RHEOLOGY AND STABILITY OF BEVERAGE EMULSIONS IN CONCENTRATED AND DILUTED FORMS

By

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August, 2006

A thesis submitted to McGill University in partial fulfillment of the requirements for the degree of Doctor of Philosophy

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Your file Votre référence
ISBN: 978-0-494-32246-8
Our file Notre référence
ISBN: 978-0-494-32246-8

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RHEOLOGY AND STABILITY OF BEVERAGE EMULSIONS

Dedicated to my beloved family Soudabeh,
Nassim, Nima, Shabnam and Neusha

ABSTRACT

Consumer's demand for more natural and high quality food products products, presenting health benefits, has increased over the years. Besides the nutritional aspects, an appealing appearance and texture is also required. Cloudiness or opacity (cloudy appearance) is an important citrus drinks property (orange, lime, lemon, etc.), since it gives natural fruit juice appeal. This property can be achieved through addition of clouding agents, which also help in uniform distribution of flavors throughout the liquid beverage. A common problem in the beverage industry is producing cloud or flavor emulsions that remain stable over the desired shelf life. Beverage cloud emulsions are oil-in-water emulsions to provide cloudiness and are prepared in a concentrated form, but diluted prior to the consumption.

Optical and rheological properties of beverage cloud emulsions as a function of water-phase and oil-phase concentrations were investigated. The specific gravity of phases, particle size distribution and creaming stability of prepared emulsions in diluted forms were evaluated. The rate of cloud emulsion creaming by determining the rheology of water phase, difference in specific gravities of the phases and droplet properties of the emulsion in presence and absence of weighting agents (sucrose acetate isobutyrate and brominated vegetable oil) or/and xanthan gum was studied. Flow and dynamic rheological properties of single-phases and emulsions containing modified starch and arabic gum as surface active hydrocolloids as well as xanthan and tragacanth as stabilizers gums were investigated. Finally, stability of cloud emulsions in orange juice drink was examined.

Oil-phase concentration had a significant effect ($P < 0.05$) on increasing the opacity of emulsion. Raise in viscosity of emulsions was more pronounced as oil concentration increased and shear thinning behavior of oil added emulsions was associated with droplet flocculation. Creaming in acidified sugar solution of 11^{0}Bx and pH 3 was observed when the oil-phase specific gravity decreased and sedimentation occurred at the lower viscosity of water phase. Addition of xanthan gum into the water phase decreased the flow behavior index (n) form 0.88 down to 0.31 and increased elastic modulus (G') over 20 times at elevated frequency ($\omega = 50$ rad/s) and perk up the stability of the emulsion.

The xanthan gum added emulsion indicated smaller average particle size and demonstrated 14 and 5 times slower separation compared to the emulsions without or with the addition of weighting agents respectively. Starch-xanthan stabilized emulsion and associated water phase at 1.5:1 surface active gum to oil ratio demonstrated viscoelastic behavior ($G' \geq G''$) with lower droplets coalescence and creaming rates, 0.013 nm/day and 0.02 percent backscattering/day respectively. Conversely, arabic-xanthan stabilized emulsion at 1:1 gum to oil ratio showed the highest rate of droplets coalescence at 0.057 nm/day and greater degree of creaming at 0.61 percent transmission/day. While creaming were associated with arabic gum stabilized emulsions, after 3 month storage, modified starch illustrated appropriate shelf stability with no sign of creaming in orange juice drink.

RÉSUMÉ

Les consommateurs exigent, de plus en plus, des aliments naturels possédant des propriétés nutritionnelles. L'opacité (apparence opaque) est une caractéristique importante des boissons à base d'agrumes (orange, pamplemousse, citron,..), car elle assure une apparence naturelle aux jus de fruits. Cet attribut visuel peut être obtenu grâce à l'incorporation d'agents opalescents à base d'huile végétale, tout en assurant une distribution uniforme des saveurs dans les boissons.

Un des problèmes commun de l'industrie des boissons est la production des émulsions à base d'huiles essentielles (saveurs) ou végétales (agents opalescents), lesquels doivent rester stables durant la période prédéterminée du produit sur les tablettes. Les émulsions à base d'opalescents pour les boissons sont des émulsions huile dans l'eau pour générer l'opacité. Elles sont préparées sous forme de concentré pour être ensuite diluées avant leur consommation.

Les propriétés optiques et rhéologiques de ces émulsions de boisson ont été examinées en fonction des concentrations des phases aqueuses et huileuse. La densité des phases, la distribution de tailles des particules dispersées et la stabilité au crémage des émulsions diluées ont été étudiées. La cinétique de crémage des émulsions a été étudiée l'étude combinée de la rhéologie de la phase aqueuse, la différence de densité des phases et les propriétés des gouttelettes d'huile de l'émulsion avec ou sans agents de poids (isobytyrate d'acétate de sucrose, huile végétale bromée). Les propriétés rhéologiques d'écoulement et dynamiques des phases individuelles et des émulsions contenant de l' amidon modifié ou de la gomme arabique comme hydrocolloides tensio-actifs et les gommes tracacanthe et xanthan comme agents stabilisants ont été examinées. La stabilité physique de ces émulsions opalescentes dans des boissons a été également quantifiée.

La concentration de la phase huileuse a eu un effet significatif ($P < 0.05$) sur l'augmentation de l'opacité de l'émulsion. L'augmentation de la viscosité des émulsions était plus prononcée avec l'augmentation de la concentration de l'huile et le comportement rhéofluidifiant de l'huile ajouté à l'émulsion était associé avec la floculation des gouttelettes. Le crémage dans une solution de sucre acidifié de 11 ^{o}Brix

et pH 3.0 était noté lorsque la densité de la phase huileuse diminuait et le phénomène de sédimentation apparaissait avec la diminution de la densité de la phase aqueuse. L'addition de la gomme xanthan dans la phase aqueuse diminuait l'indice d'écoulement (n) de 0.88 à 0.31 et, en parallèle augmentait le module (G') de 20 fois à des fréquences élevées (ω = 50 rads/s) et ainsi favorise la stabilité de l'émulsion.

Les émulsions contenant de la xanthan possédaient des tailles de particules réduites et des cinétiques de séparation de 14 et 5 fois plus lentes que les émulsions contenant aucun ou avec agents de poids, respectivement. Les émulsions à base de xanthan et d'amidon et les phases aqueuses correspondantes dans des proportions de 1.5:1 pour gommes tensioactives et/ huile démontraient des comportement viscoélastiques (G'/G''). De plus, le phénomène de coalescence était minimisé et la cinétique de crémage de 0.013 nm/jour et 0.02 backscattering (%)/jour, respectivement. Quant aux émulsions à base de xanthan et gomme arabique dans des proportions 1:1 pour gomme et huile, une cinétique accrue de la coalescence des gouttelettes était notée à 0.057 nm/jour ainsi qu'un crémage prononcée à 0.61 transmission (%)/jour. Le crémage apparaît essentiellement associé avec l'utilisation de la gomme arabique, après 3 mois d' entreposage, l'amidon modifié, quant à lui, résultait en une excellente stabilité physique sans aucun signe visible de crémage dans les boissons à base d'agrumes.

CONTRIBUTION OF AUTHORS

Most chapters of this thesis have been presented at several conferences and are in process of publication in peer reviewed journals. Three authors committed their involvement in preparation of this thesis. Ali R. Taherian is the Ph.D. candidate who planned and conducted the experiments, collected and analyzed the results, and wrote manuscripts for scientific publication. Dr. H. S. Ramaswamy is the thesis supervisor, under whose guidance the overall research was carried out. He was, as well, involved editing and reviewing the manuscripts. Dr. Patrick Fustier offered technical assistant and provided resources to carry out experiments at Food Research and Development Center.

LIST OF PUBLICATIONS AND SCIENTIFIC PRESENTATIONS RELATED TO THE THESIS

PART OF THIS THESIS HAS BEEN SUBMITTED FOR PUBLICATION:

1. Taherian A.R., Fustier P. and Ramaswamy H.S., 2006. Effect of added Oil and Modified Starch on Rheological Properties, Droplet Size Distribution, Opacity and Stability of Beverage Cloud Emulsions. Journal of Food Engineering, 77, 3:687-696.
2. Taherian A.R., Fustier P. and Ramaswamy H.S., 2006. Effects of added weighting agent and xanthan gum on stability and rheological properties of beverage cloud emulsions formulated using modified starch. Journal of Food Process Engineering 2006, Accepted October 2006, In Press.
3. Taherian A.R. and Ramaswamy H.S., 2006. Steady and dynamic shear rheological properties, and stability of non-flocculated and flocculated beverage cloud emulsions. Journal of Food Properties. Submitted, August 2006.

PART OF THIS THESIS HAS BEEN PRESENTED I SCIENTIFIC CONFERENCES:

1- Taherian A.R., Fustier P. and Ramaswamy H.S., 2004. Rheology and stability of beverage emulsions in the abcence of weighting agents. Food in 21st Century. Iranian Food Scientist Association Conference. Teheran, Iran, May, 2004.

2- Taherian A.R., Fustier P. and Ramaswamy H.S., 2004. Rheology of fluid foods "beverage emulsions". Texture and rheology of food products, La Fondation des Gouverneurs, St-Hyacinthe, November, 2004.

3- Taherian A.R., Fustier P. and Ramaswamy H.S., 2004. Effect of added Oil and Modified Starch on Rheological Properties, Droplets Size and Distribution, Opacity and Stability of Beverage Cloud Emulsions. ABET Conference March, 2005, St-Hyacinthe.

4- Taherian A.R., Fustier P. and Ramaswamy H.S., 2005. Rheology of beverage emulsions. Workshops in 3 major cities (Teheran, Esfahan and Shiraz), May 2005, Iran.

5- Taherian A.R., Fustier P. and Ramaswamy H.S., 2005. Physical stability of emulsions in simulated citrus beverage as an influence of hydrocolloids types. Association of professional nutritionist and experts in dysphagia, Ste-Anne Hospital, Quebec, November, 2005.

6- Taherian A.R., Fustier P. and Ramaswamy H.S., 2006. Rheology and Physical Stability of O/W Emulsions in Citrus Drink. La Fondation des Gouverneurs, St-Hyacinthe, Encapsulation et enrobage, CRDA, 1 février 2006.

7- Taherian A.R., Fustier P. and Ramaswamy H.S., 2006. Stability and Rheological Properties of Citrus Beverage Emulsions in Presence and Absence of Weighting Agents: Effect of Modified Starch & Xanthan Gum. CIFST, Montreal, Quebec, May 2006.

ACKNOWLEDGEMENTS

I would like to extend my appreciation and sincere thanks to Dr. H.S. Ramaswamy (Professor, Food Science Department), my thesis supervisor for his helpful support, keen intellect, encouragement, valuable guidance, and professional advices throughout the possession of my doctoral program. I am privileged to have been under his guidance.

Sincere thanks are also extended to my colleagues Dr. Patrick Fustier and Dr. M.R. Zareifard for their kind support, encouragement, and friendly advices through my PhD program. I am as well deeply grateful to the other distinguished members of my dissertation committee: Dr. Inteaz Alli, Dr. V. Yaylayan, and Dr. W.B. Marshall (From Food Science Department) and Dr. S. Grabowski (Senior Food Engineer, Food Research and Development Center, St-Hyacinthe, Quebec) who contributed their time, knowledge and expertise.

I express my gratefulness to Dr. F.R. van de Voort (Professor, Food Science Department), Dr. S. Kermasha (Chair, Food Science Department) Mr. Eby Noroozi for their encouragement and Ms. Lise Stiebel and Barbara Laplaine, Food Science Department secretaries, for all the professional administrative and secretarial help they extended to me.

I would like to thank Dr. Christian Toupin (Research Manager, Food Research and Development Center, St-Hyacinthe), Dr. André Bégin (Research Scientist, Food Research and Development Center, St-Hyacinthe), Dr. Michel Britten (Research Scientist, Food Research and Development Center, St-Hyacinthe) Dr. Kian Fadaie (International devision of Agriculture Canada), as well as Captain Réal Lavoie, Mr. Pascal Sauvé, Dr. Yousef Karimi and all my colleagues in FRDC for their encouragement and support.

I also wish to convey my profound gratitude to all in our Food Processing Group who have been helpful in the persuasion and completion of my study

This thesis is dedicated to my wonderful, lovely wife Soudabeh and my children, Nassim, Nima, Shabnam, and Neusha, also my beloved parents, to my brothers Reza and Abdolreza, and my sister Mariam who always remain in my heart.

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NOMENCLATURE

γ	Interfacial tension, dyne/cm
V	Volume of the emulsified liquid, m^3
d	Droplet diameter, µm
$\gamma_{o/water}$	Interfacial tension of a pure oil-water interface, dyne/cm
$\gamma_{surface\ active\ molecule}$	Interfacial tension in the presence of emulsifier, dyne/cm
π	Surface pressure, dyne/cm
r	Droplet radius, µm
ΔS	Increase in surface area, μm^2
T_K	Temperature, °Kelvin
T	Temperature, °C
U_{Stoke}	Velocity of creaming or sedimentation, $m\ s^{-1}$
θ	Contact angle
ρ	Density, kg/m^3
ϕ	Volume ratio
η	Viscosity, Pa.s
$\dot{\gamma}$	Shear rate, s^{-1}
n	Flow behaviour index
m	Consistency coefficient, Pa.
η_r	Relative viscosity
G'	Storage modulus, Pa.
G''	Loss modulus, Pa.
δ	Phase shift angle, G''/G'
σ	Shear stress, Pa.
G^*	Complex modulus, $G'+jG''$, Pa.
t	Time, s
a,b,c...	Variables
P	weight fraction of weighting agent (weight of weighting agent/weight of oil mixture),

G	Specific gravity of weighting agent,
E	Specific gravity of oil
$\eta_{app.Em}$	Apparent viscosity of the emulsion at a particular shear rate, Pa.s.
$\eta_{app.W.ph}$	Apparent viscosity of the water phase, Pa.s.
G(t)	Measured correlation point
N_{ca}	Capillary number
$N_{Re.p}$	Particle Reynolds number
ρ_w	Water phase density, g/cm^3
$[\eta]$	Intrinsic viscosity, Pa.s.
ϕ_c	Adjustable parameter related to the volume fraction at which the spheres become closely packed
ϕ_{eff}	Effective volume fraction
Sg_w	Specific gravity of water phase
Sg_{Em}	Specific gravity of emulsion
Sg_{oil}	Specific gravity of oil phase
λ	Time constant, s
N_0	Numbers of droplets per unit volume of emulsion at time 0
N_t	Numbers of droplets per unit volume of emulsion at time t
D_c	Rate of droplets coalescence (nm/day)
NTU	Nephelometric Turbidity Unit

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CHAPTER 1

INTRODUCTION

Consumer demand for more natural and high quality food products, presenting health benefits, has increased over the years. Besides the nutritional aspects, an appealing appearance and texture along with positive sensorial and rheological characteristics are also desired. As a result of this trend, the use of natural ingredients and those which do not compromise public health safety, are on the rise, while the synthetic ingredients are generally perceived as undesirable as they may be harmful and some are considered to be responsible for allergenic and intolerance reactions.

Cloudiness or opacity (cloudy appearance) is an important property in citrus beverages (orange, lime, lemon, etc.), since it gives natural fruit juice appeal. This property can be achieved through addition of clouding agents, which also help in uniform distribution of flavors in the liquid beverage. Cloud effect is due to interaction and diffusion of light by suspended oil droplets known as "beverage cloud emulsion". These emulsions are dispersions of one liquid phase in the form of fine droplets in a second immiscible liquid phase. The immiscible phase is usually oil and the continuous phase is water, so these emulsions can be classified as oil-in-water emulsions. Depending on the type of dispersion and when water becomes the dispersed phase, the emulsion is classified as water-in-oil emulsions (i.e., butter), Some other typical food emulsions are mild cream, ice cream, margarine, salad dressing, and meat emulsions (Barbosa-Cánovas et al., 1996).

Beverage emulsions, the traditional oil-in-water emulsions, have similar composition, preparation procedures, and physiochemical properties as compared to other typical food emulsions. Beverage emulsions are either flavor emulsions to provide flavor, cloudiness and color as in certain formulae or cloud emulsions to provide only cloudiness to the beverages such as fruit drinks, punches and sodas (Garti et al., 1991; Chanamai and McClements 2000; Chanamai and McClements 2001; Tan, 2004).

The oil phase (internal or dispersed phase) consists of some combination of vegetables oil, flavor oil, weighting agent, and antioxidants whereas the water phase (external or aqueous phase) consists of water, various types of hydrocolloids, citric acid, preservative, emulsifier, sweetener, and salts (Trubiano, 1995; Chanamai and McClements 2000; Tan 2004).

Tan (2004) and Buffo and Reineccius (2002) described the beverage emulsions as a unique class of emulsions which are consumed in a highly diluted form rather than in their original concentrated form. These emulsions are first prepared as a concentrate and are later diluted to produce the finished beverage. In addition to providing cloudiness and flavor, the physical stability of these emulsions in both concentrated and diluted forms is of critical importance.

It has been reported (Tan 2004) that the stability of emulsion in the concentrated form is much easier to achieve than in the diluted form. The reason is the higher viscosity of the concentrate due to the high concentration of hydrocolloids which act as stabilizers. This effect will decrease when the emulsion concentrate is dispensed in a second water phase (i.e, fruits drinks). For a beverage emulsion, therefore, the most critical criterion of stability is its stability in the finished beverage (diluted form).

Creaming or ringing, a common deterioration sign for beverage emulsions, is the formation of a whitish ring around the neck of the container. Oiling-off which is the formation of shiny oil slick on top of the product is also considered a quality defect. Both defects have been related to a range of physiochemical mechanisms that take place within the beverage emulsion. Gravitational separation, flocculation and coalescence are the results of these mechanisms. Lifting and striation are two others phenomena related to creaming. Lifting occurs when the emulsion in the bottle of beverage lifts up from the bottom and shows a clear layer of liquid below. Striation occurs when the emulsion in the bottle shows two or more distinctive layers of different degree of cloudiness (Tan, 2004; McClements, 2005).

The origin and nature of these instability mechanisms are categorized as:

Gravitational separation: This is due to the fact that the oil droplets in an emulsion have a density different from that of the liquid which surrounds them and so a net gravitational force acts upon them (Dickinson 1992). If the droplets have a lower density than the surrounding liquid, they have a tendency to move upward which is referred to as creaming. Conversely, if they have a higher density than the surrounding liquid they tend to move downward which is referred to as sedimentation (Chnamai and McClement, 2000a; Chnamai and McClement, 2001; Tan, 2004; McClements, 2005, Taherian et al., 2006). The densities of most edible oils are lower than that of water and so there is a tendency for oil to accumulate at the top of an emulsion and water at the bottom. Gravitational separation could also enhance flocculation and coalescence by causing droplets to come into close contact for extended period.

A rare situation which can be found in beverage is sedimentation or downward creaming, unless the added amount of weighting agents (density adjuster) increases the density of oil fraction to make density gradient, $\rho_{oil} - \rho_{water}$, to become a positive value (Taherian et al., 2006). It also happens when the weighting agents separate from the oil droplets and become precipitated in the beverages.

Flocculation: This results from the existence of attractive forces between the oil droplets. There are no changes in basic droplet size or distribution but the buildup of aggregates of droplets within the emulsion (Tadros and Vincent 1983).

The forces which draw these droplets together to form aggregates are primarily the long-range London-van der Waals forces and electrostatic forces around the droplets (Tan, 2004). In the case of beverages, when the intermediate droplets concentration is low and flocs do not substantially interact with one another, flocculation tends to increase the creaming velocity because the flocs have a larger effective size than the individual droplet and because the density difference between the flocs and the surrounding liquid is reduced. In concentrated emulsion, before introducing to the final beverage solution, the viscosity may increase when flocculation occurs. In the finished beverage system, the droplet concentration is so low that the flocculation is often reversible. The aggregates can be readily redispersed because the interaction forces between the droplets are week. Flocculation, however, accelerates the rate of gravitational separation in beverage emulsion which is undesirable because it reduces the shelf life (Tan and Holmes, 1988; Tan, 2004; McClements, 2005).

Coalescence: This is the process whereby two or more oil droplets merge together to form a larger droplet. In this stage, there is localized distribution of sheathes around the neighboring droplets of the aggregates and this results in a change in the initial droplet size distribution. Coalescence thus involves the elimination of the thin liquid film of the water phase which separate two droplets in contact in an aggregate or a close-packed array (Tan, 2004; McClements, 2005; Tadros and Vincent, 1983). Coalescence causes emulsion droplets to cream or sediment more rapidly because of the increase in their size. The use of a proper hydrocolloid in water phase could prevent the emulsion to reach this stage. The reason is that the hydrocolloid, such as gum arabic, has a good film-forming ability and will form film around the oil droplets in addition to providing viscosity in the water phase (Tan, 1998; Tan, 2004).

The rate of creaming could also be enhanced by other factors such as: oil droplet viscosity, polydispersity, electrical charge and zeta potential, particle size characterization, surface activity and emulsion rheology.

Stokes' law indicates that the velocity at which droplet moves is proportional to the square of its radius. Therefore the stability of an emulsion can be enhanced by reducing the droplet size. This is especially true for beverage emulsions which have to be stable in both concentrated and diluted forms. Consequently, the size distribution of the droplets has a great effect on stability of emulsions. For beverage emulsions, the determination of particle size distribution could serve two purposes; first estimation of the quality of the emulsion concentrates, and second prediction of the stability of the emulsion in the finished product. For example, in a beverage a particle of 0.1 μm in diameter will travel upward 100 times more slowly in the bottle than a particle of 1.0 μm in diameter (Tan and Wu Holmes, 1988).

The interfacial region which separates the oil from the aqueous phase has also a direct influence on the bulk physiochemical and sensory properties of food emulsions, including their formation, stability, rheology and flavor. The surface active molecules such as proteins, polysaccharides, alcohols and surfactants which can accumulate at the interface are able to alter the properties of the emulsions. These surface-active molecules are able to adsorb to the surface of the emulsion droplets and form a protective membrane that prevents them from aggregating (flocculating and/or coalescing) with one another. In addition, an emulsifier reduces the oil–water interfacial tension, thereby facilitating the disruption of emulsion droplets during homogenization (Walstra, 1993 and Walstra 2003; McClements, 2005).

Rheology of emulsion and its water phase is one of the most important study which helps to understand the physical stability of emulsion. Although the oil is responsible for providing the opacity in beverages, one of the main reasons why the oil is used in the form of emulsion rather than in its original state is that a much wider range of rheological characteristics and consistencies can be achieved with an emulsion. The water phase of an emulsion contains polysaccharide which could provide specific rheological properties affecting stability of the emulsion. For instance, many hydrocolloids used to prepare emulsion are shear-thinning, that is, they have a high viscosity at low shear rates, and the viscosity decreases dramatically as the shear rate is increased. This property is important because it means that the droplets are prevented from creaming, but that the food emulsion still flows easily when poured from a container.

While substantial work has been done on studying emulsions and factors that influence their stability, the process of making emulsions is still treated more as an art than a science. Product and legal constraints put severe limits on the materials that can be used to insure emulsion stability, particularly regarding the introduction of weighting agents into the oil phase (Buffo et al., 2001). Weighing agents (density-adjusting agents) are lipophilic compounds with specific gravity greater than 1. Sucrose acetate isobutyrate (SAIB), Ester Gum (EG), and brominated vegetable oil (BVO) are most widely used weighting agents. These products have limitation of use because of perceived health risk disadvantage, rosin-like taste and prone to oxidative instability (FAO/WHO joint reports, 1970, 1975, 1996 and 1997).

Thus, the stability concern of beverage emulsions is a chronic problem faced by the flavor and beverage industries. The main focus of this research is characterization of rheology of beverage emulsions for achieving better stability of these products without relying on the use of weighting agents both in the concentrated and diluted forms.

The specific objectives are detailed below:

I. To investigate the effect of added oil and modified starch on the opacity, specific gravity, rheological and droplets properties of the oil and water phases, alone and in form of emulsions, in the presence of weighting agents. The aim is to find out the relationship between investigated properties and stability of emulsions in concentrated and diluted forms,

II. To compare the physical properties of emulsions with and without the weighting agents, and find alternative replacements for the health restricted weighting agents. With this regards, improve the rheological properties of water phase via addition of high shear thinning and elastic xanthan gum and examine the consequent shelf stability

III. To explore the contribution of the rheological and surface properties of water phases to the stability of emulsion in concentrated and diluted forms (simulated juice drink) in the absence of weighting agents. In addition, to study the resulting emulsion systems over a period of two weeks to identify the changes in rheological and particle size properties associated with storage stability, and

IV. To evaluate the ability of formulated emulsions to confer cloudiness and stability in orange drink in the absence of weighting agents. The aim is to use combinations of naturally occurring components and to overcome health restrictions on the formulation of beverages.

CHAPTER 2

LITERATURE REVIEW

2.1 Food emulsions

Definition

Emulsions (oil/water or water/oil) can be defined as macroscopic dispersions of two immiscible liquids, one of which forms the continuous phase of the system and the other the dispersed phase. In most foods, the diameters of the droplets usually lie somewhere between 0.1 and 100 micron (Dickinson, 1992, McClements, 2005).

The emulsions used in the agri-food sector are among the most complex. They are also the most difficult to stabilize. Foods exhibit an infinite number of microstructures in the various compositions of proteins, carbohydrates, fats and lipids. Research is increasingly focussing on the impact of the principles of the science of colloids and surfaces on the technical problems inherent to the agri-food sector.

Amphiphilic molecules play a key role in the stabilization of many food colloids. It is therefore essential to properly understand the interface behaviour of these molecules to ensure the stability of foods. Surfactants and emulsifiers are used in a wide range of food products to play very specific functions in order to stabilize emulsions. Examples include improving the stability of emulsions to minimize agglomeration and stabilize aerated systems, modifying the texture and consistency of fat-based products by altering the polymorphism behaviour of fats and the structure of crystals, improving shelf life against the retrogradation of starch products by forming complexes with amylose, the formulation of beverage emulsions to ensure the distribution of flavour and opalescence in beverages, etc (Marangoni, 2002; Bais et al., 2005; Valdez et al., 2005, Paraskevopoulou et al., 2005).

Emulsions are considered macroscopic dispersions of two immiscible liquids, one of which forms the continuous dispersing phase of the system and the other, the dispersed phase. A distinction is made between oil-in-water (O/W) emulsions, where water is the continuous phase, such as beverage emulsions, and water-in-oil (W/O) emulsions, where oil is the continuous phase, such as margerin.

Emulsions are formed by the action of emulsifying agents, which create a layer at the interface, reducing the interfacial tension between two immiscible liquids. Emulsifying agents include low-molecular weight surfactants, such as ionic and non-ionic molecules, and macromolecules, such as proteins, carbohydrates and other polymers. The oil content of emulsions ranges from 0.5% (skim milk) to 80% (mayonnaise). This explains why the methods used to stabilize emulsions can vary from one product to another. Three concepts of stabilization are generally recognized: 1) steric stabilization, including the physical characteristics at the interface, referred to in the literature as the "skin effect," 2) charge stabilization or the "zeta potential," including the surface charge of a dispersed medium, which will result in an electrostatic repulsion and, finally, 3) the contribution of rheology control through the viscosity of the continuous phase, or the "liquid effect."

Some products (W/O emulsions) are stabilized by steric and viscous effects to prevent gelation and creaming; while liquid or semi-solid salad dressings (O/W emulsions) are stabilized against coalescence by the use of hydrocolloids and proteins to form an effective cover or steric membrane and to control rheological behaviour. For each product, a very specific emulsion is therefore required to ensure its physical stabilization (Diftis et al., 2005).

Other much more complex types of emulsions, such as multiple emulsions, i.e., a double emulsion in which water is the continuous phase and a W/O type emulsion is the dispersed phase, are also stabilized in the food sector (Stang, 1996). An example of a W/O/W emulsion would be low-fat mayonnaise, where the fats of an O/W emulsion are partially replaced by water (Matsumoto, 1986).

Regarding the immiscibility of these two components, an emulsion is a thermodynamically unstable system. Emulsification therefore involves adding a certain amount of energy to the system to create interfaces between the two media while, over time, the system tends to return to its thermodynamically stable state.

In order to successfully carry out the emulsification process, it is therefore necessary to:

a) implement a mechanism for creating an interface by providing a certain quantity of energy to the emulsion by means of mixers, homogenizers and colloid mills.

b) slow down the reverse process as much as possible, since once mechanical mixing stops, the droplets will tend to rise to the surface by gravity, unless surface-active agents or emulsifiers are incorporated in the mixture.

Theoretically, the energy necessary to create an interface is given by Friberg, (1976)

$$E = \gamma \times \Delta S \qquad \text{and} \quad \Delta \mathrm{S} = \frac{6\mathrm{V}}{\mathrm{d}} \tag{1}$$

where γ is the interfacial tension, ΔS is increase in surface area, V is volume of the emulsified liquid and d is the droplet diameter.

The interfacial tension depends heavily on the type of present components (dispersed and dispersing medium, emulsifier, macromolecules, etc.). The energy E is, therefore, inversely proportional to the diameter of the droplets. However, it is recognized that the energy that must be provided for the emulsion is significantly higher than that indicated by the formula since other factors such as the type of mechanical agitation (colloid mill versus homogeniser for example), the difference in density between the two immiscible liquids and the viscosity of the continuous phase have a significant impact on the energy required (Friberg, 1976; McClements 2005).

2.2 Emulsion stability

Definition

Emulsion stability is a measure of the rate at which an emulsion creams, flocculates or coalesces. The rate of these changes can be measured by determining the rheology of component phases, oil droplet particle size and distribution and density difference of water and oil phases. A stabilizer can be defined as single or mixed chemical component that confers long-term stability on emulsions. Stabilisers may operate by acting as emulsifiers or as texture modifiers (Huang et al., 2001 and McClements, 2005). Emulsifiers are surface-active ingredients that adsorb to the surface of emulsion droplets and prevent them from aggregating. Texture modifiers are ingredients that increase the viscosity of the continuous phase of emulsions so as to slow down the gravitational separation of the droplets. Polysaccharides are widely used as thickening, emulsifying and stabilizing agents in the beverage cloud emulsions for their biocompatibility, biodegradability, and non-toxicity. Polysaccharides are natural polymers which can display different behaviors once dissolved in water owing to their molecular structure. In particular, their mechanical properties are influenced by the polysaccharide backbone and its side subunits. The type of bond between sugar rings can result in random coil shapes (such as dextran solutions), semi-flexible chains (such as cellulose derivative solutions), or interrupted helical structures such as amylose (Lapasin and S. Pricl, 1995; Morris et al., 1996).

Polysaccharides (hydrocolloid gums) are mostly hydrophilic polymers, which do not exhibit significant surface activity (Dickinson and Stainsby, 1998). However, as a stabilizer in food emulsions, some gums were found to migrate slowly to the air–water and oil–water interfaces and exhibit some surface and interfacial activities (Garti, 1999). These researchers have further suggested that hydrocolloid gums, although water-soluble, rigid and very hydrophilic, can precipitate/adsorb onto oil droplets and sterically stabilize emulsions against flocculation and coalescence. Polysaccharides are frequently employed to stabilize aqueous suspensions or O/W emulsions, and. There are different mechanisms by which these polymers can stabilize an emulsion. Thus, the formation of an extended hydrogel network reflects into high viscosity of the continuous phase at low shear, thus slowing down the droplet motion (Whistler, 1993); such a polymeric structure surrounds the oil droplets, ensuring effective steric hindrance of their coalescence (Whistler 1993, McClements 1999). Another contribution to the stabilization is provided by non-adsorbing depletion mechanism, due to the pronounced hydrophilicity, low flexibility, and low surface activity of these polymers (McClements, 1999 and Garti et al., 1999). Finally, due to the presence of some impurities, such as hydrophobic groups or proteinic moieties, an additional stabilizing effect can derive from the formation of a viscoelastic adsorbed layer (Garti et al., 1999).

Polysaccharides and surfactants act through different stabilization methods once added to the continuous phase of an emulsion, so that simultaneous use of these additives should improve the stability of these systems. Moreover, surfactants are also employed as rheology controllers of the polysaccharide hydro-gel, in order to tune the viscoelastic properties of the system and obtain the desired mechanical characteristics for the final product. Nevertheless, when all these additives are employed together, incompatibilities, preferential adsorption of one additive respect to the others (Wilde, 2000; McClements 2005), or the formation of polysaccharide–surfactant complexes can have a detrimental effect on the stability of the emulsion, inducing phase separation (Wilde, 2000). To obtain an emulsion with good mechanical and stabilizing properties, it is necessary to consider all these aspects and, consequently, the choice of the constituent components should be made carefully (Dickinson, 2003).

2.3 Surface activity

The interface of each droplet has free surface energy (Chanamai, 2000; McClements, 1999; Dickinson, 1992; Krog, 1977). A system is thermodynamically stable when this free surface energy is at a minimum. Reduction of the interfacial area, decreasing this free surface energy, is therefore an impulsive phenomenon (Wastra, 1996). Any reduction in the total interfacial area will result in fusion of the droplets until complete separation of the two phases occurs. This is the destabilization of an emulsion. An emulsion is therefore a system where the number and arrangement of the droplets change during storage. Some emulsions (such as cake batter) have a limited lifespan, while others (such as salad dressings, beverage emulsions, etc.) must remain stable for months. Stability therefore implies that there are few structural changes. Hence, this is an objective to be attained through an in-depth knowledge of colloidal dispersions, more specifically the role and functional properties of stabilizers and emulsifiers (Garti and Rerchman, 1993; Parker, 1991).

As mentioned earlier, three main factors can be distinguished that will influence the stability of an emulsion: the charge effect, the steric effect and the viscosity effect. The viscosity effect refers to the viscosity contribution of the continuous phase; a very viscous solution can reduce the number and energy of collisions between droplets and thereby inhibit the kinetics of coalescence. In the case of an oil/water emulsion, the difference in density between the continuous and dispersed phases can be minimized by using oil whose density is similar to or higher than water in order to reduce the vertical creaming movement.

In addition, in an emulsion, the dispersed particles will have a surface charge, the zeta potential, which will permit electrostatic repulsion between particles. This repulsion will also decrease the kinetics of coalescence of the particles. The potential energy of this repulsion depends on the magnitude of the surface charge and also on the ionic strength of the continuous phase. The presence of proteins at the surface can alter the surface charge. However, the zeta potential is not equal to the sum of the net charge of the proteins and uncovered oil particles (Riddick, 1968).

It should be noted that the value of the oil/water interfacial tension can also indicate the elasticity or rigidity of the surface, which will affect the contact angle between the colliding particles. The magnitude of this angle can give us an indication of the tendency of the particles to coalesce during a collision, since a small contact angle corresponds to a high interfacial tension and vice versa (Friberg, 1978).

The reduction of interfacial tension by the presence of a surface active molecule is referred as surface pressure which is (McClements, 2005):

$$\pi = \gamma_{\text{o/w}} - \gamma_{\text{surface active molecule}} \tag{2}$$

where $\gamma_{\text{o/water}}$ is the interfacial tension of a pure oil-water interface and $\gamma_{\text{surface active molecule}}$ is the interfacial tension in the presence of emulsifier. Therefore an increase in surface pressure could be related to the activity of surface active molecule presented at the emulsion.

2.4 Factors influencing emulsification

At the interface between the two immiscible phases, the molecules are subject to unequal forces. A strong tension is therefore created, which is called the interfacial tension. During the formation of the dispersed system, it is necessary to increase the interfacial area. Emulsification is a process whereby large droplets are broken into small droplets in order to reduce the interfacial tension. To reduce the size of a droplet diameter, the mechanical stress to be applied must exceed the pressure of the droplet. Hence, the smaller the droplet, the more difficult it is to break.

As discussed previously, several factors will influence the quantity of energy to be applied for achievement of the desired size. In addition to the viscosity parameters of the continuous phase and the differences in density of the two phases, these factors may also include the volume of the dispersed phase, the rate of adsorption of the oil, the temperature (an increase will reduce the viscosity of the oil), the pH and the ionic strength of the aqueous phase, the type of oil (melting point and hydrophobicity), the concentration and type of emulsifying agents and their emulsifying properties (Wastra, 1987; Dickinson, 1992).

2.5 Emulsion instability mechanisms

The destabilization of an emulsion occurs according to different processes of varying importance that influence each other and occur more or less simultaneously (Fennema, 1996).

2.5.1 Molecular diffusion and disproportionation

The majority of surfaces or interfaces found in the food emulsions are curved rather than planer. The curvature of an interface alters its characteristics in a number of ways. According to Hunter (1986), the interfacial tension tends to cause an emulsion to shrink in size so as to reduce the unfavourable contact area between the oil and water phases. As the droplet shrink, there is an increase in its internal pressure because of the compression of the water molecules. Eventually, equilibrium is reached where the inner stress due to the interfacial tension is balanced by the outer stress associated with compressing the bonds between the liquid molecules inside the droplet. This depends on the diffusion of the molecules of the dispersed phase from small droplets to large droplets, from high pressure to lower pressure. The internal pressure of the droplets or bubbles increases with decreasing droplet size according to the Laplace equation (McClements, 2005):

$$\Delta P = \frac{2\gamma}{r} \tag{3}$$

where γ is interfacial tension and r is droplet radius.

The pressure, and consequently the solubility of the dispersed material, is higher for smaller droplets. This is more specifically referred to as Ostwald ripening. This process will continue until the fine droplets disappear. The rate of diffusion depends on the solubility of the dispersed phase in the continuous phase (Halling, 1981; Acton et al., 1971). In addition, the solubility of the dispersed phase in the continuous phase will increase with the volume of the dispersed phase. For example, the water solubility of oil increase as the radius of an oil droplet decreases (Dickinson 1992, McClements, 2005):

$$\frac{S}{S^*} = exp\left(\frac{2\gamma v}{rRT_K}\right) \tag{4}$$

where S is the water solubility of the oil in the droplet, S^* is the water solubility of bulk oil, v is the molar volume of the oil, r is droplet radius, R is the gas constant and T_K is temperature (Kelvin).

This will also result in accelerated molecular diffusion of the dispersed phase in the surrounding medium and/or accelerated diffusion of relatively small droplets into relatively large droplets (Princen, 1979). This process is influenced by the solubility of the dispersed phase in the continuous phase and also by whether or not surfactants are present. By lowering the interfacial tension, surfactants decrease the pressure differential, which has the effect of reducing the tendency to diffusion. Surfactants can also play a role by sterically preventing the molecules in the dispersed phase from crossing the interface (Friberg, 1976).

Owing to the very low solubility of oil in water, this destabilization process is very limited. This explains why the destabilization process, i.e., creaming, flocculation and coalescence, are the main causes of destabilization of an O/W emulsions. However, a better understanding of the origin and nature of these instability mechanisms would enable beverage manufacturers to develop products with enhanced shelf lives. Pursuing the sources of instability aspects is discussed:

2.5.2 Creaming (ringing)

In creaming, the two liquids separate under the action of gravity. The best-known example of this de-emulsification process is that of milk in cream and in skim milk. Creaming is not a breaking of the emulsion, but rather a separation of the emulsion into two emulsions, one which is richer in the dispersed phase and another which is poorer in the dispersed phase than the original emulsion. The oil droplets then form a dense layer at the surface of the emulsion without change in droplet size. This process is the result of the difference in density between the oil and the aqueous phase. The rate of ringing or creaming of an oil droplet in sugar solution may be determined by equating the force of gravitation with the opposing hydrodynamic force as given by Stokes' law (Chanamai. and McClements, 2000; Chanamai. and McClements 2000a; Chanamai and McClements 2001; Tan, 2004; McClements 2005; Taherian et al., 2006):

$$U_{Stoke} = \frac{2\,g\,r^2(\rho_{oil} - \rho_w)}{9\eta_w} \tag{5}$$

where U_{Stoke} is the rate of creaming or sedimentation, g is the acceleration of gravity, r is the oil droplet radius, ρ_{oil} is the density of the oil phase, ρ_w is the density of the water phase, and η_w is the viscosity of the water phase.

The sign of U_{Stoke} determines whether the particle move upward (+) or downward (-). An example of the use of Stokes' law is formulation of soft drink with orange flavor emulsion. Typically orange oils have a density of 0.85 g / cm^3, and the sugar solution in the soft drink has a density of 1.04 g / cm^3 for a 10% sugar solution or 1.048 g / cm^3 for a 12% sugar solution. Applying these density data to Stokes' law the resulted U_{Stoke} carries a negative sign, which indicate the emulsion will ring.

The Stoke equation also demonstrates that the more the droplets are uniform, the slower the creaming process. This phenomenon is very pronounced if the two phases have very different densities where the dispersing or continuous medium is very fluid.

However, this equation applies only in the case of the motion of a single droplet. Since most food emulsions are polydispersed (i.e., they contain a series of particles of different sizes), a more appropriate mathematical treatment must therefore be used to address the different creaming kinetics for each droplet.

In this review, I will limit myself to mentioning that this law provides the same conclusions as Stokes' law with respect to the effect of the reduction in droplet size and the increase in viscosity of the continuous phase on the kinetics of separation. We must also consider the flow of the liquid in the opposite direction and, especially, hydrodynamic interactions between the droplets, and the different sedimentation rates depending on the size of particles that promote collisions. This creaming process occurs for O/W emulsions of low volume ratio or "ϕ" (volume percent of the dispersed phase). The droplets can thus rise to the surface of the continuous phase. In the opposite case (highϕ), it is instead the dispersing phase that flows around the droplets; this is then referred to as drainage.

2.5.3 Flocculation

Flocculation refers to the aggregation of droplets in three-dimensional clumps, under the influence of attractive forces, without altering the original size of the droplets, i.e., all the droplets retain their integrity and remain individual entities. This phenomenon occurs when there is not a sufficiently large differential in the densities of the immiscible liquids or when the viscosity of the medium is too high to cause sedimentation. The droplets can nonetheless aggregate due to Brownian motion.

Friberg (1976) estimated that in an oil/water emulsion (1:1), the time to reduce the number of droplets by half is 1 second, in the absence of an energy barrier of approximately 25 kT (k: Boltzmann's constant, T: absolute temperature). To significantly extend shelf life (for example from six months to a year), this barrier must be adjusted (Parker, 1987).

Halling (1981) reported that the DLVO theory, from the names of its main authors (Desjaguin, Landau, Verwey and Overbeek), provides a more detailed explanation of this energy barrier concept. Indeed, the stability of colloidal dispersions depends on two types of long-distance interactions between dispersed particles, namely the Van der Waals attraction and the electrostatic repulsion between the electrical double layers of the same sign.

To preserve the stability of an emulsion, the repulsive forces must therefore be as strong if not stronger than the Van der Waals forces in order to keep the droplets apart. In an emulsion, this role can be performed by the action of ionic emulsifiers such as proteins and other compounds. In addition, the electrical charges on the droplets in the emulsions are generated by ionization, absorption or frictional contacts. In the absence of emulsifiers, only frictional contacts are capable of charging the droplets. Note that in an O/W type emulsion, since the water has a higher dielectric constant than the oil, the water will be positively charged and the oil negatively charged. Charges of the same sign at the surface of the droplets will cause repulsion between them (Dickinson and Stainby, 1982).

In addition, the larger the droplets, the stronger the Van der Waals attractive forces will be. The DLVO theory combines the repetitive effect of the electrical double layer with the Van der Waals attraction in a two-dimensional mathematical model which explains the stability of emulsions in terms of an energy barrier that must be overcome to prevent physical instability (Friberg, 1976; Parker, 1986). The sum of these two energies yields the total energy of interaction between the particles, which depends primarily on the distance between the particles. The DLVO theory is further discussed in section 2.6.7 (Electrical charge and zeta potential).

As flocculation proceeds, there is a decrease in the total number of particles (monomers + aggregates) in the emulsion, which can be described by the following equation (McClements, 2005):

$$\frac{dn_T}{dt} = -\frac{1}{2}FE \tag{6}$$

where dn_T/dt is the flocculation rate, n_T is the total number of particles per unit volume, t is the time, F is the collision frequency, and E is the collision efficiency.

In the case of emulsions containing liquid particles, it is also important to take into account for the energies of short-distance interactions such as the chemical bonds between interface molecules in the form of ionic, covalent or hydrogen bonds, physical attachments of molecules by dipolar interaction, hydrophobic bonds formed by the association of two non-hydrated species in a aqueous medium, etc. Certain factors affecting flocculation must be delayed by a high viscosity and a strong electrostatic charge. The type and concentration of the surfactant, the presence of electrical charges at the interface (ionic surfactant) and the electronic forces of attraction and repulsion represent cases of repulsion between particles. In cases where the surfactant has excess long-chain molecules in continuous medium, bonds between droplets may also be formed (Nielloud, 2000; Dickinson, 1982).

2.5.4 Coalescence

Brownian coalescence corresponds to the collision of small droplets that will clump together following creaming or flocculation (Wastra, 1993). Breaking due to the thermodynamically spontaneous coalescence of the droplets results in the formation of increasingly large droplets until the two phases separate; the surface of the interface is then at a minimum. In this case, the droplets must remain in contact for a certain time, hence a simple collision due to Brownian motion is not sufficient to ensure re-dispersion of the particles. In order to minimize this phenomenon, use of a surfactant to reduce the interfacial tension is recommended. This leads to a smaller decrease in the free energy resulting from the reduction in surface area caused by coalescence. The dynamic surface properties also play an important role, hence when two droplets clump together, integrity is ensured by the dynamic surface properties; for example, there is a positive correlation between the shear resistance of a film and its stability (Dickinson and Stainby, 1982).

Flocculation, disproportion, coalescence and creaming are phenomena which can occur simultaneously (Krog, 1977) and result in coalescence, which is undoubtedly the most serious problem of destabilization of an emulsion, namely the formation of two separate layers. Any increase in collision speeds, flocculation, and reduction in the mechanical integrity of the interfacial surface will have the effect of altering the kinetics of coalescence.

2.6 Factors affecting emulsion stability

Numerous factors will affect the movements of particles and more specifically the kinetics of creaming or sedimentation. Dickinson (1988) described the major factors with their relative impact on creaming, flocculation, coalescence and rheology.

2.6.1 The physical nature of the interfacial film

The oil droplets in the dispersed phase are in constant motion due to Brownian motion and creaming effects. Consequently, collisions between dispersed droplets are frequent. If the interfacial film between the two droplets is broken during these collisions, the droplets will then coalesce and form large particles. This reduces the free energy of the system. It is therefore essential that the interface be characterized by a film of high elasticity. Purified surfactants generally produce interface films that are loosely packed and hence not too strong mechanically. This explains why the combination of two or more surfactants produces more stable emulsions.

2.6.2 The steric or electrical barrier

As discussed earlier, the presence of a surface charge on the droplets constitutes an electrical barrier. In emulsions prepared with non-ionic surfactants, the charge on the oil droplet may be generated by absorption of the ions of the continuous phase or by friction contacts between the droplets and the continuous phase. The presence of the surfactants' lateral chains can modify the behaviour of the droplets in proximity. In this way, steric hindrance can prevent the coalescence of the particles of the dispersed phase. Note also that the oil can acquire charges through the ionization of local groups at the surface, such as the use of gum arabic, which has COO^- groups, as an encapsulant.

2.6.3 Viscosity and rheological behaviour

Three categories of studies are of vital importance when we consider food emulsions: a) formation of the emulsion, b) stability of the emulsion, and c) use of this emulsion for a given product. Viscosity is an essential parameter in each of these cases. When an emulsion is produced by homogenization, then the viscosity, initially of the dispersed phase (oil) and subsequently of the total emulsion, controls the efficiency of droplet rupture. In addition, kinetic stability also depends on viscosity, since higher values delay coalescence.

A high-viscosity vegetable oil initiates the rupture of the oil droplets very significantly, while any increase in the viscosity of the continuous phase reduces the efficiency of droplet rupture, although to a lesser degree (Pandolfe, 1981).

The rheological properties of an O/W interfacial film are far from being a negligible factor: droplet deformation is controlled by this interfacial membrane, which also controls the rheology of the emulsion (Chen et al., 1993; Oosterbroek et al., 1981). The viscosity of an emulsion depends on the concentration of the dispersed phase, particle size distribution and particle-particle interactions. The latter are a function of pH/ionic strength, temperature as well as the nature of the continuous phase (Princen, 1983). In addition, it appears that this interaction can be addressed, at least partially, by measuring the contact angle between adjacent films. Any increase in the viscosity of the continuous phase by the addition of gums to the continuous phase will reduce particle motions, resulting in fewer collisions.

2.6.4 Oil droplets viscosity

Unlike a rigid droplet, the liquid within a droplet can move when a force is applied to the surface of the droplet. This reduces the frictional forces that opposes the movement of a droplet and increase the creaming velocity as (Dickinson and Stainsby 1982):

$$U = U_{Stokes} \frac{3(\eta_{oil} + \eta_w)}{(3\eta_{oil} + 2\eta_w)} \tag{7}$$

If the viscosity of the droplet is much less than that of the water phase ($\eta_{oil} \ll \eta_w$) the creaming rate is 1.5 times faster than that predicted by Stokes' law. Conversely, when the viscosity of the oil droplet is much greater than that of the water phase ($\eta_{oil} \gg \eta_w$) the rate of creaming will be the same as Stokes' law (McClements, 2005).

Since Stokes' law has been used to calculate the velocity of an isolated rigid spherical particle in an ideal liquid, it is then necessary to consider the droplet acting as rigid spheres by surrounding them with viscoelastic interfacial layer which prevents the fluid within them from moving (Walstra 1993).

2.6.5 Particle size distribution

According to Stokes' law, the formation of small droplets in an emulsion promotes stability since the kinetics of emulsion predicts that small particles take more time to increase in volume. Particle size distribution is also important. The smaller this distribution, the more stable the emulsion will be, since large particles have more limited interfacial surfaces per unit of volume than small dispersed particles. When an emulsion has large and small particles, a "bimodal" uniform size distribution prevails; the largest particles tend to grow at the expense of the smallest, owing to the increase in thermodynamic stability. The determination of particle size distribution could serve two proposes; first estimation of the quality of the emulsion concentrates, and second prediction of the stability of the emulsion in the finished product (Dickinson and McClements, 1995).

The most commonly used technique for the characterization of food emulsions is laser light scattering, but this is only suitable for very dilute systems ($\phi<0.05$ wt %) and dilution of more concentrated emulsions may disrupt delicate aggregates. Nuclear magnetic resonance has been used to characterize concentrated food emulsions but the apparatus is expensive and difficult to operate (Dickinson and McClements 1995, Coupland and McClements, 2001).

2.6.6 Polydispersity

Refer to droplet sizes range which mostly depends upon the concentration of droplets. In dilute system such as beverage emulsions the average creaming velocity can be estimated from the mean droplet radius (Tan and Wu Holmes 1988).

2.6.7 Electrical charge and zeta potential

The potential energy barrier for charged oil droplets in water arises from electrostatic interactions between the droplets. According to the DLVO theory (Washington, 1990; Salou et al., 1998; Ichikawa and Nakajima, 2004; Ichikawa et al., 2006) the barrier height is determined by the van der Waals force and the electrostatic force. The latter force is the sum of the Maxwell's electric field stress and the osmotic pressure. The van der Waals force and the Maxwell's stress are always attractive, whereas the osmotic pressure is usually repulsive.

Although the DLVO theory is a fundamental theory for explaining the stability of charged colloidal and emulsion particles in water, it has been reported (Ichikawa et al., 2004, Ichikawa and Nakajima, 2004) the theory has not been firmly applied to emulsion systems. McClements, (2005) stated that the DLVO theory does not take into account the short-range repulsive interactions, such as polymeric steric, hydration and thermal fluctuation, which arise between droplets when they come close together.

The difficulty in the application arises from the correct estimation of surface electrostatic potentials of approaching particles. As a result, it predicts that two liquid droplets would coalesce at close separations because of the large attraction between them. Figure 2.1 shows the change of surface charges and surface potentials during the approach of two-charged spheres in water.

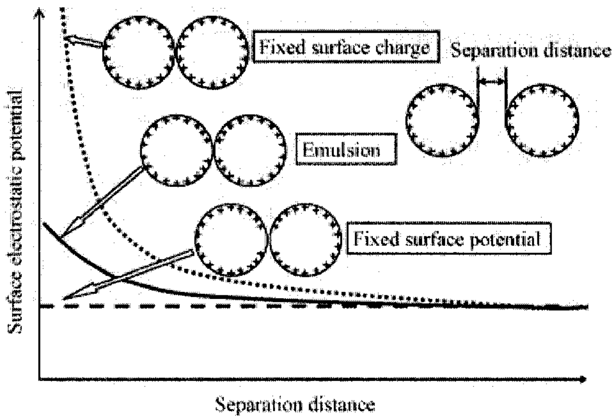


Fig. 2.1. Schematic representation of the changes of surface charges and potentials during the approach of two-charged particles (Adopted from: Ichikawa et al., 2004)

If the surface charges are moved freely like conduction electrons on metallic spheres, the migration of surface charges completely compensates the potential gradient on the surfaces. The surface potentials are, therefore, kept uniform and constant during the approach. If the migration of surface charges is completely prohibited, the surface potentials continuously increase with decreasing separation distance and become infinite at zero separation distance. The situation for emulsion droplets may lie somewhere between the two extreme cases (Ichikawa et al., 2004). In practice, many of emulsifiers used in food emulsions are capable of stabilizing the droplets through combination of electrostatic and short-range repulsive interactions McClements, 2005).

Emulsions containing charged droplets tend to move more slowly than uncharged particles. The reasons are first, repulsive electrostatic interactions between similarly charged droplets which do not allow them to get as close together as uncharged droplet and second, the cloud of counter-ions surrounding a droplet moves less slowly than the droplet itself.

The potential arises from the presence of charges in particles and the medium at the zone of shear called `zeta potential`.

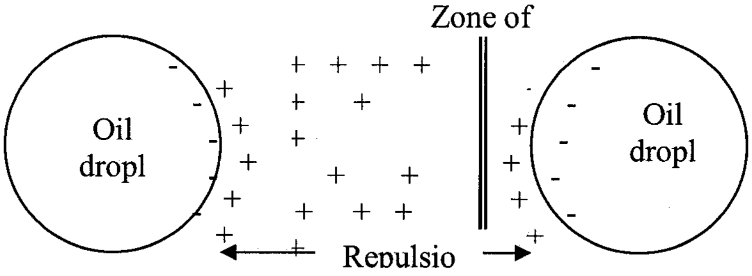


Figure 2.2. Zeta potential is a measure of the magnitude of the repulsion or attraction between particles.

Zeta potential of less than –15 mv usually represents the onset of flocculation. Hydrocolloids present in water phase have different zeta potential (eg., gum arabic zeta potential = -23 mv). However, one cannot categorically state that an emulsion will or will not be stable at a given zeta potential as some other factor such as density difference between the two phases and the droplet size should be taken into consideration (Tan and Wu Holmes 1988). Addition of minerals could also have a major effect on zeta-potential. For instance, minerals increase the ionic strength of the aqueous phase, which reduces the electrostatic repulsion between droplets through electrostatic screening. Some minerals bind to oppositely charged groups on the surface of emulsion droplets, decreasing the magnitude of their Zeta-potential and thereby reducing the electrostatic repulsion between droplets (Hunter 1986). Ion binding can increase the short-range hydration repulsion between droplets because of the additional energy required to disrupt the sheath of water molecules associated with them. At sufficiently high concentrations minerals cause alterations in the structural organization of the water molecules, which alters the strength of the hydrophobic interactions between non-polar groups (Kulmyrzaev et al., 2000). It should be noted that zeta potential reflects both the electrolytes presence in the system and the dissociated ions accompanying the original colloid particles. Addition of cation electrolytes could neutralize the zeta potential and cause aggregation to occur due to the van der Waal's-london forces (McClements, 2005).

2.6.8 Phase volume ratio of the dispersed phase

Any increase in this value is accompanied by an expansion of the interfacial film. This has the effect of increasing the instability of the system. If the volume of the dispersed phase exceeds that of the continuous phase, the emulsion will invert. The addition of an emulsifying agent can then be considered to remedy this problem and maintain the desired type of emulsion.

For instance, in one emulsion, there are one thousand dispersed particles of 1 micron diameter, and one particle of 10 micron diameter. By population, this 10 micron particle is only 0.1 percent of the total population. When expressed in volume percentage, this 10 micron particle having 50 percent of the total dispersed volume as the volume of one thousand 1 micron particle is equal to thsat of the one 10 micron particle. In the beverage if this 10 micron particle floats to rhe surface and ring, it is almost a negligible number in the total population, because it is only 1 in 1001 particles or 0.1 percent of the total population rings. But, in ters of volume, it is 50% of the total oil volume in the ring. It is a serious problem (Tan and Holmes, 1988).

2.6.9 Temperature

Any change in the temperature of an emulsion will cause changes in the interfacial tension between the two films, the viscosity of the two phases and the interfacial film and also the relative solubility of the surfactants in the two phases. The effects of temperature must therefore be rigorously controlled during the preparation and analysis of emulsions. Emulsifying agents are generally more effective near the point of minimum solubility in the solvent in which they will be dissolved, since it is at this point that they have greater surface activity (Nielson, 1958). Any increase in temperature can reduce the viscosity of the oily phase (the surfactant will then move more quickly at the interface) as well as increase the solubility of the surfactant in the oil.

Temperature control is also a major parameter for preventing protein denaturation. In addition to temperature, environmental factors also play an important role. These include pH and ionic strength, which influence the charge as well as the conformation of the proteins, and hence their emulsifying properties (Dickinson, 1987).

2.6.10 Emulsifying agents (surfactants or surface-active agents or stabilizers)

There are several types of surface-active agents that can be used to stabilize emulsions Dickinson, 1988). The main surfactants include anionic surfactants that have negative charges (carbohydrates), cationic surfactants that have positive charges (amine salts), non-ionic surfactants, with no apparent charges, such as monoglycerides, sugars, alcohols, phenols, glycols and zwitterionic surfactants that have positive or negative charges such as proteins. Hence, these surfactants simultaneously possess certain "polar" hydrosoluble characteristics due to the carboxyl and hydroxyl groups and certain "non-polar" fat-soluble characteristics of the hydrocarbonated chains. It is energetically favourable for these molecules to orient themselves at an oil/water interface rather than remain in one phase or the other (Doublier, 1989).

In this review, we will focus mainly on the emulsifiers of importance in the beverage field, namely vegetable oils and their hydrophobicity, proteins and gums (Grovens, 1999).

These surfactants generally act at the level of short-distance interactions by modifying the physical state of the oil/water interfaces. Macromolecules can be used, as well as finely divided solid particles, to modify the mechanical properties of the interfaces. Generally, surface-active agents completely adsorbed at the level of the interfaces are used because of their amphiphilicity. To be effective, they must have the following characteristics:

a) Good surface activity in order to effectively reduce the interfacial tension in the system used. More specifically, they must have a tendency to migrate to the interface rather than remain discrete in one of the two phases. A balance of lipophilic and hydrophilic components is therefore required and any excess solubility in either of the two phases will make them less effective (Chen et al., 1993),

b) They must form a condensed protective film at the interface. This film will be formed either by one agent or a combination of surface-active agents. This condensed film increases elasticity at the interface and, consequently, emulsion stability. This kinetics of migration is heavily dependent on the phase that contains the surfactant and also on the temperature and viscosity of the solvent (Halling, 1981).

To succeed in preparing emulsions that have different proportions of water and fats, the emulsifiers must exhibit variable solubilities in the two solvents and the choice of emulsifier depending on the type of emulsion is based on the HLB or hydrophilic-lipophilic balance system. Theoretically, the HLB values of the main emulsifiers range from 1 to 20. The lower value of HLB corresponds to the more lipophilic emulsifier.

2.7 Commercial oils and their hydrophobicity

Oils are hydrophobic by nature. However, some lipids are not completely non-polar. The effect of the carboxyl groups of the fatty acids in terms of hydrophobicity, for example, is greatly reduced by the length of the non-polar hydrocarbonated chains.

The presence of monoglycerides which can crystallize and behave like solid particles is an example of stabilization of solid particles. For an oil/water interface, this solid stabilizer will be even more effective to the extent that it will form a 90° angle with the interface. The interfacial energy due to the presence of a solid particle at the interface is given by the equation (Friberg, 1988):

$$W = \pi r^2 \gamma (1 + \cos\theta) \tag{8}$$

where r is particle radius, γ is surface tension and θ is the contact angle. We can therefore conclude that W will be almost nil for θ equal to 90°, which corresponds to the maximum stability.

Commercial oils contain different lipid species (Myers, 1989). The triglycerides of oil represent approximately 90% of the hydrophobic core of the oil droplet used for the formation of an emulsion. These triglycerides therefore play a structural role in maintaining droplet integrity and also contribute to the rheological properties of the emulsion. Phospholipids (3-9%), for their part, form an outer shell of the polar material separating the triglycerides from the aqueous environment (Friberg, 1978). This layer located at the oil/water interface is mainly involved in oil/surfactant/emulsifier interactions. Consequently, the characteristics of the phospholipid phase are of vital importance for the stability of an emulsion. Sterols/sterol esters (0.3 to 0.4%), monoglycerides and diglycerides, fatty acids and hydrocarbons and a small percentage of unidentified lipids complete the distribution of oil components. Of these latter components, sterol esters and monoglycerides also play an important role. An oil droplet in an emulsion therefore contains several types of lipids. In the case of corn oil, for example, these lipids arrange themselves in the droplets according to their relative hydrophobicity, with the most active surface groups at the surface of the droplet near the aqueous phase. The presence of phospholipids and sterols at the interface will constitute films whose nature depends on the arrangement of the molecules relative to one another.

In terms of relative importance to the stability of an emulsion, phospholipids are the predominant species:

a) They have a greater surface activity and reduce the interfacial tension more than triglycerides, i.e., a lower interfacial tension that is accompanied by smaller droplet size distribution, which increases the viscosity of the emulsion and hence its stability.

b) They can form liquid crystalline phases or a condensed film called multilayer.

   In fact, certain oil-emulsifier-water mixtures (trinary) can constitute crystalline mesophases at the interface. These different phase transitions of emulsifier-water mesophase due to the solubilization of soybean oil correspond to very different organized structures and physical states (Doublier, 1989). This is the phenomenon of mesomorphism.

The stability of an emulsion will therefore depend greatly on the structure of the interfacial film (liquid crystalline interfaces) and also on the concentration of phospholipids and sterols, which varies from one oil to another, and hence on the hydrophobicity of the oil. The type of mesophase will therefore determine the stability of the emulsion or more specifically the lipid-emulsifier interactions since the rheological properties of the interface (viscosity and elasticity) will vary according to the physical state of the mesophase (Krog, 1976).

These lipid-emulsifier interactions are altered by these crystalline phases of the phospholipids; hence in the case of lipid-protein interactions, the type of mesophase will dictate the force of the interactions with the proteins. Similar behaviour is noted between phospholipids and non-protein emulsifiers (ionic and non-ionic surfactants, monoglycerides, carbohydrates, etc.) and their impact on the properties of the emulsion (i.e., rheological characteristics of the droplet surface). Thus, the gel and lamellar mesophase phases of the phospholipids have different properties of permeability, molecular motion, and degree of hydration and protein bonds. These differences can therefore have a dramatic effect on the emulsifying function of emulsifiers containing phospholipid crystals. Several lipids inherent to oil, particularly monoglycerides and sterol esters, can exist in different mesophase forms that will be defined by water content, choice of temperature, etc. (Krog, 1975). In addition to existing in the form of different types of lyotropic, thermotropic and other mesophases (Friberg, 1998), several lipids therefore exhibit the phenomenon of polymorphism, i.e., structural changes induced under the influence of heat in the absence of solvents. This is the case of pure triglycerides, sterol esters, etc. and very often, different polymorphic crystalline forms are noted for a given molecular species. This polymorphic behaviour is explained by variations in the angle of inclination of the hydrocarbon chains; the chains are successively displaced relative to the adjacent chains and the inclination angle is increased or decreased. Thus, for triglycerides, the two most common packing arrangements correspond to the crystalline forms of the orthorhombic and triclinic type. These two forms have very different characteristics (Krog, 1975).

Consider an oily phase composed of natural food oil; if the oil that contains a prerequisite quantity of phospholipids is exposed to appropriate conditions, a liquid crystalline phase will then be obtained at the oil-water interface. A known method for obtaining these crystalline phases is to use an exogenous ionic surfactant to emulsify the dispersed phase. The ionic surfactant contributes to the surface charges, which are accompanied by a compression of the electrical double layer. Since the phospholipids are now more spaced out because of the added charges, a new liquid crystalline phase can be formed at the oil/water interface with a high capacity to solubilize the water. It is this emulsifier-water interaction that will place a decisive role in obtaining double layer planar packing, thus forming a protective emulsifier layer at the interface (Sjöblom et al., 1996, Friberg et al., 1997).

It worthily noted that the exogenous and endogenous emulsifier mixtures such as phospholipids can have a major effect on the rheological properties of an emulsion. In addition, the viscosity of an emulsifier in the crystalline phase form can be up to 100 times higher than the viscosity of an emulsifier that does not have crystalline properties, thereby improving the stability of an emulsion by giving it a more rigid surface, which will inhibit the phenomenon of coalescence. Also note that the polymorphic forms of triglycerides have very different densities (Flack, 1976).

2.8 Proteins as emulsifying agents

As discussed earlier, emulsification properties include the capacity to disperse two immiscible phases and maintain them in a dispersed state (Dickinson, 1992; Angelo, 1989; Bennett et al., 1968). These two functional characteristics of proteins are well correlated with steric parameters and various measurements of hydrophobicity (Kato and Nakai, 1980).

It is possible to link the structure of a protein and its emulsifying properties (Utsumi et al., 2002; Salgado et al., 2005), namely:

- primary structure/hydrophobicity and ability to form an emulsion;
- tertiary structure/surface hydrophobicity and formation/stabilization of emulsions.

These emulsifying properties could be attributable to the protein's ability to modify its structure for the stabilization of the interface created (Dickinson, 1987). This structure, which will vary depending on the conditions of the medium at the time of emulsification, is a key factor, but its ability to adapt to new conditions (pH, ionic strength, temperature) is equally important.

In an oil-in-water emulsion, at the presence of emulsifier (proteins), the direct contact between oil and water molecules is replaced by contact between the nonpolar segments of the emulsifier and oil molecules and between the polar segments of the emulsifier and water molecule. This in turn causes a decrease in free energy and hence decreases in interfacial tension. Therefore a decrease in surface tension could be related to the activity of surface active molecule presented at the emulsion (McClement, 2005).

The intermolecular forces that will contribute to the viscoelasticity of the film at the interface, i.e., to the protein/protein and protein/interface associations, are attributable to the combination of ionic bonds, Van der Waals forces and hydrophobic interactions (Dickinson, 1992 and 1987). We can then refer to surface gelification and protein denaturation (Dickinson, 1992).

Each amino acid differs from the others because of the R group. It is this group that determines the relative hydrophobicity, polarity and charge of the amino acids. The interactions between these groups, namely hydrogen bonds, ionic bonds (i.e., electrostatic attraction of opposite charges), hydrophobic interactions between non-polar groups and disulfide bonds, help to stabilize the three-dimensional structure of the protein (Lehninger, 1975).

The charge of the proteins is important in terms of electrostatic interaction. At the isoelectric point (IP), this net charge is nil; as pH increases, the net charge becomes more negative, and vice versa with a reduction in pH. The pH has a pronounced effect on charge and zeta potential, thus for serum bovine albumin, the zeta potential at pH 3.64, 4.96 and 6.55 will be 67.3, -7.1 and -51.5 mV respectively (Myers, 1989).

Ionic strength influences protein solubility, the quantity of bound water as well as the hydrophobic and electrostatic interactions. The chloride ions of sodium chloride are more easily bound to protein than sodium ions; consequently, above the IP, protein swelling can occur because of the bond between the water (instead of the Na+) and the negative charges on the protein (Fennema, 1996). Hydrophobicity is an important factor in protein conformation and functionality. Bigelow (1969) determined the hydrophobicity of the various proteins by measuring the hydrophobicity of each amino acid. While the majority of the hydrophobic groups are buried within the protein molecule, a few are located at the surface, partially or totally exposed to the aqueous medium (Klotz, 1970). These surface groups are important for oil/water interface interactions (Keshavarz and Nakai, 1979).

There is a relationship between interfacial tension, the emulsifying activity of the protein and its hydrophobicity. During protein/interface interactions, i.e., denaturation of the surface, additional hydrophobic groups are exposed to the surface. This will have the consequence of increasing the emulsifying activity (Kato and Nakai, 1980).

In the case of proteins, there is an adsorption phenomenon at the interfaces. The presence of these macromolecules will therefore limit the flocculation and coalescence of the emulsified droplets. These macromolecules appear to form a skin at the surface of the droplets during adsorption. Non-globular proteins, such as β casein for example (reliable structuring without SS bonds) are adsorbed at low concentrations at the water-oil interface according to the linear chains-loops-ends model and are thus described as flexible proteins. However, if these globular proteins are adsorbed at the interface, they can retain part of their secondary and tertiary structure (Friberg, 1998).

This model is therefore not adapted for all proteins (Dickinson, 1992). During the emulsification process, the protein diffuses at the O/W interface and spreads out there, to eventually form a continuous and cohesive film around the fat particles. The hydrophobic regions then orient themselves toward the polar phase, while the polar segments associate with the aqueous phase. This bridging at the interface can lead to denaturation of the protein, due to the unfolding of the tertiary structure (Erdem, 2006)., which improves surfactant power. Since most proteins are hydrophilic in nature, partial denaturation with unfolding of the tertiary structure will improve the surface properties since the hydrophobic residues are no longer buried within the molecule, which exposes the bonding sites (Kato and Nakai, 1980; Wastra, 1987; Wastra and Fennema 1996).

To exhibit emulsifying properties, proteins must therefore diffuse rapidly at the interface, unfold there and orient themselves in such a way as to reduce the tension generated by the interface of the hydrophobic and hydrophilic components. In addition, the adsorbed proteins must interact cooperatively to form a protective film around the fat droplets, which will have sufficient integrity and elasticity to ensure stabilization. Depending on the tertiary and quaternary structure of the protein, different degrees of molecular unfolding (changes in conformation in certain segments of the protein) can occur, giving rise to different interfacial structures.

Proteins are used in food emulsions to ensure better kinetic stability. This improvement is apparently attributable to an increase in viscosity of the continuous phase (possibly electrical charges on the dispersed phase and particularly rheological properties on the membrane or interfacial skin formed by the denatured proteins at the surface).

The method of homogenization will also affect the role of the proteins. For instance, high pressure will alter protein denaturation, which will facilitate emulsification. Temperature is another important factor, since it controls protein behaviour and more specifically hydrophobic interactions. Consequently, a complex behaviour can be obtained depending on the relative proportion of hydrophobic and hydrophilic residues in the protein and their arrangement in the three-dimensional structure (Keshavarz and Nakai, 1979).

2.9 Hydrocolloid gums

Hydrocolloid gums (polysaccharides) are mostly hydrophilic polymers, which do not exhibit significant surface activity (Dickinson and Stainsby, 1998). However, as a stabilizer in food emulsions, some gums were found to migrate slowly to the air–water and oil–water interfaces and exhibit some surface and interfacial activities. It has been further suggested that hydrocolloid gums, although water-soluble, rigid and very hydrophilic, can precipitate/adsorb onto oil droplets and sterically stabilize emulsions against flocculation and coalescence (McClements, 2005).

The contribution of polysaccharide (hydrocolloid gums) to the stability of food emulsions has also been traditionally related primarily to their rheological effects on the continuous phase. In most of the cases the stability of emulsions prepared with hydrocolloid gums was considered to be a non-adsorbing 'depletion stabilization'. Hydrocolloid gums are known to have significantly less surface activity in comparison to proteins (Dickinson and Stainsby, 1998). This inferiority is related to their pronounced hydrophilicity, low flexibility and monotonic repetition of the monomer units in the backbone (Huang et al., 2001). A hydrocolloid gum may show considerable surface activity, only if it contains auxiliary hydrophobic groups (methyl, acetyl, etc.) or if it is contaminated either with proteineous moieties attached to the biopolymer or with glycolipids (Dickinson and Stainsby, 1992).

Certain hydrocolloids are high-molecular weight polysaccharides which are used to stabilize droplets against the phenomenon of coalescence by interacting with the water, ions and other polymers and groups located at the interfaces (Dickson, 1988; Grovens, 1999). In addition, they are rarely used alone as emulsifying agents because of their weak surface activity (Wilson et al., 2000; Shukla et al., 1981; Tan, 1988).

Gum arabic and modified starch are mainly used in beverage emulsions for flavour microencapsulation (Kim et al., 1996). If the proportions of essential or vegetable oil with these two gums are respected (i.e., 1:1 to 4:1), this will facilitate the formation of a viscoelastic interfacial film. This film will permit encapsulation of the oils and hence retention of the flavours for a long period (Garti and Reichman, 1993).

These two gums in synergy with gums such as xanthan, guar, pectin, carrageenan and others as stabilizing agents will promote the elasticity and pseudoelasticity of emulsions, two rheological attributes that are desirable for the physical stability of the emulsion and hence will minimize the phenomenon of coalescence of the particles, which will tend to remain isolated from each other. Under any physical influence (pressure, vibration, etc.), the elasticity of the particles is desirable since it ensures their stability (as opposed to a particle that is too rigid and becomes more susceptible to rupture).

Arabic gum, the dried exudates from certain species of the acacia tree, is one of the most widely used biopolymer on an industrial scale. It is considered to be unequalled in many of its properties including the ability to form stable emulsions over a wide pH range and in the presence of electrolytes. Gum arabic is a complex mixture of polysaccharide, protein and arabino galacto protein species. Many studies have been performed on its structure and functionality in an effort to understand its excellent emulsification properties (Jayme et al, 1999). Therefore, gum arabic not only enhances the viscosity of the aqueous medium like most other polysaccharide gums but also forms a thick macromolecular layer around the emulsion droplets resulting in good steric stabilization. However, it is a poor emulsifier compared with food proteins and the amount required to make a stable emulsion corresponds to 1:1 w/w gum to oil while one tenth of this amount is necessary in the case of protein (Dickinson et al., 1991)

Maltodextrins, low converted products of starch hydrolysis, is used in various emulsions to provide desirable viscosity, texture, mouthfeel and stability. Maltodextrins are defined as starch hydrolysis products with dextrose equivalent less than 20. Dextrose equivalent (DE value) is measure of reducing power of starch derived oligosaccharides expressed as percentage of D-glucose on dry matter of hydrolysate and is inverse value of average degree of polymerisation (DP) of anhydro glucose units. As products of starch hydrolysis maltodextrins contain linear amylose and branched amylopectin degradation products, therefore they are considered as D-glucose polymers joined by α-(1,4) and α-(1,6) linkages. Starch degradation products in maltodextrins extend from oligomeres to macromolecules and different DE value maltodextrins have different physicochemical properties like solubility, freezing temperature, viscosity etc (Dokic et al., 1998). Maltodextrins can form weak gels that are results of interactions between amylose fractions characterised by helical regions and branched and linear chains of amylopectin molecules. Maltodextrins with lower dextrose equivalent show higher tendency to form gels due to higher percentage of long oligosaccharide chains. As maltodextrins have ability to form gels, they could be used in producing emulsions as texture modifiers, bulking agents and particularly in food emulsions to certain extent for substitution of fat. Still in formulations of emulsions many factors and influences should be taken into consideration from emulsification conditions to interactions that may take place between components in emulsions. Under certain conditions they could result in stabilisation/destabilisation of emulsions (Kasapis et al., 1993). All the mentioned effects of maltodextrins can be supposed to strongly influence emulsification of oil in combined emulsifier/maltodextrin solution in water and droplet size and rheological properties of final emulsions.

Covalent interactions between polysaccharides and proteins adsorbed at the O/W interface can also be evidenced by measurements of surface rheology. For instance, the addition of propylene glycol alginate (PGA) to sodium caseinate on a n-hexodecane/water interface demonstrates that when PGA is introduced in the aqueous phase after formation of the emulsion, the rate of increase in surface viscosity is significantly higher compared to that observed for caseinate alone (Sharma, 1981; Hennock et al., 1984). This is caused by the accumulation of PGA at the interface, which apparently forms a secondary layer complexed to the adsorbed caseinate by means of electrostatic interactions between the polysaccharide and the protein, which has a positive charge at pH levels below the isoelectric point (Dickinson, 1992).

2.10 Rheology of food emulsions

The science of rheology has many applications in the fields of food acceptability, food processing, and food handling. A number of food processing operations depend heavily upon rheological properties of the product at an intermediate stage of manufacture because this has a profound effect upon the quality of the finished product (Barbosa-Cánovaset et al., 1996 and Bourne, 2002). Rheological properties of food systems are also the key factor for improving food quality and stability as well as development of new product. Foods, however, are complex materials structurally and rheologically and, in many cases, they consist of mixtures of solids as well as fluid structural components (Finney, 1972). For example, the rheology of bread dough, milk crud, and meat emulsions are important aspects in the manufacture of high-quality bread, cheese, and sausage products (Bourne, 2002). Unique rheological properties of various foods have been reported and summarized in many publications (Tempel, 1963; Cross, 1965; Krumel and Sarkar, 1975; Steffe et al., 1986; Rao and Steffe, 1992; Steffe, 1992; Lapasin and Pricl, 1995; Mason et al., 1996; Nielsen, 1998; Larson, 1999; Chen et al., 1999; Marcotte et al., 2001a and 2001b; Bourne 2002; Buffo and Reineccius, 2002; Klinkesorn et al., 2004; McClements 2005; Taherian et al., 2006).

Rheology concerns the flow and deformation of substances and, in particular, to their behavior in the transient area between solids and fluids. Moreover, rheology attempts to define a relationship between the stress acting on a given material and the resulting deformation and/or flow that takes place. Rheological assessment becomes extremely crucial when the sensitive ingredients (edible oils, nutraceutical, probiotiques, vitamins and aroma components) are incorporated in to a food system. It is as well concerned with how all materials respond to applied forces and deformations. Basic concepts of stress (force per area) and strain (deformation per length) are keys to all rheological evaluations. Stress (σ) is always a measurement of force per unit of surface area and is expressed in units of Pascals (Pa). The direction of the force with respect to the impacted surface area determines the type of stress. Normal stress occurs when the force is directly perpendicular to a surface and can be achieved during tension or compression. Shear stress occurs when the forces act in parallel to a surface. On the other hand, strain represents a dimensionless quantity of relative deformation of a material. The direction of the applied stress with respect to the material surface will determine the type of strain. Normal strain (ε) occurs when the stress is normal to a sample surface. Foods show normal strain when compressed (compressive stress) or pulled apart (tensile stress) (Nielsen, 1998).

Rheological properties are determined by measuring force and deformation as a function of time. The science of rheology can be applied to any product and in fact was developed by scientists studying printing inks, plastic, rubber, and similat material and they can be measured either fundamentally or empirically (Bourne, 2002). The difference between fundamental and empirical rheological methods is that, unlike the latter, the former accounts for the magnitude and direction of forces and deformations, placing restrictions on acceptance of sample shapes and compositions. Fundamental tests have the advantage of being based on known concepts and equations of physics. Empirical methods are often used when sample composition or geometry is too complex to account for forces and deformations. These methods are of value if they correlate with a property of interest, whereas fundamental tests determine true physical properties. Bourne (2002) has classified the application of rheology in the three major categories of food acceptability:

- Appearance. Because certain structural and mechanical properties of some foods can be determined by appearance; for example how well maple syrup pours from the bottle and cover the pancake.
- Flavor. The manner of food breakdown in the mouth can affect the rate of release of flavor components.
- Touch. We hold foods in the hand and from the sense of deformability and recovery after squeezing frequently obtain some idea of their textural quality.

Indeed the main tool available for consumer to judge the quality and select the food products is to measure texture and rheology by using the senses. Emulsions are mixtures of two immiscible fluids consisting of droplets of one phase dispersed into the other. They are metastable systems and tend to come back to their equilibrium state of biphasic mixture. They belong to the class of non equilibrium systems and are subjected to aging and slow destruction (Larson, 1999). The shelf life of many food emulsions depends on the rheological characteristics of the component phases, for example, the creaming of oil droplets in oil-in-water emulsions is strongly dependent on the viscosity of the aqueous phase (McClements, 2005). The rheological behavior of emulsion systems depends on the liquid fraction of the dispersed phase. At low volume fraction, the droplets are Brownian and the emulsion is Newtonian with a viscosity close to that of the continuous phase.

There are 5 major aspects which determine emulsion rheology (Tan, 2004; McClement, 2005):

Rheology of component phases: The viscosity of an emulsion is directly proportional to the viscosity of the water phase, and so any alteration in the rheological properties of water phase has a corresponding influence on the rheology of whole emulsion.

Oil phase volume fraction: The viscosity of an emulsion increases with oil phase volume fraction in a linear manner.

Droplet size: The mean droplet size and polydispersity have a significant influence on the rheology of concentrated emulsion (McClements, 2005). The effect of both droplet size and droplet size distribution on the rheology of an emulsion depends upon oil phase volume fraction and the nature of colloidal interaction. At the same volume fraction, polydispersed emulsion has a lower viscosity than monodispersed emulsion.

Colloidal interactions: Colloidal interaction govern whether emulsion droplets aggregate or remain as separate forms, as well as determine the characteristics of any aggregate formed. The rheological properties of an emulsion depends upon the relative magnitude of attractive (van der Waals, hydrophobic and depletion) and repulsive (electrostatic, steric and thermal flocculation) interactions between the droplets. These properties can be control by manipulating the colloidal interactions between the droplets. For instance, the viscosity of emulsion has been increased due to addition of biopolymers which causes increase in: depletion attraction, bridging and flocculation. (McClements, 2005).

Particle charge: When a charged droplet move through a fluid the cloud of counter-ions surrounding it become distorted and causes an attraction between charged droplets and cloud counter-ions. This attraction opposes the movement of the droplet and causes an increase in viscosity.

The influence of particle packing (Volume ratio or the ratio of droplet volume to the emulsion volume) on the rheology of colloidal dispersion containing rigid spherical particles has also been categorized by McClement (2005):

- In dilute system where the volume ratio (ϕ is less than 0.05 the emulsion is a fluid with a relatively low viscosity that is dominated by the viscosity of the continuous phase.
- In concentrated system where $0.05 < \phi < 0.49$ the emulsion is still fluid with a viscosity that become increasingly high as the particle concentration increases.

- In partially crystalline system where $0.49 < \phi < 0.54$ the particle separate into two distinct phases of crystalline (closely packed) and liquid (loosely packed).
- In glassy system where $0.58 < \phi < 0.64$ the particles can be considered to be trapped and emulsion can exhibit both solid-like and liquid-like behaviors. Acting like a solid at low shear stresses and a fluid once a critical yield stress has been exceeded.
- In crystalline system where $\phi > 0.64$ the emulsion behave like an elastic solid.

Fluid emulsion, however, could range from low viscosity emulsion such as milk to high viscosity emulsion such as mayonnaise. The rheological properties of liquid emulsion could be characterized as follow:

- Newtonian or ideal liquid emulsions: the liquid flow as long as the stress is applied and the viscosity is independent of shear rate and of the length of timethat liquid is sheared. The shear stress is proportional to the rate of shear and therefore:

$$Vis\cos ity = \frac{Shear\ Stress}{Shear\ Rate} \text{ or } \eta = \frac{\sigma}{\dot{\gamma}} \tag{9}$$

- Non-Newtonian liquid emulsion: the viscosity of emulsion depends upon applied shear rate (Time Independent) and/or time over which shear stress is applied (Time Dependent).

The time-independent liquid emulsions are classified as:

1. Shear thinning or pseudoplastic fluid emulsion where the apparent viscosity of emulsion decreases as shear rate increase.
2. Shear Thickening or Dilatants fluid where the apparent viscosity of emulsion increases as shear rate increase. In both cases the viscosity at any given shear rate can be calculated by:

$$\eta = \mathrm{m}\,\dot{\gamma}^{(n-1)} \tag{10}$$

The constants m and n refer to consistency coefficient and flow behavior index respectively.

The time-dependent liquid emulsions are classified as;

1. Thixotropic where the apparent viscosity of fluid decreases with time at application of constant shear rate.
2. Rheopeptic where the apparent viscosity of fluid increases with time at application of constant shear rate.

Plastic behavior

Plasticity is also another type of rheological behavior of food emulsion where the semi-fluid emulsion (mayonnaise) has elastic properties below a certain applied stress which is known as Yield Stress and flows when this stress exceeded. The plastic property is also classified as 1) Bingham or ideal plastic in which the fluid exhibit Newtonian behavior above the yield stress and 2) Non-ideal plastic in which the fluid exhibit non-Newtonian behavior (ie, pseudoplastic, dilatant, thixotropic and rheopeptic) above the yield stress.

Viscoelasticity

This type of emulsions exhibit both viscous and elastic behaviors at the same time. On the other word, when a force is applied to a viscoelastic emulsion it does not instantaneously adopt its new dimensions nor does it instantly return back to its original no deformed state when the force removed. The rheological properties of viscoelastic materials, therefore, are consisting of elastic and viscous components and are characterized as:

$$G^{*} = G' + iG'' \tag{11}$$

where G’ is known as storage and G” as loss modulus.

The viscoelastic properties can be determined by the sinusoidal method: the value of G′, the real component of the complex modulus, also called conservative modulus, translates the elastic component of the behaviour, and G″, referred to as dissipative modulus, and translates the elastic component. The larger the values of G′, the more physically stable the emulsion. With respect to pseudoelasticity, which is determined by the flow mode, the smaller the value of n, the more pseudoplastic the system; this is then referred to as laminar flow.

Generally, a high value of G′ combined with a low value of n yields the most physically stable emulsion (Chanamai and Clements, 2000).

These adjustments of the values G′ and n can be achieved by a judicious choice of stabilizers (xanthan, carrageenan, guar gum, etc.) and emulsifying agents (protein, gum arabic, PGA, etc.) (Yilmazer et al., 1991; Hennock et al., 1984; Coia and Stauffer, 1987).

Several studies have characterized rheological properties of food emulsions with steady state shear viscosity. Chanamai and McClements, (2000) described that the apparent viscosity of concentrated emulsions ($\phi > 20\%$) containing smaller droplets was significantly greater than emulsion containing larger droplets and decreased with increasing shear rate while the apparent viscosity of dilute emulsions ($\phi < 20\%$) was relatively independent of the applied shear stress. Suzuki et al 1991 and Klinkesorn et al 2004 , studied the rheology and stability of corn oil-in-water emulsions and explained that the apparent viscosity of emulsions are affected by volume concentration of the dispersed phase, nature of emulsifying agent, emulsifying conditions and above the critical flocculation concentration , emulsions are highly viscous with strong shear thinning behavior.

The effect of oil phase concentration on emulsion rheology has been described by Barnes, (1994) and Mason et al. (1996). When the volume fraction of the dispersed phase is increased, droplets come into contact and their interfaces are deformed. When subjected to small strain rates, they can support an additional interface deformation and thus store energy, which results in an elastic response. At higher strain rates, they finally flow irreversibly. The transition between these two regimes occurs at a critical stress δ_0, called the yield stress. Below the yield stress δ_0, the shear rate is zero. The emulsion does not flow and its rheological response is purely elastic. Above δ_0, droplets rearrange irreversibly and the emulsion starts to flow.

The behavior of the flow in the surrounding area of the yield stress is still not clearly understood. The inception of the flow could be seen as an abrupt transition between a solid-like state that remains jammed and does not flow, and a liquid-like state that flows, following a Bingham-fluid behavior. Another description of the transition is characterized by the existence of an inhomogeneous flow resulting from the coexistence of both solid-like and liquid-like states in a defined range of shear rates. Moreover, the existence of slippage of the emulsion at the walls can complicate the analysis of the rheological data (Barnes, 1995).

It is of particular importance to mention that the particles in a food emulsion are fluid and deformable and because various types of attractive and repulsive forces act between the droplet will not necessarily follow the above critical volume fractions. But from an industrial point of view, determining the particle–particle interaction potential in concentrated suspensions from rheological data is useful for two main reasons, (a) prediction of how particle size, concentration or ionic strength influence the rheological functions and; (b) the possibility of on-line characterization (Berli et al., 2002). Buffo and Reineccius, 2002, stated that the rheology of concentrated beverage emulsions, where the concentration of oil phase is around 5%, can be confidently modeled through the Einstein equation or its exponential expansion.

In Einstein equation for relation between viscosity of a rigid spheres suspension to its composition it has been assumed that the liquid is Newtonian, the particles are rigid and spherical, there is no particle-particle interaction, there is no slip at particle-fluid interfase and the particle motion effects are not important.

$$\eta = \eta_1(1 + 2.5\phi) \tag{12}$$

where η_1 is the viscosity of the external phase (water phase) and ϕ is the volume fraction of internal phase (oil phase).

Nevertheless, the Einstein equation gives excellent agreement with experimental measurement for suspensions of particle concentrations of about 5% or $\phi < 0.05$ and could be used in case of beverage emulsions (McClements, 2005).

2.11 Beverage emulsions

Emulsions used for beverages serve to incorporate flavours based on essential oils, and vegetable oils as opalescent agent as well as fat-soluble colours, e.g., β-carotene (Jasentullyana et al., 1988; Kaufman, 1984).

These O/W type emulsions contain a dispersed phase or oily phase (essential oil, vegetable oil and weighting agents (BVO, SAIB, ester gum) and a continuous phase (water, gum arabic or modified starch, citric acid, preservatives and colours). Each ingredient has its own function: citric acid for adjusting the pH and optimizing the bacteriostatic activity of the preservatives, colours for the esthetic aspect, gum arabic or modified starch as stabilizing and/or emulsifying agents, weighting agents for adjusting the density of the essential and vegetable oils as flavours and opalescent agents, respectively (Tan, 1988).

During preparation of the dispersed phase, the proportion of weighting agents, soluble in the oils, is governed by the permissible standards for beverages in Canada, for example, 15 ppm BVO (density 1.23-1.33 g/cc), 300 ppm SAIB (density 1.146 g/cc).

Beverage emulsions (O/W) are no exception to the rule. They are prepared in the form of concentrates and subsequently diluted in beverages. These emulsions provide the reconstituted beverages with opacity, flavour, colour and even fat-soluble vitamins. They must possess long-term stability in concentrate form as well as when diluted in the beverage. In addition, they can be stored for a period of several months before being incorporated in the beverage, at low concentrations, i.e., less than 2% w/w. (Tan and Holmes 1988 and Tan, 2004).

2.11.1 Phase components of beverage cloud emulsion

Beverage cloud emulsions are composed of two immiscible phases namely oil phase (internal phase or dispersed phase) and water phase (external phase or aqueous phase).

2.11.1.1 Oil phase

One of the most important ingredients in beverage emulsion is the oil component. It is the oil which provides significant part of opacity in beverage cloud emulsions, with cloudiness. It has been reported that that vegetable oils at concentration of 9% weight/weight (w/w) is able to provide desirable cloudiness to citrus beverages (Taherian et al., 2006). The ingredients use to form oil phase are:

- Oils: pure and deodorize oil (canola, coconut, corn oils) are used to provide cloudiness appearance in beverage cloud emulsions. Edible waxes and terpene hydrocarbon are also used as oil phase in cloud emulsion (Tan, 2004; Kaufman and Garti, 1984).
- Weighting agents: or density adjusters are oil soluble materials which has a significantly higher specific gravity than that of vegetable oils. This materials should not contribute to the odour or color of finished product and the level of usage should be approved by regulatory agency of the country in which the product is to be consumed (Tan, 2004). Brominated Vegetable Oil (BVO), Sucrose Acetate Isobutyrate (SAIB), Ester gum and Damar gum are the mostly used weighting agent in beverage industries.

2.11.1.2 Water phase

Water: the water phase is the major component of cloud emulsion which comprises the amount of 60-80% of the formulation. The quality of water is an important issue in which the carbonate hardness or alkalinity should not exceed from 50 mg of $CaCO_3$ per litter. The water phase components are:

- Hydrocolloids: water soluble polysaccharides are served as stabilizer, viscosity adjuster, film formation, steric hindrance and electrostatic interaction (Dickinson, 2003; Tan, 2004, McClements, 2005). The widely used hydrocolloids in cloud beverage emulsions are; gum Arabic, Modified Food Starch, gum Tragacanth, Propylene Glycol Alginate, Xanthan gum, Pectin, Gellan gum, Guar gum and Carboxymethylcellulose. Several hydrocolloid gums have been studied and their activities and specifications have been reported by a number of authors (Tse and

Reineccius, 1995; McClements, 1999; Tan, 1998; Tan and Wu Holmes, 1988; Chanamai and McClements, 2001; Turbiano, 1995; Glicksman M., 1969; Sharma S.C., 1981; Light , 2002; Acton and Saffle, 1972)

The basic mechanisms for emulsion stabilization by hydrocolloid are:

- ✓ Viscosity effect
- ✓ Steric hindrance
- ✓ Electrostatic interaction

Hydrocolloids serve as the stabilizer in the cloud emulsions. When a proper hydrocolloid is used in the water phase the breakdown of the emulsion will seldom reach at coalescence stage. The reason is film forming ability of hydrocolloid around droplet of oil particles. To perform as an effective stabilizer for beverage emulsion the hydrocolloid must have the following properties (Tan, 2004 and Taherian et al., 2006):

- ✓ Readily soluble with high solubility in cold water
- ✓ Low viscosity in water (to cover the droplet surfaces by a sufficiently high concentration of hydrocolloid)
- ✓ High emulsifying property
- ✓ Will not thicken or gel on aging

Hydrocolloids are selected based on their effectiveness to act as either stabilizer or surface active hydrocolloids as are listed below:

Thickener and stabilizers hydrocolloids

1. Microbial Food Gum

- ➢ Xanthan Gum: Commercial xanthan gum is a yellowish powder completely soluble in cold and hot water, producing relatively high viscosity opaque solutions at low concentrations. Xanthan gum gives citrus and fruit-flavored beverages enhanced mouthfeel with full-bodied taste and good flavor release.

1. Marine Colloids

- ➢ PGA (Propylene Glycol Alginate) LV (Low Viscosity): PGA can act as an emulsifier in citrus punches to avoid separation and rise of flavor oils to the top of the container. It possesses good stability at pH from 3 to 4 and at room temperature. It is readily soluble in hot and cold water due to their large concentration of carboxylate anions. PGA dose not experience gelation until the pH is below 3.0. Recommended use is 0.1% to2.5%.

2. Plant Seed Gums
   - Guar Gum: Powdered guar gum hydrates well in cold water and fine grind will hydrate faster than intermediate and coarse grinds. Viscosity of guar gum increases arithmetically in solution of up to 0.5%, but in excess of 0.5% increases exponentially. Guar gum exhibits synergism when mixed with xanthan gum. This property makes it very useful in food system, since the functional properties of both gums are enhanced and a broader range of applications is therefore possible.
   - Tara gum: Similar to guar gum, tara gum is also galactomannans extracted by grinding the endosperm portions of the seeds of the legume plants Caesapinia spinosa. The property of this gum has been studied in resent studies (Sittikiyothin et al., 2005).

Surface active hydrocolloids

1. Plant Gum Exudates
   - Gum Arabic: Gum Arabic is highly soluble in cold water and solubility increasing as the temperature increases. Because of its effective emulsifying properties, gum Arabic has been effectively used in the formulation of oil-in-water (Cloud) emulsions. Gum Arabic has a broad range of compatibilities and can be used in combination with most gums, starches, carbohydrates and proteins. It is incompatible with sodium alginate and gelatin.

It has also shown promise as a stabilizer for cloud and flavor emulsions in beverages.

2. Modified Food Starches
   - Purity Gum Be: This Type of starch is a white bland tasting, odourless powder. It is cold water soluble (dissolve better at 35 °C) and the solution is low viscosity.

- **Purity gum 2000:** This Type of starch is a white bland tasting, odorless powder. It is cold water soluble and the solution is very low viscosity. At concentration less than 20%, its solution has a viscosity about equal to that of gum Arabic at the same concentration.

Acids

Acids are used in cloud emulsion to lower the pH, provide the taste and lower the chance of contamination. Citric acid is used most commonly in beverage cloud emulsion because of its close flavour to citrus fruits. Other acids such as phosphoric acid, malic acid, tartaric acid, acetic acid and lactic are seldom used in cloud emulsions.

Preservatives

The sodium salt of benzoic acid is often used as preservative for cloud emulsion. This salt is water soluble and could be more effective at pH lower than 4.5 (Tan, 2004).

2.11.2 Stability problems of a beverage emulsion

Emulsions, in both the concentrated and diluted forms, must remain stable for an extended period of time. Because of the low density of vegetable and essential oils, a poorly controlled preparation of the emulsions will result in physical instability problems, which will be manifested by creaming (ring around the neck of the bottle), flocculation or coalescence.

a) *Creaming:* When creaming occurs, two liquids separate under the action of gravity; an emulsion then separates into two emulsions; one which will be richer in the oily phase than the original emulsion, and the other, conversely, will be richer in the aqueous phase. During creaming, the oil-rich emulsion will form a creamy layer containing essential oils and/or vegetable oils at the surface of the beverage. In some cases, when the bottles are stored in a vertical position, without agitation, in the refrigerator at 4°C, Brownian motion and thermal convection of the emulsion particles will be responsible for striation, i.e., the formation of several layers exhibiting different appearances of opacity.

b) *Flocculation*: Flocculation occurs when the oil droplets of the dispersed phase form aggregates without coalescence. At this stage, the droplets still maintain their original identity. The forces that bring the droplets together are mainly associated with the Van der Waals and electrostatic forces. These aggregates behave like single large droplets; the creaming rate is accelerated in systems in which there is a sufficient differential in density of the aggregates of the continuous phase. In concentrates, an increase in viscosity of the emulsion can then be observed when flocculation occurs. Even if the flocculation changes, the physical properties of the emulsion and particle size distribution remain unchanged. In the beverage itself, the concentration of droplets is so low that flocculation is reversible; the aggregates can easily be redispersed when the interactions between droplets are weak.

c) *Coalescence:* This can be described as the localized rupture of the envelopes of the droplets comprising the aggregates, thus the oil droplets will come together to form a larger droplet. This results in a reduction in the number of oil droplets and eventually in breaking of the emulsion. Adding a hydrocolloid to the aqueous phase will prevent this breaking since certain gums such as gum arabic and modified starch have the potential to form a film around the oil droplets, as well as increase the viscosity to the aqueous phase.

2.11.3 Stabilization of a beverage emulsion

As discussed earlier, any instability of this emulsion results in the formation of a ring around the neck of a beverage bottle. Certain considerations must be studied to ensure their long-term stabilization:

a) Stokes' law

The kinetics of creaming or of sedimentation are determined by Stokes' law. This law stipulates that if the density of the oil is lower than that of the beverage, the value of U_{Stoke} will be negative and hence creaming will occur (section 11.3.1.2). In the opposite case, sedimentation will occur. Take the case of an orange emulsion that will be incorporated in a beverage. Essential oil of orange has a density of 0.85 g/cm^3 and the final beverage has a density of 1.048 g/cc (12° Brix). Applying Stokes' law, the value of U_{Stoke} will have a negative sign, the formation of a ring will then be observed during storage in the reconstituted beverage. The kinetics of creaming U_{Stoke} will therefore be directly proportional to the difference between the density of the dispersed phase and the continuous phase as well as the radius (r^2) of the droplet. It will also be inversely proportional to the viscosity of the aqueous phase. These observations can be expressed numerically; hence, in a beverage where the particle size is 0.1 μm in diameter, the particles will migrate 100 times more slowly than 1.0 μm particles. When U_{Stoke} is less than 1 mm per day, creaming can be considered negligible relative to Brownian motion.

In order to adjust the density of the oils, the Pearson rule is generally used to minimize the Archimedes effect.

Component	**Density g^{-cm3}**	**Density (beverage g^{-cm3})**	**Proportion (by volume)**
vegetable oil	**0.84**	**1.02**	**31 (oil)**
weighting agents	**1.33**		**18 (w.a.)**

Figure 2.3. Application of Pearson square method for adjustment of the density of the oil phase.

b) Adsorption at the interfaces

The gum arabic or modified starch commonly used in this type of emulsion produces a film at the oil interface. This interfacial film may be viscoelastic and after a few days of maturity may form a solid film, possibly a multi-layer film (Shorton, White, 1963; Chanamai, 2000). These authors pointed out that the film formed by gum arabic had a thickness of 0.1 μm and exhibited elastic characteristics. In addition, the use of this gum increased the weight of the oil droplet and therefore its density.

The formation of an interfacial film by hydrocolloids such as gum arabic is intended to stabilize the emulsion by preventing the phenomenon of coalescence. The layer of gum adsorbed on the surface promotes droplet separation to minimize the Van der Waals attractive force. When an emulsion is stabilized sterically by polymers such as gum arabic, this improves the physical stability of the final product. Note also that gum arabic does not have the polar and non-polar groups typical of emulsifiers that are adsorbed at the interface of the oil droplets, but nonetheless acts in the same way, although to a lesser degree.

c) *Electrostatic interaction*

Oil droplets can acquire an electrical charge through ionization of the charged groups adsorbed at the surface. For instance, the carboxyl group (COO^-) of gum arabic provides a negative charge to the droplets. The adsorption and dissolution of ions in the aqueous phase can also be a source of electrical charge. Since anions have a greater tendency to be adsorbed than cations (since the latter are normally more hydrated, they will remain in the continuous phase). The mechanism of friction is also a factor; in this case, any substance that has a high dielectric constant will be positively charged in the presence of another substance with a low dielectric constant. In the case of an O/W emulsion, since water has a higher dielectric charge, the oil droplets will therefore have a negative charge.

Ion distribution is modified in the proximity of an electrically charged surface in contact with an aqueous solution of electrolytes. The counter-ions (opposite charges) are attracted preferentially to the surface and the co-ions (ions of same charge) tend to be repelled.

The system composed by the charged surface and the zone of unequal distribution of co-ions and counter-ions near the surface is called the electrical double layer.

This double layer is therefore composed of two distinct regions: an internal immobile region (the Stern layer) where the ions are strongly adsorbed and a mobile external region (the diffuse layer) composed of ions distributed according to the balance between kinetic and potential electrical energy (Dickinson, 1992). The zeta potential corresponds to the electrical potential, at the "shear surface" between the surface of the charged particle and the dispersing aqueous phase. It is determined by particle electrophoresis. This parameter can be used to predict emulsion stability; according to Peddick (1968), a minimum zeta potential of - 40 mV would ensure physical stability because of the mutual repulsion between the particles. Any increase in this value, e.g., - 60 to - 100 mV, would increase the stability of a dispersed system. It should also be noted that although gum arabic has a zeta value of - 23 mV, other factors such as the density differential between the particles can also intervene to ensure stabilization.

The value of the zeta potential reflects the presence of the electrolytes in the system as well as of the ions in the particles. The presence of the electrolytes will mainly influence the stability of the emulsion in the beverage (diluted form). In the case where a cationic electrolyte is added to an emulsion containing negatively charged particles, the electrolyte will be adsorbed and thus will neutralize the zeta potential to cause an aggregation of the particles. This will mainly influence the stability of the emulsion in the diluted form (the beverage), since the concentration of gum arabic is very low.

Ion valence has a pronounced effect on zeta potential; trivalent ions (Al^{+3}) will be 10 to 100 times more influential than divalent ions (Ca^{++}) at equal concentrations (Tan, 1988). This observation supports the use of treated water for the formulation of emulsions and beverages.

d) Oil particle size

Stokes' law demonstrates that there are several ways of inhibiting the kinetics of creaming in a diluted emulsion: reducing droplet size, reducing the density differential between the continuous and dispersed phases, and increasing the viscosity of the continuous phase.

The particle size distribution profile can be determined using a Coulter counter. This is therefore a key method for predicting the physical stability of a diluted emulsion. Generally, the smaller the particle size, the greater number of particles available to distribute the flavour uniformly: a large number of particles will provide greater opacity in a beverage (Melillo, 1977).

Note that it is preferable to express the results by volume since this clearly distinguishes the quantity of droplets by volume. For example, an emulsion containing 1,000 droplets of 1μm and 1 droplet of 10 μm, by population, this 10 μm occupies only 0.1% of the total population and by percent volume; 10 μm droplets occupy 50% of the dispersed volume since the volume of 1,000 1 μm droplets is equivalent to that of the 10 μm droplet (Johnson, 1982).

PREFACE TO CHAPTER 3

The opalescent agents or cloud emulsions are added to fruit beverages to provide the similar appealing appearance as fruit juice. Weighting agents or density adjusters are also added to the oil phase to obtain the desired stability.

While the focus of the most studies have been the stability of cloud emulsions by varying the concentrations of different weighting agents or their effects on stability, this the first time that the physical properties of cloud emulsions in the presence of weighting agents at restricted level of use has been investigated.

The study was conducted by preparing two series of emulsions, one varied in starch concentrations and the other in oil concentrations. The vegetable oil was loaded with the identical amount of weighting agents for both series. In starch added emulsions, the amount of oil is constant for each emulsion and the only variable is the concentration of starch. This amount of oil was calculated base on 1) Pearson Square Method to obtain a density of 1.04 for the oil phase and 2) the more important, the amount of SIAB and BVO allowed in the beverages (300 and 15 p.p.m. respectively).

In oil added emulsions where both level of starch and weighting agents are constant, due to a decrease in the density of the oil phase, as the oil level increases the creaming values increases accordingly. We found that the oil concentration is readily responsible for providing the opacity to the emulsion and hence the final product. The relation between opacity and oil concentrations was also found and carried out through all investigations for the next chapters.

The results of this research was presented at different conferences and published in Journal of Food Engineering (Taherian et al., 2006). The experimental works, data analysis and writing the paper were carried out by the candidate under supervision of Professor H.S. Ramaswamy. Dr. P. Fustier was engaged in technical and resources support as well as scientific advices.

CHAPTER 3

EFFECT OF ADDED OIL AND MODIFIED STARCH ON RHEOLOGICAL PROPERTIES, DROPLET SIZE DISTRIBUTION, OPACITY AND STABILITY OF BEVERAGE CLOUD EMULSIONS

3.1 ABSTRACT

Optical and rheological properties of beverage cloud emulsions as a function of water-phase and oil-phase concentrations were investigated. The specific gravity of phases, particle size distribution and creaming stability of prepared emulsions in diluted forms were evaluated. Combinations of emulsions with added starch (3.74-18.7% w/w, with oil at 3.74% w/w) and oil (7.48-18.7% w/w with starch at 11.2% w/w) were used. The specific gravity of oil phase was adjusted using a constant combination of weighing agents [sucrose acetate isobutyrate and brominated vegetable oil] and different level of coconut oil. Oil-phase concentration had a significant effect ($P < 0.05$) on increasing the opacity of emulsion. Increase in modified starch concentration for all water phases decreased the flow behavior index while oil phase at any given concentration of coconut oil contributed to a Newtonian behavior. Increase in viscosity of emulsions was more pronounced as oil concentration increased and shear thinning behavior of oil added emulsions was associated with droplet flocculation. Creaming in acidified sugar solution of 11°Bx and pH 3 was observed when the oil-phase specific gravity decreased and sedimentation occurred at the lower viscosity of water phase. Examination of dynamic rheological properties of emulsions revealed that all oil added emulsions showed viscous behavior with the delta degree (G"/G') greater than 74 at maximum frequency level (50 rad/sec) and decreased along with increasing the oil level. The solid or elastic behavior was related to those emulsions that exhibited sedimentation with the delta degree lower than 35.

3.2 INTRODUCTION

Emulsion stability is an important quality criterion and ringing (creaming) a major quality defect in citrus drinks and beverages. Beverage emulsions are primarily used to give opacity to clear beverages or to enhance their juice-like appearance. These emulsions are different from other food emulsions in that they are consumed in a highly diluted form. The low concentration of droplets in diluted beverage emulsions (<0.3 wt %) accounts for their slightly turbid or "cloudy" appearance and their viscosities are similar to that of the aqueous solution that surrounds the droplets (McClements, 1999, Chanamai and McClements, 2001).

Oil phase is the flavor oil, terpenes or a vegetable oil and water phase is a solution of highly functional hydrocolloids, such as specialty food starch or gum Arabic (Trubiano, 1995). Modified food starches are the most widely accepted alternative to gum Arabic for use as the beverage emulsion stabilizer. They are a group of specially designed starch derivatives with balanced lipophilic and hydrophilic groups on the starch molecules (Tan, 1997). Purity gum (National Starch, Bridgewater, N.J. U.S.A.), used in this study, is an octenyl succinate derivative of waxy-maize which consists primarily of amylopectin that has been chemically modified to contain non-polar side-groups and has a surface activity almost as high as gum arabic (Chanamai and McClements, 2001). The concentration of modified starch in cloud emulsion is an important consideration and should be sufficiently high in order to cover the oil droplets (McClements, 1999).

However, these types of oil in water (o/w) emulsions are inherently unstable due to the difference in specific gravity between the oil droplets and the water medium (Hernandez et al., 1991). The specific gravity of citrus drink usually varies from about 1.038 to 1.054 and depends on the emulsion refractive index. Even though vegetable oil can be emulsified and uniformly dispersed, the large difference in the specific gravity between the two (oil and aqueous) phases can cause the deterioration of beverage emulsion and gives rise to "ringing" and "oiling-off". Ringing or the formation of a whitish "ring" around the neck of the container and "oiling-off" or the formation of shiny oil slick on the top of the product are the result of gravitational separation, flocculation, and coaleascence (Tan 1997, 1998; McClements, 1999; Chanamai and McClements, 2000). Stoke's law (Equation 1) has been employed to express the velocity of ringing and sedimentation (Tan, 1997 and McClements, 2000):

$$U_{Stokes} = -\frac{2gr^2(\rho_1 - \rho_2)}{9\eta_2} \quad (1)$$

where U is the creaming velocity, η_2 is the viscosity of water phase, r is the particle radius, g is acceleration due to gravity, ρ_1 is the density of oil phase, and ρ_2 is the density of water phase.

Therefore, reducing particle size along with increasing density of oil droplet and viscosity of water phase can enhance the stability of beverage emulsion. Specific gravity of vegetable oil can be adjusted by addition of weighting agents or density adjusting agents in order to maintain a stable dispersion of the oil (Tan, 1997; McClements, 1999; Chanamai and McClements, 2000; Huang et al., 2001).

Several studies have characterized rheological properties of food emulsions with steady state shear viscosity. Chanamai and McClements (2000) described that the apparent viscosity of concentrated emulsions ($\phi > 20\%$) containing smaller droplets was higher than that of emulsion containing larger droplets and decreased with increasing shear rate while the apparent viscosity of dilute emulsions ($\phi < 20\%$) was relatively independent of the applied shear stress. Buffo and Reineccius (2002) stated that the rheology of concentrated beverage emulsions ($\phi \sim 5\%$) can be confidently modeled through the Einstein equation or its exponential expansion. Suzuki et al (1991) and Klinkesorn et al. (2004) studied the rheology and stability of corn oil-in-water emulsions and explained that the apparent viscosity of emulsions are affected by volume concentration of the dispersed phase, nature of emulsifying agent and emulsifying conditions, and above the critical flocculation concentration emulsions are highly viscous with strong shear thinning behavior.

Nevertheless, there has not been that much attention given to change in dynamic rheological properties of beverage emulsions which can give a more complete rheological description. On the other hand, some of the ingredients such as brominated vegetable oil (BVO) and sucrose-diacetate-hexa-isobutrate (SAIB), widely used as weighting agents, are being withdrawn or limited to certain levels and/or certain countries. The permitted level of use in different countries has been reported to be 15 ppm for BVO and 50 to 500 ppm for SAIB (Turner, 1972; Kufman and Garti, 1984; Tan and Wu Holmes, 1988; Garti et al., 1991; Tan, 1997). The cloud emulsions must also contribute to the opacity of the formulated citrus drink without affecting the stability of the cloud, color, taste or odor of the finished product. These requirements, together with restrictions on the choice of weighting agents, are difficult to meet and there is a need for further investigation of factor affecting cloud emulsions stability.

Therefore, the objective of this study was to examine the opacity, droplet size and distribution, as well as flow and dynamic rheological properties of both the oil and water phases alone and in combination, in form of emulsions, at different level of gum and oil concentrations. The outcomes were then related to the stability of emulsions prior to and after dispersion in simulated beverages (acidified sugar syrup).

3.3 MATERIALS AND METHODS

3.3.1 Materials

Commercially available coconut oil, brominated vegetable oil (BVO) and sucrose acetate isobutyrate (SAIB) were obtained from Univar and Daminco Inc., PQ, Canada and modified starch (Purity Gum Be) was obtained from National Starch and Chemical (Bridgewater, NJ). Food grade citric acid was used to adjust the acidity in all prepared emulsions.

3.3.2 Preparation of emulsions

Different water phase starch based preparations were made by mixing modified starch at various levels (3.74-18.7% w/w) in double-distilled water. The mixtures were kept 24 h at room temperature to allow full hydration and then stirred until complete dissolution. Using a 50% (w/w) solution of citric acid, pH of each water phase adjusted at 3 prior to any examination. The oil phases were prepared by dispersing a measured amount of BVO and SAIB (to give 15 ppm and 300 ppm, respectively in the final product) into different level of coconut oil and stored at room temperature for 24 h to assure entire removal of air bubbles before any test. The oil phase was added to the water phase starch base at a fixed level of coconut oil (3.74% w/w). In addition, different oil phase emulsions were also prepared by blending varied quantities of oil phase (3.74-18.7%, w/w) with a 11.2% (w/w) water phase starch base. Oil droplets sizes were reduced using first Polytron laboratory scale homogenizer (Kinematica, Kriens-Lucerne, Switzerland) at highest speed for 3 min. Further reduction of particles size was obtained with the aid of high pressure homogenizer (Emulisiflex-C5, Avestin, ON, Canada) at 3500 psi over one pass.

3.3.3 Particle size distribution

The particle size distribution of emulsion was determined by the integrated light scattering technique using a ZetaSizer 4 (Malvern Instruments Ltd., Malvern, UK). The emulsions were analyzed right after preparation in duplicate. The instrument used the method of photon correlation spectroscopy (PCS) to measure particle size in constant random thermal, or Brownian, motion. This motion causes the intensity of light scattered from the particles to vary with time. Large particles move slowly than small ones, so that the rate of fluctuation of the light scattered from them is also slower. PCS uses the rate of change of these light fluctuations to determine the size distribution of the particles scattering light. The particle diameter range and number of photon counts per second [Emission strength or kilo Count per second (kCps)] were evaluated at room temperature when the volume fraction of oil in the diluted emulsion was about 1:1000 for all the cases.

3.3.4 Evaluation of opacity and specific gravity

Emulsions were diluted (1:1000) for measurement of absorbance at 660 using a Beckman DU 640 Spectrophotometer. Opacity was then calculated from the absorbance at 660 nm (Kaufman and Garti, 1984 and Garti et al., 1991). Number of photons count per second (kCps) obtained from ZetaSizer was also used as a measure of opacity and outcomes form both instruments were correlated. Specific gravity of each constituent alone and together was evaluated at the existing concentrations using a 25 ml specific gravity bottle [Fisherbrand, Ottawa, Canada].

3.3.5 Flow and dynamic rheological measurements

Measurement of rheological parameters such as flow behavior index (n), consistency coefficient (m) and shear viscosity (η_γ) as well as storage modulus (G'), loss modulus (G") and delta degree (G"/G') were carried out using an AR2000 Rheometer (TA Instrument, New Castle, DE, U.S.A.). The instrument was equipped with a 60 mm cone of 2° and solvent trap. Flow curves (shear stress vs. shear rate) were determined at increasing shear rates (0.1-100 s^{-1}) within 3 min.

The apparent viscosity of oil phase and water phase alone, and together in form of emulsions at fixed ($\phi \approx 0.04$) and varied level of volume ratio ($\phi \approx 0.08$-0.2) was measured as a function of shear rate ($\dot{\gamma}$). Experimental flow curves were compared to Power's law model, which is the typical equation to characterize shear thinning fluids:

$$\eta = m\,\dot{\gamma}^{(n-1)} \qquad (2)$$

where n <1 for a shear-thinning fluid and n = 1 for a Newtonian fluid. The variations of consistency coefficient (m) and flow behavior (n) were then determined at five level of starch and four level of oil concentrations.

For dynamic oscillatory evaluation a frequency sweep from 1 up to 50 radians per second was carried out where the oscillation stress was fixed at 1 Pascal (obtained from the development of stress sweep in the linear region). All the flow and dynamic rheological parameters are the mean of six measurements per duplicates emulsions.

3.3.6 Emulsion stability

Creaming and sedimentation values were calculated from the ratio of cream and sediment volumes over total volume of emulsion samples up on standing. Duplicate samples containing 60 ml of prepared emulsion were stored in 100 ml Wainthropp tube for 48 h at 25 ±1°C. The results were expressed as percentage of the total height of the emulsions in the tube (H_E): Creaming Index = 100 × (H_C/H_E) and Sedimentation Index = 100 × (H_S/H_E) (Radford et al., 2004 and Klinkesorn et al., 2004)

Gravity creaming of emulsion samples was also monitored visually after dilution into the simulated beverage (acidified sugar syrup with 11°Bx at pH 3) over a period of 1-5 weeks. Glass bottles of 330 ml were filled with simulated beverages containing 2% of emulsion of known composition. The filled bottles were then pasteurized at 90°C for 12 min and stored at room temperature. Samples were graded as + and ± when creaming was observed after 1 and 3 weeks respectively. The stable emulsions with no sign of creaming after 5 weeks were rated negative. Monitoring was performed in duplicate with a total of 6 bottles for each prepared emulsion.

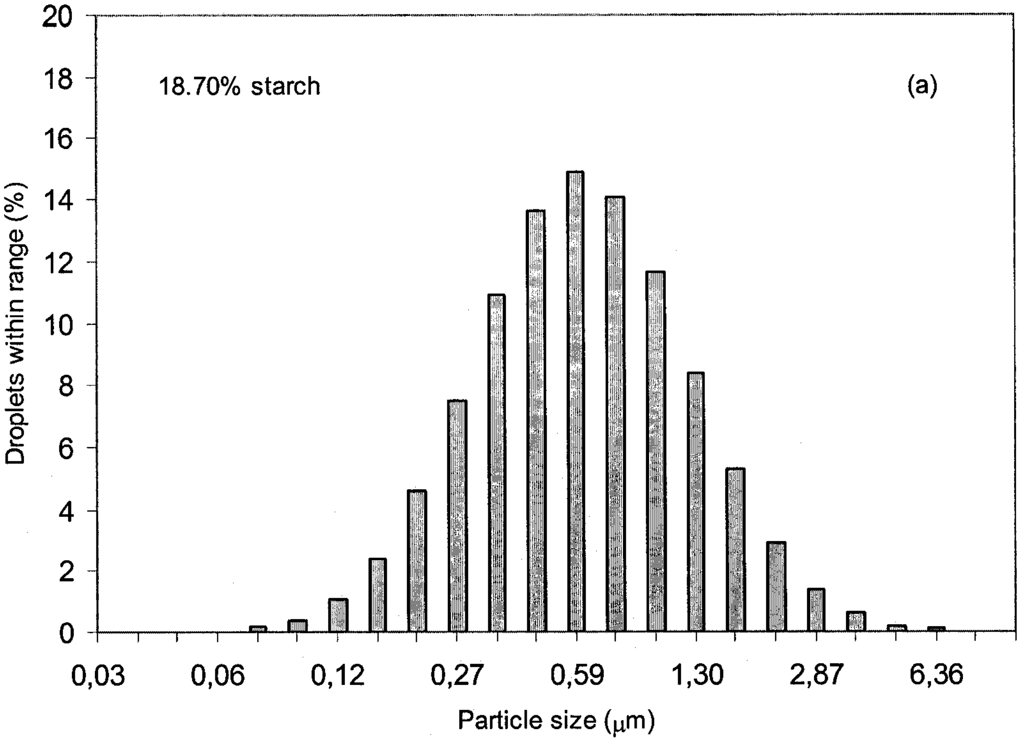
3.3.7 Statistical analysis

The effect of oil and starch concentration on the opacity of emulsions was statistically tested using the regression and ANOVA - two-factors with replication, and the means were compared at a significant level of 5%. Statistical analysis was done using Microsoft Excel and experiments were performed in duplicate.

3.4 RESULTS AND DISCUSSION

3.4.1 Starch and oil effects on particle size distribution and opacity of emulsions

The effect of starch and oil concentration on particle size distribution was investigated for five concentrations of starch and four concentrations of coconut oil, where each one experienced the identical method of preparation. The results for emulsions prepared with maximum starch and oil concentrations, are shown in Figures 3.1a and 3.1b, respectively. It can be seen clearly that neither of the emulsions could be considered as mono-dispersion; i.e., the droplets were not of the same size. Since the droplet size varied, an average droplet size was considered to compare the changes in particle size for all emulsions. Figure 3.2 compares the contribution of starch and oil at



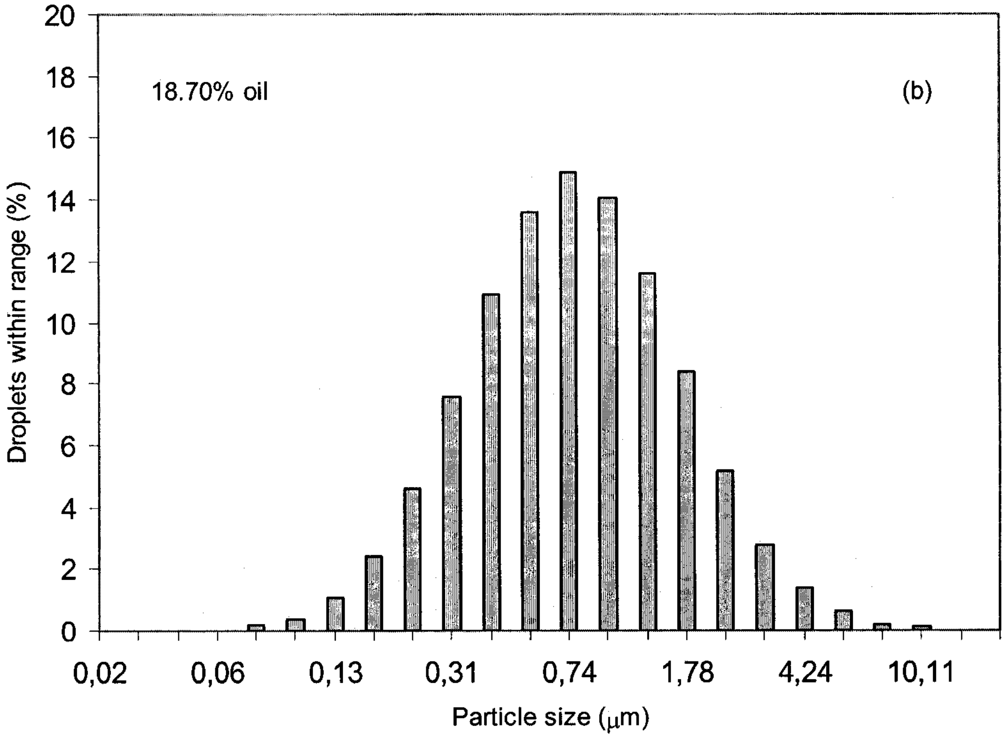


Figure 3.1. Particle size and distributions for added starch (a) and added oil (b) emulsions at maximum levels of concentration.

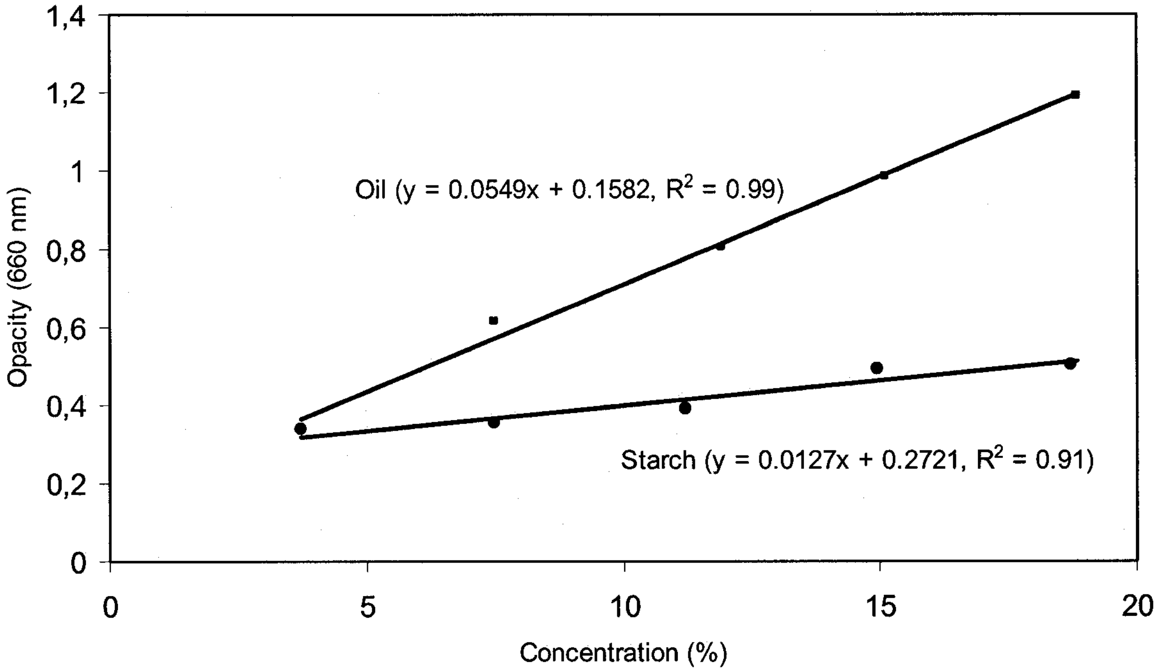


Figure 3.2.Contribution of oil and starch concentration to the opacity of diluted emulsions.

various levels of concentrations to the opacity of prepared emulsions. Figure 3.3 demonstrates that variation in starch concentration resulted in relatively smaller affects on both the average particle size and concentration (number of counts). Number of counts is a measure of the intensity of the scattered light (photon emission strength) and is directly related to the opacity of emulsion. It also appears that the starch concentration build-up was able to increase the coating of the droplets as count per second did not change to the same extent as of average particle size. Both Figure 3.2, as a function of absorbance at 660 nm and Figure 3.3, as a function of kilo count per second, demonstrate the agreement in term of their contribution trend to the opacity. While increases in opacity of both series of emulsions were linear, the oil concentration contributed significantly ($P < 0.05$) to increase the opacity to the emulsion as compared to that of added starch. By comparing the slopes of the absorbance at 660 nm versus oil and starch concentrations in emulsions, it can be realized that oil contributed 4.3 times more opacity than starch with correlation coefficients of 0.99 and 0.91, respectively. Similar comparison for opacity change as a function of kilo count per second showed a greater contribution by oil compared to the starch with correlation coefficients of 0.97 and 0.98, respectively.

3.4.2 Influence of starch and oil concentrations on creaming and sedimentation stability

The representative results concerning both stability and specific gravity for nine formulated emulsions containing starch and oil at various levels are presented in Table 3.1 and 3.2. The selection of starch concentrations, for starch added emulsions, was based on the weight ratio of gum/oil at five levels where the specific gravity and amount of oil phases were constant at 1.04 and 3.74 % (w/w). The specific gravity was adjusted by combining 50.53 % (w/w) oil with 47.1 % (w/w) SAIB and 2.41 % (w/w) BVO at specific gravities of 0.950, 1.146 and 1.24 respectively. This proportion was derived from accepted level of BVO and SAIB after dilution in final drink (15 and 300 ppm) and calculated by the use of Pearson's square method [Equation 3 (Melillo, 1977)]:

$$P = \frac{\mathrm{G}}{1.04}\left(\frac{1.04 - \mathrm{E}}{\mathrm{G} - \mathrm{E}}\right) \tag{3}$$

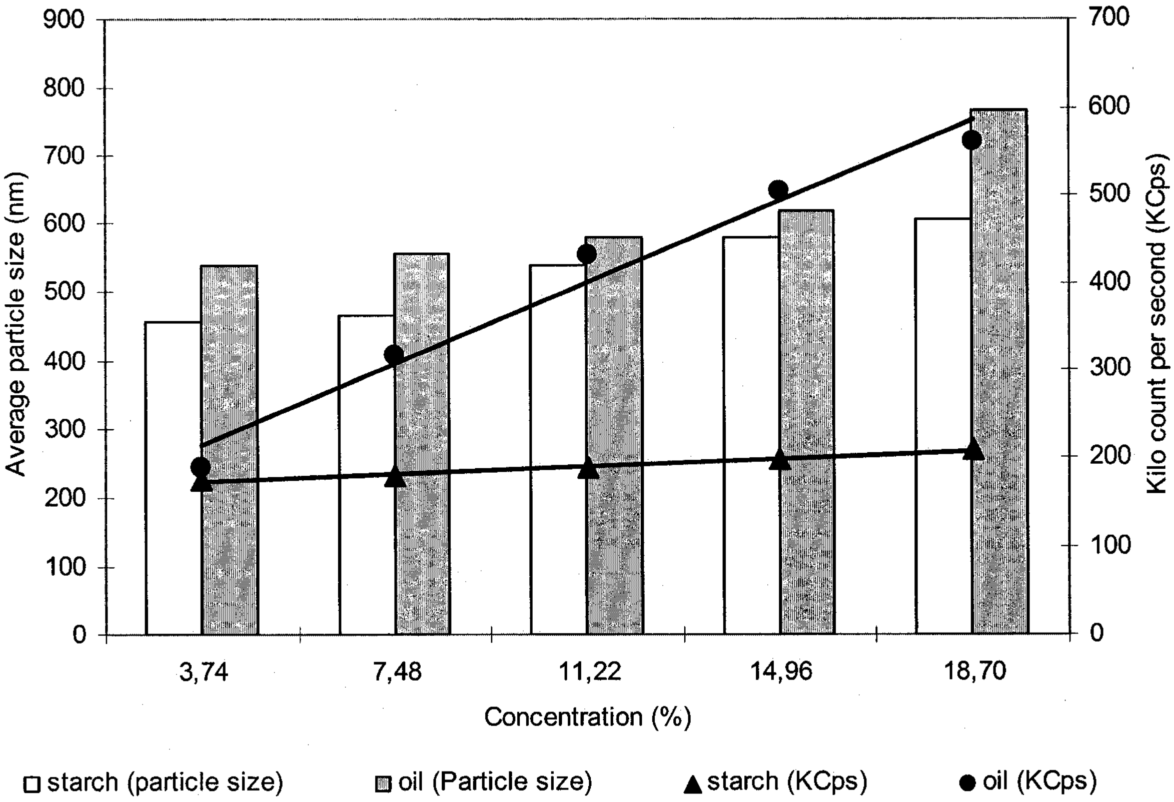


Figure 3.3. Particle size and photons count of emulsions as influence of starch and oil concentrations.

Table 3.1. Comparison of emulsion properties as a function of starch concentration.

Properties	Starch Concentration				
	3.74 %	7.48%	11.22 %	14.96 %	18.70 %
Oil phase Specific g	1.04 ± 0.02	1.04 ± 0.02	1.04 ± 0.02	1.04 ± 0.02	1.04 ± 0.02
Water phase Specific g	1.023 ± 0.02	1.032 ± 0.01	1.045 ± 0.01	1.068 ± 0.01	1.093 ± 0.01
Mean Particle size (nm)	456 ± 5.06	465 ± 3.70	540 ± 6.20	581 ± 0.95	606 ± 6.45
Opacity (660 nm)	0.33 ± 0.006	0.35 ± 0.003	0.38 ± 0.008	0.49 ± 0.002	0.50 ± 0.004
Creaming (%)	0.00	0.00	0.00	0.00	0.00
Sedimentation (%)	0.97 ± 0.08	0.76 ± 0.07	0.00	0.00	0.00
Ringing in bottle	-	-	-	-	-

Table 3.2. Comparison of emulsion properties as function of oil concentration.

Properties	Oil Concentration			
	7.48%	11.22 %	14.96%	18.70 %
Oil phase Specific g	0.990 ± 0.05	0.974 ± 0.02	0.969 ± 0.02	0.965 ± 0.06
Water phase Specific g	1.053 ± 0.01	1.059 ± 0.01	1.061 ± 0.03	1.063 ± 0.02
Mean Particle size (nm)	556 ± 7.10	580 ± 0.45	620 ± 7.35	767 ± 0.15
Opacity (660 nm)	0.64 ± 0.02	0.80 ± 0.01	0.99 ± 0.03	1.06 ± 0.02
Creaming (%)	4.56 ± 0.36	6.90 ± 0.71	8.23 ± 0.66	9.30 ± 0.63
Sedimentation (%)	0.00	0.00	0.00	0.00
Ringing in bottle	±	+	+	+ +

where P is the weight fraction of weighting agent (weight of weighting agent/weight of oil mixture), G is specific gravity of weighting agent, E is specific gravity of oil and 1.04 is the desired specific gravity for our case.

The oil concentrations, for added oil emulsions, were selected to be equal to that of starch concentrations for the first series. The water phases contained the identical amount of starch (11.2 % w/w) at which no sedimentation was observed for starch added emulsions (Table 3.2). Creaming and sedimentation values were then monitored by visual observation after 48 h storage at the room temperature and prior to the high pressure homogenization. The reason for measuring the creaming and sedimentation at this step was to obtain a rapid response to the degree of stabilization of emulsion in concentrated forms. Huang et al. (2001) reported that concentrated emulsions with small droplets (high pressure homogenized), which normally does not show any sign of instability during long term storage, could be evaluated by centrifugation assay.

However, this centrifugation method was not successful in this study; hence the stability assay was done prior to high pressure homogenization. This observation also confirmed the significant effect of particle size on stability of beverage cloud emulsions in concentrated form. Nevertheless, for the starch added emulsions no indication of creaming was found and sedimentation occurred when the density of the oil phase was higher than that of the water phase. For oil added emulsions (Table 3.1b), conversely, creaming was associated with all prepared emulsions indicating that stability of concentrated beverage emulsions are significantly affected by difference in specific gravity of both oil and water phases.

In order to examine the stability of emulsions in diluted form, certain amounts of each homogenized emulsion was diluted in acidified sugar solution where the level of BVO and SAIB in solution did not exceed from 15 ppm and 300 ppm, respectively. The acidified sugar solution was at 11°Bx with pH of 3 and specific gravity of 1.04. As illustrated in Table 3.1, for starch added emulsions, no sign of instability (ringing or sedimentation) was accompanied with any diluted emulsion indicating if the specific gravity of emulsion is equal to that of water phase and the average particle size are less than one micron the desired level of stability could be achieved. However, as it was mentioned earlier, starch added emulsions had significantly lower contribution to the opacity of final drink and use of starch at a level of more than 14% may not be feasible for industrial preparation. Table 3.2 summarizes the creaming stability associated with the oil added emulsions in diluted form. As the specific gravity differences between the oil and water phases increased presences of whitish cream (ringing) was, accordingly, more pronounced in diluted forms.

3.4.3 Flow and dynamic properties

Flow characteristics

Table 3.3 compares the flow properties of emulsions and related phases at selected concentrations of starch. The determination coefficients (R^2) for all measurement were more than 0.97 (not shown), indicating a high level of relation between measuring points. Increase in starch concentration contributed to change the flow behavior of water phase from Newtonian to slightly shear thinning ($n = 0.99$ to 0.85), while the oil phase and oil emulsions contributed to build up of Newtonian viscosity (Figures 3.4 and 3.5). Higher consistency coefficient and apparent viscosity of water phase ($m_{.W.ph}$ and $\eta_{app.W.ph}$) and emulsion ($m_{.Em}$ and $\eta_{app.Em}$) at low shear rate ($0.1s^{-1}$) was due to increase in starch concentrations. This effect was consistent across the whole shear rate as shown in Figure 3.4. Table 3.4 and Figure 3.6 compare the flow properties and viscosity of both phases and emulsions, for oil added emulsions, at low and across the whole shear rate range, respectively. Slight and sharp increase in consistency coefficients of water phase and emulsions ($m_{.W.ph}$ and $m_{.Em}$) were related to the replacement of water with oil in emulsion formulations. Conversely, oil phase consistency coefficient decreases as a result of increase in oil and decrease in weighting agents (BVO and SAIB) concentrations as illustrated in Figure 3.5. The dependence of viscosity of oil phase on concentration of coconut oil in oil phase can be explained by a power type relationship:

$$\eta_{oilphase} = a\,C^{b} \qquad (4)$$

where a and b are empirical constant at 53.70 and -1.65 respectively.

Figure 3.6 compare the shear dependency of viscosity at selected shear rate range

Table 3.3. Flow properties of oil and water phases alone and together in form of emulsions as a function of starch concentrations.

Properties	Starch Concentration				
	3.74 %	7.48%	11.22 %	14.96 %	18.70 %
$n_{W.ph}$	0.99 ± 0.006	0.95 ± 0.004	0.90 ± 0.01	0.87 ± 0.01	0.85 ± 0.02
$n_{O.ph}$	1.00 ± 0.002	1.00± 0.002	1.00 ± 0.002	1.00 ± 0.002	1.00 ± 0.002
n_{Em}	1.00 ± 0.004	0.98 ± 0.003	0.98 ± 0.005	0.98 ± 0.003	0.98 ± 0.004
$m_{W.ph}$ (mPa)	3.22 ± 0.06	6.66 ± 0.32	18.1 ± 0.21	39.3 ± 0.30	98.8 ± 0.81
$m_{O.ph}$ (mPa)	74.6 ± 3.53	74.6 ± 3.53	74.6 ± 3.53	74.6 ± 3.53	74.6 ± 3.53
m_{Em} (mPa)	3.62 ± 0.04	8.55 ± 0.28	24.0 ± 0.31	56.0 ± 0.40	143 ± 0.92
$\eta_{app.W.ph}$ 0.1 s^{-1} (mPa.s)	3.30 ± 0.09	7.48 ± 0.40	22.8 ± 0.78	53.0 ± 1.62	140 ± 7.57
$\eta_{app.O.ph}$ 0.1 s^{-1} (mPa.s)	74.6 ± 3.53	74.6 ± 3.53	74.6 ± 3.53	74.6 ± 3.53	74.6 ± 3.53
$\eta_{app.Em}$ 0.1 s^{-1} (mPa.s)	3.62 ± 0.04	8.95 ± 0.3	25.1± 0.62	58.7 ± 1.05	146 ± 4.60
$\eta_{relative}$0.1 s^{-1} (mPa.s)	1.10 ± 0,02	1.20 ± 0,04	1.10 ±0,03	1.12 ± 0,03	1.12 ± 0,05

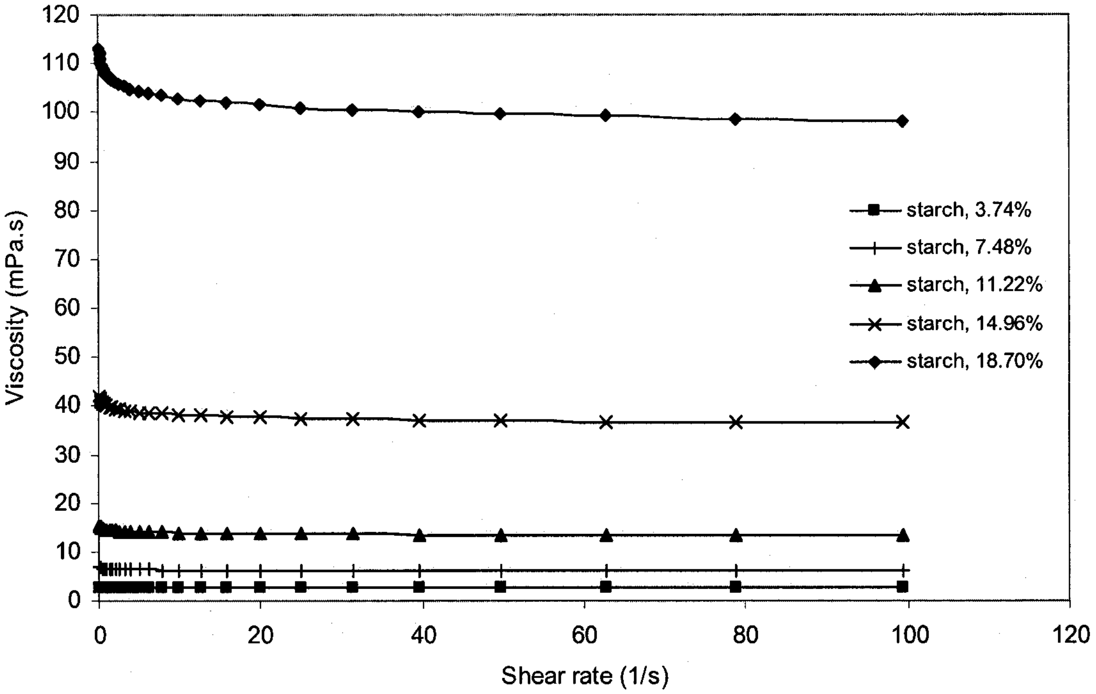


Figure 3.4. Apparent viscosity of emulsions at selected starch concentration as an influence of shear rate.

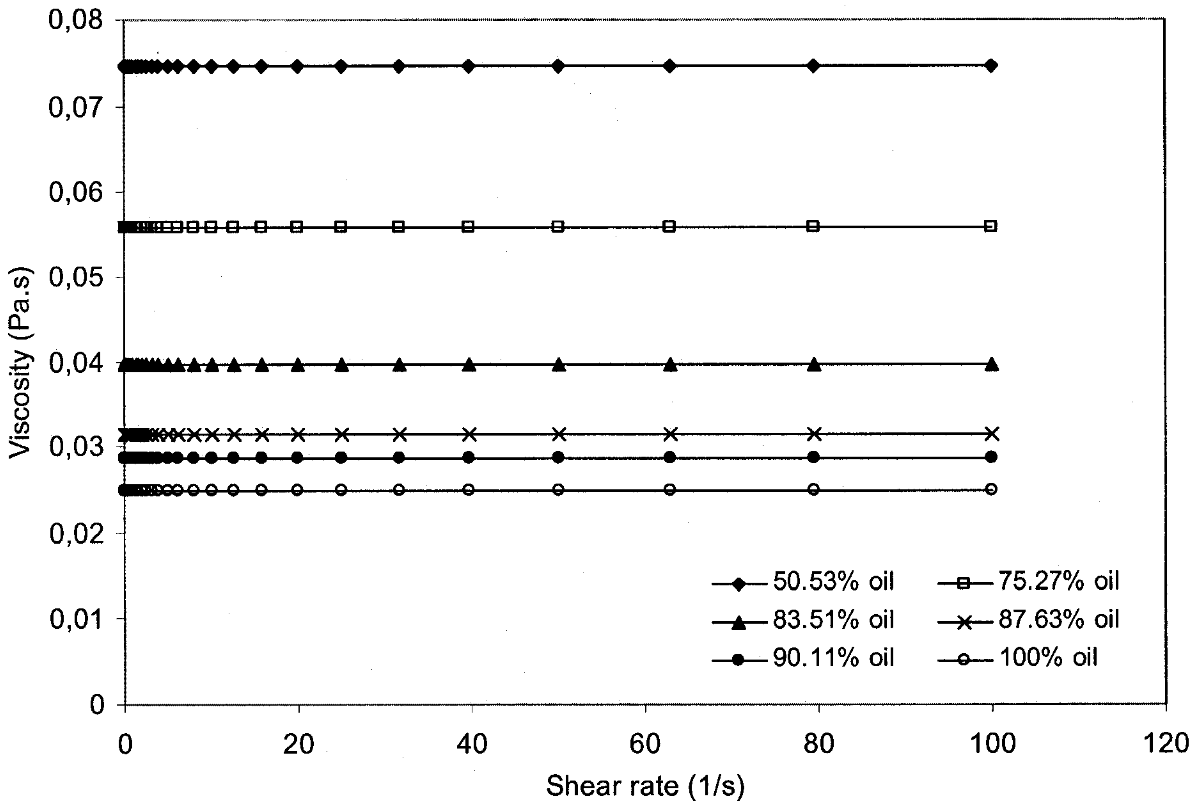


Figure 3.5. Apparent viscosity of oil phase at selected oil concentration as an influence of shear rate.

Table 3.4. Flow properties of oil and water phases alone and together in form of emulsions as a function of oil concentrations.

Properties	Oil Concentration			
	7.48%	11.22 %	14.96%	18.70 %
$n_{W.ph}$	0.89 ± 0.01	0.86 ± 0.02	0.84 ± 0.02	0.82 ± 0.02
$n_{O.ph}$	1.00 ± 0.001	1.00 ± 0.002	1.00 ± 0.002	1.00 ± 0.001
$n_{Em.}$	0.94 ± 0.01	0.84 ± 0.01	0.80 ± 0.03	0.70 ± 0.04
$m_{W.ph}$ (mPa)	20.4 ± 0.54	24.5 ± 0.58	25.5 ± 0.17	26.3 ± 0.86
$m_{O.ph}$ (mPa)	55.9± 0.74	39.7 ± 0.12	31.4 ± 1.8	28.6 ± 0.20
$m_{Em.}$ (mPa)	32.3 ± 0.84	69.3 ± 1.21	107 ± 2.14	447 ± 4.32
$\eta_{app.W.ph}$ 0.1 s^{-1} (mPa.s)	26.5 ± 1.57	33.9 ± 2.34	37.4 ± 1.48	39.7 ± 0.54
$\eta_{app.O.ph}$ 0.1 s^{-1} (mPa.s)	55.9± 0.74	39.7 ± 0.12	31.4 ± 1.8	28.6 ± 0.20
$\eta_{app.Em}$ 0.1 s^{-1} (mPa.s)	37.0 ± 1.74	100 ± 2.33	170 ± 1.89	892 ± 7.50
$\eta_{relative}$0.1 s^{-1} (mPa.s)	1.40 ± 0.15	2.70 ± 0.13	4.54 ±0.14	22.4 ± 0.12

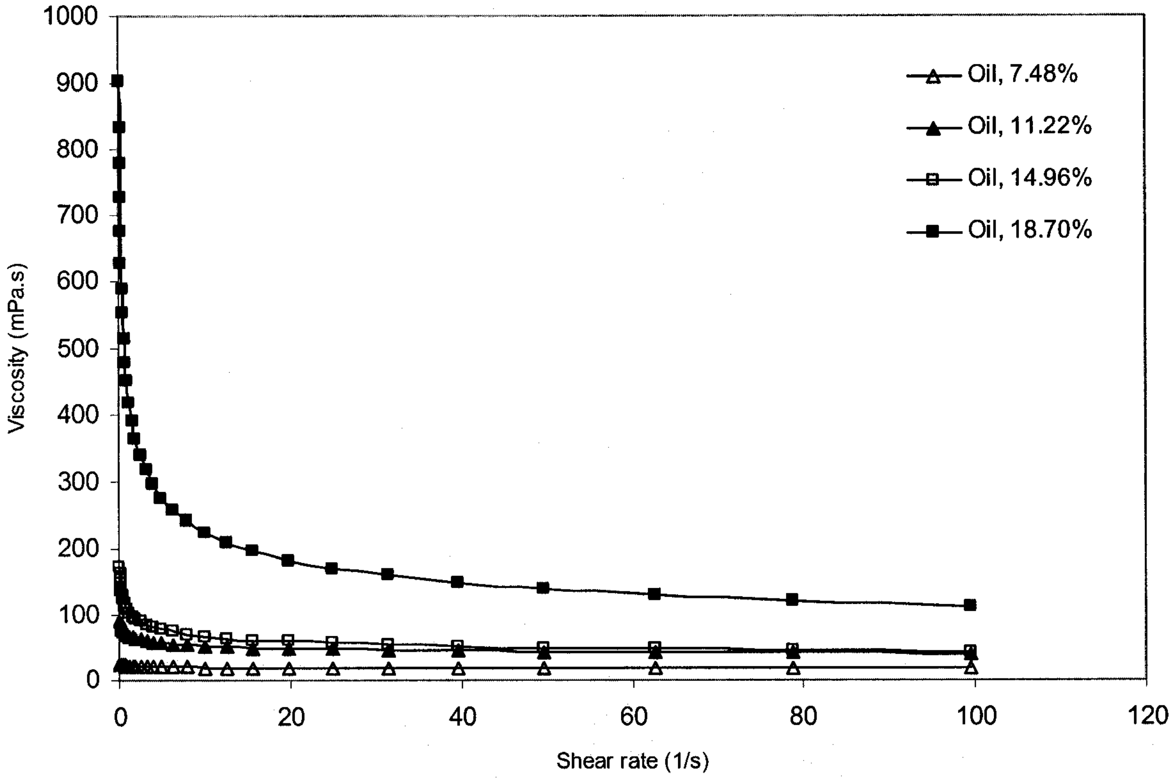


Figure 3.6. Apparent viscosity of emulsions at selected oil concentration as an influence of shear rate.

for oil added emulsion. The flow behavior index decreased when oil concentration increased in oil phase indicating a pronounced shear thinning effect at higher concentration of oil phase. This phenomenon has been explained to be related to droplet flocculation through domination of the attractive forces over repulsive forces which in turn become greater than the thermal energy of the system (McClements, 1999). Small hydrodynamic forces at low shear rate are not able to disrupt the flocs and as an effect of increasing the shear rate the hydrodynamic forces will dominate and disrupt the flocs causing a reduction in viscosity (Sherman, 1983; McClements, 1999).

The relative viscosity of emulsions was also calculated in order to examine the influence of droplets on emulsion rheology:

$$\eta_{app.relative} = \frac{\eta_{\mathrm{app.\,Em.}}}{\eta_{\mathrm{app.\,W.ph}}} \tag{5}$$

where $\eta_{\mathrm{app.Em}}$ is the apparent viscosity of the emulsion at a particular shear rate and $\eta_{\mathrm{app.W.ph}}$ is the viscosity of the water phase at the same shear rate.

The relative viscosity for starch added emulsions was slightly higher than unity as could be expected for a non-flocculated oil-in-water emulsion. This is in consistent with Einstein equation

$$\eta_{relative} = 1 + 2.5\,\phi \tag{6}$$

which is approximately 1.10 for starch added emulsions since $\phi \approx 0.04$ (Sherman, 1983; McClements, 1999; Klinkesorn et al., 2004).

For oil added emulsions, on the other hand, the relative viscosity at low shear rate was greater than unity and increased along with increasing the oil concentration.

However the relative viscosity decreased by increasing the shear rate, which in turn can be attributed to progressive disruption of the flocs when the shear rate was increased. Increase in relative viscosity of an emulsion has been related to droplet flocculation for the reason that the effective volume fraction (ϕ_{eff}: is related to the size of floc and the fractal dimension) of the particles in the system is increased due to the presence of the continuous phase (water phase) trapped between the droplets in the flocs (McClements, 1999; Klinkesorn et al., 2004). The results for both series of emulsions hence are in agreement with the creaming stability outcomes in concentrated and diluted forms as explained earlier.

Dynamic characteristics

Dynamic measurement was conducted to obtain a better description of rheological properties of emulsions under studied. To insure storage modulus (G') and loss modulus (G") are reliable and accurate a stress sweep test was first conducted. This way the linear region, where the dynamic parameters (G', G" and phase shift angle δ) are independent of the magnitude of applied stress, was investigated and proper measuring parameters were selected. The focus in this study was to compare the phase shift angle or delta degree of starch and oil added emulsions. The use of phase shift angle or delta degree (δ) in viscoelastic systems is based on the measurements of G' and G" modulus. Thus in a purely viscous system (i.e., water) δ is 90 °, and subsequently G' = 0 and G" = G*, where G* is the complex modulus. Eventually, if the system is purely elastic δ is 0 °, and subsequently G' =G* and G" = 0.

Figures 3.7 and 3.8 demonstrate the effect of starch and oil concentrations on frequency dependence of phase angle (δ) of emulsions at constant level of oil and starch respectively. Figure 3.7 indicates that the δ is not only frequency dependent, but also dependent on concentration of starch; it decreases as a function of the frequency and increases as a meaning of starch concentration. The appropriate way to describe this occurrence is to look at both specific gravity and viscosity of the oil phase reported earlier. As shown, the δ of emulsions at low concentration of starch (3.74% and 7.48%) and elevated levels of frequency is much lower than 45°, suggesting that solid like elastic behavior dominates these samples over liquid like viscous behavior. These emulsions, as described earlier, indicated sedimentations in concentrated form since the specific gravity of the oil phase was higher than the water phase. Increasing the starch concentration lowered the specific gravity and viscosity differences between the oil and water phases. Consequently, the loss modulus (G") dominated the elastic modulus (G') and the delta degree (*δ)* increased. The *δ* of the oil add emulsions slightly decayed with increasing the oil concentration over the whole frequency range and accompanied the domination of the viscose over the elastic behavior (G" > G' > 45^o). Thus, high concentration of weighting agents in oil phase, for starch added emulsions, was accountable for solid like behavior of droplets and sedimentation in concentrated form. However, at elevated concentrations of both starch and oil added emulsions, liquid like behaviors were identical; indicating increase in starch concentration alone cannot be considered as a factor for cloud emulsion stability. Starch concentration, on the other hand, had minor effect on the opacity of cloud emulsion and with the limitation in use of weighting agents modification of rheological properties of water phase may be an alternative to increase the stability of the cloud emulsion.

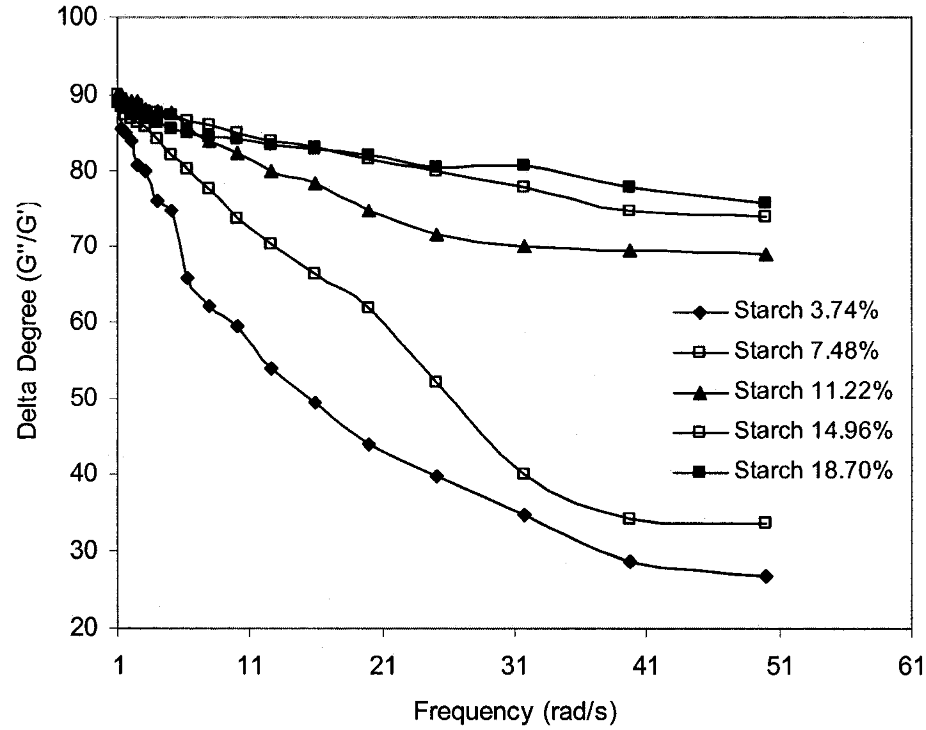


Figure 3.7. Frequency development of the delta degree δ of emulsions as a function of starch concentrations.

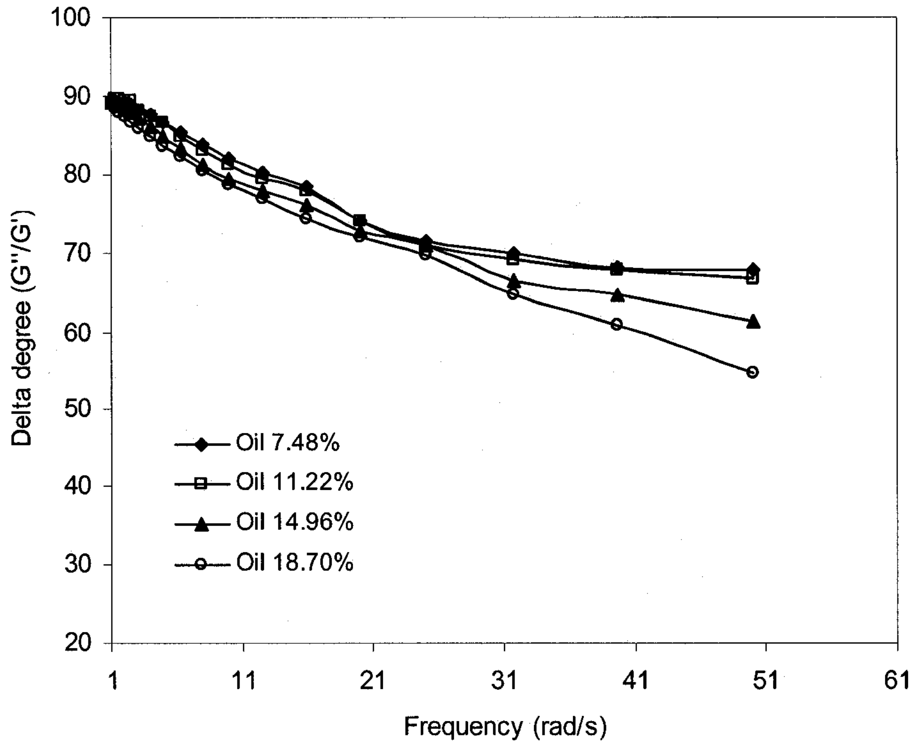


Figure 3.8. Frequency development of the delta degree δ of emulsions as a function of oil concentrations.

3.5 CONCLUSIONS

Increase in oil concentration affected the opacity and showed that oil content is readily responsible for the opacity of emulsions and hence the final product. At the constant level of weighting agents (BVO and SAIB), the specific gravity of oil phase decreased when the oil concentration increased and resulted in augmentation of the creaming values accordingly. When the specific gravity of oil phase was adjusted at 1.04, none of the starch added emulsions indicated creaming, and sedimentation occurred when the specific gravity of the oil phase was higher than that of the water phase. Addition of weighting agents, however, is restricted and practically the density of oil phase cannot be adjusted at the elevated oil level. Increase in starch concentration cannot, adequately, increase the cloudiness of emulsion. As a result, shear thinning behavior of emulsions was associated with creaming and solid like behavior with sedimentation. Modified starch was able to provide polymeric steric hindrance to the oil droplets, but did not contribute to the elasticity of covered droplets at any selected concentration.

PREFACE TO CHAPTER 4

As detailed in Chapter 3 the oil was readily responsible for providing the opacity to the final beverage. It was also found that there is a linear relation between opacity and oil concentration. As also mentioned, cloud emulsion are added to the beverage to provide suitable opacity.

Therefore, in this chapter we used the obtained results to first find out the oil concentration which could provide the identical appealing appearance as natural fruit juice. The physical properties of emulsions in presence and nascence of restricted level of weighting agents and/or xanthan gum, at the identical level of oil concentration, were then investigated.

The results of this study were presented in joined conference of AAFC-CIFST on May 2006.

A manuscript has been submitted for publication:

Taherian A.R., Fustier P., and Ramaswamy H.S., 2006. Stability and rheological properties of beverage cloud emulsions formed by modified starch: effects of added weighting agent, and xanthan gum. Journal of Food Process Engineering (Accepted October 2006, In Press)

Writing the paper, experimental work and data analysis were completed by the candidate under supervision of Professor H.S. Ramaswamy. Dr. P. Fustier support the technical resources and provided scientific advices.

CHAPTER 4

EFFECTS OF ADDED WEIGHTING AGENT AND XANTHAN GUM ON STABILITY AND RHEOLOGICAL PROPERTIES OF BEVERAGE CLOUD EMULSIONS FORMULATED USING MODIFIED STARCH

4.1 ABSTRACT

Stability of beverage emulsion is measured by the rate at which the emulsion creams, flocculates or coalesces, and is generally dependent on rheology of water phase, difference in specific gravities of the two phases and droplet size/distribution of the emulsion. Effect of weighting agents (sucrose acetate isobutyrate and brominated vegetable oil) and xanthan gum on modified starch based emulsions were evaluated in this study. Emulsion were formed by addition of 9% coconut oil, in presence or absence of weighting agents, into the water phase containing modified starch at 10, 12 or 14% without or with the addition of 0.3% xanthan gum. Stabilities of emulsions were evaluated both in the concentrated form used for storage and dilute form used in beverages. Addition of xanthan gum into the water phase decreased the flow behavior index (n) form 0.88 down to 0.31 and increased elastic modulus (G′) over 20 times at elevated frequency ($\omega = 50$ rad/s) and elevated the stability of the emulsion. The xanthan gum added emulsion had smaller particle size and demonstrated 14 and 5 times slower phase separation compared to the emulsions without or with the addition of weighting agents, respectively. When elastic modulus was larger than viscous modulus ($G' > G''$), the emulsions demonstrated greater stability. In dilute beverage solutions, creaming was observed in the absence of xanthan gum.

4.2 INTRODUCTION

Beverage emulsions are classified as oil-in-water emulsions and are prepared by dispersing flavor or vegetables oils in water phase containing various types of hydrocolloid, acid, preservative, and coloring. Stability of cloud or flavor emulsions for a desired period of time is a common issue in the beverage industry. Ringing is a frequent defect in beverage cloud emulsions mostly caused by gravitational separation, flocculation, and coalescence (Tan & Wu, 1988; Chanamai & McClements, 2001; Tan, 2004; McClements, 2005; Taherian et al., 2006). Finished beverages are prepared by dilution of the concentrated beverage emulsion in acidified sugar solutions. The emulsion in both concentrated and diluted forms must be stable at least for 6 months as required by beverage industry (Tse and Reineccius, 1995 and Tan , 2004).

Stoke's law states that the velocity at which a droplet moves is directly proportional to the square of its radius and density difference of oil and water phases, and inversely proportional to the viscosity of water phase. McClements (2005) demonstrated that Stoke's law is applicable to beverage emulsions since the oil phase has a much higher viscosity than the water phase ($\eta_2/\eta_1 > 5$). The stability of beverage emulsions is therefore highly dependent on the specific gravity, droplet size and distribution and the rheological characteristics of component phases (Tan & Wu, 1988; Chanamai & McClements, 2000; Buffo and Reineccius, 2002; McClements, 2005; Taherian et al., 2006).

The water phase of beverage emulsions contains hydrocolloids which could provide specific rheological properties for achieving stability of the emulsion. Hydrocolloids such as amphiphilic gum arabic or hydrophobically modified starch serve as the surface active gums in the cloud emulsions. These hydrocolloids have the ability of film forming around droplet of oil particles and their usage could prevent the breakdown of the emulsion due to steric stabilization thereby delaying the coalescence (Acton & Saffle, 1972; Tan & Wu, 1988; Turbiano, 1995; Chanamai & McClements, 2001; Huang et al., 2001; Tan, 2004; Taherian et al., 2006). To be an effective steric stabilizer for beverage emulsions, the hydrocolloid must have low viscosity in water to cover the droplet surfaces by a sufficiently high concentration of hydrocolloid, capacity to lower the tension at the oil-water interface, and should not thicken or gel on aging (Glicksman, 1969; Krumel & Sarkar, 1975; Sharma, 1981; Dickinson, 2003; Tan, 2004; McClements, 2005).

Our previous study (Taherian et al., 2006) demonstrated that modified starch can provide polymeric steric hindrance to the oil droplets. This starch is the octenyl succinate derivative of waxy-maize and consists primarily of amylopectin that has been modified to contain nonpolar side-groups. These side-groups anchor the molecule to the droplet surface, while the hydrophilic starch chains stick out into the aqueous phase and protect droplets against aggregation through steric repulsion (Trubiano, 1995; Chanamai & McClements 2001; Tesch et al., 2002). This starch, however, did not contribute to the elasticity of covered droplets at any selected concentration (Taherian et al., 2006).

It has also been known that the oil concentration is responsible for providing the opacity in beverages (Garti et al., 1991 and Taherian et al., 2006), and the oil is used in the form of emulsion rather than in its original state to provide a wider range of rheological characteristics in an emulsion (Garti & Reichman, 1993; Valdez et al., 2005, McClements, 2005).

Many hydrocolloids used to stabilize emulsion are shear-thinning, and generally have a high viscosity at low shear rates which decreases dramatically as the shear is increased. This property is important because it means that the droplets are prevented from creaming, but the food emulsion still flows easily when poured from a container (van den Tempel, 1963). With this regards, stabilization effect of xanthan gum has been the subject of several studies (Yilmazer & Kokini, 1991; Yilmazer et al., 1991; Pettitt et al., 1995; Xie & Hettiarachchy, 1997; Bryant & McClements, 2000; Ye et al., 2004)

Commercial xanthan gum is a yellowish powder completely soluble in cold and hot water, producing relatively high viscosity opaque solutions at low concentrations. Xanthan gum strongly affects solution rheology because of its unique ordered structure. Ma and Barbosa-Cánovas (1997) found solid-like behavior (G' or storage modulus, predominated over liquid-like behaviour, G'' or loss modulus) for xanthan solutions under small amplitude oscillation rheometry. Kaufman & Garti (1984) described that xanthan gum gives citrus and fruit-flavored beverages enhanced mouthfeel with full-bodied taste and good flavor release. It has also shown promise as a stabilizer for cloud and flavor emulsions in beverages.

Weighting agents are used in these beverage emulsions to increase the density of oil phase. In our previous study (Taherian et al., 2006), brominated vegetable oil (BVO) and sucrose acetate isobutyate (SAIB) were used as weighting agents at a restricted level of 15ppm and 300 ppm in finished beverage (maximum permitted), respectively. The study showed that addition of weighting agents at these restricted levels, the density of oil phase could not be raised to the desired level. Little published information is available on stability of beverage cloud emulsion in the absence of weighting agents. Furthermore, the effect of dynamic rheology of component phases on the stability of beverage emulsions has not been well researched. Therefore, the objective of this study was to understand the role of added xanthan gum and/or weighting agent on the stability of modified starch based beverage cloud emulsions.

4.3 MATERIALS AND METHODS

4.3.1 Materials

Modified starch (Purity Gum Be) and Xanthan gum (TIC PRETESED® TICAXAN®) were obtained from National Starch and Chemical (Bridgewater, NJ) and Nealanders Inc. (Montreal, PQ), respectively. Commercial brands of coconut oil, brominated vegetable oil (BVO) and sucrose acetate isobutyrate (SAIB) were obtained from Univar and Daminco Inc. (Boucherville, PQ). Adjustment of acidity was done by food grade citric acid.

4.3.2 Preparation of emulsions

The modified starch (10, 12 and 14 % weight/weight, w/w) and xanthan gum (0.3 %w/w) were dissolved separately in de-ionized water and stored overnight for complete hydration. Using a 50% (w/w) solution of citric acid, pH of each starch solution was adjusted to 3 prior to any examination. Oil phases were prepared by either dispersing a measured amount of BVO and SAIB (to give 15 ppm and 300 ppm, respectively in the final product) into 9 %w/w of coconut oil, or similar amount of oil without addition of weighting agents. Crude emulsions were formed by stirring the oil phase into the starch solution for 15 min. The solution of xanthan gum was then added to the emulsions which did not contain weighting agents followed by a 3 min pre-homogenization at highest speed using Polytron laboratory scale homogenizer (Polytron, PT 10-35, Kinematica, AG Ltd. Switzerland). Oil droplet size was further reduced with the aid of high pressure homogenizer (Emulisiflex-C5, Avestin, Ottawa, ON) at 3500 psi over 2 passes. Emulsions were prepared in duplicates and tested three times immediately after preparation.

4.3.3 Particle size distribution

An integrated light scattering technique was used to determine particle size distribution of emulsions employing a ZetaSizer 4 (Malvern Instruments Ltd., Malvern, UK). This instrument used the method of photon correlation spectroscopy (PCS) to measure particle size in constant random thermal, or Brownian, motion. This motion causes the intensity of light scattered from the particles to vary with time. Large particles move slowly than small ones, so that the rate of fluctuation of the light scattered from them is also slower. PCS uses the rate of change of these light fluctuations to determine the size distribution of the particles scattering light. Samples of emulsions were analyzed in duplicate right immediately preparation when the volume fraction of oil in the diluted emulsion was about 1:1000 for all the cases. The particle diameter range and emission strength [number of photon counts per second expressed as kilo-count per second (1 kCps = 1000 Cps)] as well as polydispersity (width of distribution) were evaluated at room temperature.

4.3.4 Evaluation of opacity degree and selection of oil concentration

Opacity was evaluated based on the method described by Kaufman and Garti (1984) and Garti et al., (1991). For selection of oil concentration, fresh orange juice with no pulp was purchased from local market and its opacity degree was measured from the absorbance at 660 nm using a spectrophotometer (Cary, 300-Bio, UV-Visible Spectrophotometer, Varian, Australia). The results obtained were then compared to the opacity of simulated citrus drinks containing 2 % weight/weight (w/w) of emulsions at 3 different levels of oil concentrations (4, 9 and 14% w/w). Both fresh orange juice and simulated beverage (pH 3, 11^{oBx} and 2% w/w emulsion of 9 % w/w oil and 14% w/w modified starch) indicated closest absorbance values of 0.87 and 0.86 respectively.

4.3.5 Specific gravity

Method of evaluation of specific was described in Chapter 3.

4.3.6 Emulsion stability

Instrumental test

Prior to the high pressure homogenization, and right after pre-homogenization step, 6 ml of sample from each preparation was poured into a flat-bottom cylindrical glass jar (100 mm height, 16 mm internal diameter) and the back scattering of light was measure in an optical scanning instrument (Quick Scan, Coulter Crop., Miami, FL). The back scattering of monochromatic light (λ = 850 nm) from the emulsions was measured as a function of their height in order to quantify the creaming rate. Gravitational creaming values were calculated from the height of the interfaces between the opaque droplet-rich layer and the transparent droplet-depleted layer as a function of time. Creaming was then expressed as slope of absolute thickness of layers over time.

Observation

After dilution of emulsion into the simulated beverage (acidified sugar syrup with 11^{oBx} at pH 3), gravity creaming of emulsion samples was also monitored visually over a period of 1-5 weeks. Glass bottles of 330 ml were filled with simulated beverages containing 2% of emulsion of known composition. The filled bottles were then pasteurized at 90°C for 12 min and stored at room temperature. Samples were graded as + and ± when creaming was observed after 1 and 3 weeks, respectively. The stable emulsions with no sign of creaming after 5 weeks were rated negative. Monitoring was performed in duplicate with a total of 6 bottles for each prepared emulsion.

4.3.7 Flow and dynamic rheological measurements

The rheological properties of emulsions were determined using a stress-controlled rheometer (AR2000 Rheometer, TA Instrument, New Castle, DE) fitted with a stainless steel 60 mm cone of 2° and solvent trap. The measurement temperature was kept at 22 °C using a circulating bath and a controlled peltier system. The emulsion was loaded to the rheometer immediately after being prepared. Steady-state flow parameters including flow behavior index (n), consistency coefficient (m) and shear viscosity (η_γ) were determined at increasing shear rates (0.1-100 s^{-1}) within 3 min.

The apparent viscosity of oil phase and water phase alone, and together in form of emulsions at fixed volume ratio ($\phi \approx 0.09$) was measured as a function of shear rate ($\dot{\gamma}$). Experimental flow curves were compared to Power-law model, which is the typical equation to characterize shear thinning fluids:

$$\eta = m\,\dot{\gamma}^{(n-1)} \tag{1}$$

where n <1 for a shear-thinning fluid and n = 1 for a Newtonian fluid. The variations of consistency coefficient (m) and flow behaviour (n) were then determined for each component phase and through the steps of preparation.

The dynamic oscillatory evaluation a frequency sweep from 1 up to 50 radians per second was also carried out where the oscillation stress was fixed at 1 Pascal (obtained from the development of stress sweep in the linear region). The dynamic properties such as storage modulus (G'), loss modulus (G") and delta degree (G"/G') were also examined for each sample. All the flow and dynamic rheological parameters are the mean of six measurements per duplicates emulsions.

4.4 RESULTS AND DISCUSSION

4.4.1 Particle properties and opacity of emulsions

Typical particle size distribution for weighting agents added emulsions containing 10, 12 and 14% modified starch (Purity gum Be) with a constant volume ratio *($\phi \approx 0.09$)* are shown in Figure 4.1a, 4.1b and 4.1c. It can be seen clearly that the emulsions in any

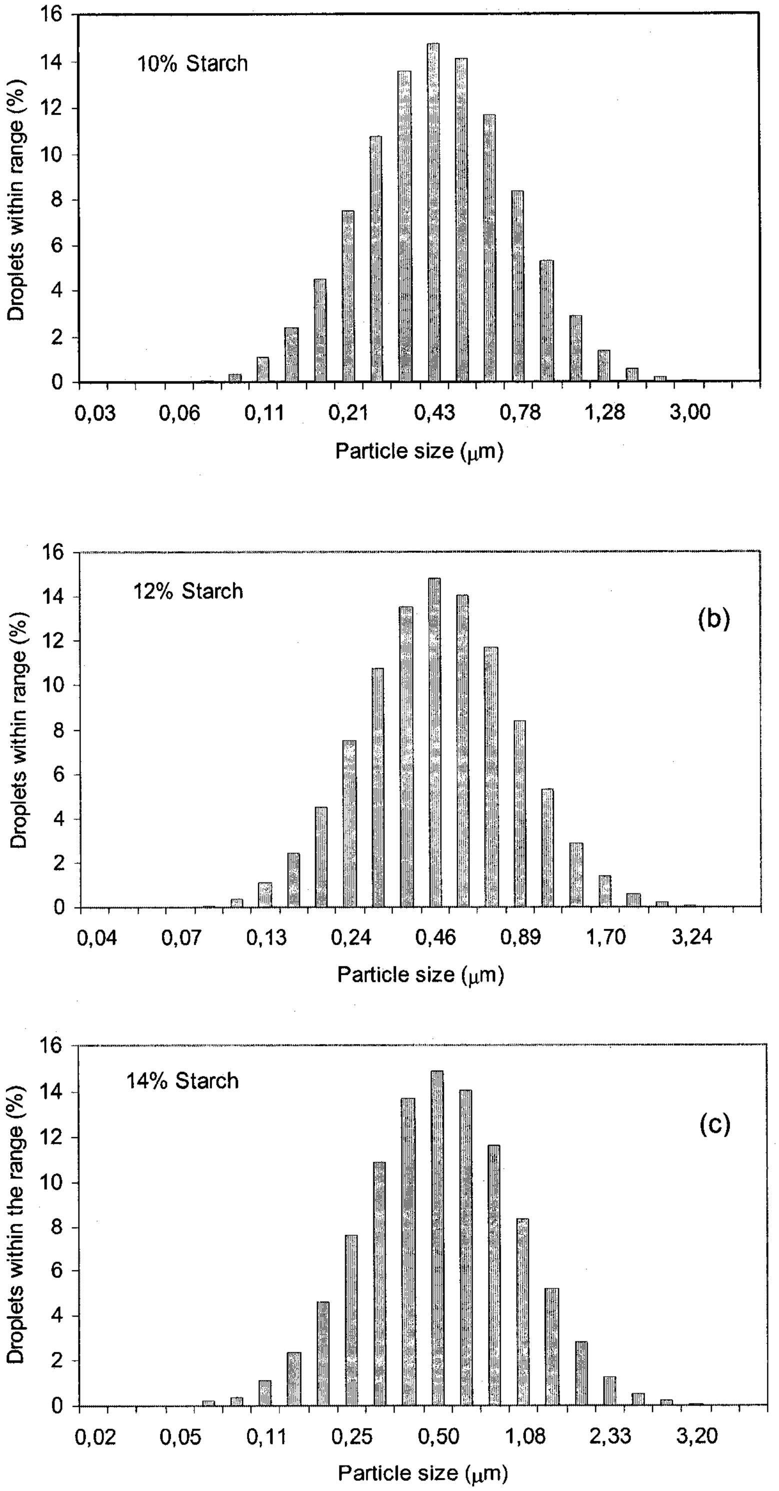


Figure 4.1. Particle size distribution for weighting agents added emulsion at different starch concentrations.

given concentration of modified starch are not mono-disperse, which means, all droplets are not homogeneous or of the same size. Since the results were consistent for all prepared emulsions, the average particle size (Z-average size), polydispersity index (PDI) and emission strength were considered for further quality comparison. Z-average size (also known as the cumulants mean) is the result of cumulants analysis and the fit of a polynomial to the log of the normalized correlation function (ZetaSizer 4, User Manual):

$$Log = (\frac{G_2(t)}{B} - 1) = a + bt + ct^2 + \ldots \qquad (2)$$

where G(t) is the measured correlation point, B is the baseline and a, b, c are the coefficients of the cumulants fit. Poly-dispersity index (the coefficient of the squared term, c, when scaled as $2c/b^2$) is a measure of the width of the distribution, and emission strength is a measure of the intensity of the scattered light and directly related to the opacity of the emulsion.

Table 4.1 compare the particle properties and opacity of the emulsions. The first information which can be drawn is a slight increase in average particle size when increasing the starch concentration. This is due to the presence of hydrophobic side chains on the octenyl-succinate starch molecule which can adsorb to the interface of water and oil (Tesch et al, 2002). It is also consistent with our previously reported data where we indicated this type of modified starch was able to increase the coating of the droplets as the oil concentration was constant for all the cases (Taherian et al., 2006). In this Table, the opacity of emulsions is demonstrated as emission strength and absorbance at 660 nm. The overall average particle sizes are smaller for xanthan added emulsion compared to the others. It is worthy to note that addition of xanthan into the emulsion was after the pre-homogenization step and prior to high pressure homogenization to allow modified starch for the identical film forming around the particles, suggesting that the starch coating enhances the steric repulsion effects between the droplets. The lower average particle size and poly-dispersity as well as higher opacity of xanthan added emulsions could be thus related to the reversible shear thinning viscosity of these emulsions which help for a better distribution of oil droplets and prevention of droplet coalescence after removal of applied shear by high pressure homogeniser. A study by Yilmazer et al. (1991) indicated that the

Table 4.1. Effect of added xanthan gum and weighting agents on particle properties and opacity of emulsions at different starch concentrations.

Emulsion containing 10 wt % modified starch			
	Starch alone	Xanthan added	Weighting agents added
Average partcle size (nm)	510.20±5.10	400±3.80	430±4.20
Opacity (kCps)	314.52±0.65	509.60±0.80	431.92±0.89
Polydispersity (index)	0.43±0.05	0.29±0.02	0.31±0.03
Opacity (660 nm)	0.69±0.01	0.76±0.02	0.62±0.02
Emulsion containing 12 wt % modified starch			
Average particle size (μm)	630.30±5.100	420.80±3.80	460.50±4.10
Opacity (kCps)	322.71±0.90	546.40±0.30	482.80±0.80
Polydispersity (index)	0.41±0.06	0.24±0.01	0.32±0.03
Opacity (660 nm)	0.74±0.04	0.82±0.02	0.69±0.03
Emulsion containing 14 wt % modified starch			
Average partcle size (μm)	780±3.80	480±2.80	500±4.20
Opacity (kCps)	345.43±0.60	551.28±0.40	508.60±0.70
Polydispersity (index)	0.398±0.04	0.211±0.03	0.318±0.03
Opacity (660 nm)	0.83±0.03	0.89±0.05	0.71±0.03

emulsion stabilized with 0.4% xanthan gum had the predominance of smaller particles. The results are also in agreement with Pettitt et al. (1995) who reported smaller particle size for emulsions containing 0.33% xanthan gum compared to the emulsion made without xanthan gum (3 μm vs 10.17 μm). The higher opacity of xanthan can also be related to the formation of aggregates by xanthan gum which promoted the scattered light (Bryant and McClements, 2000).

4.4.2 Stability of emulsions

Investigations of gravitational stability of prepared emulsions were carried out on pre-homogenized concentrated emulsions for a rapid response to the degree of stabilization. The backscattering of the light from concentrated emulsions was measured as a function of their height over a period of 5 days. The stability of emulsions in diluted forms, however, was premeditated after dilution of 2% homogenized emulsion in simulated beverage following by pasteurization and upon standing at room temperature.

Gravitational stability of beverage cloud emulsions in both concentrated and diluted in acidified sugar solution are presented in Table 4.2. Additions of weighting agents to the oil phase reduced the specific gravity difference between water phase and oil phase from 0.15 to 0.12. This change had a slight effect on gravitational separations as weighting agents added emulsions indicated creaming after three weeks in acidified sugar solutions.

Figure 4.2 illustrates the typical backscattering profiles for emulsions with or without weighting agents and xanthan gum at identical starch concentrations. Depletion flocculation of starch coated oil droplet occurs in beverage emulsions due to close distance of droplets which results the aggregation of droplets and increase in creaming velocity. The profiles show thicker aggregates for emulsions prepared with or without weighting agent addition compared to the one containing 0.3% xanthan gum. Figure 4.2c also indicates a jump in the plateau value of the backscattering from the day zero which may be related to rapid rate of aggregation in the first 24 h. By computing the absolute thickness of each aggregate the creaming velocity profile was then compared. Figure 4.3 shows the time evolution of the backscattering for emulsions at 3 different starch concentrations. Since 14% starch indicated slower aggregation (shallower slope), stability comparison was

Table 4.2. Gravitational separation of diluted emulsions as functions of starch concentrations, weighting agents and xanthan gum.

Emulsions	Emulsions		
	Oil phase Specific gravity	Water phase Specific gravity	Ringing in bottle
10% Starch	0.96 ± 0.03	1.04 ± 0.04	+ +
12% Starch	0.96 ± 0.03	1.06 ± 0.02	+ +
14% Starch	0.96 ± 0.03	1.11 ± 0.63	+
14% Starch + Weighting agents	0.99 ± 0.06	1.11 ± 0.63	±
14% Starch + Xanthan	0.96 ± 0.03	1.05 ± 0.54	-

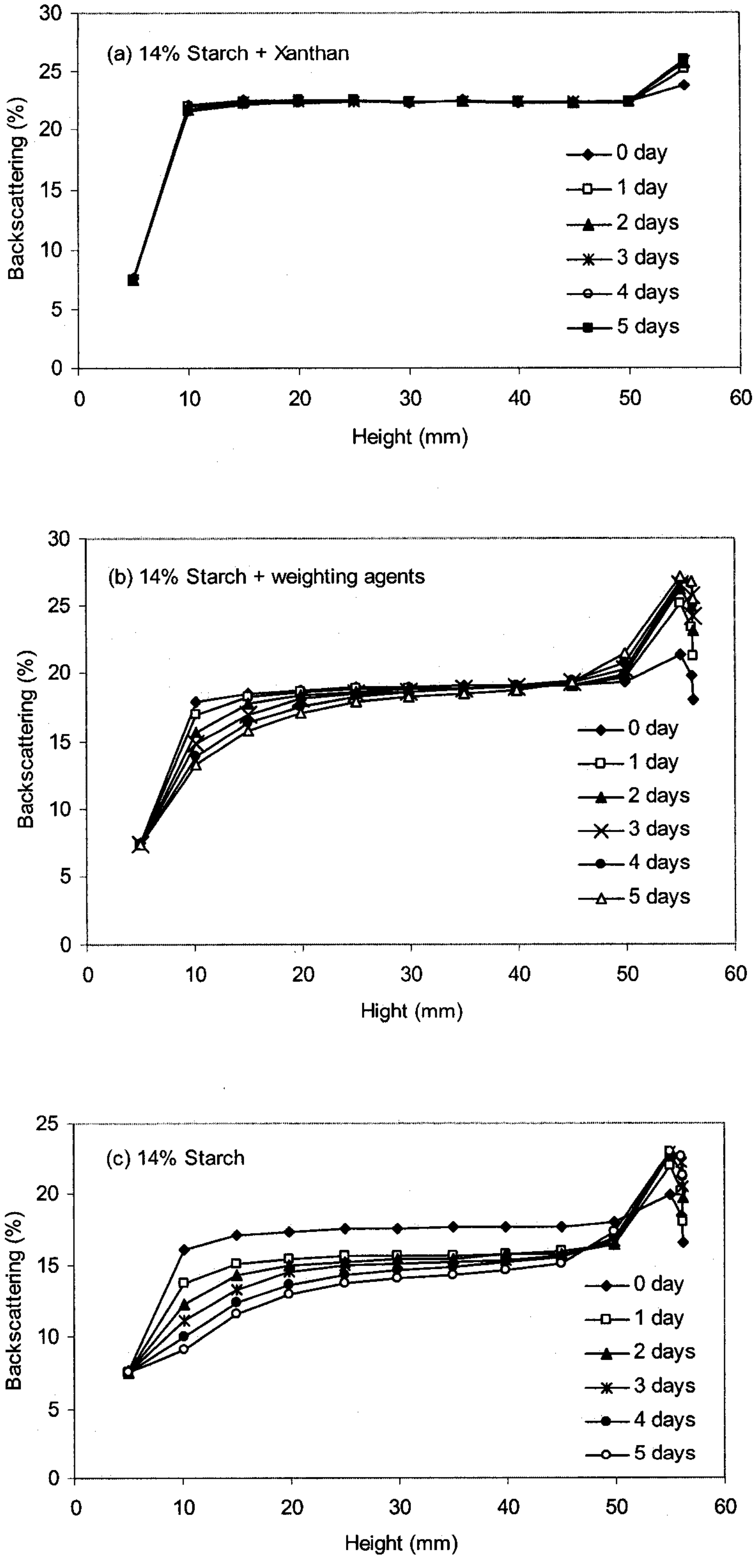


Figure 4.2. Backscattering profiles for concentrated coarse emulsions at identical starch concentration with xanthan gum (a), weighting agents (b) additions and starch alone (c).

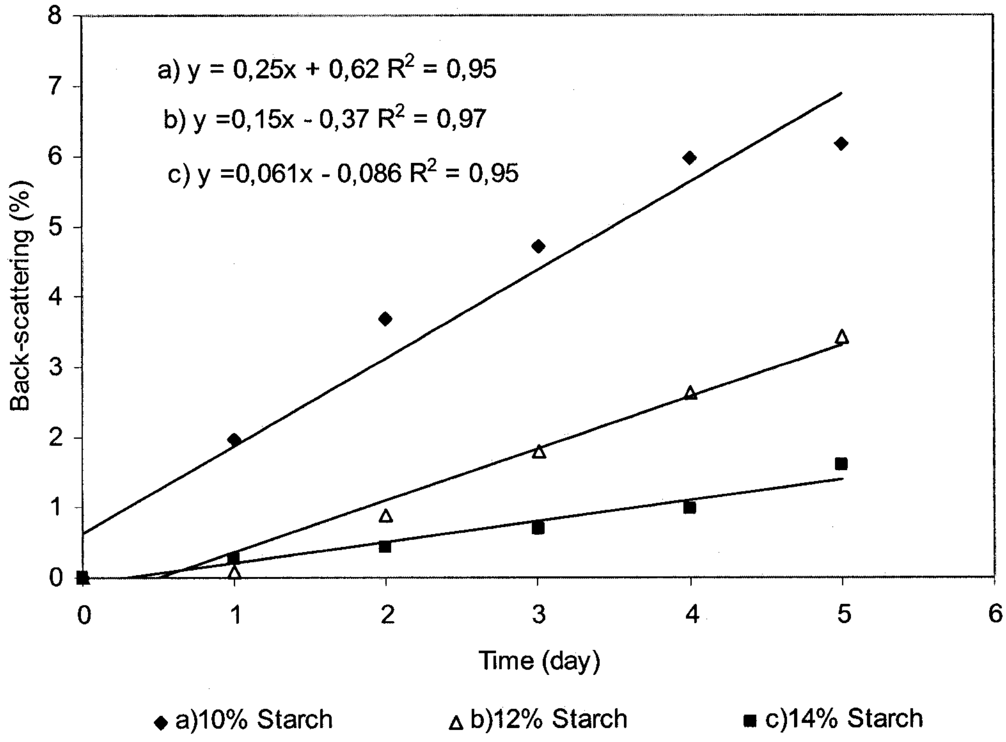


Figure 4.3. The time evolution of the backscattering for emulsions at different starch concentrations.

conducted at the same concentration. At this concentration of starch, however, the film forming around the oil droplets is thicker and it is believed that the specific gravity of oil phase is greater (Trubiano, 1995).

The time evolution of the backscattering for emulsions with or without weighting agents and xanthan gum are compared in Figure 4.4. The xanthan added emulsion indicated 14 and 5 times slower separation compared to emulsions without or with addition of weighting agents, respectively. The inhibition of creaming in presence of xanthan gum can be attributed to immobilization of the starch-coated oil droplets in a weak gel-like network as been described by Dickinson (2003).

The stabilization effect of xanthan gum has been attributed to its molecule structure by Xie and Hettiarachchy (1997) who studied the emulsification properties of soy protein isolate in presence of xanthan gum. The molecule has a cellulosic backbone that is rendered water soluble by the presence of trisaccharide side chain attached to every second glucose residue in the main chain. The authors concluded that xanthan gum contributed to the emulsion stability by its adsorption at the oil/water interface which demonstrates the protective effect on soy protein isolate.

Figure 4.5 also represent the gravitational separation of emulsions in both concentrated and diluted forms after 3 month storage. Visible serum separations are exhibited for both emulsions with or without weighting agents at identical starch concentration of 14%. In the case of weighting agent added emulsions the serum was slightly cloudy, indicating the presence of a small residual amount of oil droplets. There was no sign of separation or creaming for xanthan added emulsion containing 14% of starch in the long run.

4.4.3 Rheological properties

Flow characteristics

In our previous study on beverage cloud emulsions (Taherian et al., 2006), we investigated the rheological perception of starch and oil added emulsions in presence of accepted level of weighting agents. We found that octenyl-succinate starch was able to

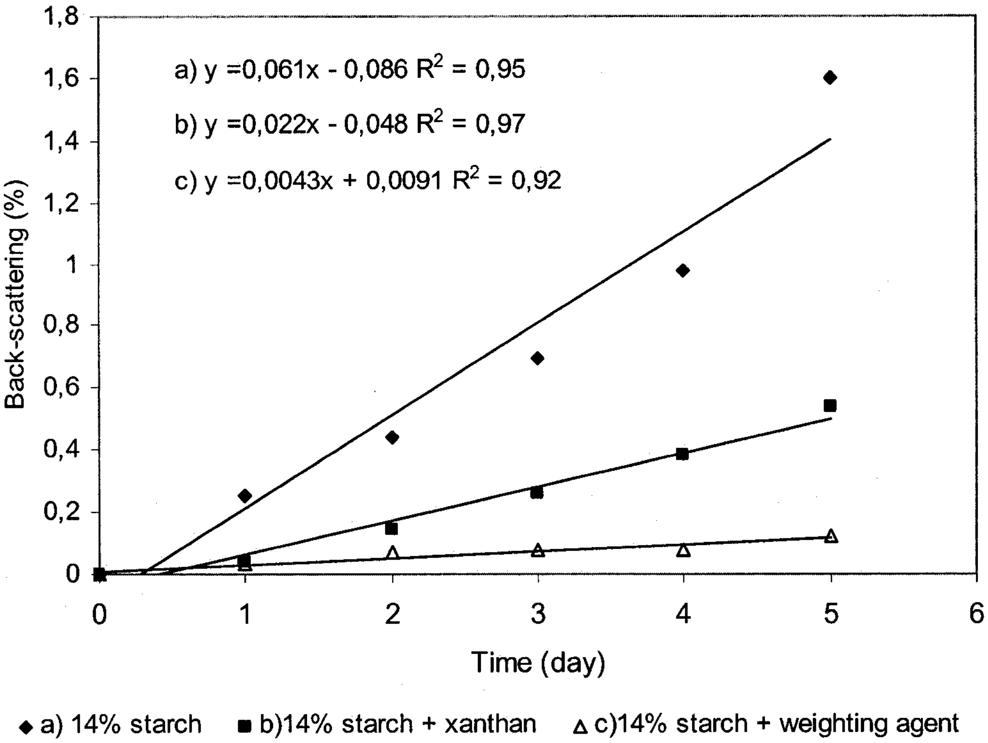


Figure 4.4. The time evolution of the backscattering for concentrated coarse emulsions at identical starch concentration with or without weighting agents or xanthan gum addition.

Figure 4.5. Gravitational separation of emulsions containing 14% starch in concentrated and diluted forms after 3 month upon standing at room temperature.

provide polymeric steric hindrance to the oil droplets, but did not contribute to the elasticity of covered droplets at any selected concentration. Here we attempt to study the effect of addition of a highly shear thinning and elastic hydrocolloid as an alternative to replace the weighting agents.

At the start, the flow behaviour of each component phase was evaluated. Table 4.3 shows the Power-law parameters and indicates a major decrease of flow behaviour index for water phase ($n_{W.ph}$) after addition of 0.3% of xanthan gum. The consistency coefficients of water phase also shifted up with the addition of xanthan gum. Both oil phases with or without addition of weighting agents indicated Newtonian behavior ($n_{O.ph} = 1$) with an increase in consistency coefficient ($m_{O.ph}$).

The shear rate dependence of viscosities of water phases and resultant emulsions are shown in Figure 4.6. The apparent viscosities of both water phases and emulsions decreased with increasing shear rate indicating shear thinning behaviors. There was a slight decrease for flow behavior index of emulsions in the absence of xanthan gum compared to the related water phase, and xanthan added emulsions indicated inverse behavior. This could be explained by breakage of flocculated droplets through the application of shear for unstable emulsions. The shear thinning behavior of emulsions, however, has been widely reported for suspensions containing rigid particles and for poly-disperse emulsions (Chanamai and McClements, 2000). This could also confirm the thick coating of the starch surrounding the oil droplets.

The influence of droplets on emulsion rheology was also examined by computing the relative viscosity:

$$\eta_{app.relative} = \frac{\eta_{\text{app. Em.}}}{\eta_{\text{app. W.ph}}} \qquad (3)$$

where $\eta_{app.Em}$ is the apparent viscosity of the emulsion at a specific shear rate and $\eta_{app.W.ph}$ is the viscosity of the water phase at the same shear rate. The relative viscosity for xanthan added emulsion, weighting added emulsion and emulsion prepared with starch alone containing 14% starch, at the shear rate of $0.1\ s^{-1}$, were found to be 1.38, 2.39 and

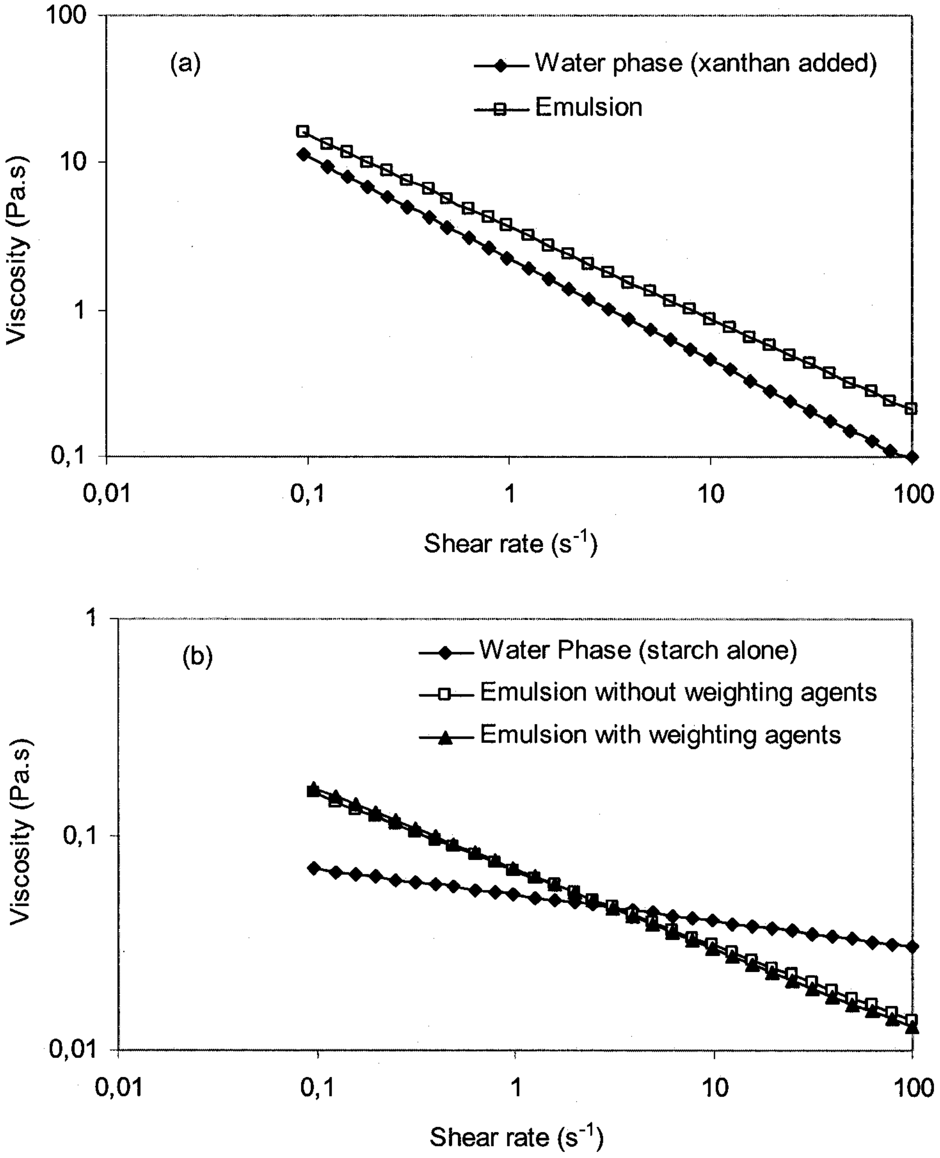


Figure 4.6. Dependence of viscosity on shear rate for emulsions and water phasesas a function of xanthan gum (a) and weighting agent (b) additions with identical starch concentration of 14%.

2.25, respectively. The relative viscosity of emulsions prepared without addition of xanthan gum, however, decreased significantly at the higher shear rates, with the cross over point occurring at an apparent relative viscosity of 1.7 and shear rate of 1.0 s^{-1}. Considering Einstein equation for non-flocculated oil in water emulsions:

$$\eta_{relative} = 1 + 2.5\,\phi \tag{4}$$

the relative viscosity should be close to 1.23 since the volume ratio ($\phi \approx 0.09$) was consistence for all prepared emulsions. The xanthan added emulsion, with a relative viscosity ratio of 1.38, was the closest one which could fit the characteristic of a non-flocculated emulsion. This could also mean the Einstein equation is not really appropriate for these emulsions. Taylor in 1932 (Pal, 2000) corrected Einstein equation taking in to account the internal dissipation within the droplets as:

$$\eta_{app.\,relative} = \frac{\eta_{\mathrm{app.Em.}}}{\eta_{\mathrm{app.W.ph}}} = 1 + \left[\frac{2 + 5.0\,\mathrm{p}}{2(1+\mathrm{p})}\right]\phi \tag{5}$$

where p is the ratio of oil phase viscosity over water phase viscosity of the system. The results using this equation indicated lower and more converging values of relative viscosity for all samples (1.09-1.16) but not really representing the true value of o/w emulsions used in this study. Klinkesorn et al., 2004; McClements, 2005 attributed this decrease to progressive disruption of the flocs when the shear rate was increased. A study by Yilmazer et al., (1991) on stabilization effect of xanthan gum on o/w emulsions indicated a little change for viscosity of xanthan added emulsion over period of study. They suggested distribution of oil droplets did not change with aging time. Long term stability of xanthan added emulsion could, therefore, be related to immobilization of particle due to unvarying high viscosity and the absence of flocculated particles.

Dynamic characteristics

The dynamic rheological parameters (G′, G″ and phase lag angle δ) of components

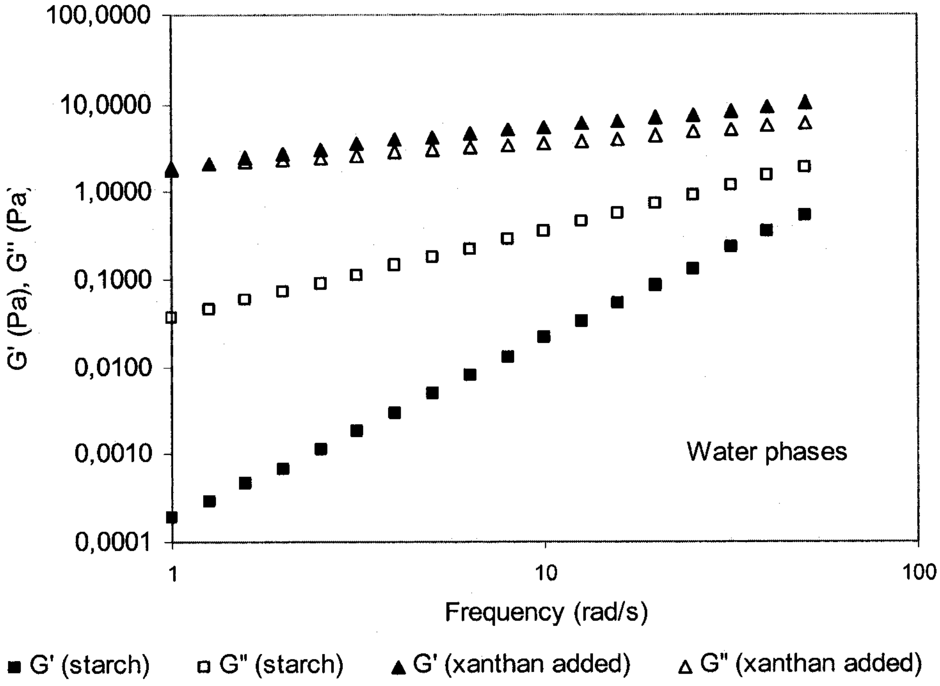


Figure 4.7. Frequency dependence of storage modulus (G′) and loss modules (G″) for water phases with or without addition of 0.3% xanthan containing identical amount of starch concentration at 14%.

phases and emulsions were evaluated in the linear viscoelastic region. The rheological parameters were first measured as a function of stress amplitude at a fixed frequency. After establishment of linear viscoelastic region, measurements were then made at fixed stress amplitude (1 Pa) as a function of frequency.

Figure 4.7 shows the frequency dependence of storage modulus (G′) and loss modulus (G″) for the hydrocolloid solutions which formed the water phases of the emulsions. The starch concentration was maintained at 14% for all water phases and similar water phases were used to prepare emulsions with or without addition of weighting agents.

For all the cases the modules (G′ and G″) increased with increasing frequency. For water phase without addition of xanthan gum the loss modulus (G″) fell above the storage modulus (G′), but for xanthan gum added water phase G′ was higher than G″. This indicates the predominant elastic behavior of the xanthan added water phase over the water phase prepared with starch alone which shows superior viscous behavior (G″ > G′). Addition of xanthan increased the elastic attribute of water phase over 20 times (form 0.52 Pa to 10.42 Pa) and controlled the size of aggregates. Increase in elastic modulus as a result of frequency development has been related to the closer packing of micro-gelled colloidal particles leading to greater friction forces between the droplets subjected to shear (Valdez et al., 2005).

Although the viscosity and elasticity of emulsion prepared with the addition of xanthan gum was considerably higher than the other emulsions, the highly shear thinning behavior of xanthan gum solution at selected concentration caused a slight increase in residence time of emulsion inside the homogeniser. This caused the formation of smaller particle as was indicated earlier. Dickinson (2003) reported that once an emulsion of small droplets has been formed, the molecular characteristics of the adsorbed biopolymer as a strong barrier play the dominant role in long term stability of emulsion and consideration of surface activity or interfacial tension gradients are no longer relevant.

Figure 4.8 signifies that elastic properties of xanthan added water phase remained after addition of oil phase and formation of emulsion. This suggested that addition of xanthan increased the elastic component of the interfacial film and introduced a strong barrier to drainage and coalescence of oil droplets. There was a slight increase in elastic

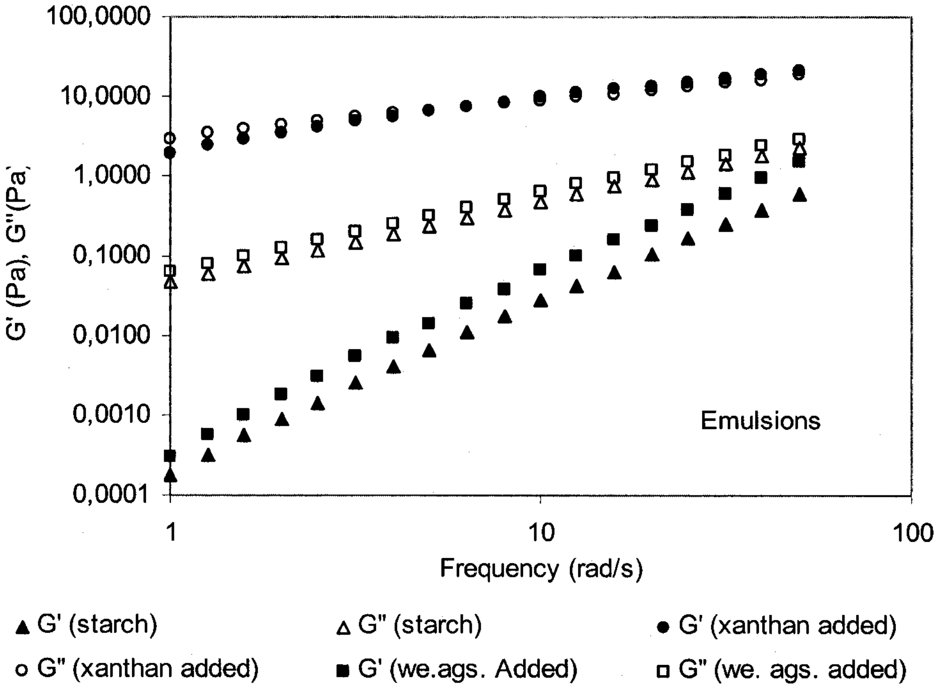


Figure 4.8. Frequency dependence of storage modulus (G′) and loss modules (G″) for emulsions in the presence or absence of xanthan gum and/or weighting agents containing identical amount of starch concentration at 14%.

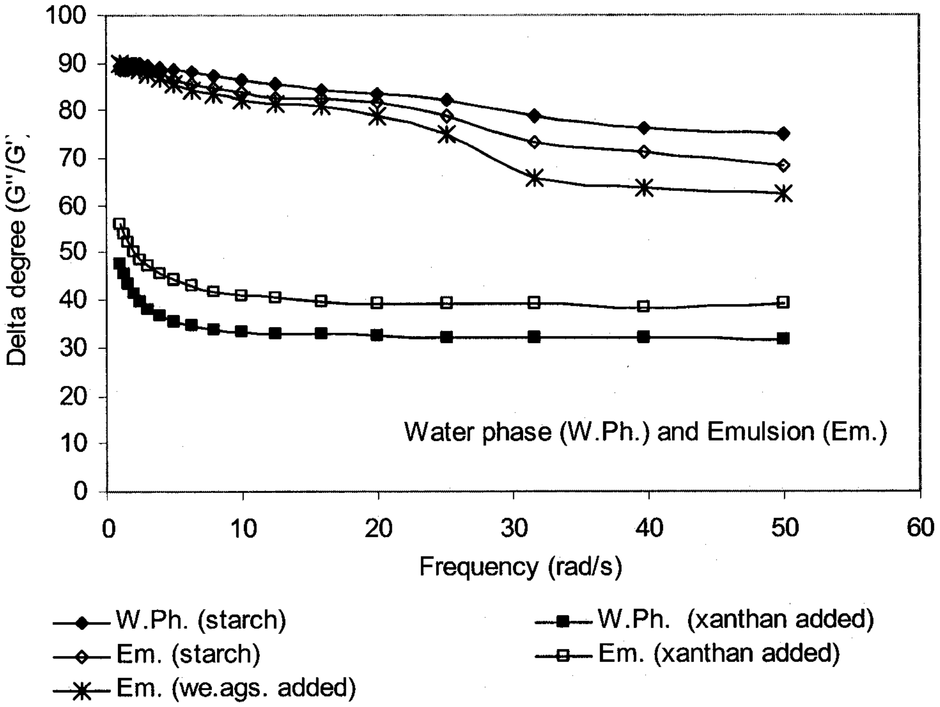


Figure 4.9. Frequency dependence of the delta degree δ for water phases and emulsions in the presence or absence of xanthan gum and/or weighting agents containing identical amount of starch concentration at 14%.

and viscous modulus of emulsions prepared with addition of weighting agents. This minor increase was due to high viscosity of added weighting agents which had a minor impact in stability of prepared emulsion. The phase angle (δ) development of water phases and emulsions was also measured (Figure 4.9). This measurement confirms the domination of elastic characteristic by xanthan added emulsion as both water phase and emulsion indicated lower phase angel compare to the others. All these characteristics are obvious evidence that indicate the formation of micro-gel network for xanthan added emulsion since the phase angle was below 45^{o} as frequency increased. The results are, therefore, in agreement with long term stability of xanthan added emulsions as mentioned earlier.

4.5 CONCLUSION

This study indicated that modification of rheological characteristic of continuous aqueous phase can play an important role in relation to the storage stability of beverage emulsions. Highly shear thinning and elastic properties of xanthan gum, even at very low concentration, is able to provide a micro-gel network and influences the state of flocculation and prevents coalescence of the droplets. In particular, for a beverage emulsion to possess an acceptable stability, the system must acquire a solid-like character, in the sense that $G' > G''$ for water phase. Octenyl-succinate starch also showed superior potential as an emulsifier. It was able to adsorb at interfaces, provided a thick coating and thus enhanced stabilizing of the droplets against gravitational separation and creaming. Xanthan gum added emulsions had a small volume-surface mean particle size and a narrow size distribution. As well xanthan gum was found to be an excellent alternative to replace weighting agents which have restricted level of use due to the health disadvantages.

PREFACE TO CHAPTER 5

In Chapter 3 the relation between oil concentration and opacity and emulsion was found and in Chapter 4 the results were then used to investigate the physical stability of emulsions in presence and absence of weighting agents. It was demonstrated that addition of weighting agents at restricted level failed to provide desirable stability, whereas replacing the weighting agent with micro-gel forming xanthan gum illustrated a promising stability.

In this Chapter 5, we examined the rheological properties and stability of different surface active and stabilizer gums at found level of oil concentration. The aim was to provide a rheological model for selection of surface active and stabilizer hydrocolloid gums concentrations in order to obtain desirable stability in practical application.

Part of this research was presented in 2005, scientific conference series of Food Research and Development Center of Agriculture and Agri-Food Canada, St-Hyacinthe, Quebec. A manuscript has also been submitted for publication:

Taherian A.R. Fustier P. and Ramaswamy H.S., 2006. Steady and dynamic shear rheological properties, and stability of non-flocculated and flocculated beverage cloud emulsions. Journal of Food Properties (Submitted, August 2006).

Writing the paper, conducting the experimental work and analyzing the data were performed by candidate under supervision of Professor H.S. Ramaswamy.

CHAPTER 5

STEADY AND DYNAMIC SHEAR RHEOLOGICAL PROPERTIES, AND STABILITY OF NON-FLOCCULATED AND FLOCCULATED BEVERAGE CLOUD EMULSIONS

5.1 ABSTRACT

Rheological properties of single-phase, and emulsions containing modified starch and gum arabic as surface active hydrocolloids as well as xanthan and tragacanth gums as stabilizers were evaluated under steady and dynamic shear testing conditions using a control stress rheometer. Emulsions were formed 9% and 14% gum concentrations with oil concentration maintained at 9% thus giving a 1:1 and 1.5:1 surface active agent to oil ratio, respectively. The rates of droplet coalescence and creaming, for a total of 8 emulsions, as a function storage time before and after dilution in a simulated fruit beverage were then investigated. Steady shear (flow curve) was well described by the Carreau model at shear stress ranging from 0.01 up to 100 Pa.

All prepared water phases indicated a zero-shear viscosity plateau followed by shear thinning behavior with flow behavior index (n) ranging from 0.51 to 0.79 for 14% starch-0.3% xanthan and 14% gum arabic-0.8% tragacanth stabilized emulsions, respectively. The water phase flow property data were well fitted by the Einstein equation and its expansions. The dynamic rheological properties of water phase and emulsions were also evaluated for $G'(\omega)$ and $G''(\omega)$ from 1 to 50 rad/s. Similar curves were obtained with varying degrees of deviations (G' from G'') for different emulsions. Starch-xanthan emulsion and associated water phase at 1.5:1 agent to oil ratio demonstrated viscoelastic behavior ($G' \geq G''$) with lower droplet coalescence and creaming rates. On the other hand, gum arabic-xanthan emulsion at 1:1 agent to oil ratio showed the highest rate of droplet coalescence and a greater degree of creaming.

It was speculated that the lower stability of gum arabic-xanthan emulsion could be related to the denaturation of proteinaceous part in the gum and loss of emulsification capacity due to lower pH and pasteurization.

5.2 INTRODUCTION

A stable beverage emulsion is characterized by long term stability in the diluted form, or absence of ringing resulting from raised coalesced droplets around the neck of the beverage bottle. Since ban and/or restriction on use of density adjusting weighting agents in 1970 for producing cloud or flavor emulsions, their stability over the desired shelf life has become a common problem in the beverage industry (Trubiano, 1995; Tan & Wu, 1988; Chanamai & McClements, 2001; Tan, 2004; McClements, 2005; Taherian et al., 2006).

Beverage cloud emulsions are oil-in-water emulsions comprising of vegetable oil to provide opacity, and in the oil phase are a combination of weighting agents to increase the oil phase density. The water phase is formed by water and amphiphilic polysaccharides to reduce surface tension and grant steric stabilization, added stabilizer gums prolong the stability and control rheological properties and citric acid is used to adjust the acidity.

Several studies concerning emulsion stability have indicated that the use of a proper polysaccharide in the water phase could prevent the breakdown of the emulsion and it will seldom reach the coalescence stage (Glicksman, 1969; Sharma, 1981; Buffo et al., 2001; Tan, 2004). Furthermore, to perform as an effective stabilizer for beverage emulsion, the surface active hydrocolloids must be readily soluble in cold water, and should have a low viscosity in water (to cover the droplet surfaces by a sufficiently high concentration of hydrocolloid), a high emulsifying power, and should not thicken or gel on aging.

Gum arabic, which has been known as the most hydrocolloid emulsifier, is highly soluble in cold water and its solubility increases at higher temperatures. Because of its effective emulsifying capacity and the well known film forming ability gum Arabic has been widely used in the soft drink industry for emulsifying flavour oils under acidic conditions. It is mainly produced from the species *Acacia Senegal*, and *Acacia Seyal* produces the rest. The surface activity is due to the branched arabino-galactan blocks attached to a polypeptide backbone. Chanamai and McClements (2002) reported that the hydrophobic polypeptide chain anchor the molecules to the droplet surface and the hydrophilic arabino-galactan blocks extend into the solution, providing stability against droplet aggregation by steric stabilization and electrostatic repulsion. Buffo et al. (2001) and Dickinson (2003) indicated that gum Arabic is an indisputable emulsifier that grants functionality not by modifying the rheology of the water phase but by leading the formation of a macromolecular stabilizing layer around the oil droplets. Despite its functionality, gum arabic is a fairly expensive ingredient and there have been many attempts for its replacement by hydrophobically modified starch or other gums.

In this study we used a modified starch (Purity gum; National Starch, Bridgwater, NJ) known as octenyl-succinated starch or OSA. It is made by esterification of starch with anhydrous octenyl-succinic acid under alkaline conditions (Tesch et al., 2002). It consists primarily of amylopectin that has been modified to contain non-polar side-groups. These side-groups anchor the molecule to the droplet surface, while the hydrophilic starch chains stick out into the aqueous phase and protect droplets against aggregation through steric repulsion. The Purity gum is mildly anionic in aqueous solutions and has a surface activity that is almost as high as gum arabic (Chanamai and McClements 2001).

Therefore, polysaccharides such as amphiphilic gum arabic or hydrophobically modified starch serve as the surface active and steric stabilizer in the cloud emulsions while xanthan and tragacanth gums could control the rheological properties of the emulsions (Tan & Wu, 1988; Chanamai & McClements, 2001; Tan, 2004; Sahin and Ozdemir 2004; Paraskevopoulou et al., 2005).

Xanthan gum is a microbial exocellular polysaccharide approved by FDA for use in food. Tragacanth gum, a Persian gum, is a complex mixture of polysaccharides, mostly poly-D-galacturonic acid and bassorin. A part of it is miscible and a part forms a gel of exceptional quality. Both xanthan and Tragacant gums have been recognized as cold water soluble gums with good stability to salt and acid (Coia and Stauffer, 1987; Tischer et al., 2002).

Several studies have attempted to correlate the rheological properties and stability of emulsions (Quemada and Berli, 2002; Bais et al., 2005; Pal, 2000). Tempel and Van Den, (1963) reported that many hydrocolloids used to stabilize emulsion are shear-thinning, that is, they have a high viscosity at low shear rates which decreases dramatically as the shear rate is increased. This property is important because it means that the droplets are prevented from creaming, but that the food emulsion still flows easily when poured from a container. They have also indicated that information about the size of the aggregates and the strength of the bonds between flocculated droplets can be determined from steady state flow tests over a large range of shear rates. Xie and Hettiarachchy (1997) studied the effect of xanthan gum on emulsifying properties of soy protein isolate. They mentioned that xanthan gum contributed to the emulsion stability by its adsorption at the oil-water interface which resulted in decreasing the surface tension as well as formation of liquid crystalline lamellae in the water phase to trap the oil droplets in the micro-gel matrix. A study by Chen and Dickinson (1999) on effect of emulsifiers on the viscoelastic properties of heat-set whey protein emulsion gel revealed that by decreasing the mean droplet size the adsorbed polymer stabilizing layer gives rise to an effectively larger volume fraction and produce a gel of higher elastic modulus. Buffo and Reineccius (2002) indicated that an appropriate stability of concentrated beverage emulsion could be achieved by adjusting the viscosity of the system through the hydrocolloid concentration. Dickinson (2003) pointed out that emulsions with low volume fraction (5-10%) favor the destabilization by flocculation when the aqueous phase contains a non-gelling hydrocolloid or gelling hydrocolloids at a concentration below the gelation threshold. Paraskevopoulou et al. (2005) studied the stability of olive oil – lemon juice emulsion stabilized by xanthan gum as stabilizer and gum arabic and propylene glycol alginate as emulsifiers, and emphasized the importance of continuous phase rheology in determining the rheological and creaming behavior of emulsions. Batista et al. (2006) studied the rheological properties of added lutein and phycocyanin in colored oil-in-water emulsions and highlighted the contribution of each component on the quality of formed emulsions.

The production of high quality food emulsions, consequently, depends on the knowledge of the contribution of the components both individually and in combination on the properties of the end product (McClements, 2005).

So far most studies on stabilizing beverage emulsions have aimed at using different weighting agents; but those dealing with the shelf life of beverage emulsions without weighting agents are limited. The objective of this study was to investigate the effect of the viscosity modifiers (starch and gum) and surface active agents (emulsifiers) on the rheology and stability of beverage emulsions both in the concentrated and dilute (simulated juice drink) forms in the absence of weighting agents.

5.3 EMULSION RHEOLOGY

Beverage emulsions are considered to be low internal phase emulsions containing deformable particles which could exhibit shear-thinning and viscoelastic properties. The droplets of emulsions carry two opposing effects under a steady shear flow. The first one is viscous stress, $\eta_w \dot{\gamma}$, that has a tendency to elongate the droplet and the second one is a physical stress, σ / R, that tends to maintain the droplet in a spherical shape. The equilibrium shape of droplet is, therefore, the ratio of the two stresses which is refered to as cappilary number (N_{Ca}, the capillary number represents the relative effect of viscous forces and surface tension acting across an interface between two immiscible liquids) (Pal, 2000a; Pal, 2003):

$$N_{ca} = \eta_w \dot{\gamma} R / \sigma \tag{1}$$

where η_w is the water phase viscosity, $\dot{\gamma}$ is the shear rate, R is the droplet radius, and σ is the interfacial tension.

Reynolds number is the ratio of inertial forces to viscous force and for beverage emulsions, oil-in-water, (Pal, 2000a):

$$N_{\mathrm{Re}.p} = \rho_w \dot{\gamma} R^2 / \eta_w \tag{2}$$

where $N_{Re,p}$ is the particle Reynolds number and ρ_w is water phase density.

According to Pal (1998) and Pal (2000b), the relative viscosity, η_r, of emulsions can be expressed in the form of a rheological equation when Coulombic and van der Waals interactions are negligible:

$$\eta_r = f(K, \phi, N_{Ca}, N_{\mathrm{Re}.p}) \tag{3}$$

where ϕ is volume fraction of oil phase. The relative viscosity (η_r) can be calculated from the ratio of the emulsion viscosity (η_{Em}) over water phase viscosity (η_w):

$$\eta_r = \frac{\eta_{Em}}{\eta_w} \tag{4}$$

and K is the ratio of the oil phase viscosity to that of the water phase viscosity:

$$K = \frac{\eta_{oil}}{\eta_w} \tag{5}$$

where η_{oil} is the viscosity of oil phase.

The viscosity of covered oil droplets in beverages is much greater than that of the water phase ($\eta_{oil} >> \eta_w$) and the droplets are nearly spherical (McClements, 2005). Under such conditions and under creeping flow, both Capillary and Reynolds numbers are low ($N_{Ca} \rightarrow 0$ and $N_{Re,,p} \rightarrow 0$), and the relative viscosity for unflocculated beverage emulsions can be expressed as:

$$\eta_r = f(K, \phi) \tag{6}$$

The functional form of Equation 6 was first presented by G.I. Taylor (Pal, 2000b):

$$\eta_r = \frac{\eta_{Em}}{\eta_w} = 1 + \frac{(5K+2)}{2(K+1)}\phi \tag{7}$$

This equation is valid for very dilute emulsions where the interaction of adjacent droplets is low, but may not be applicable to the beverage emulsions when the hydrodynamic interaction is considerable.

For dilute suspensions of rigid spherical particles, the Einstein equation [Eq.(6)] and its expansions have been widely used (Sherman, 1983; Pal and Rhodes, 1989; Quemada and Berli, 2002; Buffo and Reineccius, 2002; Starov and Zhdanov, 2003; Klinkesorn et al., 2004; McClement, 2005; Taherian et al., 2006):

$$\eta_{Em} = \eta_w \left(1 + \frac{5}{2}\phi\right) \tag{8}$$

This equation covers suspensions containing continuous phase (water phase) of Newtonian behavior and rigid particles.

For the dilute suspensions of fluid spherical particles the modified Einstein Equation is given by (McClement, 2005)

$$\eta_{Em} = \eta_w \left[1 + \left(\frac{\eta_w + 2.5\eta_{oil}}{\eta_w + \eta_{oil}}\right)\phi\right] \tag{9}$$

For concentrated suspensions of non-flocculated particles and in the absence of long-range colloidal interactions the following two equations have been given to define the relative viscosity of concentrated beverage emulsions:

$$\eta_{Em} = \eta_w \left(1 + a\phi + b\phi^2 + c\phi^3 + \ldots\right) \tag{10}$$

The value of the constants *a*, *b*, *c*, and …can be determined either experimentally or theoretically. The values *a* and b for rigid particles were established as 2.5 and 6.2, respectively (Buffo and Reineccius, 2002; McClements, 2005) and

$$\eta_{Em} = \eta_w \left(1 - \frac{\phi}{\phi_c}\right)^{-[\eta]\phi_c} \tag{11}$$

where ϕ_c is an adjustable parameter related to the volume fraction at which the spheres become closely packed and $[\eta]$ is the intrinsic viscosity. If the flocs are assumed to be approximately spherical, then $[\eta] = 2.5$ and $\phi_c = 0.65$ (Buffo and Reineccius, 2002; McClements, 2005).

The effective volume fraction (ϕ_{eff}) of a fractal floc, on the other hand, is related to the size of the floc and the fractal dimension (Buffo and Reineccius, 2002; McClements, 2005):

$$\phi_{eff} = \phi\left(\frac{R}{r}\right)^{3-D} \tag{12}$$

where R is the floc radius and r is the droplet radius. In the presence of long-range repulsive interactions (electrostatic, steric) where the droplets are prevented to become close together and collide which results in increasing the effective volume fraction of the droplets - a modified Dougherty and Krieger equation has been suggested (Buffo and Reineccius, 2002):

$$\phi_{eff} = \phi\left(1+\frac{\delta}{r}\right)^{3} \tag{13}$$

where the δ is half the distance of closest separation between the droplets and for steric stabilization which is approximately equal to the thickness of adsorbed layer.

Buffo et al. (2002) reported that determination of layer thickness based on viscosity is prone to error due to different degree of poly-dispersity and packing density at the oil/water interface among the samples, as well as dissimilar electrolyte contents which can reduce the effective volume fraction. Later, Buffo and Reineccius (2002) justified the assumption of layer thickness to be one eighth of the particle radius: δ =r/8 and $\delta_{eff} = 2.68\delta$. Therefore,

$$\eta_{Em} = \eta_w(1-4.12\phi)^{-1.125} \qquad \text{(Model I)} \tag{14}$$

In term of complex shear modulus (G^*) and in the linear viscoelastic region, the following equation is suggested by Pal (2000c) and Pal (2002):

$$G^* = G_w^* \left[\frac{1 + \frac{3}{2}\phi}{1 - \phi} \right] \tag{15}$$

where G_w^* is the complex shear modulus of water phase and G^* defined as

$$G^* = G' + jG'' \tag{16}$$

where G' is the storage modulus, G'' is the loss modulus and j is the complex number.

For a dilute suspension of solid spherical particle, the complex shear modulus (G^*) in the linear viscoelastic region is given by (Pal, 2002):

$$G^* = G_w^* \left[1 + \frac{5}{2}\phi H \right] \tag{17}$$

Equation 17 is known as Palierne model (Pal, 2000c and Pal, 2002) and H is given by

$$H = \frac{2(G_{oil}^* - G_w^*)}{2G_{oil}^* + 3G_w^*} \tag{18}$$

where G_{oil}^* is the complex shear modulus of the oil phase.

For dilute suspensions of rigid spherical particles ($G_{oil}^* \to \infty$), H is unity and Equation 17 is given by

$$G^* = G_w^*(1 + 2.5\phi) \tag{19}$$

Pal (2002) developed another equation for suspensions of rigid particles as

$$\left(\frac{G^*}{G_w^*}\right)\left(\frac{G^* - G_{oil}^*}{G_w^* - G_{oil}^*}\right)^{-2.5} = (1-\phi)^{-2.5} \tag{20}$$

Considering oil particles are rigid ($G_{oil}^* \to \infty$):

$$G^* = G_w^*(1-\phi)^{-2.5} \qquad \text{(Model II)} \tag{21}$$

In the present study, the theoretical models of emulsion viscosity for concentrated beverage emulsions consisting of different surface active hydrocolloids and identical volume ratio were compared. The complex shear moduli of emulsions were also compared to Equation (21).

5.4 MATERIALS AND METHODS

5.4.1 Materials

Coconut oil was obtained from Univar and Daminco Inc. (Boucherville, Quebec) and modified starch (Purity Gum 2000) from National Starch and Chemical (Bridgewater, NJ). Spray dried arabic and xanthan gums (TIC PRETESED® XANTHAN 200) were provided by Nealanders Inc. (Montreal, Quebec). Tragacanth gum was kindly granted by Hydrotech Inc. (Teheran, Iran). Food grade citric acid and potassium sorbate were used to adjust the acidity and reduce the chance of contamination in all prepared emulsions.

5.4.2 Preparation of emulsions

Modified starch and gum arabic as surface active emulsifying agents and xanthan and tragacanth as stabilizing agents were dissolved separately in distilled water and stored overnight for completing hydration. After hydration, the appropriate amount of citric acid in form of 50% solution and potassium sorbate solution were added to the emulsifying solutions. After addition of a constant amount of coconut oil 9% weight/weight (w/w based on final preparation) into the emulsifier solutions, each sample was stirred for 15 min. The surface active agent concentrations were based on 1:1 and 1.5:1 agent/oil ratio, thus the batches were 9 and 14% agent with 9% oil (all w/w basis final weight). The solution of stabilizer gums were, then, added to the dispersion and followed by a 3 min homogenization at high speed using Polytron laboratory scale homogenizer (Polytron, PT 10-35, Kinematica, AG Ltd. Switzerland). Further size reduction was obtained by using a laboratory scale high pressure homogenizer (Emulisiflex-C5, Avestin, Ottawa, ON) at 3500 psi and 2 passes.

5.4.3 Particle size distribution

The mean particle size and particle size distribution of prepared emulsions were determined using an integrated light scattering technique (ZetaSizer 4, Malvern Instruments Ltd., Malvern, UK). Concentrated beverage emulsions were diluted 1:1000 using DI water to prevent multiple scattering effects (Klinkesorn et al., 2004) and placed in specified glass cuvette for size measurement. The instrument used the method of photon correlation spectroscopy (PCS) to measure particle size in constant random thermal, or Brownian, motion. This motion causes the intensity of light scattered from the particles to vary with time. Large particles move slowly than small ones, so that the rate of fluctuation of the light scattered from them is also slower. PCS uses the rate of change of these light fluctuations to determine the size distribution of the particles scattering light. Determination of size was done in duplicate at room temperature and right after preparation of each emulsion.

5.4.4 Surface tension

The Du Nouy ring method was used to determine the surface tension of hydrocolloid gum solutions (Huang et al., 2001). A Fisher Surface Tensiomat (Fisher Scientific, Sainte-Foy, Quebec) was employed and the force acting on the ring was measured as it was moved upward form 3 mm below the surface of gum-air interface.

5.4.5 Opacity, specific gravity and volume fraction

Opacity of diluted emulsions (1:1000) was measured at 660 nm visible range using a spectrophotometer (Cary, 300-Bio, UV-Visible Spectrophotometer, Varian, Australia). Specific gravity of components phases were evaluated at the prepared concentrations using a 25 ml specific gravity bottle [Fisherbrand, Ottawa, Canada]. The volume fraction of each emulsion was determined based on following expression:

$$\phi = \frac{Sg_w - Sg_{Em}}{Sg_w - Sg_{oil}} \tag{22}$$

where Sg_w is the specific gravity of water phase, Sg_{Em} the specific gravity of emulsion and Sg_{oil} the specific gravity of oil phase.

5.4.6 Rheological Tests

Using a control-stress rheometer (AR2000 Rheometer, TA Instrument, New Castle, DE) equipped with a stainless steel 60 mm cone of 2° and solvent trap. The measurement temperature was constant at 22 °C using a circulating bath and a controlled peltier system. Flow and dynamic tests were conducted at the ranges of 0.001-100 Pa and 1-50 rad/sec (using constant stress value of 1 Pa, find from linear viscoelastic region) respectively. Hydrocolloid gums after 24 h hydration and emulsions immediately after being prepared were subjected to rheological measurements.

5.4.7 Physical stability

Instrumental Test

Homogenized emulsion was diluted in acidified sugar solution 2% (w/w), bottled and pasteurized (12 min at 95 °C) for stability studies. The pasteurization time was found by installing a semi-rigid thermocouple with the tip located at 1:10 of height of the bottle from the bottom. An aliquot of 6 ml of each pasteurized sample was poured into a flat-bottom cylindrical glass tube (100 mm height, 16 mm internal diameter) and subjected to an optical scanning screening (Quick Scan, Coulter Crop., Miami, FL). The transmission of monochromatic light (λ = 850 nm) from the diluted emulsion was measured as a function of their height in order to quantify the creaming rate. Creaming rate was then calculated from the height of the interfaces between the opaque droplet-rich layer and the transparent droplet-depleted layer as a function of time. Creaming rate was expressed as slope of absolute thickness of layers per unit time.

Observation in bottles

The 2% (w/w) diluted emulsion (simulated beverage) after preparation, bottling and pasteurization for 12 min at 95°C was stored at ambient temperature. The creaming stability was monitored in duplicate with a total of 6 bottles for each prepared emulsion. The samples with presence of whitish rings on the neck of the bottles after a period of one week were graded as +, and ± when creaming was observed after 3 weeks. Simulated beverages containing 2% of emulsions with no sign of creaming after 5 weeks were considered stable with negative sign.

5.4.8 Statistical analysis

The rate of coalescence of emulsion was statistically tested using the regression and ANOVA - two-factors with replication, and the means were compared at a significant level of 5%. Statistical analysis was done using Microsoft Excel and experiments were performed in duplicate

5.5 RESULTS AND DISCUSSION

5.5.1 Flow properties

The selection of concentration for stabilizing agents was based on primary steady shear rheology of xanthan and tragacanth gums at different concentrations. Xanthan gum at 0.3% and Tragacanth gum at 0.8% indicated the comparative consistency coefficients at 886 and 883 mPa, respectively. Xanthan gum, however, had a lower flow behavior index at 0.28±0.02 compared to that of tragacanth gum at 0.53±0.03. Since the measurements were carried out at shear rate that were sufficiently lower than the high shear rate plateau ($\eta_\infty \to 0$), the modified Carreau equation was used to compare the flow properties of different emulsions (Carreau, 1972)

$$\eta = \frac{\eta_0}{\left[1+\left(\lambda\dot{\gamma}\right)\right]^{1-n}} \qquad (23)$$

where η_0 is the limiting viscosity for the first Newtonian region, $\dot{\gamma}$ is the shear rate, λ is the time constant calculated from reciprocal of the shear rate at which the zero shear rate component and power-law component of flow curve intersect and n is the flow behavior index.

The emulsions flow curves for 1:1 and 1.5:1 surface active agent/oil are shown in Figures 5.1 (a, b, c and d) and Figure 5.2 (a, b, c and d) respectively. Both figures represent a shear thinning behavior with a zero-shear rate limiting viscosity (η_0) at very low shear rate ($\dot{\gamma}$). The flow curves were identical for the three measurements and a time period of two weeks after preparation. The zero-shear rate limiting viscosity slightly increased for all the emulsions after two weeks, corresponding to the upper limit of the linear viscoelastic range of the emulsion (Table 5.1). Increase in viscosity of emulsions containing tragacanth and xanthan gums as a function of storage time has also been reported by Coia and Stauffer (1987). They assumed that the initial viscosity resulted from the hydration of amorphous region of tragacanth gum containing the crystalline bodies in their solid state. The crystalline bodies that were soluble and more hydrophobic, and could migrate to the interfacial area producing a film around the droplet. The remaining crystalline bodies were unable to migrate the continuous phase and upon standing slowly hydrated producing additional viscosity. It is also possible that increase in zero-shear viscosity partially corresponded to higher degree of flocculation, thus, more stress needed to breakdown the flocs.

The zero-shear viscosity is related to application of shear stresses within the Newtonian plateau producing small deformations which were within the linear viscoelastic range. As a result, the viscosity measured at equilibrium flow corresponded to the Newtonian compliance and as long as the applied shear stress was within the linear viscoelastic range of the emulsion, the measured equilibrium viscosity was constant. Buffo and Reineccius (2002) and McClements (2005) also indicated that at low shear rates the hydrodynamic forces are not large enough to disrupt the flocs which then act

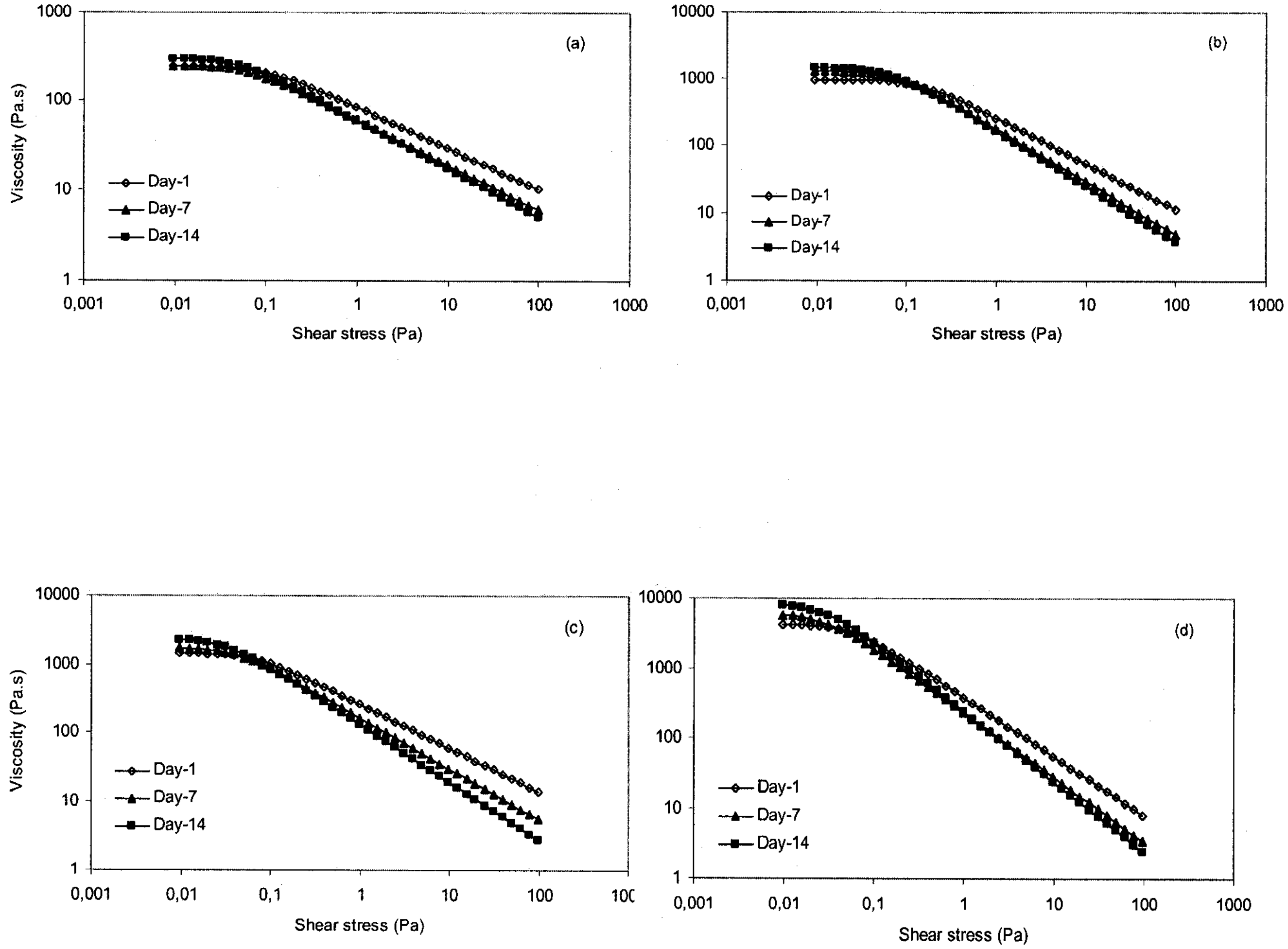


Figure 5.1. Steady-state flow curves for a) 9% arabic and 0,8% tragacanth gums, b) 9% arabic and 0.3% xanthan gums, c) 9% modified starch and 0.8% tragacanth gums and d) 9% modified starch and 0.3% xanthan stabilized emulsions.

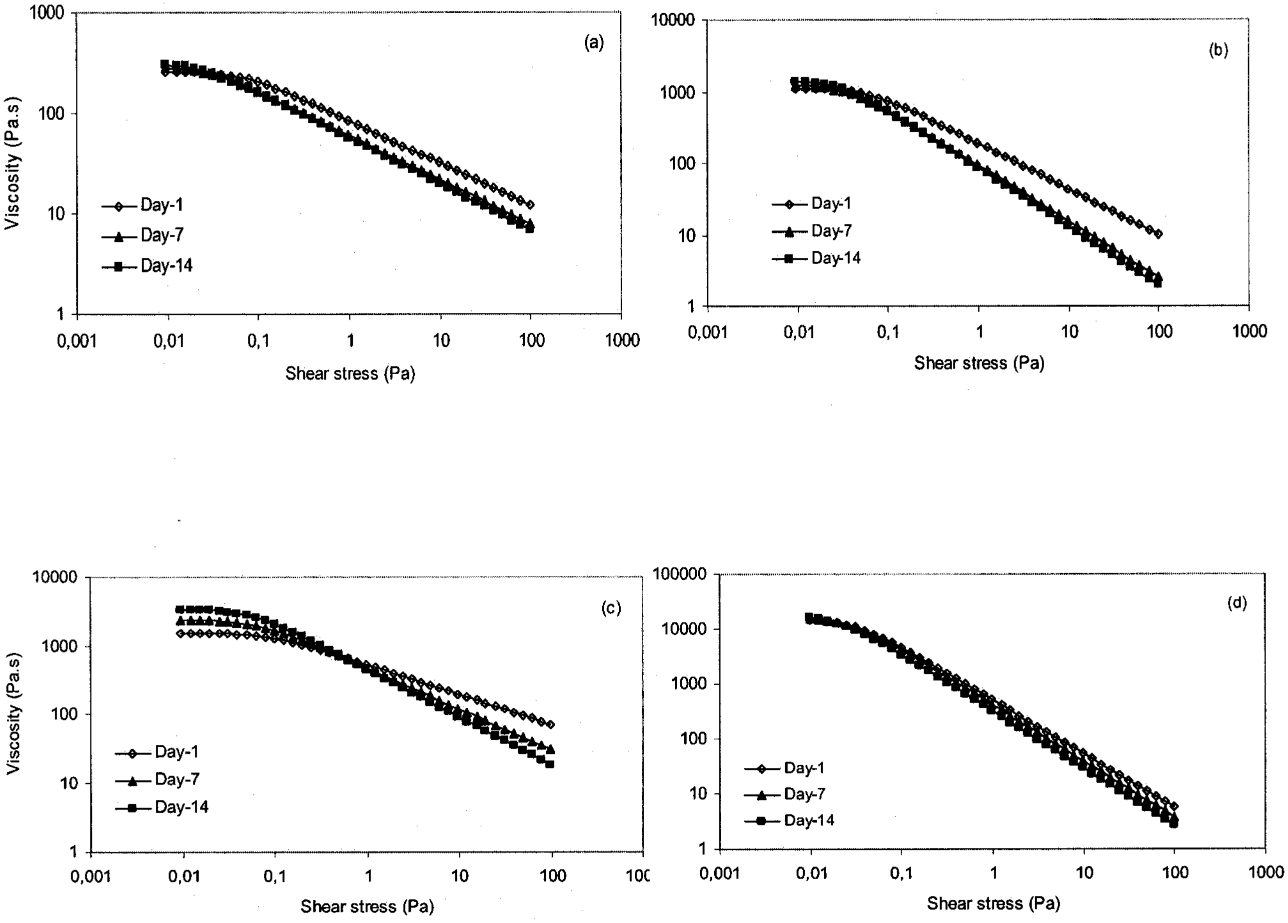


Figure 5.2. Steady-state flow curve for (a) 14% arabic and 0,8% tragacanth gums, (b) 14% arabic and 0.3% xanthan gums, (c) 14% modified starch and 0.8% tragacanth gums and (d) 14% modified starch and 0.3% xanthan stabilized emulsions.

Table 5.1. Zero-shear viscosity and flow behavior index of emulsions as a function of storage time.

Emulsions	η_0 (mPa.s) day-1	η_0 (mPa.s) day-7	η_0 (mPa.s) day-14	n (slope) day-1	n (slope) day-7	n (slope) day-14
a)	483.2±3.8	495.5±6.8	601.3±11.5	0.77±0.01	0.75±0.01	0.73±0.01
b)	1911.8±16.7	2532.2±9.2	2895.5±8.5	0.66±0.02	0.61±0.01	0.59±0.01
c)	2917.6±9.8	3503.3±23.5	4749.3±18.9	0.68±0.01	0.63±0.01	0.58±0.01
d)	8478.9±31.8	11991±40.2	16862±14.5 ***	0.58±0.01	0.54±0.01	0.5±0.00
e)	524.3±11.7	580±9.3	631.8±12.9	0.79±0.02	0.78±0.00	0.77±0.00
f)	2252.8±17.8	2532±24.7	3053.0±19.6	0.68±0.02	0.61±0.01	0.58±0.00
g)	3054.1±12.3	4771.8±18.7	6861.3±25.5	0.78±0.001	0.70±0.001	0.65±0.00
h)	31038.8±76.6	33329.2±65.2	39558.1±44	0.51±0.00	0.49±0.01	0.48±0.01

a) 9% Arabic + 0.8% Tragacant + 9% Coconut oil, b) 9% Arabic + 0.3% Xanthan + 9% Coconut oil, c) 9% Starch + 0.8% Tragacanth + 9% Coconut oil, d) 9% Starch + 0.3% Xanthan + 9% Coconut oil, e) 14% Arabic + 0.8% Tragacant + 9% Coconut oil, f) 14% Arabic + 0.3% Xanthan+ 9% Coconut oil, g) 14% Starch + 0.8% Tragacanth + 9% Coconut oil, h) 14% Starch + 0.3% Xanthan + 9% Coconut oil.

like particles with fixed size and shape, resulting in a constant viscosity. This increase was more pronounced for emulsions formed by modified starch (purity gum 2000) - tragacanth gum as well as arabic - xanthan gum combinations which could be related to the higher degree of flocculation. As the shear rate is increased and the values of stress exceeded the linear range, the hydrodynamic forces become large enough to deform and disrupt the flocs, which elongate and align with the shear field, and a rapid decline in equilibrium viscosity occurs. The shear thinning index (n) indicated a decrease after two weeks storage time period for all emulsions, the magnitude was different. This decrease was again more articulated for emulsions prepared with modified starch and tragacanth gum and/or arabic and xanthan gum at selected concentrations. The shear thinning region has been reported to be a consequence of a dramatic shear induced structural breakdown, related to the mechanism of oil droplet deflocculation (McClements, 2005; Batista *et al.*, 2006). Both findings, therefore, describe the lower stability of these emulsions compared to those prepared with modified starch and xanthan and/or gum arabic and tragacanth gum combinations.

The experimental flow curves consisting of apparent viscosity as a function of shear stress were also compared with Buffo and Reineccius model (Model I, Eq. 14). This model assumed the reduction of effective volume fraction due to different packing density of gums at the oil/water interface and similar electrolyte content. Since we used the combination of surface active and stabilizer gums, accounting for both hydrodynamic and colloidal interactions, the viscosity was predicted by including additional volume fraction term using extended Einstein equation as:

$$\eta_{Em} = \eta_w\left(1 + a\phi + b\phi^2\right) \tag{24}$$

The flow curves for day 1 and 14 along with model predicted values (Equation 24) are shown in Figure 5.3 (a, b, c and d) for stable emulsions and Figure 5.4 (a, b, c, and d) for unstable emulsions. The values of a were found to be 2, 1.8, 1.4 and 0.6 for 14% starch-0.3% xanthan, 14% arabic-0.8% tragacanth, 14% Arabic-0.3% xanthan and 14% starch-0.8% tragacanth, respectively. The values of b were constant at 6.2 for all predictions. As illustrated Model I over-predict the viscosity of emulsions, while all flow curves illustrate an excellent fit for predicted model. Stable emulsions after 14 days storage (Figures 5.3 b and d) indicate minor deviations from predicted flow curves. The unstable emulsions (Figure 5.4 b and d) illustrate this deviation along with an increasing zero-shear viscosity. Unstable emulsions, hence, indicated greater extent of flocculation associated with holding the particle together, increasing the resistance to rupture and dramatic decrease of viscosity when the flocs became elongate and aligned with the shear field.

5.5.2 Dynamic properties

In order to determine the linear viscoelastic region, the rheological parameters [storage modulus (G'), loss modulus (G") and complex modulus (G^*)] were first measured by conducting a stress sweep test at a fixed frequency. The stress of 1 Pa was then obtained from linear region and kept constant during course of measurements. The frequency development of the viscoelasticity of emulsions containing an even amount of surface active agents 1:1 or 1.5:1 gum/oil, on day 1 and day 14, are shown in Figures 5.5 (a, b, c and d) and Figure 5.6 (e, f, g and h), respectively. The storage modulus (G') and loss modulus (G″) for all emulsion systems showed very similar monotonic development at low frequency while emulsions prepared with modified starch and xanthan gum increased to a greater extent at elevated frequency (Figure 5.5d and Figure 5.6h).

For emulsions prepared with gum arabic or starch and tragacanth, there appeared to be a more divergent behavior among the loss moduli with increasing frequency. It is interesting to note that, with the exception of emulsion formed by 14% modified starch and 0.3% xanthan, the loss modulus increased after 14 days of storage while the storage modulus decreased slightly. This means that viscous component become more prominent after storage and is in agreement with the earlier results for zero-shear viscosity in steady-state flow tests. Comparing both figures, it can also be noted that the emulsions stabilized by tragacanth gum illustrated a lower storage moduli as compared to emulsions stabilized by xanthan gum. The diversity between storage modulus (G') and loss modulus (G″) for emulsions containing tragacanth gum are also more pronounced (Figures 5.5a and 5.5c and Figures 5.6e and 5.6g).

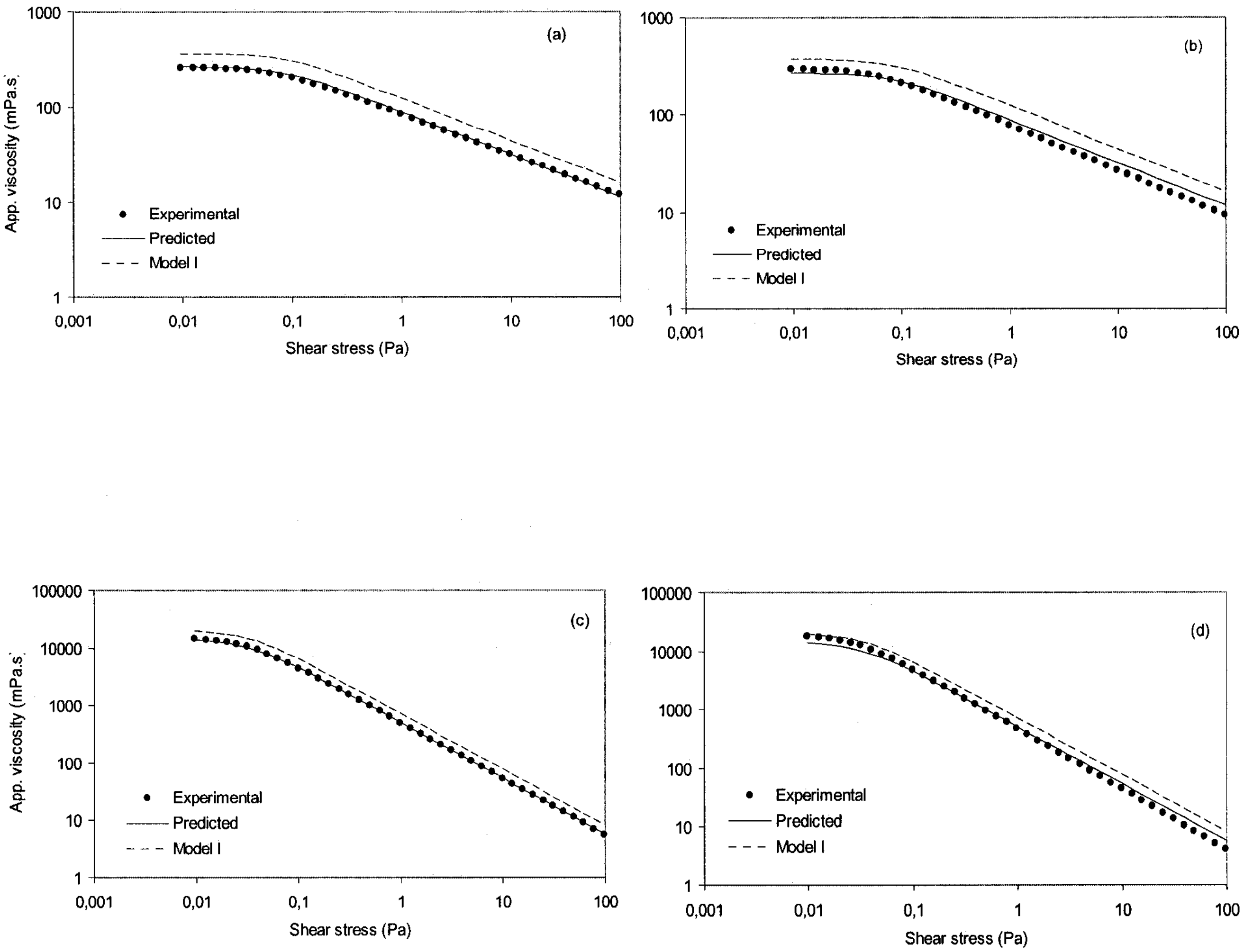


Figure 5.3. Comparison of experimental steady-state flow curve with predictions of Eq.(14) and Eq. (24), for 14% arabic-0.8% tragacanth and 14% starch-0.3% xanthan stabilized emulsions at a) day 1, b) day 14, c)day 1, and d) day 14, respectively.

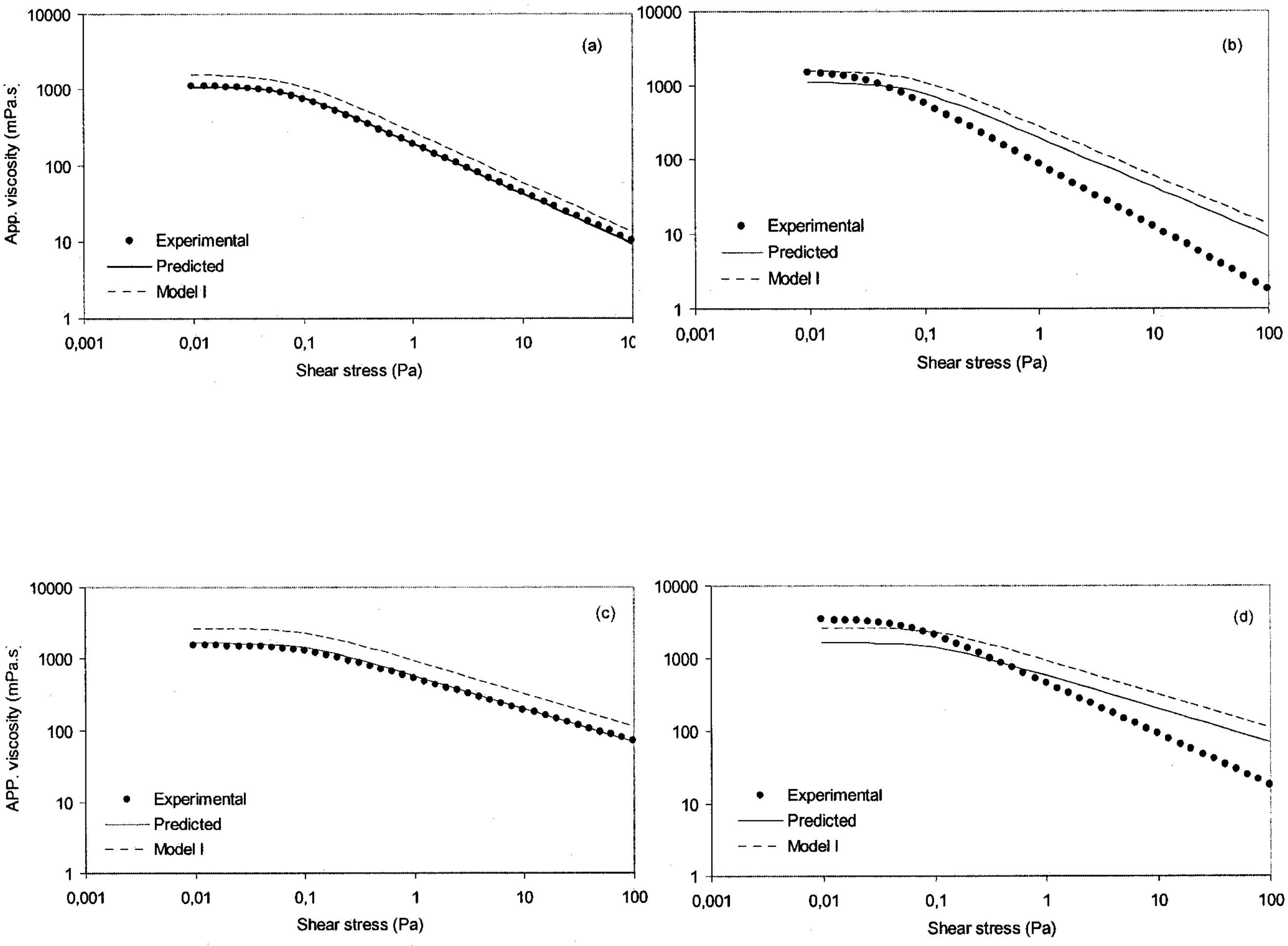


Figure 5.4. Comparison of experimental steady-state flow curve with predictions of Eq.(14) and Eq. (24), for 14% arabic-0.3% xanthan and 14% starch-0.8% tragacanth stabilized emulsions at a) day 1, b) day 14, c)day 1, and d) day 14 respectivly.

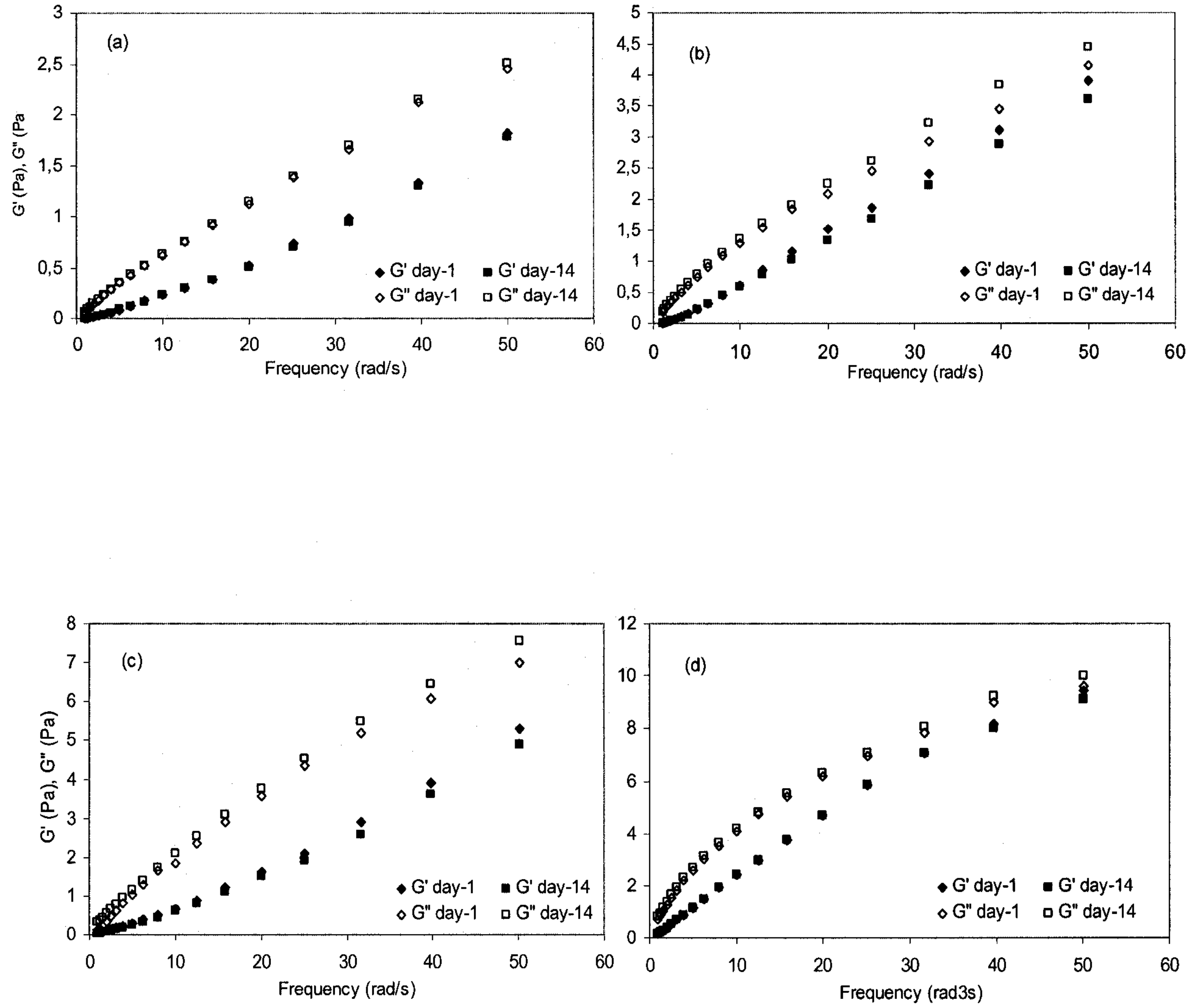


Figure 5.5. Linear viscoelastic properties of emulsions at identical oil phase concentration and a) 9% Arabic + 0.8% Tragacant , b) 9% Arabic + 0.3% Xanthan, c) 9% Starch + 0.8% Tragacanth, d) 9% Starch + 0.3% Xanthan.

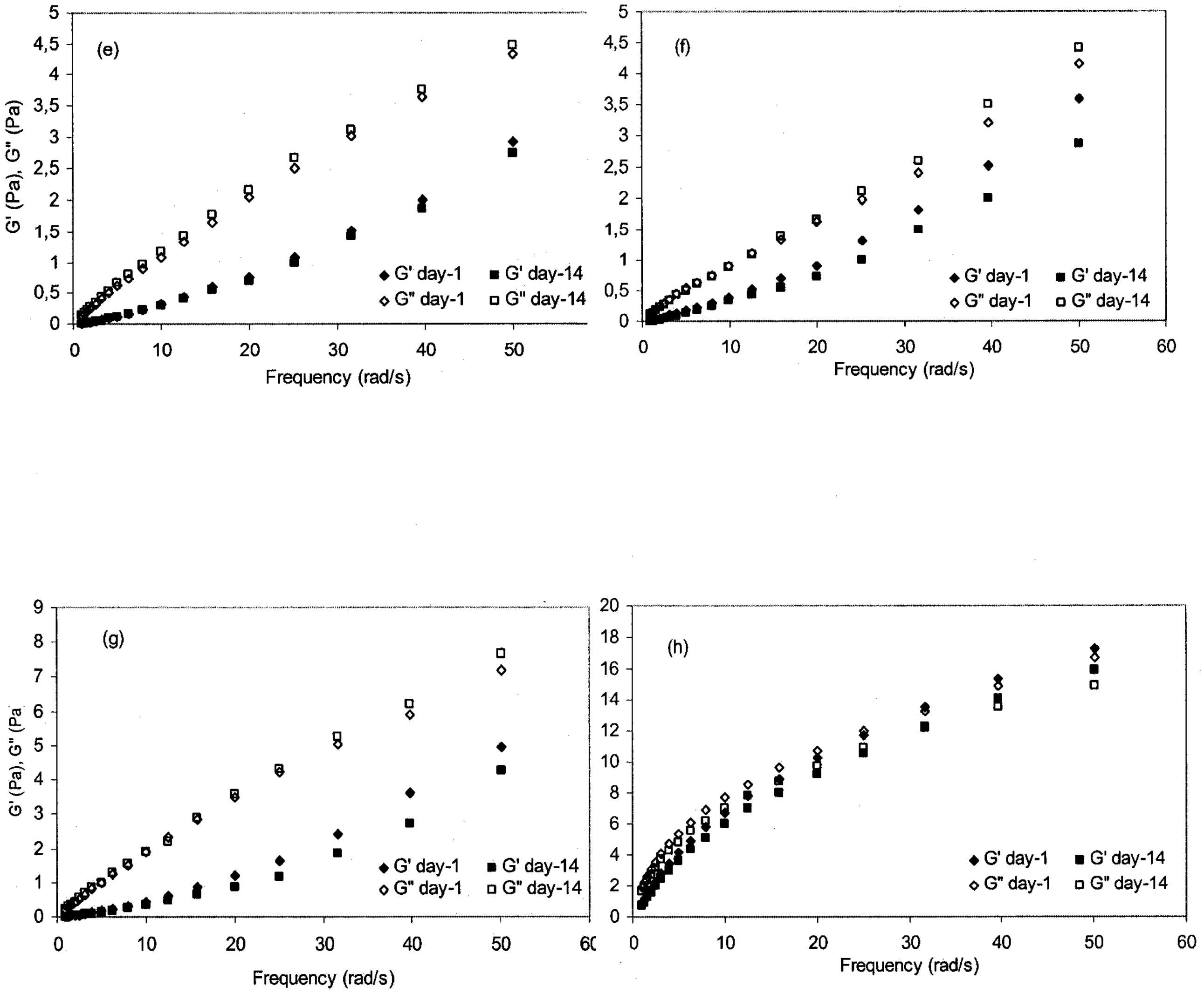


Figure 5.6. Linear viscoelastic properties of emulsions at identical oil phase concentration and e) 14% Arabic + 0.8% Tragacant, f) 14% Arabic + 0.3% Xanthan, g) 14% Starch + 0.8% Tragacanth, h) 14% Starch + 0.3% Xanthan in water phases.

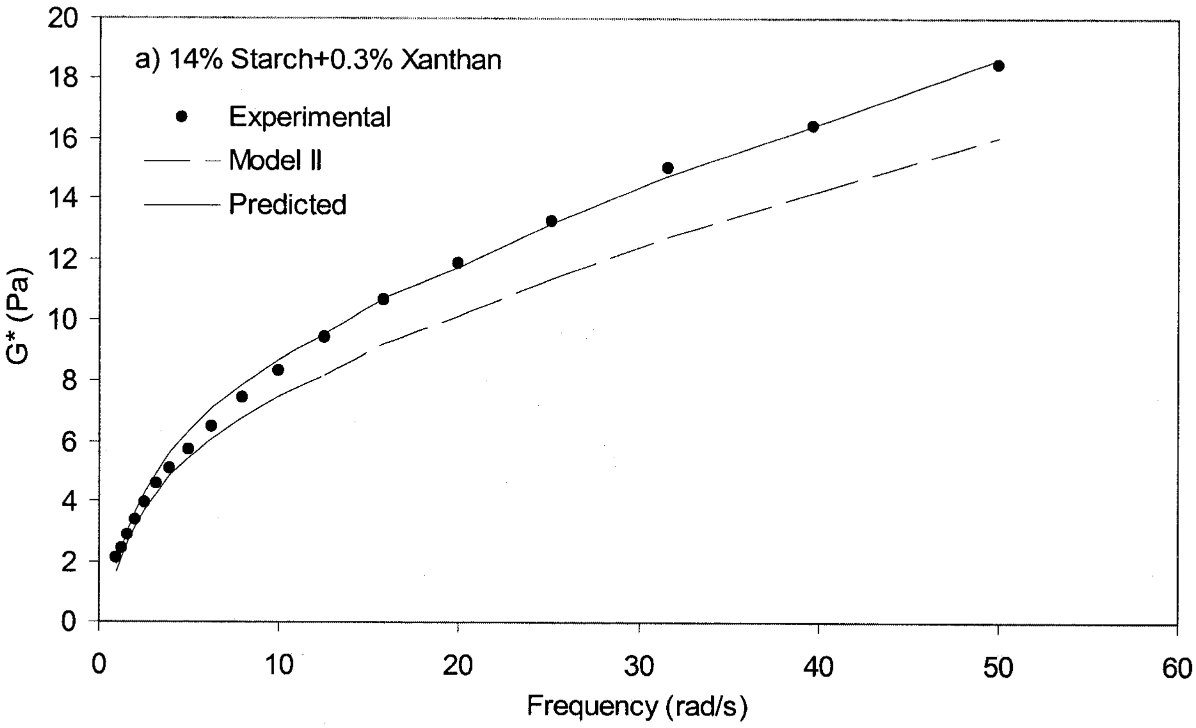
In our primary tests, xanthan gum did not reduce the surface tension of water while tragacanth gum resulted in decreasing the surface tension in a great extent (from 72.5 dyne/cm to 53 dyne/cm). Possibly, the elasticity of the covered oil droplets suspended in water phase dominated the measured viscoelasticity and, therefore, masked the viscoelastic effects of added tragacanth. For emulsions formed by modified starch and xanthan, the mechanical behavior was that of a viscoelastic liquid, where $G' \geq G''$ through the entire frequency range (Figure 5.5d and Figure 5.6h). Nonetheless, in the case of arabic and tragacanth gums, a weak-gel structure was observed where $G'' > G'$ and both moduli increase with frequency under almost the same gradient. All these features are unambiguous evidence that gel-network is being set up in modified starch coconut oil xanthan stabilized emulsions. Consecutively, the corresponding frequency developments of emulsions stabilized with arabic and tragacanth gums showed lower value of the viscoelastic moduli as compared to those of modified starch and xanthan gum stabilized emulsions. It should also be noted that the change in both moduli as influenced by storage time is lower for arabic and tragacanth gum stabilized emulsions (Figure 5.5a and Figure 5.6e) as compared to arabic and xanthan stabilized emulsions (Figure 5.5b and Figure 5.6f).

As pointed out earlier, in concentrated beverage emulsions, the colloidal interactions have been reported to be of short-range significance (Buffo et al., 2001; Buffo and Reineccius, 2002. In this situation, the particles begin to interact with each other through a combination of hydrodynamic and colloidal interactions. Hydrodynamic interactions result from the relative motion of neighboring particles and alter the viscosity of the system. In order to account for the effect of these interactions, the additional volume fraction should be added (McClements, 2005), therefore the Einstein equation can be extended as

$$G^* = G_w^*\left(1 + a\phi + b\phi^2\right) \tag{25}$$

where a and b were found to be 4.5 and 6.2, respectively, for 14% starch-0.3% xanthan and 10 and 6.2, respectively for 14% arabic-0.8% tragacanth stabilized emulsions.

Figures 5.7a and b compare experimental data of 14% starch-0.3% xanthan gum and 14% Arabic-0.8%tragacanth gum stabilized emulsions, respectively, with the



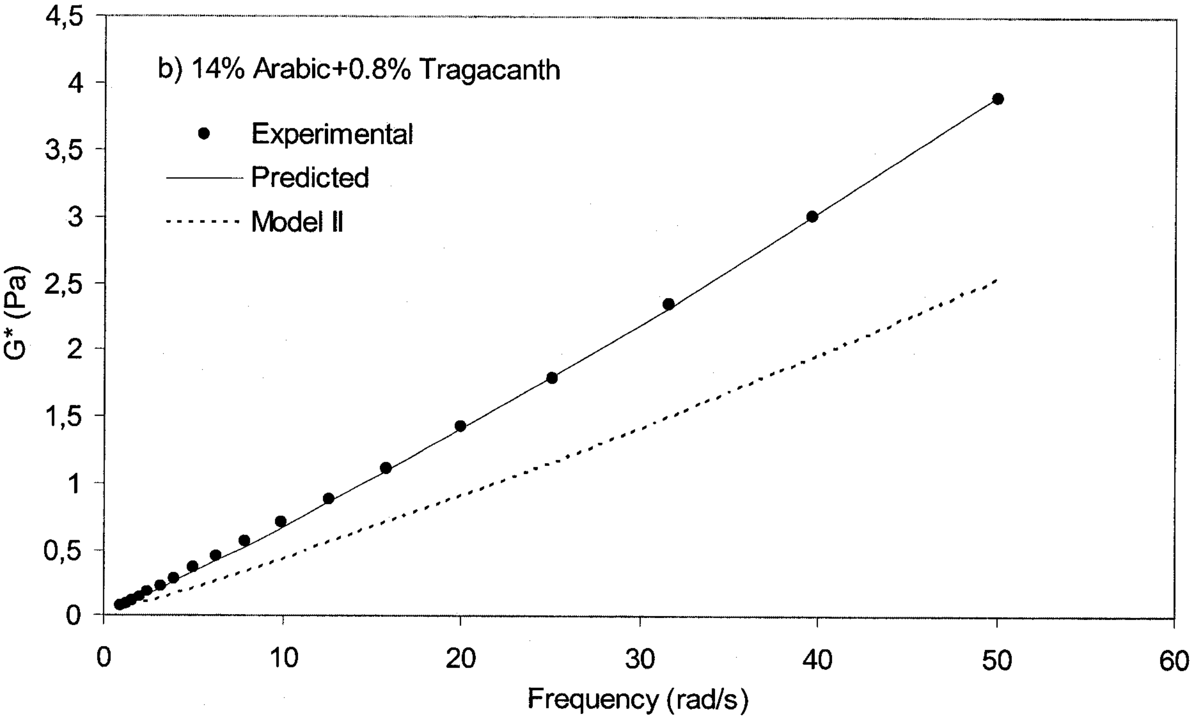


Figure 5.7. Comparison of complex shear modulus of Starch-xanthan and Arabic-tragacanth stabilized emulsions with prediction of models.

complex shear modulus, Equation (21), developed by Pal (2002) and predicted model (Equation, 25) suggested in this study. Equation (21) is referred as Model (II) in both figures. These two emulsions indicated good stability after dilution in simulated citrus beverage with no sign of ringing after 5 weeks. The experimental data consisting of complex modulus of emulsions as a function of oscillation frequency are plotted and compared with both Pal and predicted models. As illustrated, the Pal model under-predicted the complex modulus and the deviation increased with increasing frequency. It should be noted that this model represented a good fit only at low value of dispersed phase volume fraction for suspension of spherical glass beads in purified carboxymethylcellulose (CMC) Pal (2002). In our case, although the volume ratios of all prepared emulsions were lower than 0.1 (0.099 for 14% starch-0.3% xanthan stabilized emulsion and 0.091 for 14% arabic-0.8% tragacanth stabilized emulsion), the covered droplets did not act as glass beads. Figures 5.7a and 5.7b also indicate that increase in elasticity of covered droplets could reduce this divergence.

The differences in viscoelastic properties of the emulsions referred to in this study were related to the arabic-tragacanthe, starch-tragacanth, arabic-xanthan and starch-xanthan combinations. Hydrophobic interactions between the oil and proteins in tragacanth and arabic gums as well as the modified starch at the interface may account for the relaxation and overall viscoelastic properties. However, they cannot be considered as being the only responsible mechanisms controlling the degree of the aggregation of the emulsion droplets as reported by Valdez et al. (2005). Dramatic reduction of emulsification capability of gum arabic has been reported at low pH (Garti and Reichman, 1993). Even though xanthan gum did not impart in reduction of surface tension but it was the most effective gum in controlling the rheological properties.

5.5.3 Stability of emulsions in concentrated and diluted form

The stability of emulsions in diluted form against oil droplet coalescence was determined by following the change with time of the average droplets size and droplet aggregation rate. The rate of coalescence of emulsion droplets (D_c) mainly followed the first-order kinetics (Sherman, 1983; Ye et al., 2004; Paraskevopoulou et al., 2005):

$$N_t = N_0 \exp(-D_c t) \qquad (26)$$

where N_0 and N_t are the numbers of droplets per unit volume of emulsion initially and time t, respectively, and D_c is the rate droplets coalescence. In term of average droplets size, the Equation is given as (Sherman, 1983):

$$\ln D_t = \ln D_0 + \frac{D_c t}{3} \qquad (27)$$

where D_0 and D_t are the mean droplet sizes initially and at time t, respectively. Therefore D_c was determined by plotting 3(ln (D_t/D_0) versus time (t).

The results for emulsion droplet size, rate of coalescence of emulsion droplets, opacity and ringing in bottle for all prepared emulsions are tabulated in Table 5.2. The extent of droplet coalescence is associated with creaming (ringing in bottle). The rate of coalescence also indicated a high coorelation coefficient (0.97) when were ploted versus creaming rate. Emulsion stabilized by arabic-xanthan combinations indicated that the rate of coalescence in both concentrated and diluted forms were significantly different ($\rho<0.05$). Modified starch-tragacanth stabilized emulsions also demonstrated a lower stability compared to arabic-tragacanth and modified starch- xanthan stabilized emulsions. Increase in concentration of gum arabic in arabic-xanthan emulsions did not improve the emulsion stability, and additional concentration of modified starch in starch-tragacanth emulsions had a slight effect on stability improvement, possibly, due to increase in water phase viscosity. Arabic-tragacanth emulsions, despite of low viscosity of their water phases, were also among the most stable emulsions. The highest rate of coalescence was associated with arabic-xanthan emulsions and the lowest rate of coalescence was associated with the modified starch-xanthan emulsions.

In order to find an explanation for all these occurrences, the previously reported data by Garti and Reichman (1993) would be useful. They reported that "the gum arabic behaves as a typical surface active protein and anchors strongly to the oil phase via its proteinaceous part of the molecule. When the proteinaceous part is removed, denatured, or deactivated, the gum tends to lose its surface activity and emulsification capacity". It is also worthy to mention that the rheological testes on arabic gum solution indicated lower

Table 5.2. Comparison of particle size growth, volume ratio, opacity and stability in simulated beverages for prepared emulsions.

Emulsions	Average particle size, *D_t (nm)			D_c	Opacity	Ringing
	Day-1	Day-7	Day-14	nm/day	660 nm	in bottle
9%A + 0.8%T	756.2±11.7	797.4±5.6	835.6±4.1	0.023	0.71±0.01	±
9%A + 0.3%X	772.9±8.3	930.8±12.2	993.6±0.9	0.057	0.65±0.02	+
9%S + 0.8%T	354.6±5.6	380.7±2.1	412.4±5	0.035	0.24±0.01	+
9%S + 0.3%X	377.9±5.6	389.1±2.3	409.8±8.5	0.019	0.45±0.01	-
14%A + 0.8%T	614.6±7.2	633.7±13.7	667.7±6.1	0.019	0.93±0.07	-
14%A + 0.3%X	717.1±2.5	782.0±3.1	895.7±10.2	0.052	0.76±0.02	+
14%S + 0.8%T	366.5±6.3	388.4±4.9	417.6±4.0	0.030	0.25±0.01	+
14%S + 0.3%X	378.8±1.8	389.9±2.3	401.1±3.9	0.013	0.56±0.01	-

*D_o is D_t at day 1

viscosity and practically Newtonian behavior at the selected concentrations. The lower stability of arabic-xanthan emulsions may, therefore, be due to the loss of emulsification capacity of arabic gum as the influence of acidity and pasteurization temperature. Since xanthan gum as well did not indicate any surface activity, the only stabilization effect is due to the viscosity and, hence, emulsion will separate rapidly. The results are also in agreement with Chanamai and McClements (2001) who studied the depletion flocculation of beverage emulsions by gum arabic and modified starch. They reported that emulsions containing gum arabic are more susceptible to depletion flocculation compare to emulsions containing modified starch. They also reported that gum arabic has a greater aqueous phase effective volume than modified starch due to higher molecular weight and more open structure of arabic gum.

In the case of arabic-tragacanth emulsions, although the emulsions had an identical type of preparation, tragacanth gum is more surface active and is more resistant to acid and heat treatment. Therefore, the greater stability of these emulsions may be due to the residual surface activity contributed by tragacanth gum. Gum arabic stabilized emulsions also added greater opacity to the simulated beverage emulsions compared to modified starch stabilized emulsions.

The rate of creaming (aggregation) for emulsion at low and elevated concentrations of arabic and modified starch stabilized emulsions are illustrated in Figure 5.8 and Figure 5.9 respectively. As the rates of aggregations are the highest for arabic-xanthan emulsions, the results are in excellent agreement with previously mentioned coalescence rate. Once again, the modified starch-xanthan emulsion at elevated concentration of modified starch indicated the lowest aggregation rate and, hence, the most stable emulsion in both concentrated and diluted forms.

Figure 5.10 and Figure 5.11 illustrate shelf stability of pasteurized simulated citrus beverages containing 2% emulsions after 12 weeks storage at room temperature for 1:1 and 1.5:1 agent to oil combinations, respectively. As it can be observed that the ringing and aggregation are associated mostly with arabic-xanthan emulsions and slightly with modified starch-tragacanth emulsions at low and elevated surface active gum concentrations. Since the separation of starch-tragacanth stabilized emulsion was also

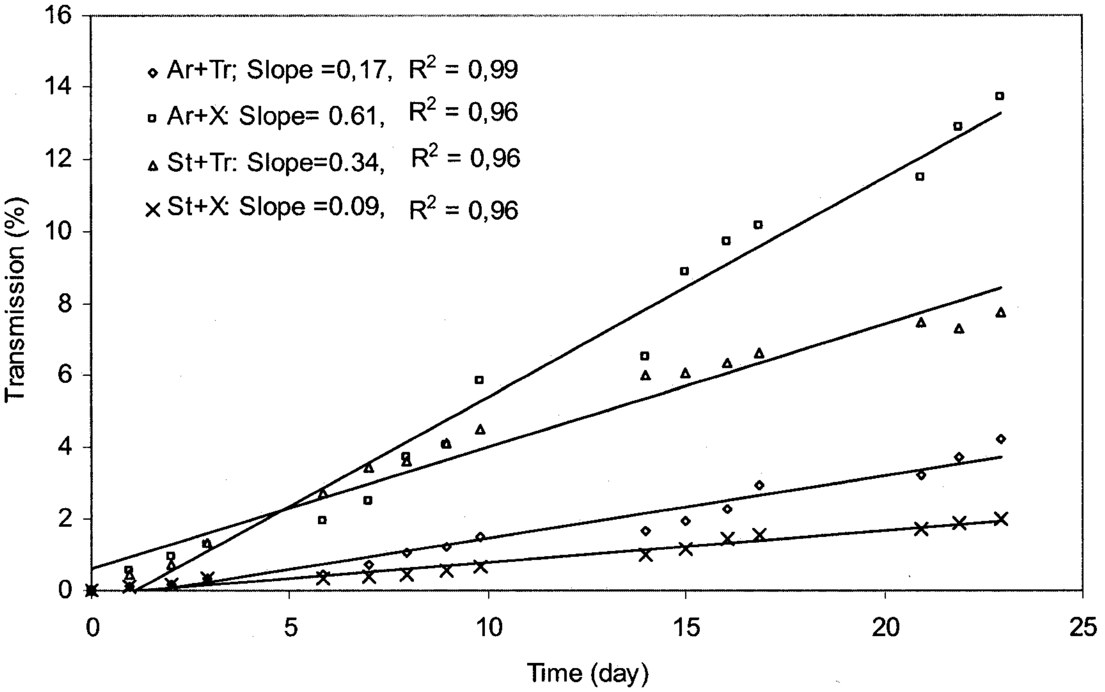


Figure 5.8. The time evolution of transmission for simulated beverages containing 2% of emulsions at 9% Starch (St), 9% Arabic gum (Ar), 0.8% Tragacanth gum (Tr) and 0.3% Xanthan gum (X) concentrations.

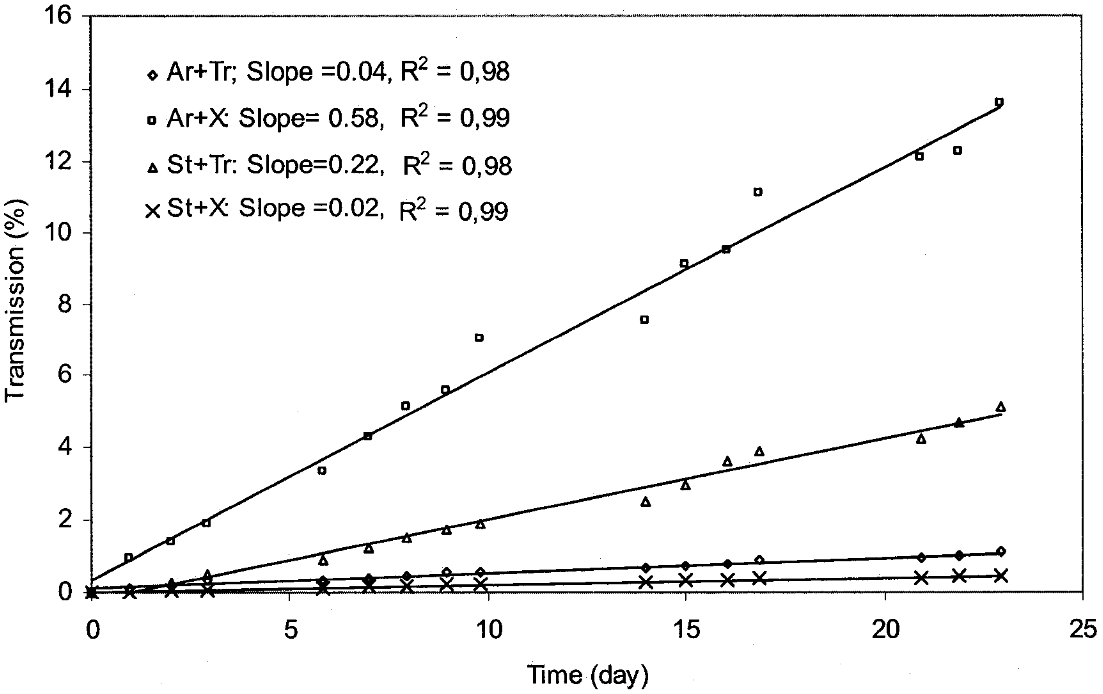


Figure 5.9. The time evolution of transmission for simulated beverages containing 2% of emulsions at 14% Starch (St), 14% Arabic gum (Ar), 0.8% Tragacanth gum (Tr) and 0.3% Xanthan gum (X) concentrations.

Figure 5.10. Shelf stability of pasteurized simulated citrus beverages containing 2% emulsions, stabilized by I) 9% Arabic and 0.3% Xanthan, II) 9% Starch and 0.3% Xanthan, III) 9% Arabic and 0.8% Tragacanth, IV) 9% Starch and 0.8% Tragacanth, after 12 weeks storage at room temperature.

Figure 5.11. Shelf stability of pasteurized simulated citrus beverages containing 2% emulsions, stabilized by V) 14% Arabic and 0.3% Xanthan, VI) 14% Starch and 0.3% Xanthan, VII) 14% Arabic and 0.8% Tragacanth, VIII) 14% Starch and 0.8% Tragacanth, after 12 weeks storage at room temperature.

observed in the concentrated form, the instability may be is due to the incompatibility or coacervation of these two hydrocolloids. As Dickinson (2003) stated the thermodynamic incompatibility implies the separation of emulsion into two distinct aqueous phases, one rich in protein and other rich in hydrocolloid. The observations, therefore, are in a good agreement with the results obtained by both rheological assessment and particle properties examinations.

5.6 CONCLUSIONS

This study demonstrated that both modified starch-xanthan and arabic-tragacanth gum combinations could be used to form highly stabilized beverage cloud emulsions. In the considered concentration range, the rheological properties of modified starch-xanthan gum combination were able to provide a gel matrix and highly stable emulsion. Arabic-tragacanth stabilized emulsions demonstrated rheological properties with fewer changes in shear thinning behavior after storage. The rheology of all prepared emulsions can be confidently modeled through the Einstein equation or its exponential expansion. The predicted model for complex shear modulus also well fitted with experimental data.

With the exception of arabic-xanthan emulsions which demonstrated the lowest stability, the creaming stability and rheology of beverage emulsions were affected by increasing surface active gum concentration. As a first approach, we venture to suggest that the lower stability of arabic-xanthan emulsions may be due to the loss of emulsification capacity of arabic gum as an influence of acidity and pasteurization temperature. In the case of arabic-tragacanth emulsions, the greater stability could be observed due to higher surface activity and higher stability to acid and heat by tragacanth gum. From practical point of view, the results provide useful information for achieving reasonable stability and opacity for concentrated emulsion and fruit beverages.

PREFACE TO CHAPTER 6

In this chapter we investigated the shelf stability of emulsions in orange beverage. The reformulation of emulsions was based on the obtained results from previous chapter for the most and the least stable emulsions.

The aims were first to confirm our previous results and, second to approach our main goal of replacement of health restricted weighting agents with natural and food grade ingredients for industrial practices.

Part of this research was presented in conference of Encapsulation et enrobage, La Fondation des Gouverneurs (CRDA), St-Hyacinthe, Quebec, 1 février 2006 and Joint Conference of AAFC-CIFST, Montreal, Quebec, 2006. This research was presented at Food Safety and Nutrition Conference (AAFC Annual Meeting for Food Safety and Nutrition) October 2006, Ottawa, Ontario.

The experimental work and data analysis were carried out by the candidate under supervision of Professor H.S. Ramaswamy. Dr. P. Fustier supported the resources and provided scientific advices.

CHAPTER 6

STABILITY OF CLOUD EMULSIONS IN ORANGE BEVERAGE

6.1 ABSTRACT

Orange beverage emulsions were prepared using gum arabic and two types of modified starches (Purity Gum Be and Purity Gum 2000) as emulsifying agents at 1:1 and 1.5:1 agent/oil concentrations. A constant amount of vegetable oil was added to each gum solution followed by addition of even amounts of xanthan gum as stabilizers.

Rheological properties, turbidity and droplet properties of each prepared emulsion were examined using TA-Rheology Instrument equipped with a 60 mm and 2° cone, turbidity-meter and light scattering respectively. After addition of 2% (w/w) emulsions in orange beverage, containing 10% orange juice, creaming stability of emulsions were tested instrumentally and via visual observation in pasteurized glass bottle.

All surface active agents were able to reduce the surface tension at the oil-water interface. Emulsion prepared with modified starch (Purity Gum Be) at 1.5:1 (gum/oil) resulted in a higher elasticity compared to the other emulsions ($G'_{Be} > G'_{2000} > G'_{Arabic}$). Both types of modified starches (Putity Be and 2000) emulsions resulted in a greater stability than gum arabic emulsions. While creaming was associated with emulsions formed with 1:1 gum/oil for both Purity 2000 and gum arabic emulsions, after 3 month storage at room temperature, Purity Gum Be emulsions at both low and elevated concentrations provided appropriate stability with no sign of ringing in orange beverage.

6.2 INTRODUCTION

There is a constant increase in market demand for convenience, valuable and nutritional juices and drinks. Among them orange beverages in the form of RTD (ready-to-drink), frozen concentrated, powder and shelf-stable concentrated (premix) should be mentioned. The classification of fruit juice, or flavor-based drinks and products, can include many products such as concentrated fruit juices, squashes, RTD (ready-to-drink) beverages, sodas and low-calorie drinks, as well as powder mix preparations.

The cloudy appearance of orange beverage is related to addition of clouding agents (emulsions) and maintaining the stability of emulsion is of great importance. Garti et al., (1991) reported that the clouding agent must contribute to the opacity of the formulated orange soft drink without affecting the stability of the cloud (no creaming, ringing or separation), color, taste or odor of the finished beverage.

A stable beverage emulsion is, therefore, characterized by long term stability, in diluted form, with absence of ringing resulting from raised coalesced droplets around the neck of the bottle. After the year 1970, due to branding and restriction in use of density adjuster (weighting agents), producing a cloud or flavor emulsion that remain stable over the desired shelf life has became a common problem in the beverage industry (Trubiano, 1995; Tan & Wu, 1988; Chanamai & McClements, 2001; Tan, 2004; McClements, 2005).

The major components of citrus beverage cloud emulsions in the oil phase are vegetable oils to provide opacity and a combination of weighting agents to increase their density. The water phase is formed by water and amphiphilic polysaccharides to reduce surface tension and grant steric stabilization, stabilizer gums to prolong the stability and control rheological properties and citric acid to adjust the acidity. The stability of beverage emulsions as affected of added proteins has been studied by several authors and surface activity of protein has been well defined (Inklaar and Fortuin, 1969; Titus and Mickle, 1971; Tornberg and Hermansson, 1977; Fang and Dalgieish, 1996; Cornec et al., 1998; Demetriades and McClements, 1999) and has been discussed in the previous chapters. The reological properties of added stabilizer gum has a significant effect on stability of final diluted emulsion and has been also discussed by several authors (Sherman; 1963; Glicksman 1983; Barnes et al., 1989; Kokini and Fischbach, 1989; Harris, 1990; Nshinari and Doi, 1992; Lopes da Silva et al., 1992; Rao and Cooley, 1993; Ma and Barbosa-Canovas, 1995; Ma and Barbosa-Canovas, 1996; Ye et al., 2004).

Among the hydrocolloids, gum arabic and modified starch have been known for their surface activity and emulsifying properties with similarity to proteins. Gum arabic has been recognized as a hydrocolloid emulsifier. It is highly soluble in cold water and the solubility increases with temperature. Because of its effective emulsifying properties and the well known film forming ability, gum arabic has been widely used in the soft drinks industry for emulsifying flavor oils under acidic conditions. It is mainly produced from the species *Acacia Senegal.* The surface activity is due to the branched arabino-galactan blocks attached to a polypeptide backbone (Chanamai and McClements, 2002). Gum arabic is an important emulsifier that grants functionality not by modifying the rheology of the water phase but also by leading to the formation of a macromolecular stabilizing layer around the oil droplets (Buffo et al., 2001; Dickinson, 2003). Despite its functionality, gum arabic is a fairly expensive ingredient and there have been many attempts for its replacement by hydrophobically modified starch or other gums (Dickinson, 2003).

The octenyl-succinate starch known as OSA starch (Purity gum; National Starch, Bridgwater, N.J.) is made by esterification of starch and anhydrous octenylsuccinic acid under alkaline condition (Tesch et al., 2002). Purity gum is mildly anaionic in aqueous solutions and has a surface activity that is almost as high as gum arabic (Chanamai and McClements 2001).

Commercial xanthan gum is a yellowish powder completely soluble in cold and hot water, producing relatively high viscosity opaque solution at low concentrations. Xanthan gum gives citrus and fruit-flavored beverages an enhanced mouthfeel with full-bodied taste and good flavor release. It has also shown promise as a stabilizer for cloud and flavor emulsions in beverages (Kaufman and Garti 1984; Alan Imeson, 1992). Rheological properties of xanthan gum are the most important determinant of the behavior of this gum in its final application (Born et al., 2005).

Gum arabic, modified starches and xanthan gum added emulsions are evaluated in this study for their ability to confer and stabilize cloudiness in orange beverage in the absence of weighting agents. Such combinations of naturally occurring components will help overcome health restrictions on the formulation of beverages.

6.3 MATERIALS AND METHODS

Canola oil, spray dried gum arabic, liquid fructose, orange oil, ascorbic acid and xanthan gum (TIC PRETESED® TICAXAN 200) were obtained from Nealanders (Montreal, Quebec). Modified starches (Purity Gum Be and Purity Gum 2000) were obtained from National Starch and Chemical (Bridgewater, NJ). A commercially available concentrated orange juice was obtained from a local source. Food grade citric acid and potassium sorbate were used to adjust the acidity and reduce the chance of contamination in all O/W emulsions. Fat soluble β-Carotene was provided by Roche Vitamin and Fine Chemicals (Nutley, New Jersy).

6.3.1 Preparation of emulsions

Preparations of emulsions have been described in previous chapters and procedures used were same in this study.

6.3.2 Preparation of juice drink

Preparation of beverages involved first the addition of dry materials into the water (citric acid was added in the end) and then the liquid ingredients. Orange oil was added to concentrated orange juice and homogenized (accounting for 10% orange juice, 11°Bx and 200 ppm orange oil). The combination was then added to acidified sugar solution and loaded with 2% weight/weight (w/w) of prepared emulsions (3×6 bottles for first replicate). Each formulated beverage was stirred for 15 min using magnetic stirrer. After preparation, the beverages were bottled and pasteurized for 12 min in boiling water. A total of 36 bottles were prepared in duplicate and stored.

6.3.3 Opacity and stability tests

These tests have been detailed in previous chapters.

6.3.4 Zeta potential and particle size distribution

Particle size distribution was measured as described in previous chapters. The same instrument equipped with ZET5104 capillary cell was use to measure zeta potential.

The instrument uses electrophoresis technique in which the movement of colloidal particles is measured when they are placed in an electric filed. The measurement can be used to determine the sign of the charge on the particles and also their electrophoretic mobility, which is related to the surface charge and zeta potential. The instrument is equipped with laser velocimeter to measure the particle velocity at the stationary layer (where the particles move with a velocity which is due solely to their own charge).

6.3.5 Turbidity

The turbidity of orange juice drinks were evaluated with a turbidimeter (HACH, 2100 Turbidimeter, Loveland, Colo). The equipment was first calibrated using standard solution for calibration at 1000 and 2000 NTU.

6.3.6 Rheological examinations

Measurement of rheological parameters such as flow behavior index (n), consistency coefficient (m) and viscosity were carried out using TA Instrument, AR1000 Rheometer equipped with 60 mm cone of 2°. The measurements were conducted at 22 °C and shear rate from 0.1 up to 200/s. Viscoelastic parameters such as storage modulus (G') and loss modulus (G'') and delta degree of each prepared emulsion were also evaluated. For these measurements, dynamic rheology tests were employed with an oscillation stress of 1 Pa (obtained from linear region of stress sweep test) while varying the frequency rate from 1 up to 25 rad/s.

6.4. RESULTS AND DISCUSSION

Two types of commercial OSA starch (Purity Gum Be and Purity Gum 2000) and spray dried gum arabic at 1.5:1 and 1:1 gum/oil were used to prepare emulsion. The main difference between two types of modified starch is the viscosity of hydrated solution. Purity Gum Be at the same concentration had a higher viscosity compare to Purity Gum 2000.

Table 6.1 and Table 6.2 summarize the relevant properties of emulsions prepared at 1:1and1.5:1gum/oil. The results in the tables demonstrate that Purity Be (modified

Table 6.1. Physical properties of emulsions at 1:1 gum/oil.

Properties	Arabic + Xanthan	Purity Be + Xanthan	Purity 2000 + Xanthan
Turbidity of 2% emulsion in orange drink (NTU)	2879±15	2469±12	2284±19
Zeta potentials (mv)	-47.9±1.2	-29.2±0.7	-29.1±0.5
Average size (nm)	974±16	504±11	715±8
App. Viscosity at 0.1/s (mPa.s)	741±18	2623±24	1678±26
Power law index (n)	0.78±0.01	0.53±0.01	0.57±0.02
Creaming (3 month)	+	–	±

Table 6.2. Physical properties of emulsion prepared at 1.5:1 gum/oil.

Properties	Arabic + Xanthan	Purity Be + Xanthan	Purity 2000 + Xanthan
Turbidity of 2% emulsion in orange drink (NTU)	2982±19	2510±17	2431±11
Zeta potentials (mv)	-48.5±1.2	-29.9±1.2	-29.7±1.3
Average size (nm)	1056±26	422±8	569±14
App. Viscosity at 0.1/s (mPa.s)	1812±15	3512±28	2568±31
Power law index (n)	0.89±0.01	0.52±0.02	0.56±0.02
Creaming (3 month)	+	–	±

starch) gives emulsions of higher viscosity and lower power law flow behavior index as compared to Purity 2000 (modified starch) and gum arabic. The degree of shear thinning (n, power law index), for both types of modified starch, slightly decreased with increasing gum concentrations. Arabic gum, on the other hand, indicated a more Newtonian behavior even at higher level of gum concentrations. The solutions of gum arabic in water, at both concentrations, were practically Newtonian (n= 0.94) and shear thinning behavior of the emulsions was due to the addition of xanthan gum which was pseudoplastic (n=0.31). Arabic gum-xanthan emulsions also showed higher turbidities, at both concentrations, compared to modified starches-xanthan emulsions, which is due to their larger average particle size.

It has been reported (Jayme et al., 1999) that stabilization of dispersion occurs via two main mechanisms that depend upon the surface association of the polymer and particle. The first is steric stabilization which results from macromolecules adsorbed to the particle surface. As two such particles approach each other, the osmotic pressure between them increases due to the spatial confinement of the adsorbed polymer molecule and manifested as a repulsive interaction. The second is electrostatic stabilization which arises from the mutual repulsion between both particles electrical double layer and is effective over distances comparable to the van der Waal‘s attraction.

Although it has been reported (Tan and Wu Holmes, 1988) that zeta potential of less than -15 mv represent the onset of flocculation and zeta potential of as low as -40 mv could form stable emulsion, one cannot categorically state that an emulsion will or will not be stable only on the basis of zeta potential. The low stability of gum arabic-xanthan emulsions in orange beverage, therefore, refers to other factors rather than zeta potential.

Figure 6.1 illustrates the frequency development of storage modulus for 1:1 gum/oil (9% modified starches-0.3% xanthan and 9% gum arabic-0.3% xanthan emulsions). Storage modulus (G') for all systems showed very similar monotonic development at lower frequency while emulsion prepared with modified starches increased to a greater extent at higher frequency levels. The surface active hydrocolloids that are able to form a dense elastic barrier can provide more stable emulsion. This means that the modified starches covered droplets carry the greater elasticity compare to that of the arabic gum.

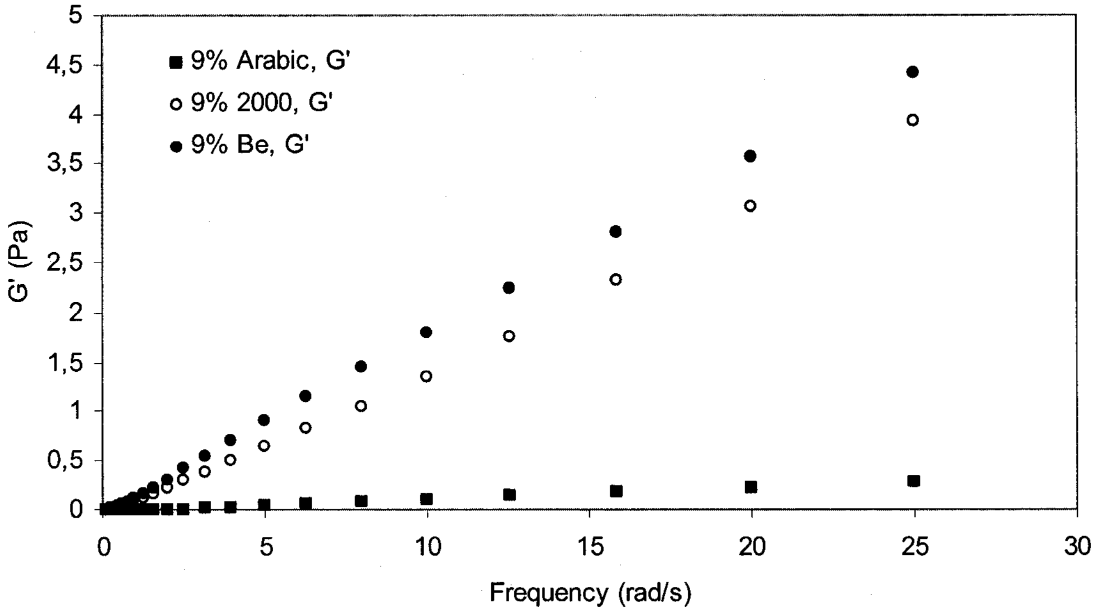


Figure 6.1. Frequency dependence of storage modulus (G') for 1:1 gum/oil emulsions.

Frequency development for emulsions at 1.5:1 gum/oil (14% modified starches 0.3% xanthan and 14% arabic gum-0.3% xanthan emulsions) is shown in Figure 6.2. As illustrated the difference between storage modulus (G') at elevated concentration of surface active hydrocolloids is more pronounced.

Gums (polysaccharides), in almost all uses, exist in an environment rich in water molecules. Thus, although polysaccharides must interact appropriately and beneficially with proteins, lipids, and other environmental molecules commonly found in foods, they must primarily and continuously react with water molecules. By such interactions polysaccharides perform their useful functions, which are those of providing viscosity, elasticity, solution stability, suspendability, emulsifying action, and gelatin (Glicksman 1982). Therefore, the mechanism by which modified starches and gum arabic impart stability to emulsions is via an electro-steric mechanism, but the steric contribution is dominant.

Results for creaming velocity of 2% (w/w) emulsions in the orange drink at 1:1 and 1.5:1 gum/oil are shown in Figures 6.3 and 6.4. The rate of creaming velocity are 0.68, 0.34 and 0.17 percent transmission/day for arabic-xanthan, starch2000-xanthan and starch Be-xanthan stabilized emulsions at 1:1 gum/oil, respectively. With the exception of arabic-xanthan emulsions, the creaming velocity decreased as the gum/oil increased. The rate of creaming velocity for arabic-xanthan, starch 2000-xanthan and starch Be-xanthan at 1.5:1 gum/oil were found to be 1.9, 0.24 and 0.05 percent transmission/day, respectively. Increase in creaming velocity of gum arabic-xanthan at elevated concentrations was also associated with a decrease in elasticity and pseudoplastisity.

Shelf stabilities of 2% (w/w) emulsions in orange drink after pasteurization and upon standing for 3 months are shown in Figure 6.5 for 1:1 gum/oil and Figure 6.6 for 1.5:1 gum/oil). The results confirm our data for rheological and creaming velocity profile assessments. As illustrated starch Be-xanthan emulsions at both low and elevated concentrations indicate higher shelf stability compared to the other prepared emulsions.

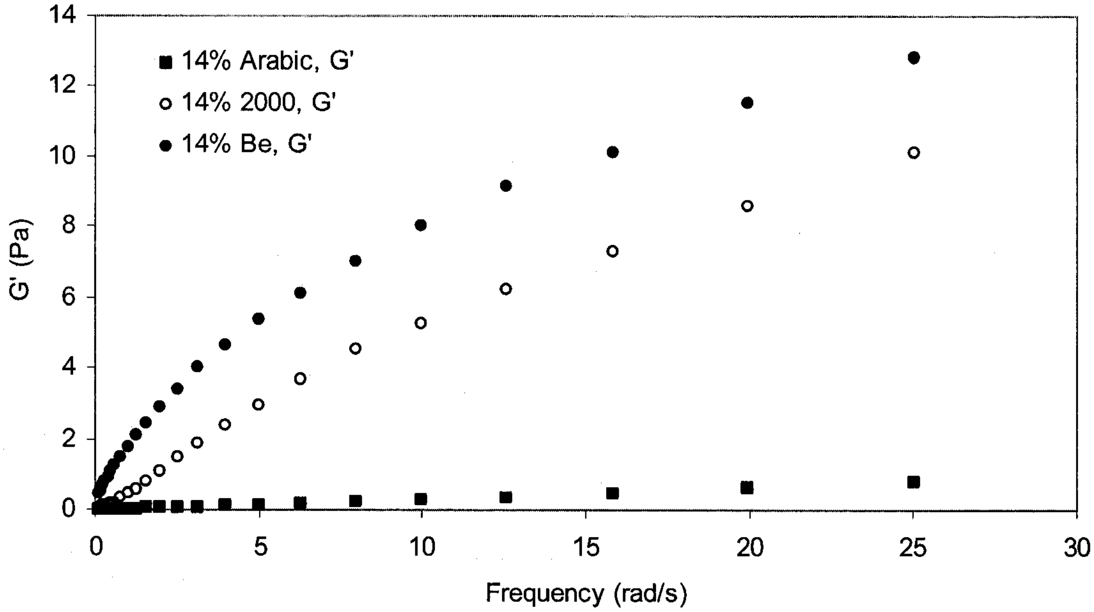


Figure 6.2. Frequency dependense of storage modulus (G') for 1.5:1 gum/oil emulsions.

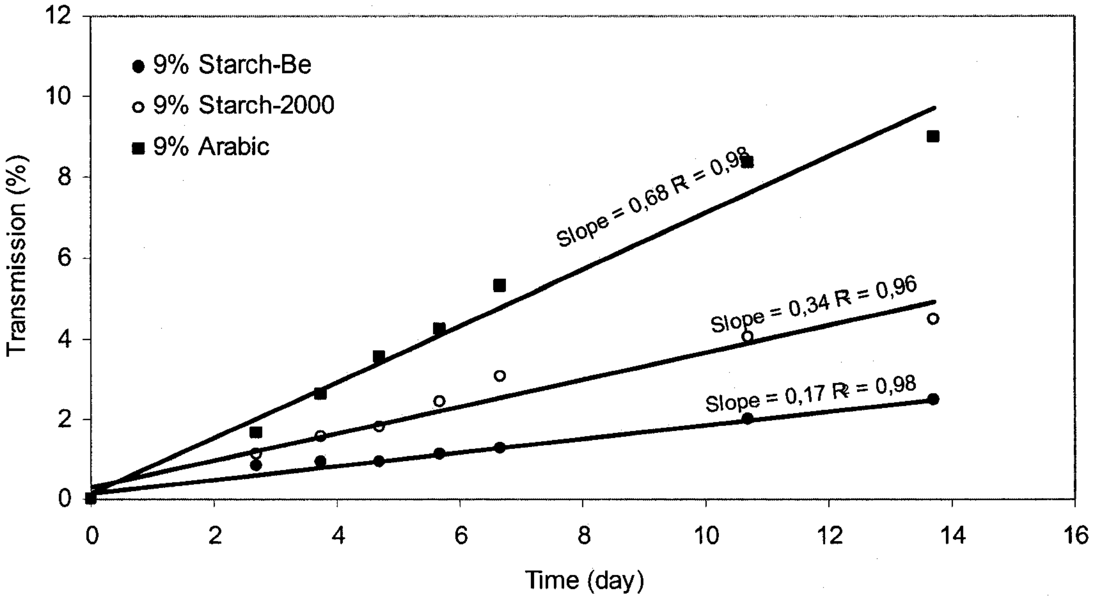


Figure 6.3. The time evolution of transmission for 1:1 gum/oil emulsions as a function of storage time.

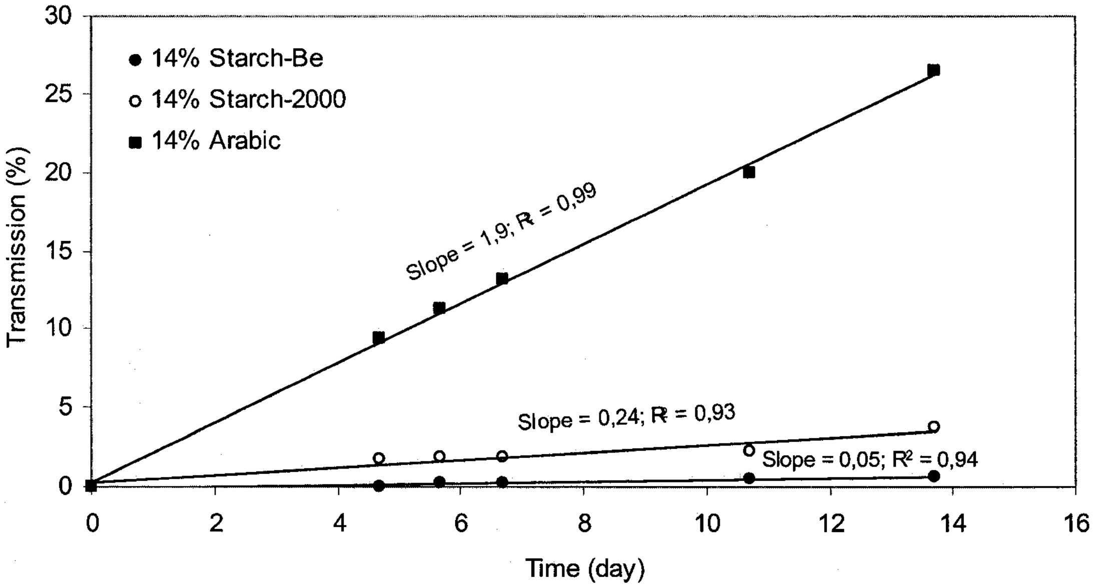


Figure 6.4. The time evolution of transmission for 1.5:1 gum/oil emulsions as a function of storage time.

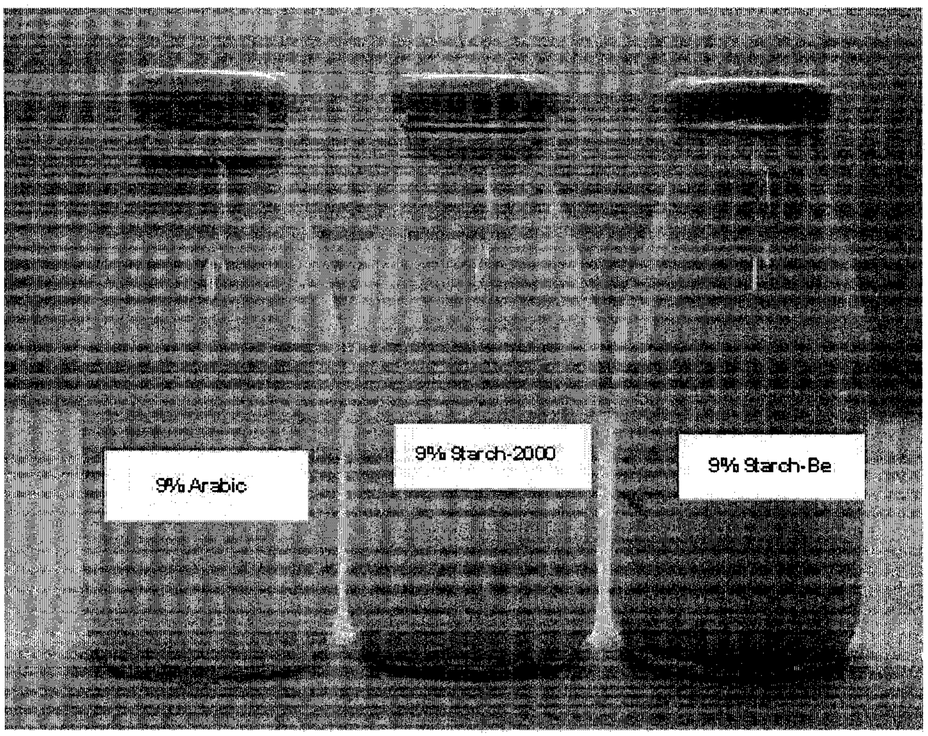


Figure 6.5. Shelf stability of 1:1 gum/oil emulsions in orange juice drink upon standing at room temperature for 3 month.

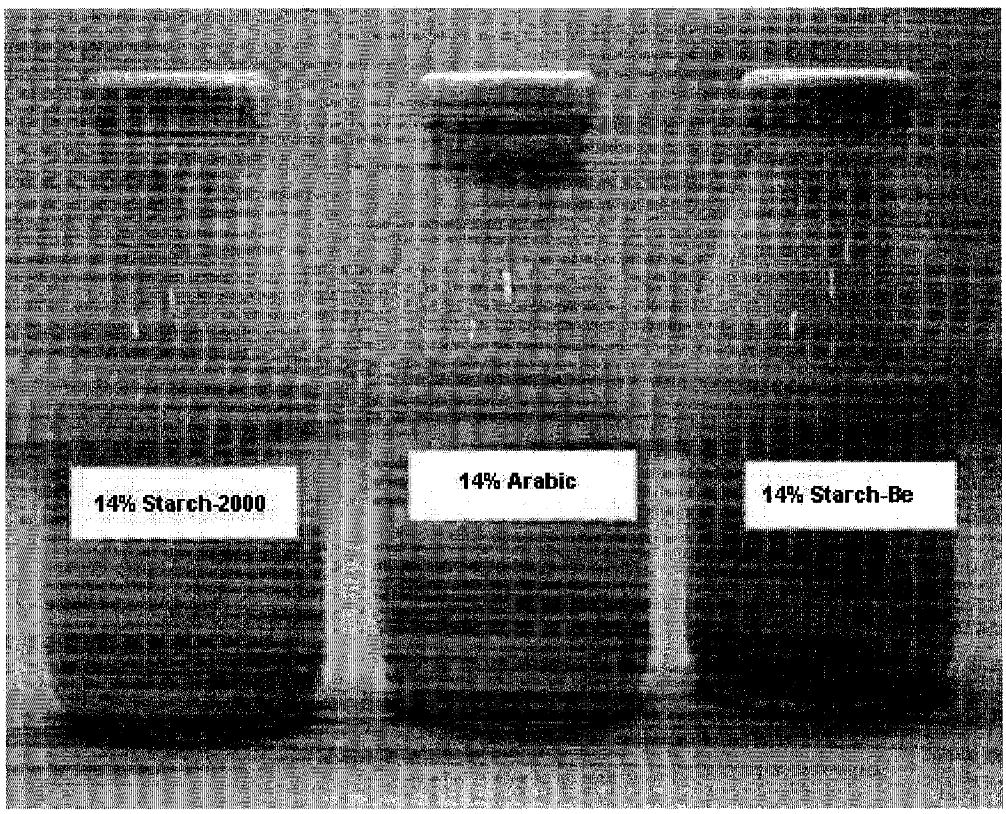


Figure 6.6. Shelf stability of 1.5:1 gum/oil emulsions in orange juice drink upon standing at room temperature for 3 month.

6.5 CONCLUSIONS

The zeta potential assessment showed that gum arabic emulsions bear a higher degree of surface charge compared to the starch stabilized emulsion. Starch-xanthan combinations could provide a viscous and elastic barrier around oil droplets. Since the steric stabilization was dominant, it was concluded that the type of hydrocolloid, concentration and combination are responsible for rheological properties of emulsions and hence stability of cloud in orange juice drink. Modified starch (Purity Gum Be) at 14 % (w/w) in combination with 0.3% xanthan (w/w) yielded the greatest stability in pasteurized orange juice drink.

The results of this study could be useful for industrial practices in order to produce suitable quality juice drink and will help to overcome health restrictions on the formulation of beverage.

CHAPTER 7

GENERAL CONCLUSIONS, CONTRIBUTION TO KNOWLEDGE AND RECOMENDATIONS

Beverage emulsions are oil/water emulsions and primarily used to give opacity to clear beverages or to enhance their juice-like appearance. These emulsions are different from other food emulsions in that they are consumed in a highly diluted form. Beverage emulsions are thermodynamically unstable and tend to breakdown during storage. Breakdown processes of beverage emulsions include gravitational separation, flocculation and coalescence. The rate at which a beverage emulsion breaks down, flocculates or coalesces, and the mechanism by which this process occurs depends on its composition and microstructure, as well as on the environmental conditions it experiences during its lifetime (e.g., processing temperature, mechanical agitation and storage condition).

Stability of emulsions is highly affected by certain physicochemical characteristics of polymeric emulsifier (gums) added into the water phase. In addition to the presence of the segments which bind strongly to the oil droplet surface the concentration of gums should be sufficiently high in order to cover the oil droplet surface and form a thick layer.

In this study the physical properties of water and oil phases as functions of added starch and oil were first examined. Increase in oil concentration affected the opacity and showed that oil content is highly responsible for the opacity of emulsions and hence in the final product. At the constant level of weighting agents (BVO and SAIB), the specific gravity of oil phase decreased when the oil concentration increased and resulted in augmentation of the creaming values accordingly. When the specific gravity of oil phase was adjusted to 1.04, none of the starch added emulsions indicated creaming, and sedimentation occurred when the specific gravity of the oil phase was higher than that of the water phase.

In the second step, we studied the rate of emulsion breakdown by determining the rheology of water phase, difference in specific gravities of the two phases and droplet properties of the emulsion in presence and absence of weighting agents (sucrose acetate isobutyrate and brominated vegetable oil) with and without added xanthan gum. This study indicated that modification of rheological characteristic of continuous aqueous phase can play an important role in relation to the storage stability of beverage emulsions. Highly shear thinning and elastic properties of xanthan gum, even at very low concentration, was able to provide a micro-gel network and influence the state of flocculation to prevent coalescence of the droplets. In particular, for a beverage emulsion to possess an acceptable stability, the system must acquire a solid-like character, in the sense that $G' > G''$ for water phase. As well xanthan gum was found to be an excellent alternative to replace weighting agents which have restricted level of use due to the health disadvantages.

We continued our investigation in third step by conducting a study on flow and dynamic rheological properties of individual phases and emulsions containing modified starch and arabic gum as surface active hydrocolloids as well as xanthan and tragacanth as stabilizer gums. The results obtained demonstrated that both modified starch-xanthan and arabic-tragacanth gum combinations could form highly stabilized beverage cloud emulsions. The modified starch-xanthan gum emulsions were able to provide a gel matrix and highly stable emulsions. Arabic-tragacanth stabilized emulsions demonstrated rheological properties with fewer changes in shear thinning behavior after storage time periods. The flow and dynamic rheological properties of all prepared emulsions were confidently modeled through the Einstein equation or its exponential expansion. The developed model for complex shear modulus also well fitted with experimental data.

The creaming stability of developed beverage emulsions was finally investigated in a simulated orange beverage in order to apply the outcomes of our investigations to an industrial practice. Gum arabic, modified starches and xanthan gum added emulsions were evaluated in this study for their ability to confer and stabilize cloudiness in orange beverage in the absence of weighting agents. Starch-xanthan combinations could provide a viscous and elastic barrier around oil droplets. Since the steric stabilization was dominant, it was concluded that the type of hydrocolloid, concentration and combination are responsible for rheological properties of emulsions and hence stability of cloud in orange beverage. Modified starch (Purity Gum Be) at 14 % (w/w) in combination with 0.3% xanthan (w/w) yielded the greatest stability in pasteurized orange juice drink.

The results of this study are useful for industrial practices in order to produce suitable quality juice drink and will help to overcome health restrictions on the formulation of beverage.

CONTRIBUTION TO KNOWLEDGE

1. After the year 1970, due to banning and restriction in use of density adjusting agents (weighting agents), producing cloud or flavor emulsions that remain stable over the desired shelf life has become a common problem in the beverage industry. Moreover, consumer's knowledge increasingly developed within the years, asking for more healthy food products.

   In response to consumer demand for natural and food grade ingredients and to solve an industrial quality problem, new cloud emulsions were developed through a series of investigations.
2. A comprehensive study was carried out to understand the effects of polymer and oil concentrations on stability and rheology of cloud emulsions. This study was conducted in presence of weighting agents within the restricted level of use. The focus was on three major aspects affecting shelf stability of cloud emulsions: density difference between oil and water phases, particle size distribution and flow and dynamic rheological properties of phases and emulsions. Looking for desirable opacity, the use of weighting agents at restricted level failed to stabilize the emulsion at elevated concentration of oil. However, the desirable concentration of oil to provide the identical opacity, as natural juice, was found and the result was carried out through out of the rest of our research.
3. By employing the desirable level of oil, the physical stability of emulsions in presence and absence of weighting agents and/or xanthan gum was then investigated in detail. The main focus was to understand the role of added xanthan gum and weighting agents on the stability of beverage cloud emulsions pre-

stabilized by modified starch using rheological properties and specific gravities of component phases and particle size distribution of prepared emulsions.

This study enabled us to find out that highly shear thinning and elastic properties of xanthan gum, even at very low concentration, was able to provide a micro-gel network and influence the state of flocculation to prevent coalescence of the droplets. As well xanthan gum was found to be an excellent alternative to replace weighting agents which have restricted level of use due to the health disadvantages.

4. Investigation went deeper by employing different surface active gums and stabilizers in the next phase of the study. From practical point of view, the results provided useful information for achieving reasonable stability and opacity for concentrated emulsion and fruit beverages.
5. Gum arabic, modified starches and xanthan gum added emulsions were then evaluated for their ability to confer and stabilize cloudiness in orange beverage in the absence of weighting agents. Such combinations of naturally occurring components assisted to overcome health restrictions on the formulation of beverages.

RECOMMENDATIONS FOR FUTURE RESEARCH

Scope of the current research could be expanded by:

1. Employing other hydrocolloids (Pectin, Tara gum, Mesquite gums etc) to stabilize cloud emulsions and study their individual and combination effects on stability.
2. Preparation and processing of emulsions by application of different preservation method such as UHT, UHP and freezing.
3. Evaluating the compatibility of stabilizer and surface active gum.
4. Evaluating the surface and interfacial property of both oil and water phase in beverage emulsions.
5. Evaluating the rheological properties of water phase and emulsion to find a more versatile model.

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