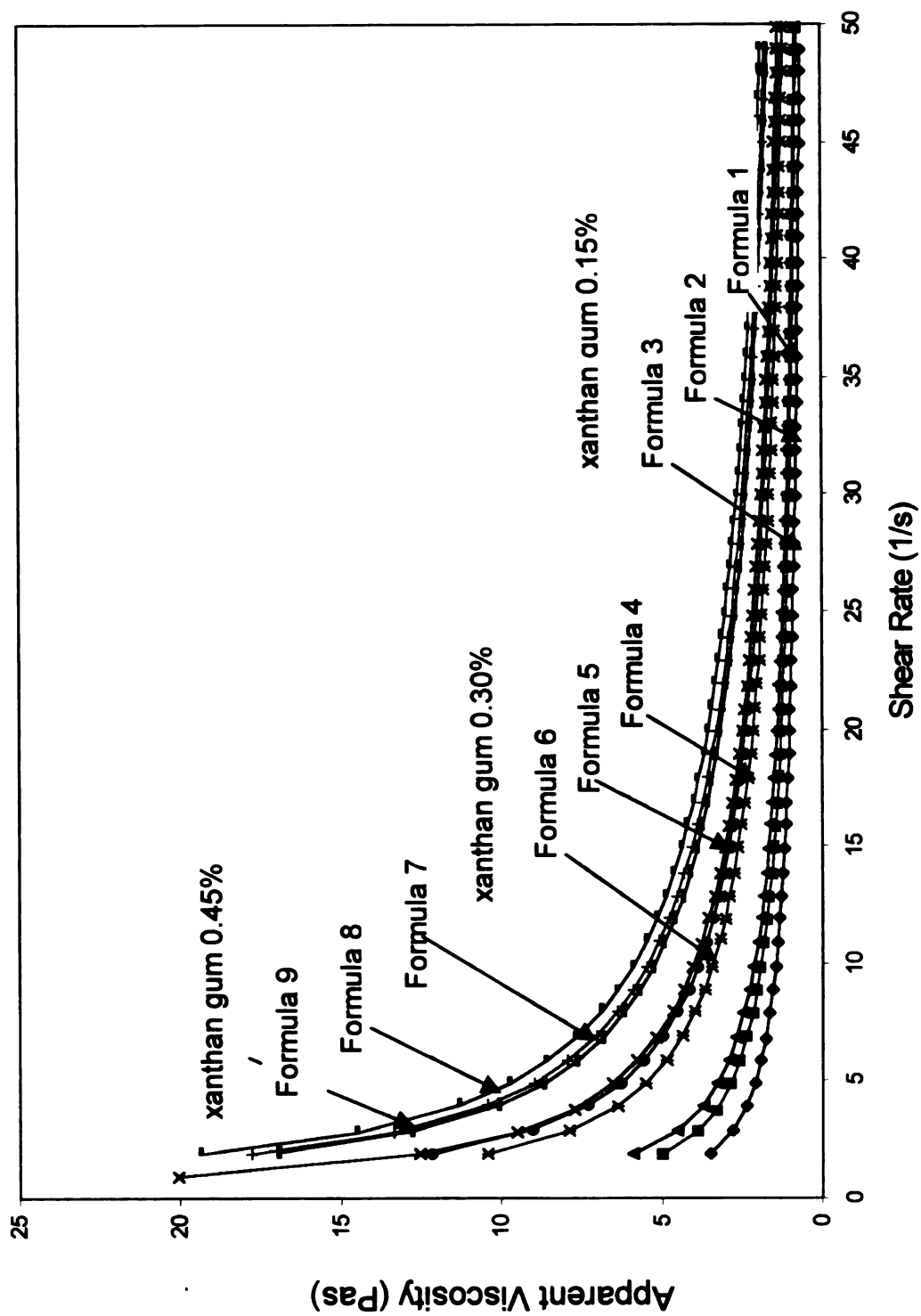


Figure 18 – Effects of Increasing egg yolk at 0%, 1.5% and 3.0% and increasing xanthan gum at 220 psi at 25°C.

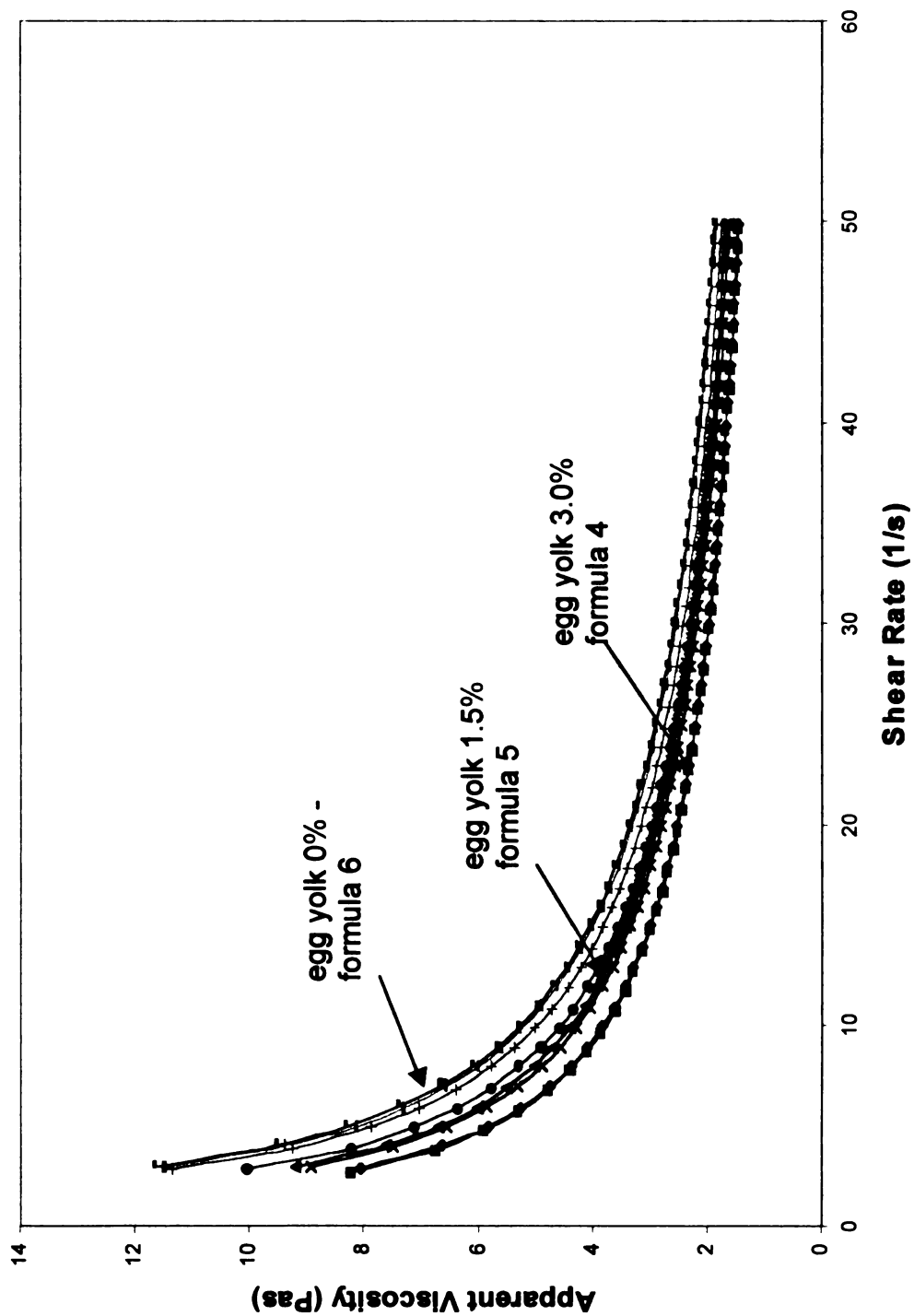


Figure 19 – Effect of processing rate increase 140, 180 and 220 psi with increasing egg yolk and xanthan gum level of 0.30% at 25°C.

necessary to obtain emulsion stability in a dressing system. Carillo and Kokini (1988) showed through creep analysis, steady shear and particle size analysis that emulsions are most stable in the presence of 2% egg yolk with 0% salt or 3% egg yolk with 2% salt. In this study at levels greater than 1.5% the effect of egg yolk on the apparent viscosity has a plateau effect, and egg yolks are not controlling viscosity.

4.1.3 Processing Rate

Model dressing samples were produced under processing rates with increasing differential pressures of 140, 180 and 220 psi. The effect of this process variable on apparent viscosity was significant but only slightly compared to xanthan gum.

As can be seen in Figure 20, at all three levels of xanthan gum, the rheogram is unchanged as the processing rate increases, while the egg yolk level is held constant at 3.0%. The fluid exhibits shear-thinning behavior, with the apparent viscosity being strongly affected by xanthan gum. The process rate does not have a significant effect on the apparent viscosity in conjunction with the other factors, or independently.

As the processing rate increase, with the egg yolk level at 0% and xanthan gum at 0.45% in formula 7, a very slight increase can be seen in apparent viscosity at 220 psi.

At 140 and 180 psi, no change was seen in an apparent viscosity at any shear rate (Figure 21). The same trend, is seen in formula 1 and 4

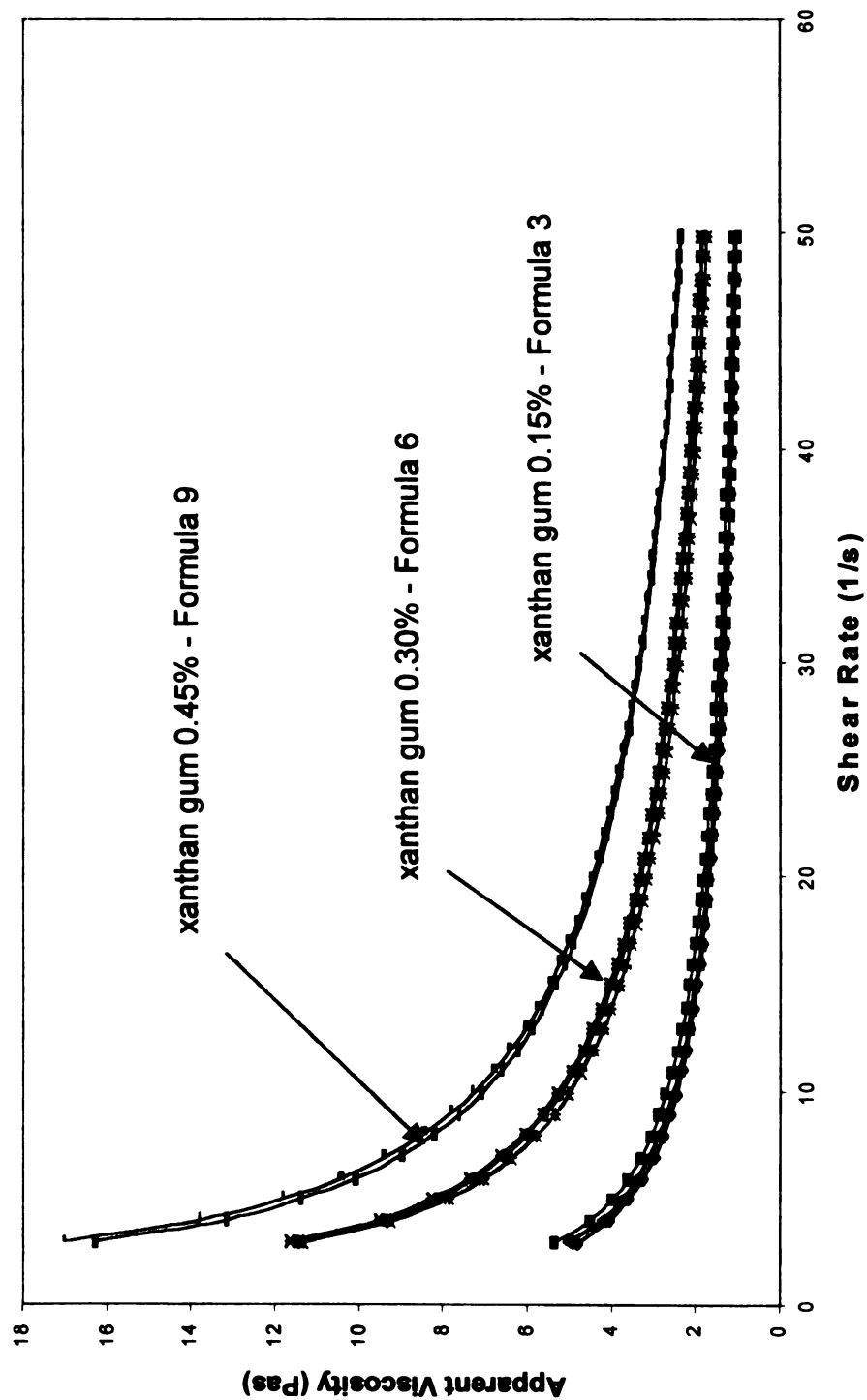


Figure 20 – Effect of increasing processing rate 140, 180 and 220 psi with increasing xanthan gum 0.15%, 0.30% and 0.45% and egg yolk level at 3.0%.

with a little change in apparent viscosity evident as processing rate or egg yolk levels increase.

In all the samples evaluated, a stable emulsion was formed through the use of the hydroshear homogenization unit under a range of differential pressures ranging from 140 – 220 psi. As the pressure variables were applied the oil droplets formed new interfaces allowing the emulsifiers, egg yolks and polysorbate 60, to diffuse to the interface and therefore lower the interfacial tension as the droplets were formed. As seen from the rheograms, the droplets formed and stabilized during processing through the hydroshear did not alter the apparent viscosity.

Response surface analysis showed that egg yolk and processing rate significantly affect the apparent viscosity but only slightly compared to the effect of xanthan gum. Response surface analysis also showed that egg yolk and the processing rate independently affect viscosity. The effect of viscosity is the same no matter what the rate or egg yolk levels are.

This study shows that the utilization of a hydroshear unit for this model system allows for production of a dressing system under a pressure range of 140 – 220 psi to be utilized without significantly affecting the product viscosity. This range is large and opens up a wide range of flexibility for the production of this dressing system due to the low impact that the processing rate on the rheological characteristics, at low and high levels of egg yolks and xanthan gum. Ultimately

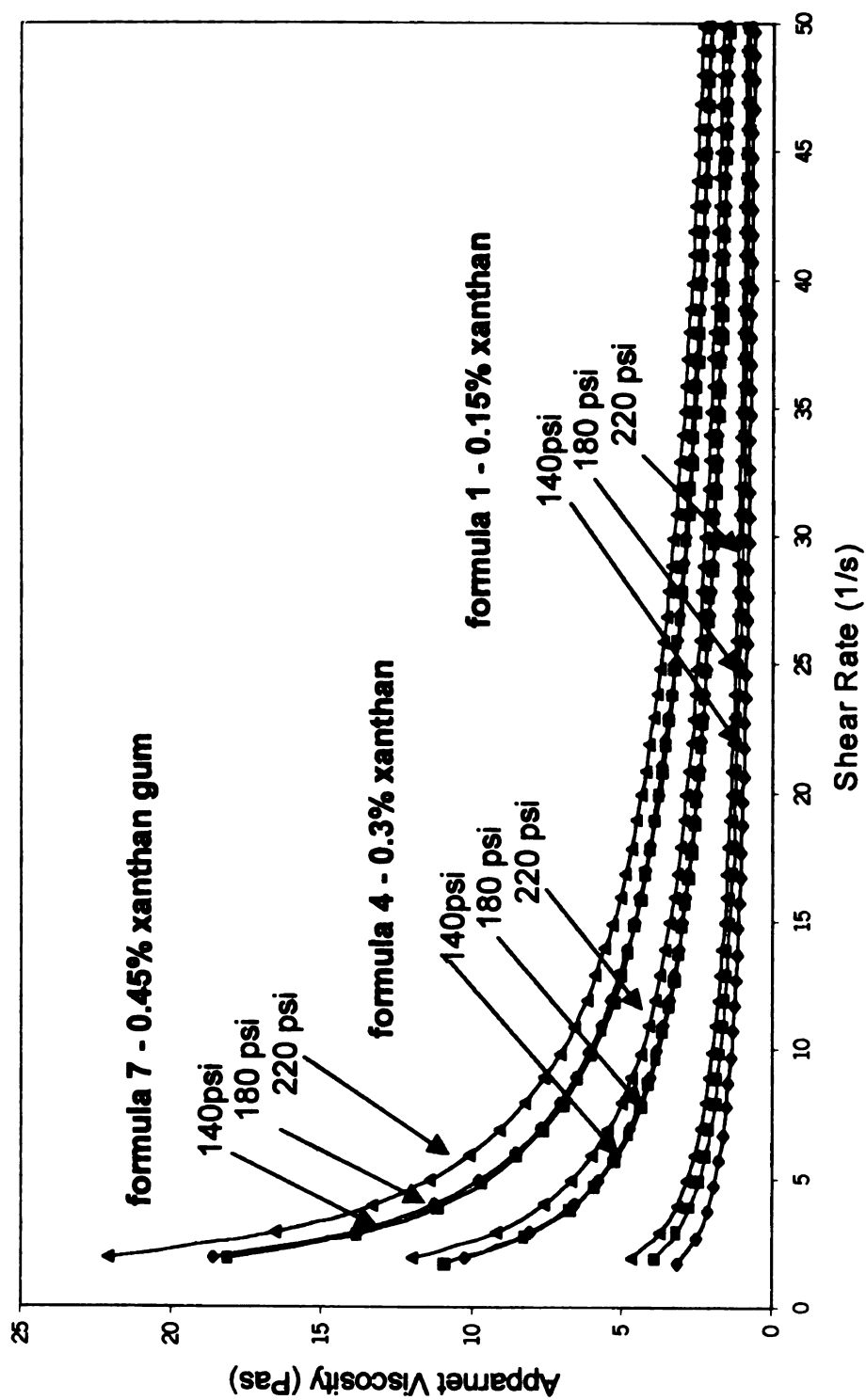


Figure 21 – Effects of increasing process rate with 0% egg yolks and increasing xanthan gum 0.15%, 0.30% and 0.45% at 5°C.

operations could run as high as 220 psi, resulting in an increase in throughput without negatively affecting the product integrity.

4.1.4 Temperature

Temperature can greatly affect the flow behavior of fluid systems. In this study, the effects of 5°C and 25°C on the rheological behavior were determined. Temperatures were chosen to mimic the typical temperatures that consumers encounter during consumption of salad dressing.

In the initial time-dependent test, temperature dependency was also evaluated, under a controlled shear rate of 10 s^{-1} for 60 seconds at 5°C and 25°C. The apparent viscosity was determined to be only slightly higher for the same sample at the colder temperature of 5°C than at 25°C, Figure 22. This shows that the model dressing system is slightly temperature dependent.

As can be seen from the rheogram, Figure 22, the apparent viscosity of the dressing is only slightly dependent upon temperature especially at 0.45% xanthan gum and 3.0% egg yolk levels at low shear rates, where the fluid exhibits shear thinning behavior. At the 0.15% xanthan gum level and 0% egg yolks the apparent viscosity becomes constant at higher shear rates. This shows that the apparent viscosity is only slightly affected by the temperature. A consumer would see little difference during pouring.

These temperature effects are important to note in developing new dressing systems and for improving upon existing systems. The effect of the

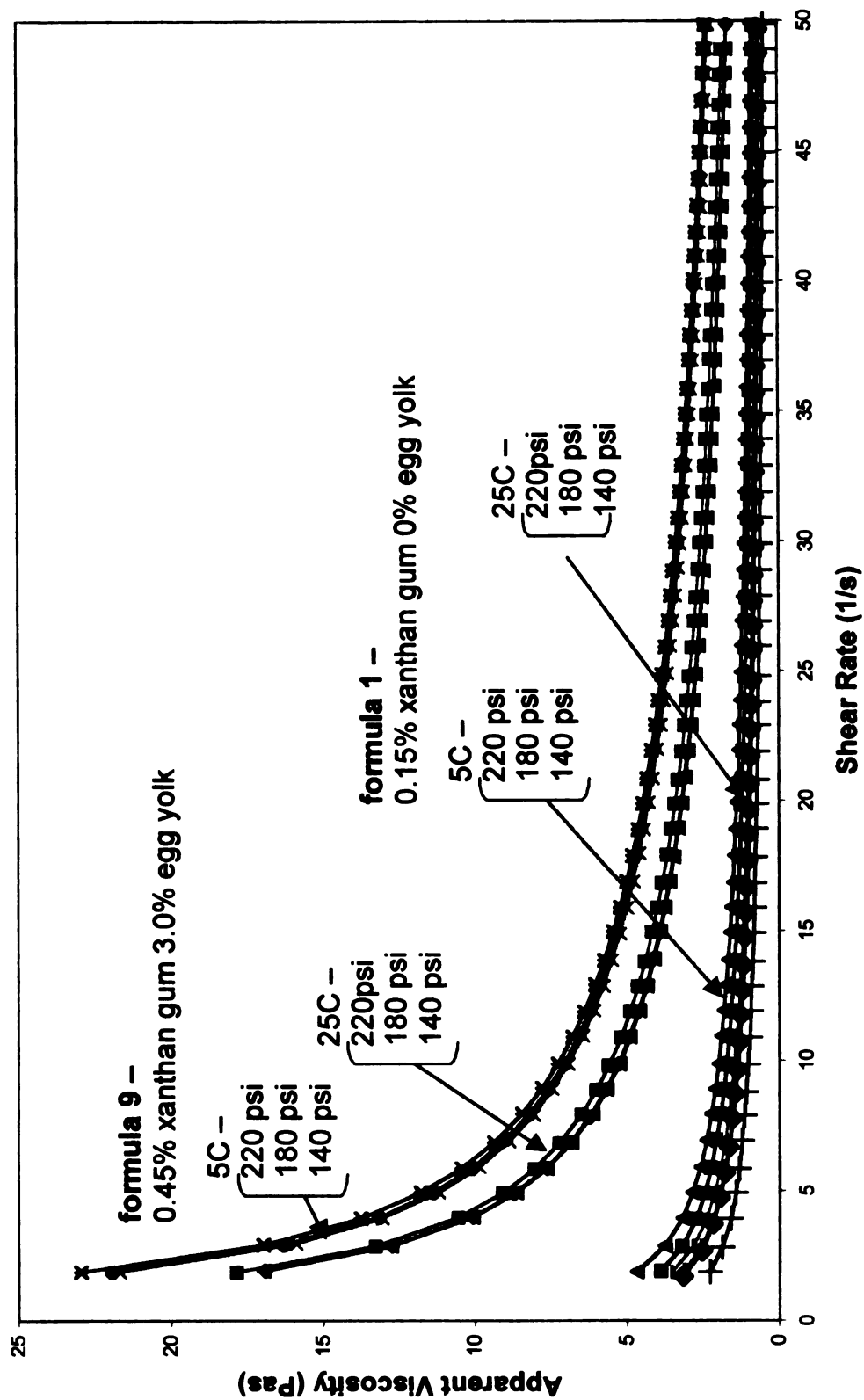


Figure 22 – Influences of temperature at 0.15% and 0.45% xanthan gum and 0% and 3.0% egg yolk levels.

varying temperature conditions is also important in maintaining similar product characteristics during the variety of temperatures seen by consumers.

4.2 Particle Size Influence

The size of the lipid particles in salad dressing is a very important characteristic due to its impact on appearance, texture, rheology, stability, and flavor. Reduction of droplet size causes a significant increase in interfacial area. Newly formed droplets will coalesce if not stabilized by emulsifiers. Analysis of the influence of the formulation including, xanthan gum, egg yolk level, and the processing rate (differential pressure) on the particle size was determined through the measurement of the lipid particle size of each formula using a light scattering particle size distribution analyzer.

To measure the particle size of the lipid droplets in each formula required dilution in two solutions. The samples were first diluted in SDS to obtain a uniform dispersion of droplets, including the breaking up of any aggregates. Particles distributed in SDS were analyzed and a mean particle size and the surface area was determine through the average of two readings per sample. The first reading was at one minute, and the second at three minutes (Table 9). Mean particle size of formulas with 0% egg yolks and 0.15% xanthan gum ranged from 5.432 μm at a processing rate of 140 psi to 4.877 μm at 220 psi. The use of SDS as a diluent for particle size analysis was successful.

The greatest range of particle size seen in a formula as a result of

increased processing rates from 140 psi to 220 psi was found in formula 5 (1.5% egg yolk, 0.3% xanthan gum). At 140 psi the particle size was 6.442 μm and at 220 psi it was 4.550 μm , giving a 1.892 μm difference. These results show that overall as the processing rate increased the particle size decreased (Figure 23). Overall response surface analysis showed that in an SDS solution, egg yolk, xanthan gum and processing rate all significantly affected the particle size. The processing rate (differential pressure) had the strongest effect on particle size (Table 9).

Particle size of each formula at each processing rate was also measured in a NaCl solution. Measurements were taken under slow and fast circulation past the laser and through the circulation pump. The mean particle size was determined through the average of one and three minute readings. Three replications were taken as a result of the variability seen during the readings.

At slow and fast circulation, the lipid particles began to aggregate spontaneously in the NaCl solution, especially under slow circulation. This caused an inaccurate measurement of the lipid particle size. The formation of these aggregates in the NaCl solution is a result of the amphilic lipid molecules being associated physically and aggregating due the NaCl ions. The mean particle sizes varied no matter how much shear was applied (by the fast or slow circulation) to break aggregates. Overall the results show that the use of NaCl as a diluent not effective due to the ionic charge of the particles in the solution resulting in spontaneous aggregation of the lipid droplets.

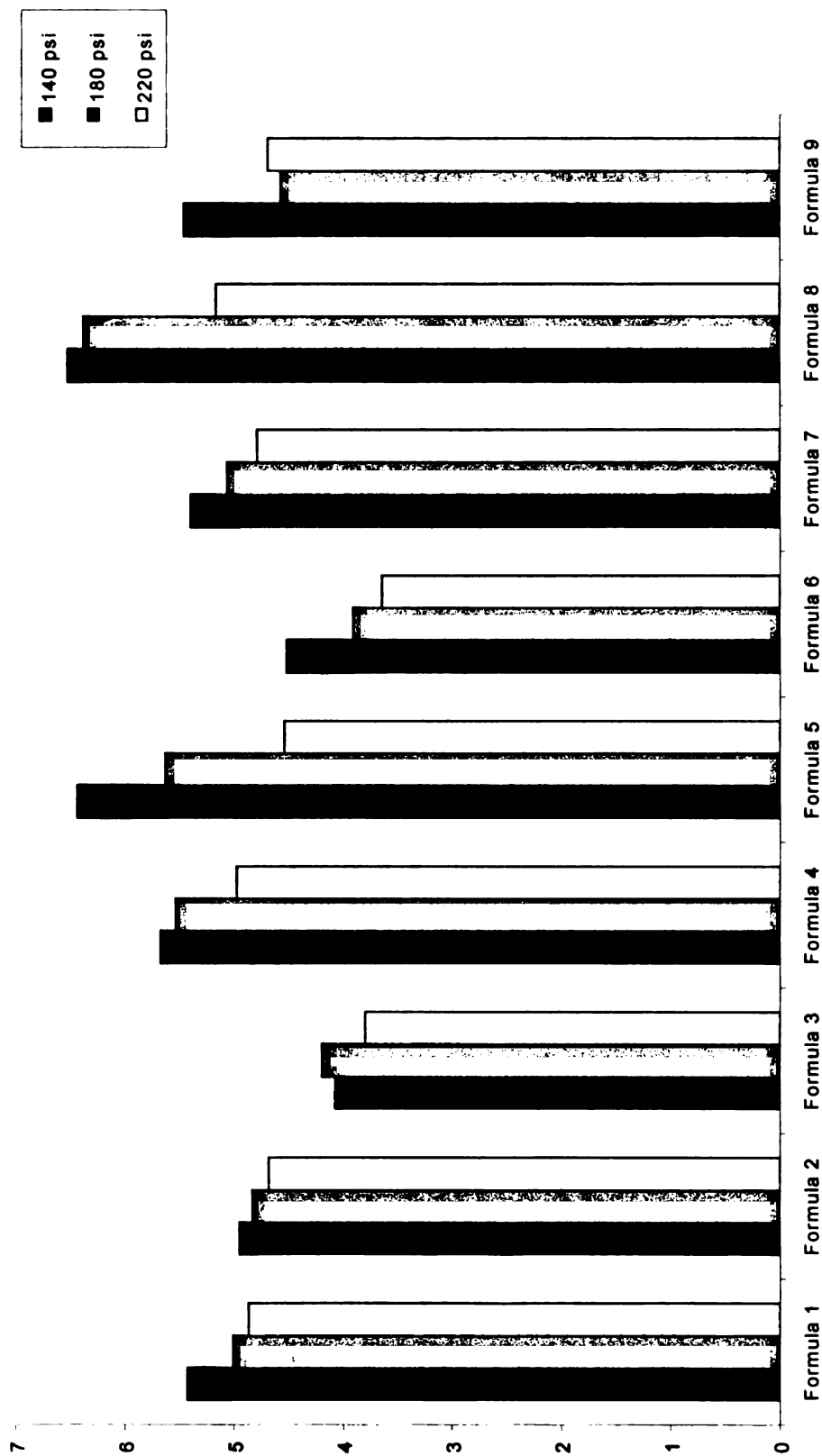


Figure 23 – Effect of increased differential pressure in the hydroshear on particle size.

Xanthan gum and egg yolks were shown to have a small effect on particle size. The particle size is the smallest at high levels of xanthan gum (0.45%) and egg yolk (3.0%). Particle size was not affected at 0% and 3% egg yolk as xanthan increased. At 1.5% egg yolk, as the xanthan gum level increases the particle size increases. The particle size for all of the samples was shown to be the largest (6.399 μm) at 1.5% egg yolks and 0.45% xanthan gum at 180 psi (Figure 24).

As egg yolk level increased from 0, to 1.5% and 3.0% the particle size was shown to decrease at any differential pressure (Figure 25). Figure 25 is a representative example, for all xanthan gum levels, showing a decrease in particle size as egg yolk levels increase at a constant xanthan gum level. These results are consistent with the study performed by Carillo and Kokini (1988). They determined that a shift in the particle size distribution towards small values was seen with addition of egg yolk and salt, and a shift towards larger values when egg yolk and salt were not present.

In this study the effect of the xanthan gum on the particle size was shown to be significant, in SDS. It was also shown that xanthan gum and egg yolks together significantly influence particle size at specific levels. At high levels of xanthan gum and high levels of egg yolk the particle size is smaller.

Xanthan gum is an effective stabilizer that affects the creaminess, viscosity and emulsion stability while the egg yolk is an effective emulsifier. The various xanthan gum and egg yolk levels resulting in different interaction effects

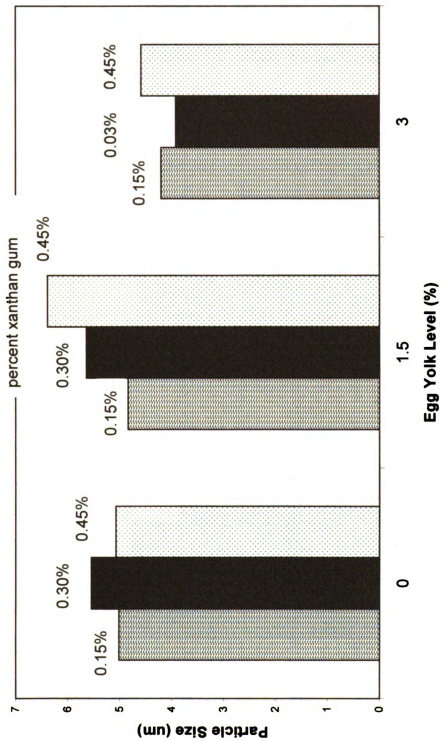


Figure 24 – Effects of increasing egg yolk and xanthan gum levels on particle size at 180 psi.

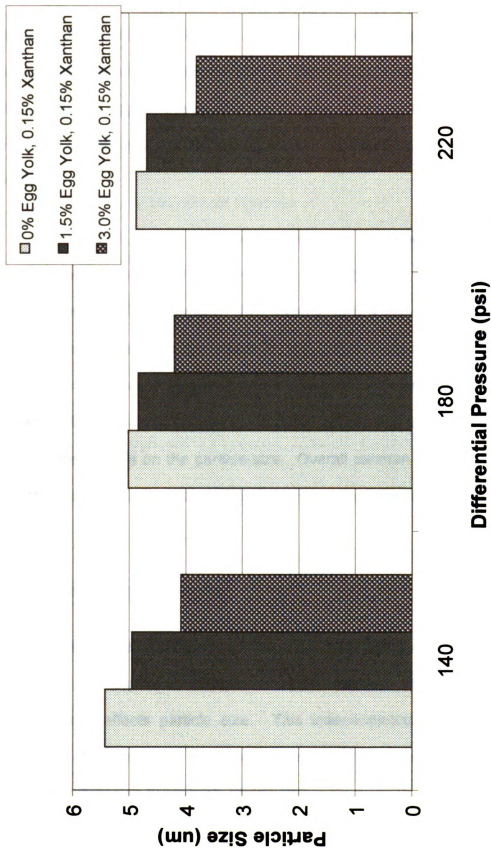


Figure 25 – Effect of increased levels of egg yolk, at a constant xanthan gum level of 0.15% on particle size.

on the particle size is important to understand to maintain the desired emulsion stability. As the lipid droplet was sheared through the hydroshear unit the lipid particle surface area increased due to the formation of new droplets. This allowed for the egg yolk to be absorbed on the droplet surface. The absorption of the emulsifier to the interface minimized coalescence of the newly formed droplets.

In addition to the egg yolk acting as an emulsifier, the dressing formulations also included the emulsifier polysorbate 60. This was held at a constant level in all of samples. Polysorbate 60 is a very fast emulsifier due to its small molecular size compared to the larger molecules of the egg yolk lipoprotein complex. The level of the xanthan gum in conjunction with the level of the egg yolk significantly influencing the overall emulsion stability, flow behavior, with minimal effects on the particle size. Overall xanthan gum and egg yolk do not affect the particle size as significantly as the processing rate (differential pressure).

4.2.1 Influence of pressure drop

Particle size decreases as the differential pressure in the hydroshear increases. Response surface analysis showed that processing rate independently affects particle size. This independence can be seen in the interaction of egg yolk and process rate: as the egg yolk increases, regardless of rate, the particle size decreases, Figure 25.

Control and reduction of particle size as a result of changing the differential pressure is important in forming a stable emulsion system. Optimizing the shear profile of the hydroshear or any other emulsification device is important in reducing the oil droplet size. This may make it possible to reduce the total oil used while maintaining a target rheological profile.

4.2.2 Influence of particle size on viscosity

As the processing rate (differential pressure over the hydroshear) was increased causing a decrease in particle size, no effect was seen on the viscosity. The particle size decreases as the processing rate (differential pressure) increases. Even as the particle size decreased the viscosity does not change, but remains flat. No correlation was seen between the particle size and the viscosity as is depicted in Figure 26. This correlation was seen with all nine formulations.

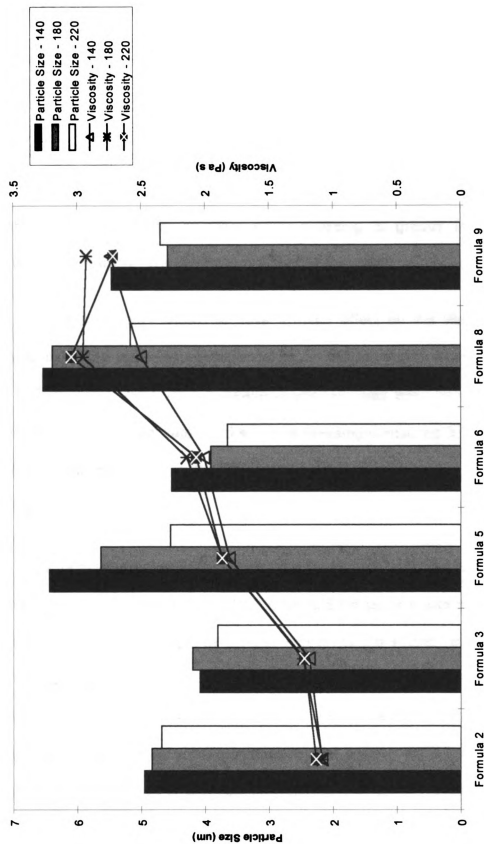


Figure 26 – Viscosity versus particle size effects with processing rate increases.

Chapter 5

Summary and Conclusions

The effect of formulation and particle size on the rheological properties of salad dressing suggests that the viscosity at 25 s^{-1} for this slightly time-dependent, shear-thinning behavior salad dressing is greatly influenced by xanthan gum. Particle size is affected by processing rate.

Temperature was shown to have a minor effect on the viscosity. Salad dressing exhibited temperature dependency as the temperature was increased from 5°C to 25°C . A 1.0 Pa s increase in viscosity was seen between the two temperatures. At a shear rate of 25 s^{-1} , for a dressing containing 3.0% egg yolks and 0.45% xanthan gum, at 220 psi, the viscosity was 2.72 Pa s at 25°C and 3.77 Pa s at 5°C .

The optimal rheological behavior was found with a formulation of 0.45% xanthan gum and 1.5% egg yolks. In this formula the particle size observed was $6.534 \mu\text{m}$ at 140 psi, $6.388 \mu\text{m}$ at 180 psi, and $5.172 \mu\text{m}$ at 220 psi. Varying the level of xanthan gum in the formulation affects the viscosity of the dressing system; hence, this ingredient must be very carefully controlled during production. While the egg yolks provide emulsion stability, as the egg yolk level is increased, concurrently with increasing xanthan gum levels, only a slight effect is seen on the apparent viscosity. Egg yolks have a very small effect on the

viscosity compared to xanthan gum.

Increasing the processing rate (differential pressure over the hydroshear) did not affect viscosity, but had a strong effect on the particle size. During processing, a differential pressure range of 140 – 220 psi could be utilized with minimal effects on viscosity. This fact means the manufacturer can operate over a wide range of pressure while still providing the desired product viscosity. The increase in process rate, due to an increase in differential pressure across the hydroshear, had the greatest effect on the mean lipid particle size, for all formulas.

Xanthan gum, egg yolks and processing rate all significantly affect particle size, however the processing rate has the greatest effect. High levels of xanthan gum and high levels of egg yolk result in a smaller particle sizes. As the egg yolk level was decreased, while the xanthan gum and processing rate were held constant the particle size decreased. Also as the processing rate (differential pressure over the hydroshear) was increased the particle size decreased and there was no change in viscosity. Even as the particle size decreased the viscosity does not change. Overall no correlation was seen between the particle size and the viscosity.

Chapter 6

Future Research

Future research in rheological characterization of salad dressings due to formulation and processing conditions could be expanded to include: further particle size testing on the existing system, measurement of the stability provided by egg yolks, measurement and comparison of other types of model dressing systems, ingredients, and emulsification equipment.

The comparison of the measurement of the particle size prior to the shear sweep and after the shear sweep, to determine the degree of permanent structural breakdown due to shear would provide further information on the system. This could also determine any aggregation, or change in particle size, that is occurring as a result of the shear rate sweep.

The stability provided by the egg yolks at each level could also be evaluated. This would yield a better understanding of the exact level of egg yolk. If proven to be significant or provide a cost savings the use of a variety of emulsifiers in dressing formulation could also be tested for product development or for product improvement.

The application and study of a wider variety of emulsification equipment, including the standard homogenizer, could be utilized to produce a product under a variety of processing conditions. This would determine the effects of different

processes on a control formulation. It would also be interesting to understand the relationship of formulation to multiple processing conditions and the resulting viscosity.

Bibliography

Association for Dressings and Sauces. Facts and Forklore – The History of Salad Dressings. [Online] Available

<http://www.dressings-sauces.org/folklore.html>, October 11, 2000.

Bistany KL, Kokini JL. 1983. Comparison of steady shear rheological properties and small amplitude dynamic viscoelastic properties of fluid food materials. J Texture Studies 14(2): 113-124.

Cadle RD. 1965. Particle Size. New York: Reinhold Publishing. p 1-30.

Carrillo AR, Kokini JL. 1988. Effect of egg yolk and egg yolk + salt on rheological properties and particle size distribution of model oil-in-water salad dressing emulsions. J Food Sci 53(5): 1352-1366.

Chang CM, Powrie WD, Fennema O. 1972. Electron microscopy of mayonnaise. J. Inst Can Sci Tech 5(3) 134-137.

Code of Federal Regulations. 21.CFR.161.

Coia KA, Stauffer KR. 1987. Shelf life study of oil/water emulsions using various commercial hydrocolloids. J Food Sci 52(1): 166-172.

Dickenson E. 1994. Emulsion stability. In: Nishinari K, Doi E, editors. Food hydrocolloids: Structures, properties and functions. New York: Plenum Press. p 387-396.

Elliott JH, Ganz AJ. 1977. Salad dressings- preliminary rheological characterization. J Texture Studies 8(3): 359-371.

Elejalde CC, Kokini JL. 1992. The psychophysics of pouring, spreading and in-mouth viscosity. J Texture Studies 23(3): 315-336.

Figoni PI, Shoemaker CF. 1983. Characterization of time dependent flow properties of mayonnaise under steady shear. J Texture Studies 14(4): 431-442.

Ford LD, Borwankar R, Martin Jr. RW, Holcomb DN. 1997. Dressings and sauces. In: Friberg SE, Larsson K, editors. Food emulsions. 3rd ed. New York: Marcel Dekker, Inc. p 361-412.

HAAKE. 1996. Viscotester VT 550 manual. Paramus, NJ.

Hasenhuettl GL, Hartel RW. 1997. Food emulsifiers and their applications. New York: Chapman & Hill. p 1-9.

Heil JR, Perkins WE, McCarthy MJ. 1990. Use of magnetic resonance procedures for measurement of oil in french-style dressings. J Food Sci 55(35): 763-884.

Hennoek M, Rahalkar RR, Richmond P. 1984. Effect of xanthan gum upon the rheology and stability of oil-water emulsions. J Food Sci 49(5): 1271-1274.

Hobart Corporation, Food Equipment. 2000. A200 Mixer. Ohio. p 1-4.

Horiba LTD. 1999. Laser scattering particle size distribution analyzer, LA-920. Bulletin:HRD-3639B.

Kiosseoglou VD, Sherman P. 1983. The rheological conditions associated with judgement of pourability and spreadability of salad dressings. J of Texture Studies 14(3): 277-282.

Kiosseoglou VD, Sherman P. 1983. Influence of egg yolk lipoproteins on the rheology and stability of O/W emulsions and mayonnaise 1. Viscoelasticity of groundnut oil-in-water emulsions and mayonnaise. J of Texture Studies 14(3): 397-417.

Krishnamurthy RG, Witte VC. 1998. Methods of making a reduced fat emulsified dressing. United States Patent 5,795,614. p 1-5.

Langton M, Astrom A, Hermansson A. 1999. Microstructure in relation to the textural properties of mayonnaise. In: Dickenson E, Patino editor. Food emulsions and foams: Interfaces, interactions and stability. New York: Plenum Press. p 367-375.

McClements DJ. 1999. Food emulsions: Principles, practice and techniques. New York: CRC Press.

Munoz J, Sherman P. 1990. Dynamic viscoelastic properties of some commercial salad dressings. J Texture Sci 21(4): 411-426.

Narwar, W. 1986. Lipids. In: Fennema O editor. Food chemistry. 2nd ed. New York: Marcel Dekker, Inc. p 139-244.

Orr C. 1988. Determination of particle size. In: Becher P, editor. Encyclopedia of emulsion technology, volume 3 basic theory, measurement, applications. New York: Marcel Decker. p 137-169.

Paredes MDC, Rao MA, Bourne MC. 1988. Rheological characterization of salad dressings 1: Steady shear, thixotrophy and effect of temperature. *J Texture Sci* 19(3): 247-258.

Paredes MDC, Rao MA, Bourne MC. 1989. Rheological characterization of salad dressings 2: Effect of storage. *J Texture Sci* 20(2): 235-250.

Peressini D, Sensidoni A, Cindio BD. 1998. Rheological characterization of traditional and light mayonnaises. *J Food Eng* 35(4): 409-417.

Phillips GO, Williams PA. 1990. *Gums and Stabilisers for the food industry* 5. Oxford: Oxford Univeristy Press.

Rao, MA. 1999. *Rheology of fluids and semisolid foods, principles and applications*. Aspen Publishers. Maryland. p 219-250.

Rao, MA, Steffe JF. 1997. Measuring yield stress of fluid foods. *Food Technology*. 51(2):50-52.

Rao, MA, Anantheswaran RC. 1982. Rheology of fluids in food processing. *Food Technology*. 36(2) 116 –126.

Rao, MA. 1977. Rheology of liquid foods – a review. *J Texture Studies* 8(2):135-168.

Sherman P. 1963. *Rheology of Emulsions*. Oxford: Pergamon Press.

Sherman P. 1967. Changes in the rheological properties of emulsions on aging II. *J. Colloid & Int. Sci.* 24:67.

Stang M, Karbstein H, Schubert H. 1996. Influence of emulsifier adsorption kinetics and emulsification machine construction on dispersity of oil-in-water emulsions. In: Dickenson E, editor. *Food Colloids: Proteins, Lipids and Polysaccharides*. New York: Plenum Press. p 382-392.

Stauffer CE. 1996. *Fats and oils*. Minnesota: Eagan Press. p 101-107.

Steffe JF. 1996. *Rheological methods in food process engineering*, 2nd ed. East Lansing, Michigan: Freeman Press.

Tiu C, Boger DV. 1974. Complete rheological characterization of time-dependent food products. *J Texture Studies* 5(3):329-338.

Tung MA, Paulson AT. 1995. Rheological concepts for probing ingredient interactions in food systems. In: Gaonkar AG, editor. Ingredient Interactions Effects on Food Quality. New York: Marcel Dekker, Inc. p 45-83.

Urlacher B, Nobel O. 1997. Xanthan gum. In: Imeson editor. Thickening and gelling agents for food. 2nd ed. London: Blackie Academic & Professional. p 285-311.

Van Den Temple M. 1963. Effect of droplet flocculation on emulsion viscosity. In: Sherman P, editor. Rheology of emulsions. New York: Mac Millan Company.

Walstra P. 1996. Emulsion stability. In: Becher P, editor. Encyclopedia of emulsion technology. Volume 4. New York: Marcel Dekker, Inc. p 1-59.

