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 μ m. 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 with from aggregating 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 among xanthan gums are the most commonly used as thickening agents in food emulsions. Guar gum is a water-soluble nonionic 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 composition. structure and 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 provided from salt were 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

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emulsified. After emulsification, the vinegar was added. Emulsions were stored at 45 °C and at ambient temperature for 30 days.

During this period the appearance and oiling-off of the samples were visually studied.

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 1. Initial	experimental	area for	the	formu	lations	(wt, %)
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Table 2. E	mulsions co	mposition	proposed	by the	four-	component	mixture	design
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Ingredient Proportion								
Formulation	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 24	0.45 0.45	0.9 0.7	0.7 0.7	97.95 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.

$$\mathbf{M} = (\mathbf{k}') \mathbf{N}^{\mathbf{n}} \tag{1}$$

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

$$Ln M = ln (k) + n ln (N)$$
(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.

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

Where $k_{\sigma_{\tau}}$ 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.

$$\gamma' = k_{\gamma}'(N) \tag{4}$$

Where k_{γ} , known as the shear rate conversion factor, depends on the numerical value of the flow behavior index (Steffe, 2006):

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

- Particle size distribution

Samples (0.05 g) were diluted with 150ml dodecyl sulfate 0.1% sodium (SDS) solution, stirred gently by a spatula until dispersed. Samples completely 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:

$$D_{4,3} = \sum n_i d_i^4 / \sum n_i d_i^3$$
 (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.

$$D_{3,2} = \sum n_i d_i^3 / \sum n_i d_i^2$$
 (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 distillated water and citric acid, then burned on the flame and cooled down ambient then to the 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 f raction (F1) was measured. The emulsion

stability was characterized as (%) (F_1/F_0) × 100. All tests were carried out in triplicate orders.

- Statistical Analysis

A mixture design based on a 4component 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 stabilizers interaction with increasing 2005). (Tornton. Stabilizers alter the rheological properties directly and increase the viscosity of continues 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 consequently. Xanthan forms viscose solution at low concentration and forms desirable rheological properties in food (Dolz et al., 2008). It exhibits a synergistic effects with guar gum (Garsia-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

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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):

$$\sigma = K. \gamma^n \tag{8}$$

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 respectively processing, (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 stressshear 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 (\mathbf{R}^2) 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 hydrolization 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 decreased. Rheological is 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)

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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

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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

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	Before thermal processing			After thermal processing		
Formulation	n	K (Pa.s ⁿ)	\mathbf{R}^2	n	K (Pa.s ⁿ)	\mathbf{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

Table 3. Power law parameters of emulsions samples (K, n)

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

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

Before thermal	Viscosity(rpm=6)	n	K	Particle size	Surface
processing	cP		Pa s ⁿ	μm	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
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After thermal	Viscosity(rpm=6)	n	K	Particle size	Surface
After thermal processing	Viscosity(rpm=6) cP	n	K Pa s ⁿ	Particle size µm	Surface tension mN/m
After thermal processing Sum of squares	Viscosity(rpm=6) cP 1.526E+010	n 0.0043	K Pa s ⁿ 2.923E+005	Particle size μm 246.38	Surface tension mN/m 787.71
After thermal processing Sum of squares DF	Viscosity(rpm=6) <u>cP</u> 1.526E+010 3	n 0.0043 3	K Pa s ⁿ 2.923E+005 3	Particle size μm 246.38 3	Surface tension mN/m 787.71 3
After thermal processing Sum of squares DF Mean of squares	Viscosity(rpm=6) cP 1.526E+010 3 5.086E+009	n 0.0043 3 0.014	K Pa s ⁿ 2.923E+005 3 97425.17	Particle size μm 246.38 3 82.13	Surface tension mN/m 787.71 3 262.57
After thermal processing Sum of squares DF Mean of squares	Viscosity(rpm=6) cP 1.526E+010 3 5.086E+009	n 0.0043 3 0.014	K Pa s ⁿ 2.923E+005 3 97425.17	Particle size μm 246.38 3 82.13	Surface <u>tension mN/m</u> 787.71 3 262.57
After thermal processing Sum of squares DF Mean of squares F value	Viscosity(rpm=6) cP 1.526E+010 3 5.086E+009 19.36	n 0.0043 3 0.014 1.56	K Pa s ⁿ 2.923E+005 3 97425.17 1.99	Particle size μm 246.38 3 82.13 1.72	Surface tension mN/m 787.71 3 262.57 4.11
After thermal processing Sum of squares DF Mean of squares F value Standard deviation	Viscosity(rpm=6) cP 1.526E+010 3 5.086E+009 19.36 16206.08	n 0.0043 3 0.014 1.56 0.096	K Pa s ⁿ 2.923E+005 3 97425.17 1.99 221.32	Particle size μm 246.38 3 82.13 1.72 6.91	Surface tension mN/m 787.71 3 262.57 4.11 7.99
After thermal processing Sum of squares DF Mean of squares F value Standard deviation	Viscosity(rpm=6) cP 1.526E+010 3 5.086E+009 19.36 16206.08	n 0.0043 3 0.014 1.56 0.096	K Pa s ⁿ 2.923E+005 3 97425.17 1.99 221.32	Particle size μm 246.38 3 82.13 1.72 6.91	Surface <u>tension mN/m</u> 787.71 3 262.57 4.11 7.99
After thermal processing Sum of squares DF Mean of squares F value Standard deviation Predicted R-squared	Viscosity(rpm=6) <u>cP</u> 1.526E+010 3 5.086E+009 19.36 16206.08 0.6010	n 0.0043 3 0.014 1.56 0.096 -0.4209	K Pas ⁿ 2.923E+005 3 97425.17 1.99 221.32 -0.0334	Particle size μm 246.38 3 82.13 1.72 6.91 -0.0801	Surface tension mN/m 787.71 3 262.57 4.11 7.99 -0.1732

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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 (Difitis & Biliaderis, 2005).Droplet coalescence could occur simultaneously when two or more droplets within the flocks merge together to form a single larger droplet (Hayahi 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 (Difitis, 2005). Some emulsions heterogeneous of the had 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 m^2/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 thermal after processing (Palmer, 1976). This behavior could be explained by increasing of kinetic of energy molecules. and therefore decreasing of inter molecular attraction interaction. Effect of temperature on surface tension is obtained by Eotvas equation:

$$y = k (T_{\rm C} - T) [d / M]^{2/3}$$
(9)





Fig. 8. Particle size distribution of eight emulsion samples



Fig. 9. Particle size distribution for 8 emulsion sample

able 5. Effect of thermal processing on size distribution of emulsions	able	5.	Effect	of thermal	processing	on size	distribution	of emulsions
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Before	ocessing	After thermal processing				
Formulation	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 processing. Following several thermal attempts to relate surface tension with viscosity, Pelofsky presented (1966) a linear relation between these two thermo physical properties:

 $\ln\sigma = \ln A + \frac{B}{\mu}$ (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 oilwater 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 The consistency coefficient of CMC). 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 (\approx 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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