

Physical and Rheological Properties of Oil in Water Heat Stable Emulsions Made from Different Stabilizers

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ABSTRACT: Oil in water emulsions have attracted considerable attention in food industry due to their large applications. In this study, the effect of thermal treatment on oil in water emulsions (o/w) containing 40% oil was studied. The emulsions were prepared using xanthan gum, guar gum and carboxymethyl cellulose as stabilizer and polyoxyethylen sorbitan monooleat as emulsifier. A mixture design was used to define the percentage of each stabilizer to simulate wide range of emulsions. The emulsions were pasteurized at 87 °C for 15 minutes. Thermal treatment had a considerable influence on rheological properties of the emulsions. Viscosity of all emulsions decreased after thermal treatment and stabilizers had increasing effect on this response. All emulsions exhibited non Newtonian pseudo plastic flow behavior that often referred to as shear thinning ($n < 1$). A non linear relation between shear rate and shear stress was observed. Shear stress versus shear rate data was successfully fitted to the Power-law model. Consistency coefficient (K) decreased and flow behavior index (n) increased after thermal processing. Thermal treatment caused an increase in particle size of emulsions because of coalescence. Some of emulsions had heterogeneous coalescence (bimodal) and some of them had homogenous coalescence (mono modal). All emulsions were stable to centrifugation and did not breakdown. It was found that surface tension was affected more by temperature than by stabilizer content. Surface tension decreased by thermal processing. Viscosity of all the samples was reduced during storage. The results showed that developed emulsions are thermally under pasteurization temperatures.

Keywords: *Emulsifier, Heat Stable Emulsion, Mixture Design, Physical Properties, Stability.*

Introduction

Many natural and processed foods exist either partly or wholly as emulsions or have been in an emulsified state at some time during their production. Emulsion consists of two immiscible liquids (usually oil and water), with one of the liquids dispersed as small spherical droplets in the other (Pal, 2000). In most foods, the diameters of the droplets usually lie somewhere between 0.1 and 100 μm . Emulsions can be conveniently classified according to the distribution of the

oil and aqueous phases (McClements, 2003). Emulsions are thermodynamically unstable systems because of interfacial tension, especially those with reduced oil content. The presence of salts and an acidic medium, usually found in food emulsions such as salad dressing, enhances the instability of these systems. Several types of instability occurs in emulsion, such as creaming (or sedimentation), flocculation, coalescence, Ostwald ripening and phase inversion (Wanlop *et al.*, 2007). Polysaccharides are usually added to the aqueous phase of low fat O/W food emulsions to improve their

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creaming stability (Garti *et al.*, 2001). Emulsifiers are also important since they affect many of the emulsion properties. An emulsifier is surface active agent and reduces the interfacial tension between oil and water and therefore facilitates the disruption of emulsion droplets during homogenization. The emulsifier adsorbs to the surfaces of emulsion droplets to form a protective coating that prevents the droplets from aggregating with each other (McClements, 2003). The most significant factors which influence the emulsions stability are the rheological behavior of the continuous phase, the nature of the particles, their concentration, their size distribution, surface and interfacial tension, and the particle-particle interactions (Dickinson, 1992). The rheology of emulsions was investigated by several authors because of its importance for the choice of formulation, process conditions and quality control (Perssini & Sensidoni, 1998). In emulsions with oil content less than 60%, rheological properties can be modified by replacing the oil with stabilizer such as guar and xanthan (Mandala & Savvas, 2004). Guar and xanthan gums are among the most commonly used as thickening agents in food emulsions. Guar gum is a water-soluble non-ionic polysaccharide (Achayuthakan & Suphantharika, 2008). Xanthan gum is a water-soluble anionic extracellular polysaccharide produced by fermentation of the bacterium *Xanthomonas campestris* (Papalamprou & Makri, 2005). A number of researchers have investigated the influence of gums on physicochemical properties of emulsions by measuring their droplet size, viscosity and stability (Hemar *et al.*, 2001; Sun, Gunasekaran, & Richards, 2007; Ye, Hemar, & Singh, 2004; Ye, Hemar, & Singh, 2004). They reported that increase in xanthan concentration caused a increase in emulsions viscosity. There are also some papers on the effect of thermal treatment on oil in water emulsions (Kiratee-u-rai & Coredig, 2009; Ven & Courvoisier, 2007;

Kristensen *et al.*, 1997). Viscosity of both the oil and aqueous phases are depend on temperature and decrease with increasing the temperature. Minimum droplet size strongly depends on proportional viscosity of continuous phase to disperse phase (Maruyama *et al.*, 2007). Moreover, Thermal treatment causes reduction in surface tension, which leads to formation of smaller droplet. However the capability of emulsifiers decreases after thermal processing protection coalescence (Peker *et al.*, 2001). Prediction of the stability of emulsions is difficult because of the structure and composition. Thermal treatment causes breakdown of emulsions. However stabilizers increase the viscosity in low concentrations and, hence increase their stability against temperature (Acton *et al.*, 2001).

In this study, the effects of stabilizers and thermal treatment on the rheological properties, particle size distribution, surface tension and stability of emulsions have been investigated.

Materials and Methods

- Materials

Polyoxyethylene sorbitan monooleate (Tween 80) emulsifier, xanthan, guar gum and CMC were purchased from Oleon (Oleon Company, Belgium). Other ingredients such as soybean oil, sugar and salt were provided from the local supermarket.

- Emulsions preparation

Emulsions with a composition similar to commercial salad dressings were prepared. A mixture design was used to cover the ratios of components in the ranges indicated in Table 1. Emulsions were formed by mixing the aqueous phase ingredients such as water, salt, sugar, stabilizers and Tween 80 (1 wt.%) as emulsifier. After that oil is slowly added and the obtained mixture is emulsified. After emulsification, the vinegar was added. Emulsions were stored at 45 °C

and at ambient temperature for 30 days. oiling-off of the samples were visually studied. During this period the appearance and

Table 1. Initial experimental area for the formulations (wt, %)

| Component | Minimum | Maximum |
|-----------|---------|---------|
| Xanthan | 0.2 | 0.45 |
| Guar | 0.5 | 0.9 |
| CMC | 0.5 | 0.9 |
| The rest | 97.75 | 98.8 |

Table 2. Emulsions composition proposed by the four-component mixture design

| Formulation | Ingredient Proportion | | | |
|-------------|-----------------------|------|------|----------|
| | Xanthan | Guar | CMC | The rest |
| 1 | 0.2 | 0.5 | 0.5 | 98.80 |
| 2 | 0.45 | 0.9 | 0.9 | 97.75 |
| 3 | 0.32 | 0.7 | 0.9 | 98.08 |
| 4 | 0.2 | 0.7 | 0.7 | 98.40 |
| 5 | 0.32 | 0.5 | 0.7 | 98.48 |
| 6 | 0.2 | 0.9 | 0.9 | 98.00 |
| 7 | 0.39 | 0.7 | 0.6 | 98.31 |
| 8 | 0.2 | 0.9 | 0.5 | 98.40 |
| 9 | 0.32 | 0.6 | 0.8 | 98.28 |
| 10 | 0.2 | 0.5 | 0.9 | 98.40 |
| 11 | 0.45 | 0.5 | 0.5 | 98.55 |
| 12 | 0.45 | 0.5 | 0.5 | 98.55 |
| 13 | 0.2 | 0.9 | 0.5 | 98.40 |
| 14 | 0.32 | 0.9 | 0.9 | 97.88 |
| 15 | 0.2 | 0.5 | 0.9 | 98.40 |
| 16 | 0.45 | 0.7 | 0.9 | 97.95 |
| 17 | 0.28 | 0.9 | 0.63 | 98.18 |
| 18 | 0.32 | 0.7 | 0.5 | 98.48 |
| 19 | 0.45 | 0.9 | 0.5 | 98.15 |
| 20 | 0.28 | 0.9 | 0.63 | 98.18 |
| 21 | 0.45 | 0.5 | 0.9 | 98.15 |
| 22 | 0.2 | 0.5 | 0.5 | 98.80 |
| 23 | 0.45 | 0.9 | 0.7 | 97.95 |
| 24 | 0.45 | 0.7 | 0.7 | 98.15 |

- Thermal processing

Samples were pasteurized at 87 °C for 15 minutes in semi rigid aluminum packaging using a water cascade retort (Steriflow, France).

- Rheological properties

Rheological properties of samples were measured by Brookfield rotational viscometer (Model RVDV-II, Brookfield Engineering Inc., USA) equipped with spindle model RV6 at speed range of 1-6 rpm. Samples were sheared at an increasing order of spindle speed (N). Flow behavior index (n) is obtained using Equation 1.

$$M = (k') N^n \quad (1)$$

Or, in the case of logarithmic form, the calculation can be performed using Equation 2.

$$\ln M = \ln (k') + n \ln (N) \quad (2)$$

Ω (radians per second) can be used in place of N (revolutions per minute) in Equation 2 and Equation 4 with no change in the calculated value of n. M is percentage of torque and k' is a constant. The average shear stress is calculated using Equation 3.

$$\sigma = k_\sigma (C) (\% \text{ Torque}) \quad (3)$$

Where k_σ , is the shear stress conversion factor, changes with the spindle number. The value of C (a dimensionless constant) depends on the total torque capacity of the instrument. The percentage of torque is the percentage of the maximum torque recorded during testing at a constant speed. Average shear rate is calculated from Equation 4.

$$\gamma' = k_\gamma' (N) \quad (4)$$

Where k_γ' , known as the shear rate conversion factor, depends on the numerical value of the flow behavior index (Steffe, 2006):

$$k_\gamma' = 0.263(1/n)^{0.771} \quad (5)$$

- Particle size distribution

Samples (0.05 g) were diluted with 150 ml 0.1% sodium dodecyl sulfate (SDS) solution, stirred gently by a spatula until completely dispersed. Samples were analyzed by a particle size analyzer (Mastersizer, 2000, Malvern Instrument Ltd, Instrument, UK). The sample solution was dispersed in distilled water at 1500 rpm until an obscuration rate of 4.15- 5.16% was obtained. Background and sample were measured for 10 s. Optical properties of the sample were defined as follows: refractive index 1.460 and absorption 0.00. The fundamental size distribution derived by this technique is volume based, which uses the Mie theory. Droplet size measurements are reported as using two indexes, $D_{4,3}$ and $D_{3,2}$.

$D_{4,3}$ represent the volume-weighted mean diameter:

$$D_{4,3} = \sum n_i d_i^4 / \sum n_i d_i^3 \quad (6)$$

Where d_i is the droplet diameter and n_i is the number of droplets of diameter d_i .

$D_{3,2}$ is the volume-surface average diameter of the emulsion droplets.

$$D_{3,2} = \sum n_i d_i^3 / \sum n_i d_i^2 \quad (7)$$

Size distribution measurement was performed in triplicate orders (Liu *et al.*, 2007).

- Surface and interfacial tension

The surface tensions of the emulsions were determined by the Du Nouy ring method using a Tensiometer (Tensiometer k9 Kruss, Germany). Surface activity effect of materials stuck to the ring were removed by washing the ring by distilled water and citric acid, then burned on the flame and then cooled down to the ambient temperature. The maximum force needed to pull the ring through the interface is expressed as the surface tension in mN/m.

- Centrifugation assay

To measure the heat stability of emulsion samples, they were centrifuged (Sigma, 2-16 centrifuge, Germany) immediately after preparation. Approximately 10 ml (F_0) of each emulsion were placed into plastic tubes and centrifuged at 3000 rpm for 15 minutes at room temperature. The weight of the precipitated fraction (F_1) was measured. The emulsion stability was characterized as $(\%) (F_1/ F_0) \times 100$. All tests were carried out in triplicate orders.

- Statistical Analysis

A mixture design based on a 4-component mixture was used (Table 1). Mixture design is an efficient method of studying the effect of several parameters to distinguish among process variables. The experimental results were analyzed using Expert Design 6.0.6 trial (Stat Ease Inc., Minneapolis, MN). An ANOVA was performed to determine the statistical significance of models.

Results and Discussion

- Rheological properties of emulsions

- Effect of stabilizers on rheological properties

Figures 1 and 4 show the effect of stabilizers on the rheological properties of the emulsions. As the total amount of stabilizers increased the emulsions viscosity increased. Similar results were obtained by Wendin & Hall, (2001). The contour plot of the viscosity response and power law parameters of emulsions samples (Fig. 4) indicated that the viscosity contour values increased toward the xanthan gum vertex where maximum viscosity contour could be observed; however, the viscosity values were similar at guar and CMC vertex. From this point of view, it could be concluded that the addition of xanthan gum in emulsions as a stabilizer enhanced the viscosity of the final product. The higher values of K and values of n were observed at higher xanthan

concentration. Briefly, the K values were increased by increasing xanthan proportion in the emulsions (Fig. 4). The results indicated that xanthan had a greater effect on the viscosity and flow parameters (i.e. K and n) of emulsions samples as compared to the other components including guar gum and CMC. Similar results were obtained by Benichou *et al.*, (2007). Mun *et al.*, (2009) showed that when a reduced fat mayonnaise was proposed by using modified starch and xanthan gum, it was indicated that the addition of xanthan gum to the reduced-fat substrate as a fat replacer, the consistency index (K) was markedly increased and the flow behavior index (n) was decreased. Besides, the structure of the low fat mayonnaise plus gum sample was very similar to that of the full fat mayonnaise. Emulsion No. 1 containing 0.2% xanthan, 0.5% guar and 0.5% CMC had the lowest viscosity and emulsion No. 14 containing 0.32% xanthan, 0.9% guar and 0.9% CMC had the highest viscosity. This behavior is due to the increase intermolecular interaction with increasing stabilizers (Tornton, 2005). Stabilizers alter the rheological properties directly and increase the viscosity of continuous phase of emulsions. This is because the stabilizers indirectly change interactions between droplets (Robins & Watson, 2002). Stabilizers increase the resistance to flow, therefore viscosity is raised in consequence. Xanthan forms viscous solution at low concentration and forms desirable rheological properties in food (Dolz *et al.*, 2008). It exhibits synergistic effects with guar gum (Garcia-Ochoa *et al.*, 2000). Therefore, in this case, viscosity of the samples was increased considerably due to the synergistic effect of the hydrocolloids. These results cause an enhanced viscosity with guar gum and at low concentrations with guar and leads to the improvement of rheological properties. Therefore, emulsion No. 9 containing 0.32% xanthan, 0.6% guar

and 0.8% CMC had higher viscosity as compared to the emulsion No. 10 that contained higher amount of CMC because of the synergistic effect of xanthan and guar gum. Guar and CMC content of emulsions No. 4 and 24 containing 0.45% xanthan, 0.7% guar and 0.7% CMC were similar but significant differences between their viscosities were observed. This phenomenon could be attribute to the xanthan contents, that was different in the two mentioned emulsions. It can be seen that the effect of xanthan on the consistency of emulsions was greater than other stabilizers. Similar results were obtained by Fonseca & Haminiuk, (2009). The combination of xanthan and guar lead to a high viscosity of emulsion. Emulsion No. 21 and 24 had the same xanthan content, and emulsion No. 24 had the lower CMC content, but it showed higher viscosity due to its high guar content. This indicates that Guar gum increased the viscosity of the samples more than CMC. All of the emulsions showed similar flow behavior (Fig. 2), which means viscosity is reduced by increasing shear rate. This showed that all samples had a shear thinning behavior. During shearing, shape of oil droplet and flock is altered and ultimately flocculated droplets are separated, thus viscosity is reduced. This result is similar to that previously reported by Lorenzo *et al.*, (2008) who observed shear-thinning behavior of low fat emulsions stabilized with xanthan/guar mixtures. Xanthan and guar gum solutions are highly pseudo plastic (Williams & Philips, 2008). When shear stress is increased, the viscosity is decreased progressively. In a concentrated emulsion, flocculation leads to the formation of a three-dimensional network of aggregated droplets. Increasing the shear rate causes progressive deformation and disruption of the aggregated particles, which in turn decreases the emulsion resistance to flow and reduces its apparent viscosity (Nikzad *et al.*, 2012). Upon the removal of the shear, the initial viscosity is recovered almost

instantaneously. Flow behavior of the emulsions is described by power law model as below (Maruyama & Sakashita, 2007):

$$\sigma = K \cdot \dot{\gamma}^n \quad (8)$$

The consistency coefficient (K) and flow behavior index (n) of emulsions, obtained by fitting the experimental shear stress-shear rate data to the power law model, are given in Table 3. The value of consistency coefficient (K), were from 99.64 to 876.555 and 61.616 to 901.445 Pa sⁿ before and after thermal processing, respectively. Flow behavior index (n), was from 0.104 to 0.493 and 0.257 to 0.655 before and after thermal processing, respectively (Table 3). Consistency coefficient (K) and flow behavior index (n) is increased by increasing the stabilizer content of the emulsions (Su & Lien, 2010). Similar results were reported in the literature where Raymundoa *et al.* (2002) optimized the composition of emulsions using different contents of the white lupin protein, xanthan gum and oil. Emulsions were a non-Newtonian, pseudo plastic fluid. The results showed that the shear stress–shear strain relationship were non-linear, indicating that the emulsions behaved as a non-Newtonian fluid. The results showed that values were lower than one indicating that these emulsions were pseudo-plastic materials. The coefficients of determination (R²) obtained were high which confirms the power law model is adequately suitable for describing the flow behavior of the emulsions. Therefore, it can be concluded that the xanthan, guar and CMC solution exhibit pseudo plasticity behavior. Pseudo plasticity behavior of xanthan is higher than the other gums (Lorenzo & Zaritzky, 2008). Xanthan has a complex structure with high molecular weight. Increasing of Xanthan content in the emulsions results in increasing pseudo plasticity. At low shear rates, solutions of xanthan gum have higher viscosity than guar gum and significantly more viscosity in comparison to CMC.

Increasing the shear rate causes progressive deformation and disruption of the aggregated particles, which in turn decreases emulsion resistance to flow and reduces its apparent viscosity. Rheological properties of emulsion No 14 before thermal processing is shown in Fig. 3. Other emulsions had the similar rheological properties.

- Effect of thermal treatment on rheological properties

Figure 1 and 7 shows the effect of thermal processing on viscosity of the emulsions. The viscosity of the emulsions decreased after thermal treatment. This behavior could be explained by the structural breakdown of the molecules due to the hydrodynamic forces generated and the increased alignment of the constituent molecules and hydrolyzation of stabilizers (Partal *et al.*, 1997). In the contour plot of the viscosity response and power law parameters of emulsions samples (Fig. 7) indicates a decrease in consistency coefficient (K) after thermal treatment indicating a decrease in apparent viscosity at higher temperature. The flow behavior index (n) also showed an increasing trend with the temperature, which indicates the emulsions were tending to have

higher pseudo plasticity at higher temperature (Razavi *et al.*, 2007). All of the emulsions showed similar flow behavior (Fig. 5), by increasing the shear rate, the viscosity is decreased. Rheological properties of emulsion No. 14 after thermal processing are shown in Fig. 6. Other emulsions had the same rheological properties.

- Particle size distribution

Analysis of variance of emulsions particle size is given in Table 4. The results showed that a linear model is well attuned to the experimental data of particle size response. A linear model was found to explain the effect of each component on particle size. The best model has low standard deviation, low predicted sum of squares and high predicted R-squared (Nikzad, 2012). Following these guides, the linear model was found the best fitted for viscosity, rheological properties (K, n), surface tension and particle size. Figure 8 shows the particle size distribution of the eight emulsions, which indicates emulsions had a greater particle size by increasing the amount of stabilizers, This behavior could be attributed

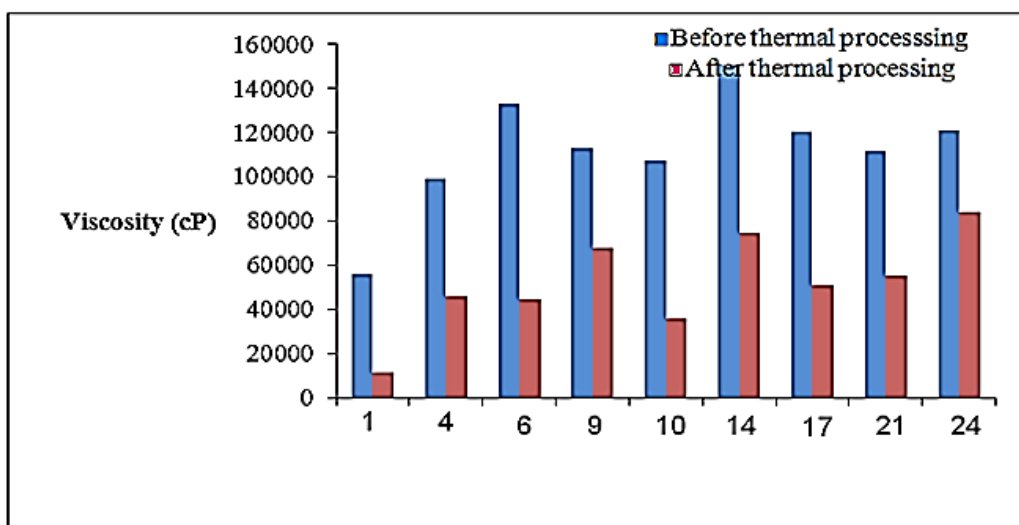


Fig. 1. Effect of thermal processing on viscosity of 9 emulsions (25 °C, 87 °C and 6rpm)

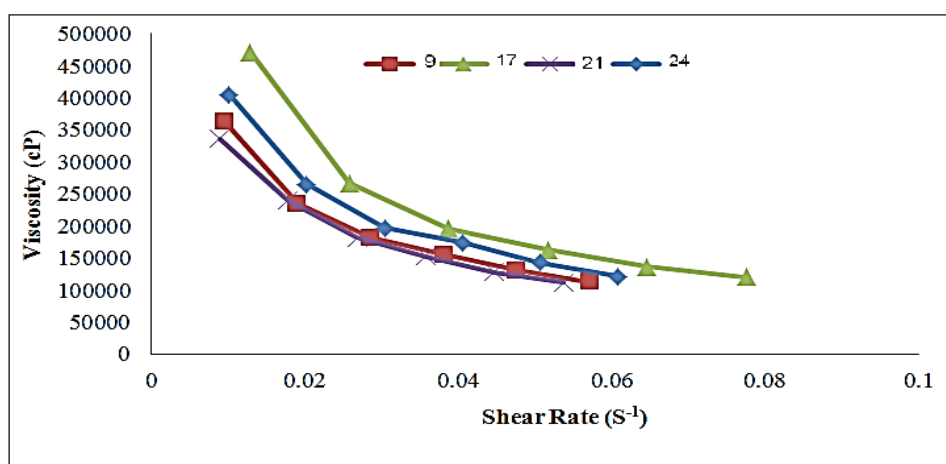


Fig. 2. Viscosity of four emulsion samples at 25 °C before thermal processing

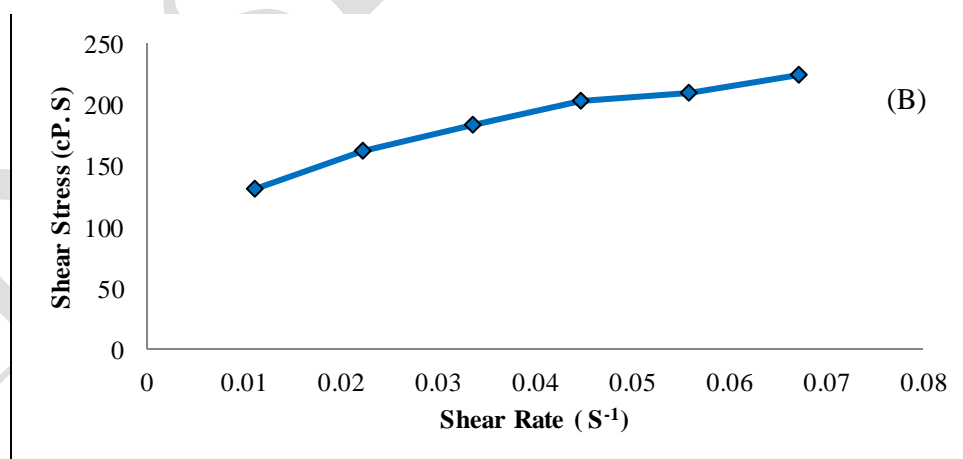
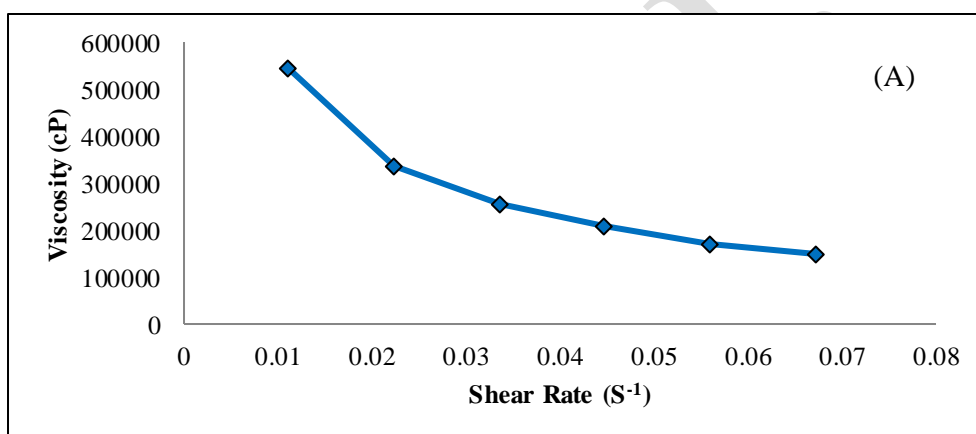
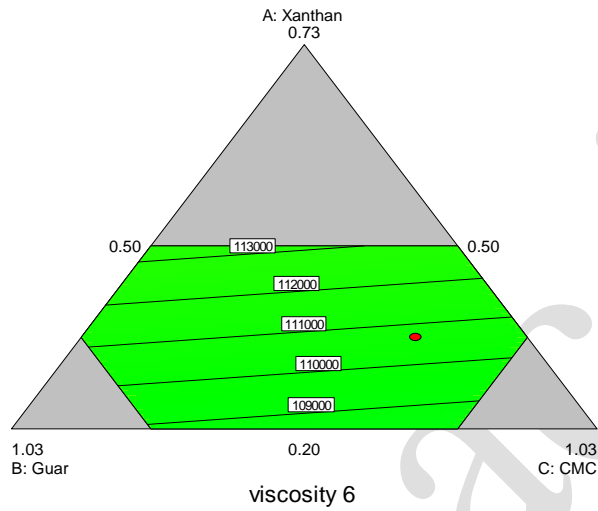
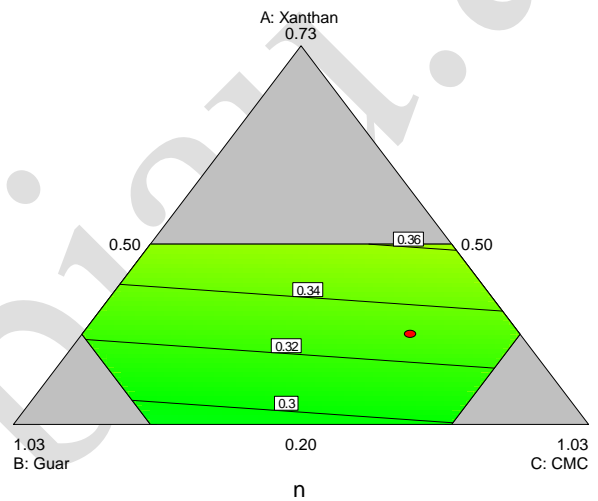


Fig. 3. (A, B). Rheological properties of emulsion No 14 at 25 °C before thermal processing

Design-Expert® Software
 Component Coding: Actual
 viscosity 6
 ● Design Points
 162925
 56007
 X1 = A: Xanthan
 X2 = B: Guar
 X3 = C: CMC
 Actual Component
 D: The rest = 98.27



Design-Expert® Software
 Component Coding: Actual
 n
 ● Design Points
 0.493
 0.104
 X1 = A: Xanthan
 X2 = B: Guar
 X3 = C: CMC
 Actual Component
 D: The rest = 98.27



Design-Expert® Software
 Component Coding: Actual
 k
 ● Design Points
 876.555
 96.64
 X1 = A: Xanthan
 X2 = B: Guar
 X3 = C: CMC
 Actual Component
 D: The rest = 98.27

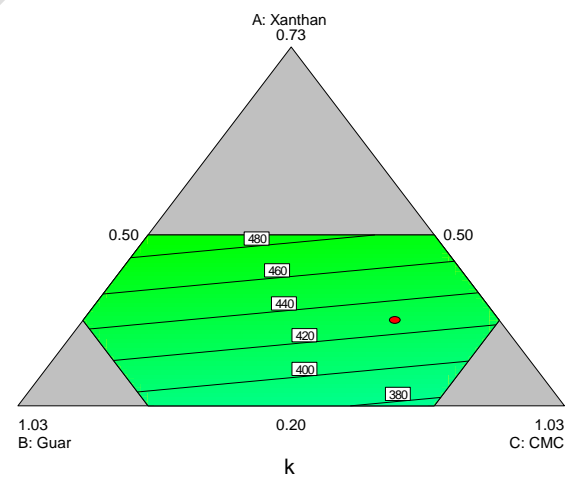


Fig. 4. Ternary contour plots of the effects of processing components on viscosity (obtained at the rpm= 6 & 25 °C (a) and power law parameters (consistency index (b) and flow behavior index (c) of the emulsion samples before thermal processing.

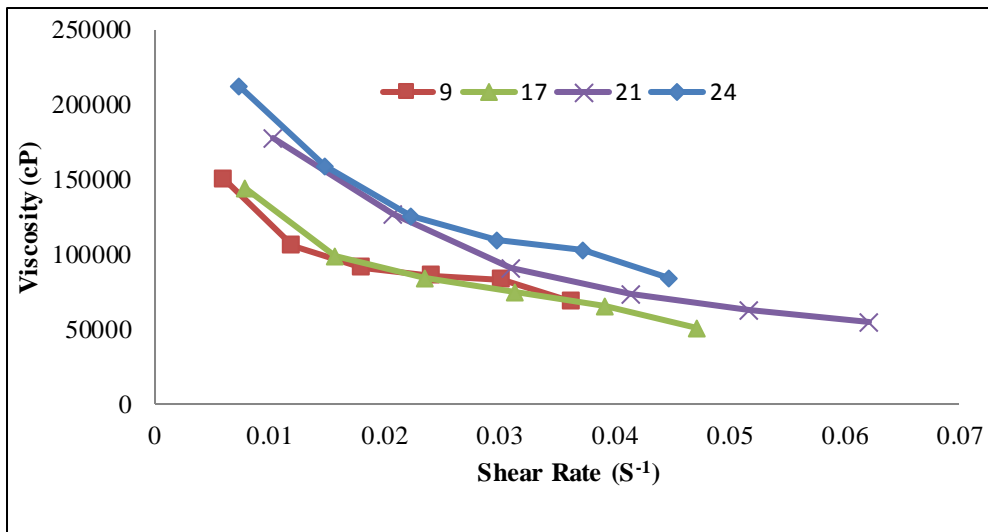


Fig. 5. Viscosity of four emulsion samples at 25 °C after thermal processing

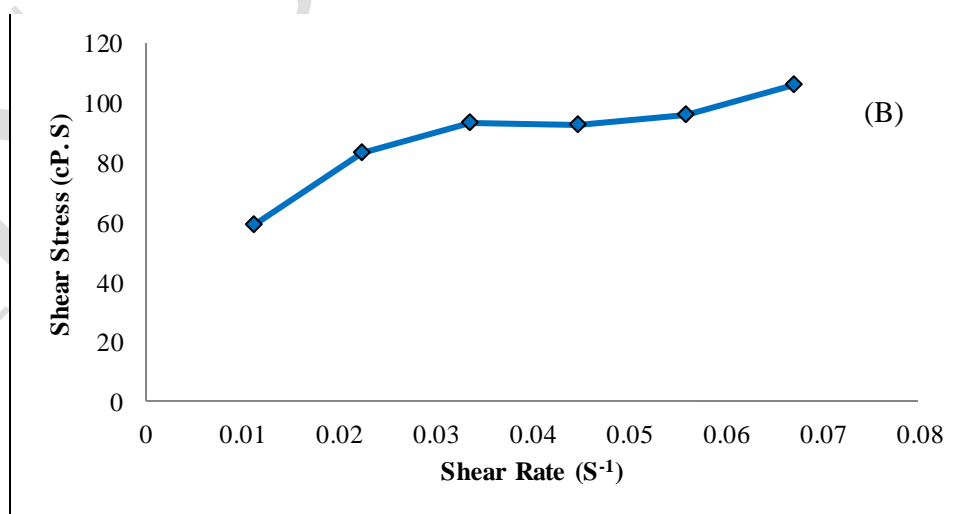
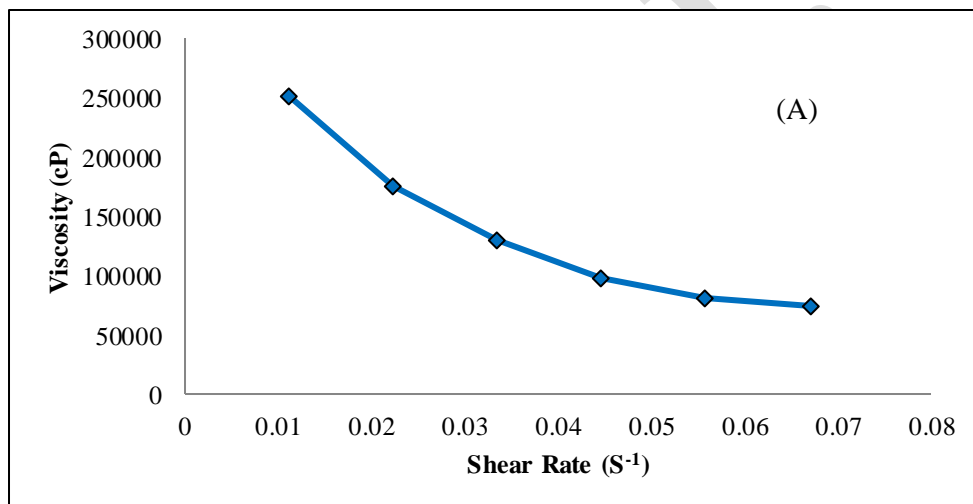


Fig. 6. (A, B). Rheological properties of emulsion No 14 at 25 °C after thermal processing
Table 3. Power law parameters of emulsions samples (K, n)

| Formulation | Before thermal processing | | | After thermal processing | | |
|-------------|---------------------------|------------------------|----------------|--------------------------|------------------------|----------------|
| | n | K (Pa.s ⁿ) | R ² | n | K (Pa.s ⁿ) | R ² |
| 1 | 0.104 | 96.64 | 0.932 | 0.465 | 69.616 | 0.973 |
| 4 | 0.259 | 294.712 | 0.973 | 0.609 | 523.742 | 0.922 |
| 6 | 0.271 | 387.997 | 0.996 | 0.441 | 237.935 | 0.996 |
| 9 | 0.365 | 479.143 | 0.993 | 0.655 | 941.995 | 0.984 |
| 10 | 0.358 | 427.092 | 0.997 | 0.454 | 207.058 | 0.983 |
| 14 | 0.296 | 499.196 | 0.997 | 0.297 | 238.173 | 0.917 |
| 17 | 0.246 | 321.822 | 0.983 | 0.469 | 334.621 | 0.951 |
| 21 | 0.396 | 535.998 | 0.985 | 0.328 | 197.156 | 0.959 |
| 24 | 0.337 | 465.445 | 0.958 | 0.502 | 569.452 | 0.998 |

K (Pa sⁿ) and n indices were obtained by fitting experimental data to power law model $\gamma' = k\dot{\gamma}^n$ (N).

Table 4. Estimations of coefficients and probabilities of linear model for rheological properties, surface tension and particle size

| Before thermal processing | Viscosity(rpm=6) cP | n | K Pa s ⁿ | Particle size µm | Surface tension mN/m |
|---------------------------|------------------------|---------|------------------------|---------------------|-------------------------|
| Sum of squares | 1.322E+010 | 0.043 | 3.676E+005 | 257.43 | 1041.46 |
| DF | 3 | 3 | 3 | 3 | 3 |
| Mean of squares | 4.408E+009 | 0.014 | 1.225E+005 | 85.81 | 347.15 |
| F value | 69.96 | 2.54 | 7.11 | 3.16 | 4.46 |
| Standard deviation | 7937.98 | 0.075 | 131.29 | 5.21 | 9.03 |
| Predicted R-squared | 0.8719 | -0.0378 | 0.3443 | -0.1231 | -0.1776 |
| After thermal processing | Viscosity(rpm=6) cP | n | K Pa s ⁿ | Particle size µm | Surface tension mN/m |
| Sum of squares | 1.526E+010 | 0.0043 | 2.923E+005 | 246.38 | 787.71 |
| DF | 3 | 3 | 3 | 3 | 3 |
| Mean of squares | 5.086E+009 | 0.014 | 97425.17 | 82.13 | 262.57 |
| F value | 19.36 | 1.56 | 1.99 | 1.72 | 4.11 |
| Standard deviation | 16206.08 | 0.096 | 221.32 | 6.91 | 7.99 |
| Predicted R-squared | 0.6010 | -0.4209 | -0.0334 | -0.0801 | -0.1732 |

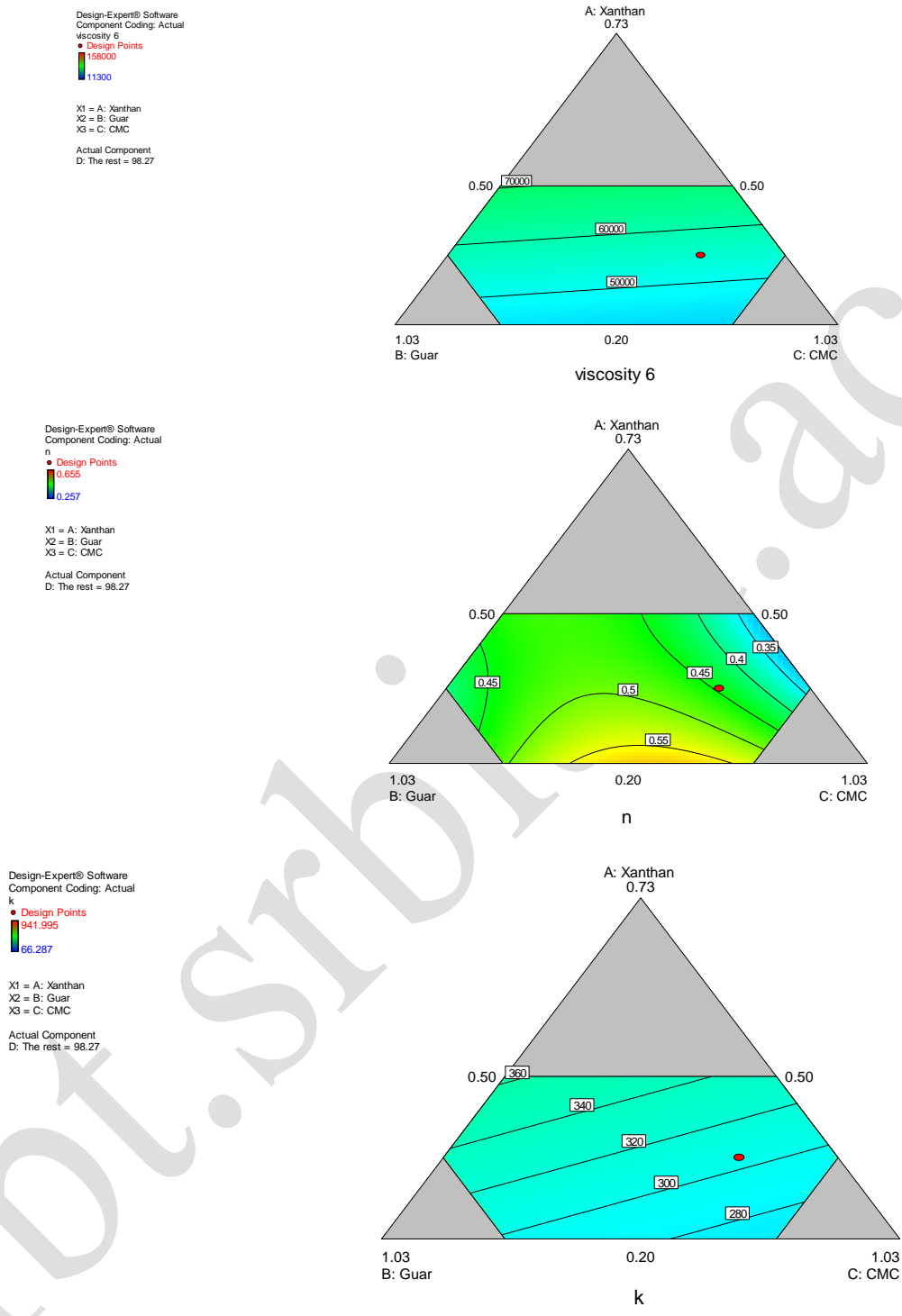


Fig. 7. Ternary contour plots of the effects of processing components on viscosity (obtained at the rpm= 6 & 25 °C (a) and power law parameters (consistency index (b) and flow behavior index (c) of the emulsion samples after thermal processing.

to the fact that stabilizers increase the viscosity of continuous phase and reduce movement rate of emulsifier into the interfaces layer and therefore particle size

increases (Samavati *et al.*, 2008). Some researcher reported that at the higher xanthan gum concentration, the increased viscosity may have lower efficiency than

homogenization process and lead to the formation of larger oil droplets (Huang *et al.*, 2001). Particle size is increased after thermal processing, mainly due to flocculation and coalescence (Diftis & Biliaderis, 2005). Droplet coalescence could occur simultaneously when two or more droplets within the flocks merge together to form a single larger droplet (Hayati *et al.*, 2007). In these tests, emulsions were diluted with SDS which can reduce coalescence and increase electrostatic depletion, which lead to a reduction in droplet size. Dilution and stirring might have partially disrupted weakly flocculated droplets, although it is unlikely that they will have disrupted more strongly flocculated droplets. Salt causes reduce electrostatic depletion between droplets. Droplet size is affected by temperature based on different ways: (i) viscosity is dependent to temperature and (ii) surface tension will decrease by temperature helping formation of the small droplets. Particle size of the emulsions depend on the percentages of gums especially xanthan gum; by increasing the stabilizer content in the emulsions, particle size increased. Emulsion No. 10 before thermal treatment and emulsion No.14 after thermal treatment had largest droplet size between emulsions. Xanthan had the highest effect on increasing the particle size. This might be attributed to the fact that xanthan is a water soluble hydrocolloids and in formulations containing low concentration of oil, they might be in crystal form switch resulted in increasing particle size of emulsions. Figure 9 shows the particle size distribution for eight emulsions. The similarity between the droplet size distribution curves of the emulsions, indicates the lack of extensive aggregation between the oil droplets and

considerable coalescence, suggesting that the gums enhanced steric repulsion effects between the droplets (Diftis, 2005). Some of the emulsions had heterogeneous coalescence (bimodal) and some of them had homogenous coalescence (mono modal) (Hayati *et al.*, 2007). Table 5 contains surface mean diameter ($D_{3,2}$), volume mean diameter ($D_{4,3}$) and specific surface area for the emulsions. Which indicates decreasing particle size, led to specific surface area increased (Huang & Kakuda, 2001). Emulsion No. 14 with the largest particle size, had small specific surface area ($2.07 \text{ m}^2/\text{g}$).

- Surface and interfacial tension

Analysis of variance of the emulsion surface tension is given in Table 4. A linear model was found to explain the effect of each component on surface tension. The emulsifier adversely influenced surface tension while xanthan, guar and CMC increased surface tension. It is obvious that all components had significant effects on surface tension. It can be also seen from Figure 10 the effect of xanthan which is higher and guar and CMC are similar in model.

Figure 10 shows the effect of thermal processing on surface tension of the emulsions. The surface tension of the emulsions decreased after thermal processing (Palmer, 1976). This behavior could be explained by increasing of kinetic energy of molecules, and therefore decreasing of inter molecular attraction interaction. Effect of temperature on surface tension is obtained by Eotvas equation:

$$\gamma = k (T_c - T) [d / M]^{2/3} \quad (9)$$

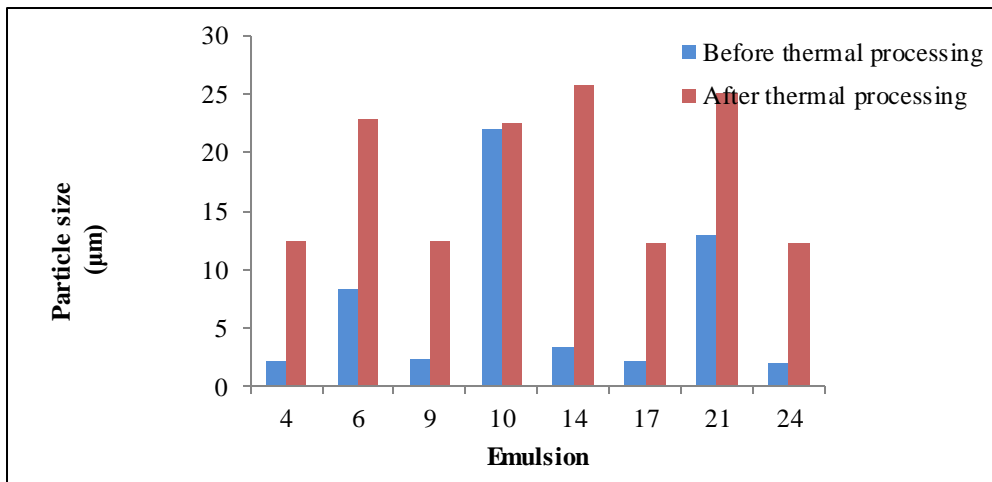


Fig. 8. Particle size distribution of eight emulsion samples

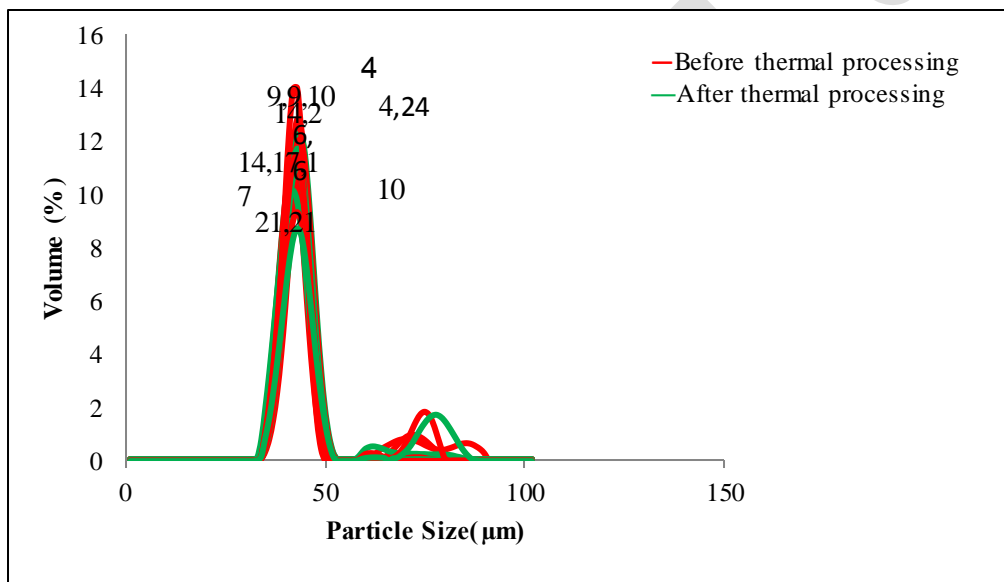


Fig. 9. Particle size distribution for 8 emulsion sample

Table 5. Effect of thermal processing on size distribution of emulsions

| Formulation | Before thermal processing | | | After thermal processing | | |
|-------------|---------------------------|------------------|------|--------------------------|------------------|------|
| | D _{3,2} | D _{4,3} | * | D _{3,2} | D _{4,3} | * |
| 4 | 1.988 | 2.244 | 2.91 | 2.061 | 12.371 | 2.62 |
| 6 | 1.872 | 8.275 | 3.4 | 2.763 | 22.855 | 2.21 |
| 9 | 2.077 | 2.385 | 2.89 | 3.073 | 12.369 | 2.89 |
| 10 | 2.437 | 21.972 | 2.81 | 3.132 | 22.446 | 2.46 |
| 14 | 1.781 | 3.446 | 3.29 | 1.822 | 25.807 | 2.07 |
| 17 | 1.870 | 2.160 | 3.11 | 1.928 | 12.248 | 3.21 |
| 21 | 2.214 | 12.982 | 2.51 | 2.391 | 25.005 | 2.11 |
| 24 | 1.841 | 2.034 | 3.08 | 1.949 | 12.246 | 3.26 |

*: Specific surface area (m²/g)

γ is the surface tension, k is constant, M is the molecular mass, T_c is the critical temperature and T is the temperature. Surface tension supposed to be zero in critical temperature. Equation 9 predicts the decrease of the surface tension with increasing temperature, which has been confirmed by the experiment. In Pippard's (1957) discussion of the temperature dependence of surface tension upon temperature, dependence upon $(T_c - T)$ was indicated. HLB of the emulsifier can be changed with the temperature. With increasing temperature hydrophilic degree increases (Palanuwech & Coupland, 2003). The other reason of decreasing of surface tension with temperature is the decrease of surface tension of water. Emulsion No. 14 had highest surface tension (67 mN/m) and viscosity (149940 cP). It can be conclude that there is a positive relationship between viscosity and surface tension. The lower the viscosity the smaller the surface tension. Viscosity is resistant against flow, but surface tension is the intermolecular force. These two parameter will decrease after thermal processing. Following several attempts to relate surface tension with viscosity, Pelofsky presented (1966) a linear relation between these two thermo physical properties:

$$\ln \sigma = \ln A + \frac{B}{\mu} \quad (10)$$

where A and B are constants, σ is the surface tension, and μ is the viscosity.

Hydrocolloids are mostly hydrophilic, which don't exhibit significant surface activity (Dickinson, 1999). However, as stabilizers in food emulsions, some gums were found to migrate slowly to the oil-water interfaces and exhibit some surface and interfacial activity (Huang *et al.*, 2001). In the emulsion, xanthan increased their surface and interfacial tension dramatically at higher concentration. It appears that at higher concentration the measurement of

interfacial activity became a problem for three gums due to the viscosity effects. The role of the surfactant is critical. It depends on surfactant nature and their concentration. It must be transported to the interface where it has lower surface tension and is adsorbed, forming surface protective layer (Krstonosic *et al.*, 2009). Tween 80 reduces surface tension in the samples. It is a nonionic emulsifier, which stabilises the emulsions firstly via steric, coalescence and hydration and then via electrostatic interactions. It is possible that the emulsifier strongly interacts with oil molecules in the interfacial region through Van der Waals force (Opawale & Burgess, 1998). Method of determination of surface tension might affect the results. For example Du Nouy ring method had different results in comparison to Wilhelmy Plate method (Kristensen *et al.*, 1997).

- Centrifugation assay

The centrifugation procedure is a rapid and convenient method but might not reflect the true emulsion stability during storage (Badolato *et al.*, 2008). Resistance of an emulsion to centrifugation depends on the difference in density between the oily and aqueous phases and also on the resistance on the interfacial film (Roland *et al.*, 2003). Centrifugation have produced an aqueous phase on the bottom, an emulsion phase in the middle and an oil phase on the top (McDermott, 1981). Emulsion samples showed a high stability to centrifugation and didn't breakdown because of the high viscosity of the aqueous phase, mainly due to adding the xanthan, guar gums and CMC that consequently slowed down oil droplets movement (Lorenzo & Zaritzky, 2008).

During the storage, the viscosities of all samples were reduced. The emulsions were stable against creaming and phase separation. Visual investigation of the samples after the storage demonstrated that all the samples had a homogenous texture. No phase concentration or any other

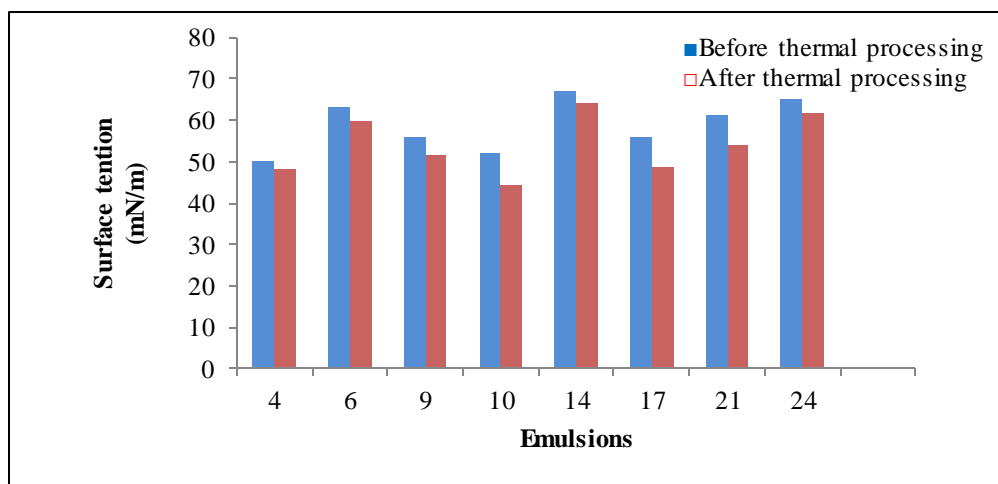


Fig. 10. Effect of stabilizers and thermal processing on surface tension of 8 emulsions

instability was observed. This is might be due to the high viscosity of the samples that prevented or limited the movements of droplets in the samples. Moreover, in these emulsions with low-fat content, creaming is usually prevented by adding a thickening agent such as a gum to the aqueous phase, in order to slow down the droplet movement.

Conclusion

It was found that the emulsions behave as non-Newtonian, shear thinning fluid and its flow can be successfully described by the power law model. Stabilizers increased the viscosity; however, the effect of xanthan was greater than other gums (i.e. guar and CMC). The consistency coefficient of emulsions increased with increasing the stabilizers level and decreasing temperature, while the flow behavior index slightly raised with increasing the temperature. The presence of three applied stabilizers in the samples increased their stability. Size of droplet had a significant effect on stability. Smaller the droplet size the higher the stability of the emulsion. Tween 80 decreased surface tension between water phase and oil phase and facilitates the formation of smaller droplet. Adding vinegar after emulsification had a significant effect on stability of emulsions. If vinegar is added to aqueous phase, emulsions will not have

the desirable texture and stability. The lower the surface tension, the higher the stability. Tween 80 has high HLB (≈ 15) and decreased the surface tension and showed strong effect on the stability of emulsions. In general, both high viscosity, small oil droplet size and low surface tension contribute to the stability of the emulsions.

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References

- Achayuthakan, P. & Suphantharika, M. (2008). Pasting and rheological properties of waxy corn starch as affected by guar gum and xanthan gum. *Food Hydrocolloids*, 71, 9–17
- Acton, J. C. & Saffle, R. L. (1970). Stability of oil in water emulsions. *Journal of Food Science*, 35, 852- 855.
- Arora, A. & Chism, G. W. (2003). Rheology and stability of acidified food emulsions treated with high-pressure. *Journal of Agricultural and Food Chemistry*, 51, 2591-2596.
- Badolato, G. G., Aguilar, F., Schuchmann, H. P. & Lerche, D. (2008). Evaluation of Long Term Stability of Model Emulsions by Multisample Analytical Centrifugation. *Progr Colloid Polym Sci.*, 134, 66-73.

- Benichou, A., Aserin, A., Lutz, R. & Gart, N. (2007). Formation and characterization of amphiphilic conjugates of whey protein isolate (WPI) / xanthan to improve surface activity. *Food Hydrocolloids*, 21, 379-391.
- Campbell, L. & Trueck, H. U. (2000). A heat stable oil-in-water emulsions and a process for its manufacture. U. S. Patent. EP0702902: 1-8.
- Coupland, J. N. & McClements, D. J. (2001). Droplet size determination in food emulsions: comparison of ultrasonic and light scattering methods. *Journal of Food Engineering*, 50, 117-120.
- Dickinson, E. (1992). Interfacial interactions and the stability of oil-in water emulsions. *Pure&App/ Chern*, 64, 1721-1724.
- Diftis, N. G. & Biliaderis, C. G. (2005). Rheological properties and stability of model salad dressing emulsions prepared with a dry-heated soybean protein isolate–dextran mixture. *Food Hydrocolloids*, 19, 1025–1031.
- Dolz, M. & Ndez, M. J. H. (2008). Creep and recovery experimental investigation of low oil content food emulsions. *Food Hydrocolloids*, 22, 421-427.
- Fonseca, V. C. & Haminiuk, C. W. I. (2009). Stability and rheological behavior of salad dressing obtained with whey and different combinations of stabilizers. *International Journal of Food Science and Technology*, 44, 777-783.
- Garcia-Ochoa, F., Santos, V. E., Casas, J. A. & Gomez, E. (2000). Xanthan gum: production, recovery, and properties. *Biotechnology Advances*, 18, 549-579.
- Garti, N. & Leser, M. E. (2001). Emulsification properties of hydrocolloids. *Polymers for Advanced Technologies*, 12, 123-135.
- Hayati, I. N. & Man, Y. B. C. (2007). Stability and rheology of concentrated O/W emulsions based on soybean oil/palm kernel olein blends. *Food Research International*, 40, 1051-1061.
- Huang, X. & Kakuda, Y. (2001). Hydrocolloids in emulsions: Particle size distribution and interfacial activity. *Food Hydrocolloids*, 15, 533-542.
- Krstonosic, V., Dokic, L., Dokic, P. & Dapcevic, T. (2009). Effects of xanthan gum on physicochemical properties and stability of corn oil in- water emulsions stabilized by polyoxyethylene (20) sorbitan monooleate. *Food Hydrocolloids*, 23, 2212-2218.
- Kristensen, D., Jensen, P. Y., Madsen, F. & Birdi, K. S. (1997). Rheology and Surface Tension of Selected Processed Dairy Fluids: Influence of Temperature. *Dairy Sci.*, 80, 2282–2290
- Lorenzo, G. & Zaritzky, N. (2008). Modeling rheological properties of low in fat o/w emulsions stabilized with xanthan/guar mixtures. *Food Research International*, 41, 487-494.
- Liu, H., Xu, X. M. & Guo, Sh. D. (2007). Rheological, texture and sensory properties of low-fat mayonnaise with different fat mimetics. *LWT*, 40, 946-954.
- Mandala, I. G. & Savvas, T. P. (2004). Xanthan and locust bean gum influence on the rheology and structure of a white model-sauce. *Journal of Food Engineering*, 64, 335-342.
- Maruyama, K. & Sakashita, T. (2007). Relationship between rheology, particle size and texture of mayonnaise. *Food Sci Technol Res.*, 13, 1-6.
- McClements, DJ. (2003). *Food Emulsions: Principles, Practices and Techniques*. CRC Press.
- McDermott, R. L. (1981). A centrifugal method for characterization of salad dressing emulsions. *Journal of Food Technology*, 81-87.
- Nikzad, V., Mazaheri Tehrani, M. & Saadatmand-Tarzjan, M. (2012). Optimization of low-cholesterol-low-fat mayonnaise formulation: Effect of using soy milk and some stabilizer by a mixture design approach. *Food Hydrocolloids*, 28, 344-352.
- Opawale, F. O. & Burgess, D. J. (1998). Influence of Interfacial Properties of Lipophilic Surfactants on Water-in-Oil Emulsion Stability. *Journal of Colloid and Interface Science*, 197, 142-150.
- Pal, R. (2000). Relative viscosity of non-newtonian concentrated emulsions of noncolloidal droplets. *Ind. Eng Chem Res.*, 39, 4933-4943.
- Palmer, S. J. (1976). The effect of temperature on surface tension. *Physics Education*.
- Papalamprou, E. M. & Makri, E. A. (2005). Effect of medium molecular weight xanthan gum in rheology and stability of oil-in-water emulsion stabilized with legume proteins."

Journal of the Science of Food and Agriculture, 85, 1967-1973.

Palanuwech, J. & Coupland, J. N. (2003). Effect of surfactant type on the stability of oil-in-water emulsions to dispersed phase crystallization. *Colloids and Surfaces A: Physicochem. Eng. Aspects*, 223, 251-262

Partal, P. & Guerrerob, A. (1997). Influence of concentration and temperature on the flow behavior of oil-in-water emulsions stabilized by sucrose palmitate. *JAOCS*, 47.

Perssini, D. & Sensidoni, A. (1998). Rheological characterization of traditional and light mayonnaise. *Journal of Food Engineering*, 35, 409-417.

Razavi, S. M. A., Najafi, M. B. H. & Alaei, Z. (2007). The time independent rheological properties of low fat sesame paste/ date syrup blends as a function of fat substitutes and temperature. *Food Hydrocolloids*, 21, 198-202.

Robins, M. & Watson, A. D. (2002). Emulsions, creaming and rheology." *Current Opinion in Colloid & Interface Science*, 7, 417-425.

Roland, I., Piel, G., Delattri, L. & Evrard, B. (2003). Systematic characterization of oil in water emulsions for formulation design."

International Journal of Pharmaceutics, 263, 85-94.

Samavati, V., Razavi, S. H. & Mousavi, S. M. (2008). Effect of Sweeteners on Viscosity and Particle Size of Dilute Guar Gum Solutions. *Iran. J. Chem. Chem. Eng.*, 27.

Steffe, F. J. (2006). *Bioprocessing Pipelines: Rheology and Analyses*. Freeman Press. USA.

Su, H. P. & Lien, C. P. (2010). Development of low-fat mayonnaise containing polysaccharide gums as functional ingredients. *J. Sci Food Agric*.

Thornton, M. (2005). Effect of emulsifiers and stabilizers in oil and vinegar salad dressing. *Food chemistry*, 453.

Wanlop, Ch., Eric, A. D. & Julian McClements, D. (2009). Influence of glycerol and sorbitol on thermally induced droplet aggregation in oil-in-water emulsions stabilized by b-lactoglobulin. *Food Hydrocolloids*, 23, 253-261

Wendin, K. & Hall, G. (2001). Influences of Fat, Thickener and emulsifier contents on salad dressing: static and dynamic sensory and rheological analyses. *Academic Press*, 222-231.

Williams, P. A. & Phillips, G. O. (1998). *Gums and stabilizers for the food industry*. The Royal Society of chemistry, Cambridge.