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Modeling the Rheological Properties of Carboxymethylcellulose Stabilized O/W Emulsions Based on Sunflower Oil and Tallow Fat

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ABSTRACT: The aim of this research was to assess the effect of fat type and concentration as well as the continuous phase viscosity on the rheological properties of an oil-in-water (O/W) emulsion. Thus, sunflower oil and tallow fat were used as the dispersed phase of the emulsion both at 10 and 50% (w/v) and CMC solutions (at 0.1, 0.3 and 0.5% w/v) were acted as the continuous phase. CMC solutions and emulsions showed a shear-thinning behavior with increasing CMC or dispersed phase concentration. The rheological behavior of all samples was well modeled by Herschel-Bulkley, Power law and Casson equations. According to Herschel-Bulkley and Power law models, an increase in the consistency index and a decrease in the flow behavior index of all samples was occurred with increasing CMC concentration (0.1 to 0.5%), fat concentration (10 to 50%) and dispersed phase change from liquid oil to a solid fat. The obtained data were compared with Einstein, Larson, Pal and Dougherty-Krieger predicting models and the results showed that Larson model well described the flow behavior of emulsions with 10% fat content, and Dougherty and Krieger or Pal equations were fitted more with the experimental data of emulsions containing 50% fat content.

Keywords: *Emulsion, Fat Type, Modeling, Rheology.*

Introduction

Many products used by consumers (mayonnaise, milk, sausages, …) are oil-in-water (O/W) food emulsions (Caporaso *et al.*, 2016), in which have a good potential for solubilizing water-insoluble materials (such as flavors, essential oils, nutraceuticals, and antioxidants) at concentrations much above the solubility power of the oil or the oil/surfactant mixtures, in an aqueous medium (Lorenzo *et al.*, 2008). However, these emulsions have limited stability due to the separation of continuous and dispersed phases over time (Caporaso *et al.*, 2016). The stability of emulsions is affected by the emulsion composition (Kim & Mason, 2017) and the procedure used for the emulsion preparation (Helgesen, 2017). In order to increase the stability of an emulsion and improve its rheological parameters, stabilizers are used in the emulsion formulation (Radi & Amiri, 2013). Polysaccharides are usually added as stabilizers to the aqueous phase of O/W food emulsions to improve their creaming stability (Lorenzo *et al.*, 2008). Stabilizers such as polysaccharides are usually high molecular weight compounds that the interactions

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between their polymeric chains as well as their high water sorption capacity, result in increasing the viscosity and therefore the stability of an emulsion (Yaseen *et al.,* 2005; Krstonosic *et al.,* 2009).

The rheological behavior of O/W emulsions is very important from different aspects, and various factors affect this parameter. Dispersed phase type, concentration, and size distribution, type and viscosity of thickening agent, the viscosity of continuous phase, temperature, and aqueous phase pH are some of these factors (Kolotova *et al.,* 2018). The impact of each of these factors needs to be accurately quantified and predicted in the emulsion rheology. For example, if the type of oil phase is changed, the change in the emulsion viscosity and therefore, emulsion flow rate in the handling tubes should be foreseeable to predict the amount of needed energy for its pumping.

Therefore, the flow properties of the emulsions need to be understood to meet the technical requirements (power consumption, mixing efficiency, etc.) encountered during the emulsions manufacturing process, such as mixing, pumping, filling, etc. On the other hand, the consumer-perceived attributes, such as pouring or extrusion of emulsions from packs, are also related to their flow properties and must be also understood (Lorenzo *et al.*, 2008).

Other examples that explain the importance of evaluating the rheological behavior of emulsions well include the formulation and stabilization of emulsions such as sauces and beverage emulsions. Beverage emulsions are a unique O/W class of emulsions that are prepared as an emulsion concentrate and are later diluted in sugar solution for consumption. The stability of beverage emulsions is an important problem of flavor and beverage industries (Buffo *et al.,* 2001). Understanding the effect of fat type and concentration on the formulation and stability of origin beverage emulsion concentrates and their rheological behavior is an important contribution to the beverage industry. Meanwhile, predicting the effect of fat type and concentration on the textural properties of the sauces can be very helpful for the food industry.

In this regard, Buffo *et al*. (2001) studied the rheological properties of gum acacia in beverage emulsions, and declared that the viscosity of the emulsions concentrate was decreased by pasteurization and increased by demineralization. Lorenzo *et al*. (2008) modeled the shear-thinning behavior of O/W emulsions stabilized with xanthan/guar mixtures, with Ellis equation. Radi and Amiri (2013) declared that CMC stabilized O/W emulsions were well modeled by Power law and Casson models. The role of various emulsifiers or thickening agents on emulsion viscosity has been extensively studied but few studies concerning the effect of dispersed phase state (liquid oil or solid fat) in combination with dispersed phase concentration on the viscosity of O/W emulsions are performed. Regarding the above statements, the major aim of this research was to examine and modeled the effect of dispersed phase concentration (10 and 50%) and type (sunflower oil as a liquid oil with lower viscosity against tallow fat as a solid, inexpensive, and affordable fat with higher viscosity) on the rheological properties of an O/W emulsion at ambient temperature. Therefore, in this study, it was investigated whether the effect of oil type and concentration as a dispersed phase on the viscosity of an O/W emulsion is predictable, which might make it much easier to work with emulsions in the food industry.

Materials and Methods

- *Materials*

The materials were supplied from Sigma–Aldrich, USA (for Commercial CMC [carboxymethylcellulose]), and a local market (for sunflower oil and tallow fat). A commercial grade soybean lecithin was used for the emulsion preparation.

- *Preparation of CMC solutions*

In order to prepare CMC solutions, certain amounts of CMC were stirred with deionized water to give solutions with 0.1, 0.3 and 0.5% (w/v) concentrations, using a magnetic stirrer at 1 atm pressure and 28 ˚C. Addition of CMC was performed gradually to give an opportunity to CMC to dissolve. Finally, the CMC solutions were transferred to a refrigerator (at 7 °C) for 24 h to complete CMC hydration process (Radi & Amiri, 2013).

- *Emulsions Preparation*

To prepare O/W emulsions, the oil phase containing lecithin (0.5% w/v in the final emulsion) was added into the CMC solutions at predetermined concentrations (0.1, 0.3 and 0.5% w/v in the final emulsions) and homogenized for 1 min (3500 rpm) and then 30 sec (7000 rpm) at 1 atm pressure and 28 ˚C using an ULTRA-TURRAX high speed homogenizer (IKA, model T25, Germany). The experiments were performed just after the preparation of the emulsions (Radi & Amiri, 2013).

- *Rheological experiments*

The viscosity and zero-shear viscosity of emulsions and their associated CMC solutions were determined according to Radi and Amiri (2013). An Ultra rotational rheometer (Brookfield Engineering Laboratories, LV-DVIII, Stoughton, MA, USA), with co-cylinder assemblies (UL or SS Adaptor) was used for this purpose.

- *Microscopic observations*

For microscopic observations, a small sample from the prepared emulsions was spread on a microscope slide which then was covered with a glass lamella and observed by a light microscope (Olympus BX40, Japan). A 5-megapixel digital video ocular camera (Kruss VOPC85, Germany) was used for taking pictures from the slides and the pictures were stored on a computer.

- *Statistical analyses*

The experiments were performed with fifteen treatments, three sampling times, and three replications. The comparison of treatment means was performed through the analysis of variance (ANOVA) at p<0.05 by Duncan's multiple range test. The SPSS software (SPSS 17.0 for Windows, SPSS Inc., Chicago, IL, USA) was used for data analysis.

Results and Discussion

According to shear stress-shear rate curves of different emulsion samples (Figure 1), it was concluded that with the addition of solid fat or liquid oil into the CMC solution, the applied shear stress increased upon shear rate increases, indicating a higher viscosity of the emulsions in comparison with the corresponding CMC solutions (Figure 1). As well, higher shear stresses were applied for samples containing solid fat than those containing liquid oil (at the same concentrations), indicating a higher viscosity for these kinds of emulsions (Figure 1). In this regard, the volume fraction of the fat phase significantly affected the viscosity of the emulsions as the viscosity increased with fat concentration from 10 to 50%. The increase of O/W emulsions viscosity due to the oil concentration has been reported previously by Kundu *et al.* (2015). Figure 1 shows that the viscosity of all samples increased remarkably with the CMC concentrations.

It is well known that the viscosity of continuous phase (as affected by CMC concentration) and the dispersed phase volume fraction have a direct effect on increasing the viscosity of an emulsion system (McClements, 1999). Furthermore, the effect of particle hardness on the viscosity and rheological behavior of a dispersed system has been mentioned in the literature (Pal, 1996; McClements, 1999; McClements, 2003).

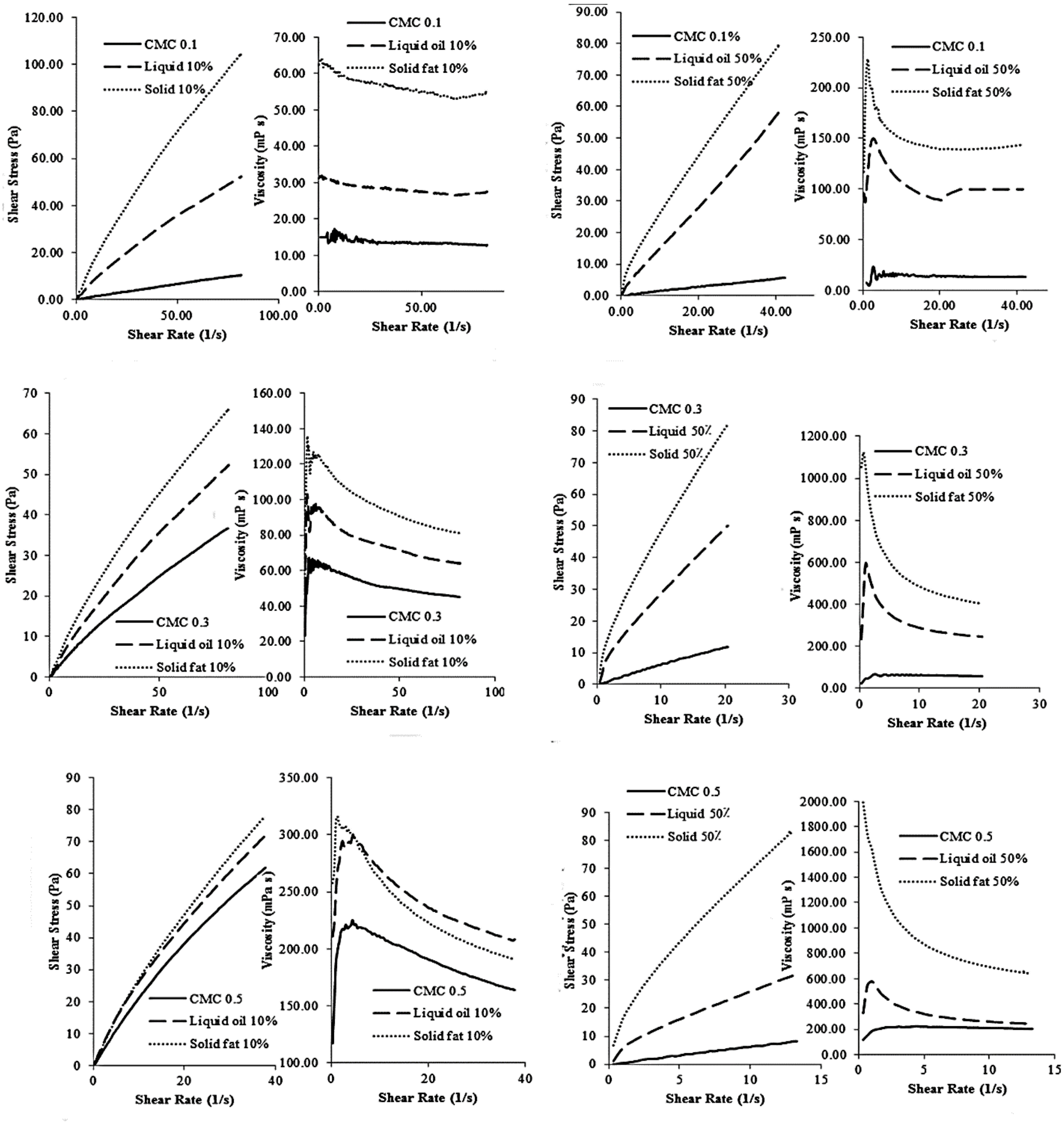

Fig. 1. Shear stress-shear rate and viscosity-shear rate relations in o/w emulsions containing 10% or 50% tallow fat or sunflower oil, stabilized with 0.1, 0.3 and 0.5% CMC.
CMC 0.1, 0.3 and 0.5% corresponds to CMC solutions (controls) containing 0.1, 0.3 and 0.5% CMC, respectively and liquid 10% (50%) or solid 10% (50%) corresponds to the emulsions containing 10 or 50% tallow fat or sunflower oil, respectively.

According to Figure 1, a constant viscosity, indicating a Newtonian behavior, was exhibited from the CMC solution at low concentration of 0.1% but the behavior was changed by either increasing the CMC concentration to 0.3 and 0.5%, or addition of fat (solid fat or liquid oil) at 10 and 50%. In this regard, a decrease in the viscosity of the samples was observed with increasing shear rate, demonstrating a shear thinning behavior. This shear-thinning behavior increased with the concentration of CMC (from 0.3 to 0.5%), fat (10 to 50%) and addition of fat. Mikkonen *et al.* (2016) also confirmed that in concentrated regimes containing high molecular weight polymers, higher concentrations of dispersed phase produce emulsions with higher viscosity.

The pseudoplastic behavior of prepared emulsions was affected by CMC flow behavior, the dispersed phase concentration and particle size distribution, and finally the type of fat phase (solid fat or liquid oil) as a dispersed phase (Pal, 1996; Derkach, 2009; Kim & Mason, 2017). The pseudoplastic behavior of CMC solutions has been reported before (Mandala & Bayas, 2004; Radi & Amiri, 2013).

In concentrated colloidal dispersions, when the particle concentration reaches a certain amount, a noticeable shear-thinning behavior is observed due to the effect of Brownian motion. At low shear stresses, Brownian motion of particles overrides the particles to make a randomly three-dimensional distribution. As the shear stress increases, the particles arrange along the flow lines, that results in the formation of particle layers with lower resistance to the fluid flow and subsequently, the viscosity of emulsion reduces (McClements, 1999; McClements, 2003). As well, the highly entangled long chain of CMC is oriented randomly in solutions corresponding to their minimum energy state. At low amounts of shear rate, the system shows resistance against any deformation, thereby exhibiting a high apparent viscosity (Buffo *et al.*, 2011). By increasing the level of shearing stress, the long chains of polymer are oriented along the streamlines, which facilitate the bulk flow. This results in the viscosity reduction with the shear rate increase, representing a shear-thinning behavior (Pal, 1996; Buffo *et al.*, 2011).

Significantly higher viscosities were obtained for emulsions containing 50% dispersed phase rather than 10% containing ones. It is reported that the volume fraction of the discontinuous phase (oil droplets) has an important influence on the viscosity and the type of viscous flow. At low concentrations of the dispersed phase, the viscosity of emulsion increases slightly, but at high concentrations, the collisions between the particles result in the viscosity increase and a stronger shear-thinning behavior (Bourne, 2002).

The higher viscosity of solid-fat-containing emulsions than those of liquid oil ones might refer to the texture of the dispersed phase. Solid fat and liquid oil droplets are supposed to be acted as “hard” and “soft” particles in emulsions, respectively. A hard particle is supposed to be incompressible and therefore its effective size is not affected by the droplet concentration or the shear rate amount. In contrast, the effective size of a soft particle as a compressible substance may decrease at high concentrations of droplets or high values of shear rates. It should be noted that the difference between the viscosity of the dispersed and continuous phases greatly affects the function of particles as whether it should be considered as a hard or a soft particle. Liquid oil droplets may act as hard particles (solid spheres) where the continuous medium viscosity is much lower than the viscosity of the dispersed phase (Derkach, 2009). Dougherty–Krieger equation describes mathematically the viscosity of dispersions with high particle concentration and repulsive interactions between the particles as follow (McClements, 2003):

$$\eta = \eta_0 \left(\frac{\Phi}{\Phi_c}\right)^{-[\eta]\Phi_c} \qquad \text{Dougherty–Krieger equation}$$

According to the equation, the particles' actual volume fraction (Φ) is replaced with the particles' effective volume fraction (Φ_{eff}). The Φ_c (critical volume fraction) value for hard particles is 63.4, which is supposed to be like the non-interacting particles (Φ_c= 63.4, Song *et al.*, 2008) but the Φ_c amount increases ($\Phi_c \geq 63.4$) when the particles are soft. Subsequently, when the volume fraction increases, soft particles are more compressed and packed, resulting in a lower viscosity for soft particles containing emulsions compared to hard particles containing ones, at the same Φ_{eff} (McClements, 2003). The other parameters of the equation are described later.

It is reported that a suspension viscosity may increase when the dispersed phase contains droplets with small particle sizes or droplets with thick shells around them. The microscopic observations (data not shown) showed that the CMC particle sizes decreased with CMC concentration. In dispersions with a high concentration of hard particles, the particles cannot be considered as isolated particles due to the importance of hydrodynamic interaction (HI) presented between the particles. The reduction of particles separation distance results in the HI increase. For example, in a dispersion with a certain concentration of particles, the particle size decrease results in the separation distance decrease, and viscosity and hydrodynamic interaction increase (Pal, 1996).

In order to evaluate the effect of fat phase and concentration (10 and 50%) as well as CMC concentration (0.1, 0.3 and 0.5%) on the flow behavior of the prepared O/W emulsions, the shear stress-shear rate curves (Figure 1) were matched with different models. According to the results, the flow behavior of produced emulsions was well modeled with the Herschel-Bulkley equation (Table 1).

$\tau = \tau_0 + k\dot{\gamma}^{n}$ Herschel-Bulkley equation (Bourne, 2002)

In the equation τ means shear stress (Pa), τ_0 stands yield stress (pa), k is consistency index (mPa.s), $\dot{\gamma}$ is shear rate (s^{-1}) and n means flow behavior index (without unit). Fluids that obey this model show yield stress. Herschel-Bulkley behavior is generally suitable for non-newtonian fluids, in which a nonlinear pattern for shear stress-shear rate plots is obtained (Bourne, 2002). The results showed that the Herschel-Bulkley model can well explain the flow behavior of samples as the experimental data were matched very well with the model [very high determination coefficients (R^2= 0.98–1.00) were obtained (Table 1)].

Table 1. Herschel-Bulkley model constants for emulsions containing tallow fat or sunflower oil, stabilized with different CMC concentrations (0.1–0.5%)

Samples	n	τ_0 (Pa)	k (mpa.s)	RSME	R^2	Samples	n	τ_0 (Pa)	k (mpa.s)	RSME	R^2
CMC 0.1%	0.87	0.00	35.20	1.69	98.12*	CMC 0.1%	0.87	0.00	35.20	1.68	98.12*
CMC 0.1-oil 10%	0.86	0.00	49.70	0.26	100*	CMC 0.1-oil 50%	0.82	0.14	157.80	0.89	98.30*
CMC 0.1-fat 10%	0.79	0.00	88.90	1.52	98.2*	CMC 0.1-fat 50%	0.79	1.15	177.10	0.13	99.90*
CMC 0.3%	0.81	0.00	105.20	0.59	99.9*	CMC 0.3%	0.81	0.00	105.20	0.59	99.9*
CMC 0.3-oil 10%	0.79	0.00	152.30	1.58	99.90*	CMC 0.3-oil 50%	0.77	1.99	382.00	1.79	99.90*
CMC 0.3-fat 10%	0.73	0.00	270.50	1.51	99.90*	CMC 0.3-fat 50%	0.75	3.90	836.00	2.23	100*
CMC 0.5%	0.77	0.00	438.30	1.92	99.90*	CMC 0.5%	0.86	0.00	438.30	1.92	99.90*
CMC 0.5-oil 10%	0.74	0.00	489.60	1.37	100*	CMC 0.5-oil 50%	0.74	3.51	318.60	1.91	100*
CMC 0.5-fat 10%	0.74	0.00	494.40	0.94	100*	CMC 0.5-fat 50%	0.71	6.02	1243	1.90	99.30*

* indicates that the model is significant for the treatment ($P < 0.05$).

The yield stress for all CMC solutions containing 0.1, 0.3 and 0.5% CMC as well as their corresponding emulsions prepared with 10% solid fat or liquid oil, was zero (Table 1), meaning that the Power model may be a better model for describing these emulsions rheological behavior. In contrast, emulsions containing 50% solid fat or liquid oil showed yield stress, of which increased significantly when solid fat was used instead of liquid oil. The additional increase in the volume fraction of dispersed phase prevents particles from moving relative to one another and in facts, the particles get stuck, exhibiting yield stress (Malvern Panalytical, 2005).

The results showed that Power law (Ostwald–de Waele model) may also be a proper model (Table 2) for describing the flow behavior of CMC solutions and their corresponding emulsions but obviously, lower determination coefficients (R^2=0.88-0.99) were obtained when compared with Herschel-Bulkley model. Table 2 shows the constants of the Power Law model.

$$\tau = k(\dot{\gamma})^n$$

Ostwald – de Waele model (Buffo *et al.*, 2011)

τ is shear stress (Pa), k is consistency index (mPa.s^n), $\dot{\gamma}$ is shear rate (s^{-1}) and n is flow behavior index (without unit).

In Herschel-Bulkley and power models, n value shows the interchain association in the semi- and concentrated solutions. This means n value can be an index of shear-thinning or shear-thickening behavior (Mandala & Bayas, 2004). When $n<1$, the solution would have a more shear-thinning behavior; for $n=1$, the solution would have a Newtonian behavior and a shear-thickening behavior is expected for $n>1$ (Mandala & Bayas, 2004; Helgesen, 2017). According to Tables 1 and 2, the CMC emulsions and solutions indicated a shear-thinning behavior due to n values lower than one. The n values decreased with increasing the CMC concentration from 0.1 to 0.5%, indicating a stronger shear-thinning behavior at higher CMC concentrations. According to n values in the Herschel-Bulkley and Power models, a more severe shear-thinning behavior was observed in emulsions due to the fat or oil addition. Kundu *et al.* (2015) obtained the same result in their studies on O/W emulsions.

According to Herschel-Bulkley and Power models, the consistency index (k) of CMC solutions and their corresponding emulsions increased significantly with the CMC concentration and the addition of fat. The phase change from liquid to solid fat also increased the k values at the same concentrations. The increase in fat concentration from 10 to 50%, increased the consistency of samples remarkably, in both models.

Table 2. Ostwald–de waele model constants for emulsions containing 10 or 50% tallow fat or sunflower oil, stabilized with different CMC concentrations.

Samples	n	k (mpa.s^n)	RSME	R^2	Samples	n	k (mpa.s^n)	RSME	R^2
CMC 0.1%	0.96	30.11	2.94	94.12*	CMC 0.1%	0.96	30.11	5.94	94.12*
CMC 0.1-oil 10%	0.89	43.10	0.14	99.40*	CMC 0.1-oil 50%	0.70	164.1	0.250	88.00*
CMC 0.1-fat 10%	0.84	66.34	3.68	95.22*	CMC 0.1-fat 50%	0.65	178.7	1.51	95.40*
CMC 0.3%	0.93	65.20	1.27	95.30*	CMC 0.3%	0.93	65.20	1.27	95.30*
CMC 0.3-oil 10%	0.89	110.80	1.51	95.40*	CMC 0.3-oil 50%	0.70	639.20	1.91	95.70*
CMC 0.3-fat 10%	0.84	174.50	1.82	95.10*	CMC 0.3-fat 50%	0.71	966.70	0.82	98.20*
CMC 0.5%	0.88	263.90	3.92	95.00*	CMC 0.5%	0.88	263.90	3.92	95.00*
CMC 0.5-oil 10%	0.85	375.30	1.58	95.40*	CMC 0.5-oil 50%	0.72	534.50	1.39	95.80*
CMC 0.5-fat 10%	0.19	395.40	4.67	96.80*	CMC 0.5-fat 50%	0.59	1805	2.38	94.60*

* indicates that the model is significant for the treatment ($P < 0.05$).

Casson equation was the other model used for evaluating the flow behavior of the emulsions:

$$\tau^{0.5} = \tau_0 + k_c (\dot{\gamma})^{0.5}$$ *Casson equation* (Bourne, 2002)

where τ is shear stress (Pa), τ_0 represents the yield stress (Pa), k_c is the consistency coefficient (mPa s)$^{1/2}$ and $\dot{\gamma}$ means the shear rate (s^{-1}).

The results showed that the rheological behavior of CMC containing samples was also well modeled by the Casson equation ($R^2 = 0.93$–0.99, Table 3). Casson consistency coefficient values showed the significant effect of the fat phase on the emulsion rheology, as the CMC containing solutions consistency index increased with the addition of fat in the same concentrations of CMC. As well, the consistency index of emulsions containing solid fat was significantly higher than that of liquid oil.

To estimate zero shear viscosity (η_0), log viscosity (η) was plotted vs. log $\dot{\gamma}$ and the intercept value of the curve at zero shear rate was reported. Figure 2 shows the η_0 values of the different treatments. The η_0 of CMC solutions increased significantly with CMC concentration increase from 0.1 to 0.5% ($p<0.05$). With increasing the CMC concentration, the chains of the polymer begin to form an entangled network, resulting in higher viscosities (Mandala & Bayas, 2004). When the concentration of the polymer is low, it is not possible for the chains to interact with each other and get entangled (Chhabra & Richardson, 2008). On the other hand, when the fat phase was added into the CMC solutions, the η_0 values increased significantly. This increase for emulsions containing solid fat was more pronounced when compared to samples containing liquid oil. The η_0 values were also affected by the concentration of fat, as it increased remarkably with an increase in the fat content from 10 to 50%. Although the description of the flow characteristics of concentrated suspensions containing hard particles in a shear flow is a long-standing problem but the most prominent feature in this regard is that the zero-shear viscosity considerably increases when the dispersed phase volume fraction (Φ) increases above Φ~0.6 (Behera *et al.*, 2017). For soft particles, only a small increase in η_0 has been reported up to Φ~0.6, indicating that the particles interact weakly in dilute regimes but at high concentrations (at volume fractions above the random close packing volume fraction $\Phi>0.6$), a dramatic increase in η_0 occurs, accompanied by significant deformation of the soft particles (Behera *et al.,* 2017; Shamana, 2017), particle interpenetration and squeezing. It is reported that even particles with the very low softness (S=0.02-0.2) may show sharp deviations from Brownian hard spheres, which may be due to the layer deformability (Vlassopoulos *et al*., 2001). This layer deformability may be the reason for lower η_0 of soft particle containing emulsions in comparison with hard particle containing ones.

Where η and η_0 represent the viscosity of emulsion and continuous phase respectively; Φ stands the dispersed phase volume fraction; η_{drop} (in Larson equation) is the dispersed phase viscosity; Φ_c (in Dougherty and Krieger equation) is the maximum packing volume fraction. This factor (Φ_c) is derived experimentally and is associated with the particle volume fraction upon which the particles become closely packed. In the Pal equation, the values of the constants, *a*=2.5 and *b*=6.2 may be derived experimentally or theoretically for dispersions containing spherical rigid particles (McClements, 2003).

Here are some other equations used for the prediction of emulsions or suspensions viscosity at different conditions:

$$\eta = \eta_0(1+2.5\Phi)$$ *Einstein equation* (McClements, 2003)

$$\eta = \eta_0\left[1 + \left(\frac{\eta_0+2.5\eta_{\mathrm{drop}}}{\eta_0+\eta_{\mathrm{drop}}}\right)\Phi\right]$$ *Larson equation* (McClements, 2003)

$\eta = \eta_0 (1 + a\Phi + b\Phi^2)$ *Pal equation* (McClements, 2003)

$\eta = \eta_0 \left(\frac{\Phi}{\Phi_c}\right)^{-[\eta]\Phi_c}$ *Dougherty and Krieger* (McClements, 2003)

The Einstein and Larson equations are used for predicting the viscosity of dilute dispersions containing rigid and fluid spherical particles, respectively. In the Einstein equation, there are no interactions between the particles. As well, no slip at the interface is observed between the particles and fluid. Neither shear rate nor particle size

Table 3. Casson model constants for emulsions containing 10 or 50% tallow fat or sunflower oil, stabilized with different CMC concentrations

Samples	τ_0 (Pa)	K (mpas)$^{1/2}$	RMSE	R^2	Samples	τ_0 (Pa)	K (mpas)$^{1/2}$	RMSE	R^2
CMC 0.1%	0.00	15.24	1.02	98.78*	CMC 0.1%	0.00	15.24	3.02	98.78*
CMC 0.1-oil 10%	0.14	22.70	1.44	99.60*	CMC 0.1-oil 50%	0.29	58.00	2.14	93.80*
CMC 0.1-fat 10%	0.22	33.31	2.01	95.66*	CMC 0.1-fat 50%	0.32	137.70	5.26	97.90*
CMC 0.3%	0.17	41.00	1.77	96.90*	CMC 0.3%	0.17	41.00	2.77	96.90*
CMC 0.3-oil 10%	0.41	55.20	2.87	97.20*	CMC 0.3-oil 50%	2.16	165.40	3.25	98.70*
CMC 0.3-fat 10%	0.90	66.80	2.49	96.50*	CMC 0.3-fat 50%	2.83	274.10	3.40	98.30*
CMC 0.5%	0.68	133.10	2.00	96.70*	CMC 0.5%	0.68	133.10	2.00	96.70*
CMC 0.5-oil 10%	0.87	173.90	3.42	97.10*	CMC 0.5-oil 50%	1.87	141.40	4.39	98.90*
CMC 0.5-fat 10%	1.24	149.40	2.36	97.30*	CMC 0.5-fat 50%	6.04	354.6	2.40	97.40*

- * indicates that the model is significant for the treatment ($P < 0.05$).

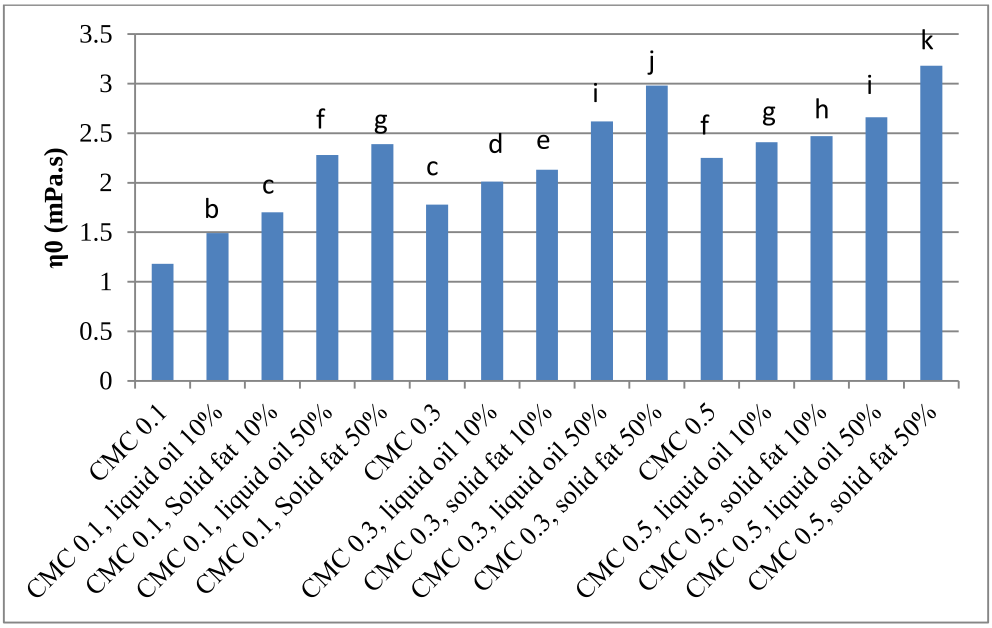

Fig. 2. The zero shear viscosity values of emulsions containing 0.1, 0.3 and 0.5% CMC, 10 and 50% tallow fat or sunflower oil measured at ambient temperature. Different letters indicate a significant difference between the treatments ($P < 0.05$).

has any effect on the Einstein equation. This equation describes that the continuous phase viscosity primarily defines the viscosity of a dilute suspension which increases with increasing the volume fraction of particles (McClements, 2003). In the Larson equation, it is assumed that the continuous and dispersed phases both have Newtonian behavior.

In most of food emulsions, the interfacial membrane has covered a droplet surrounding and can protect the dispersed phase from tangential stresses coming from the continuous phase. Subsequently, in such foods, the droplets are considered as rigid particles, in which the Einstein model is the best to describe their flow behavior at low concentrations. In such situations, if the shear stress increases sufficiently, the interfacial forces, in which keep the droplets together, might be overcome by the hydrodynamic forces, resulting in droplets deformation and disruption (McClements, 2003).

Pal or Dougherty and Krieger equations are used for predicting the viscosity of the concentrated dispersions. The rheology of concentrated emulsions is influenced by the colloidal interactions or hydrodynamic interactions (HI) existed between the droplets. Without long-range colloidal interactions, it is possible to use the Pal equation for dispersions containing up to 10% colloidal particles (Larson, 1999) whilst Dougherty and Krieger equation can be used at entire volume fractions. Subsequently, it is one of the most widely used equations (Hunter, 1986; Mewis & Macosko, 1994).

Figure 3 shows the viscosity-shear rate plots of emulsions containing 0.1-0.5% CMC in their continuous phase as determined experimentally and by four mentioned equations. Comparison of experimentally determined and predicted values of emulsions viscosities showed that for emulsions containing 0.1, 0.3 and 0.5% CMC with 10% liquid oil or solid fat as well as samples containing 0.5% CMC-50% liquid oil, Larson equation was the best equation. In this regard, the Einstein equation was also matched very well with the experimental data of 0.1% CMC-10% liquid oil emulsion. Dougherty and Krieger equation prediction was closest to the experimental data of 0.1% CMC-50% liquid oil or solid fat,0.3% CMC-50% solid fat and Pal equation was well matched with the experimental data of 0.3% CMC-50% liquid oil and 0.5% CMC-50% solid fat emulsions.

As mentioned before, Dougherty and Krieger and also Pal equations are useful for predicting the viscosity of concentrated emulsions while Einstein and Larson equations are applicable for dilute emulsions. According to the results, emulsions containing 10% dispersed phase, were well modeled with dilute regimes (Larson model) even at 0.1, 0.3 and 0.5% CMC concentrations, showing that the viscosity of continuous phase has a great influence on the emulsion viscosity and the viscosity of emulsions increased significantly with the CMC concentration increase from 0.1 to 0.5% (Figure 3).

In dilute emulsions, the viscosity of the continuous phase determines the viscosity of emulsions. In these regimes, the continuous phase prevents the collision and interaction of dispersed phase droplets. Contrary to that, in concentrated emulsions, the particles of dispersed phase collide, which increases the viscosity of the emulsions (McClements, 2003), and this was what happened in 50% emulsions in this study.

When solid fats were used instead of liquid oils, especially at higher concentrations (50%), they could act as rigid particles due to the higher viscosity of the dispersed phase than the continuous phase. In such situations, the rigid particles of solid fat are not deformed into long threads along the continuous phase flow. This significantly influences the viscosity of the emulsion and results in emulsions with higher viscosity

(Tadros, 1994; McClements, 2003; Walstra, 2003). Contrary, the soft drops of oil are deformed (from spherical shape to ellipsoidal form) due to shear stresses generated by the continuous phase higher viscosity. The higher viscosity of the continuous phase causes further drops deformation, showing that the deformation extent of the drops in a liquid flow is significantly influenced by the continuous phase viscosity (Derkach, 2009).

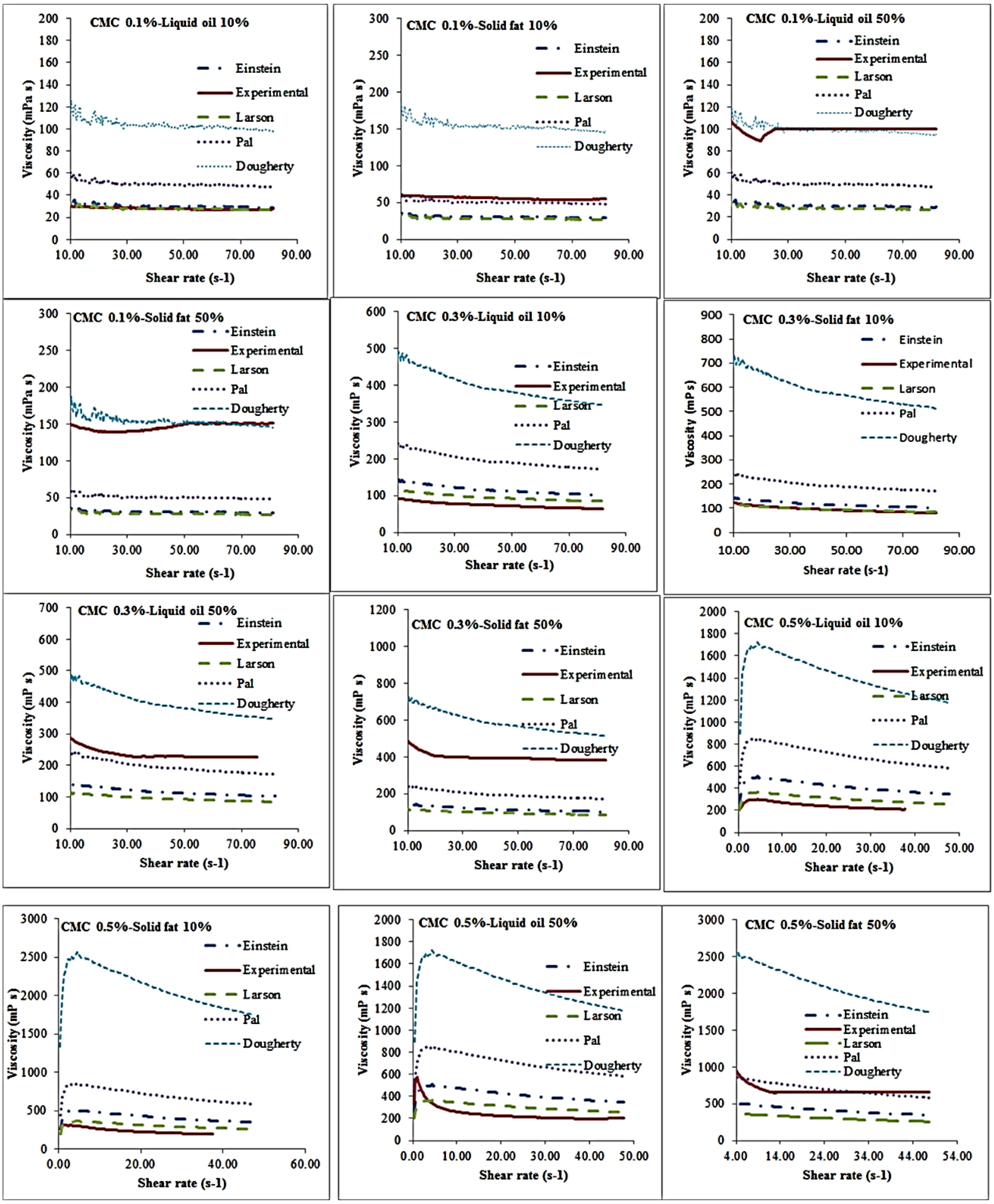

Fig. 3. Viscosity-shear rate plots of emulsions containing 0.1, 0.3 and 0.5% CMC, 10 and 50% tallow fat or sunflower oil measured experimentally and predicted by four models.

The consistency index ratios ($k_{emulsion}/k_{solution}$) of the samples are shown in Table 4. According to Table 4, the ratio increased significantly when the fat phase of emulsions was changed from liquid oil to the solid fat, at the same concentrations. This increase was remarkable at 50% fat content. As well, an increase in fat content from 10% to 50% resulted in a great increase in the ratio. The significant increase of consistency index ratios indicated the important effect of the dispersed phase on the viscosity of the emulsion. This is especially true when solid particles act as a dispersed phase, as they stand against deformation in a shear flow system. Therefore, the emulsion viscosity dramatically is influenced by the addition of a dispersed phase (Derkach, 2009). When the concentration of CMC increased to 0.5%, the consistency index ratios did not change significantly or the increase in the ratio was so slight. This result indicates that the influence of the dispersed phase on the emulsions viscosity is reduced by the high viscosity of the continuous phase. Therefore, the viscosity of the emulsions becomes close to the continuous phase viscosity.

Time-dependent fluids are fluids in which their shear stress is a function of the shear rate and the time when they are under shearing forces (Bourne, 2002). Figure 4 shows the time dependency data for CMC solutions and their corresponding emulsions (all data not shown). The behavior is time-independent when the curve on the way down retraces the same path as on the way up (Bourne, 2002). A thixotropic shear thinning behavior was observed for emulsions containing solid fat in their formulations as the curve on the way down doesn't lie exactly on the curve on the way up and a hysteresis loop was observed. In these samples, the enclosed area was small, and the time-dependent behavior of the emulsions was weak. The other samples in this study showed a non-thixotropic behavior (time-independent behavior). On the basis of our findings, CMC solutions and emulsions in diluted or concentrated forms show a time-independent behavior. These results were in accordance with the results of Radi and Amiri (2013) on CMC emulsions and Turabi *et al.* (2008) on batter cake containing xanthan.

Table 4. The consistency index ratios ($k_{emulsion}/k_{solution}$) of emulsions (the k values of herschel-bulkley model were used for estimation).

Samples	$k_{emulsion}/k_{solution}$	**Samples**	$k_{emulsion}/k_{solution}$
CMC 0.1%	-	CMC 0.1%	-
CMC 0.1-oil 10%	1.49d	CMC 0.1-oil 50%	3.81h
CMC 0.1-fat 10%	2.53f	CMC 0.1-fat 50%	9.03k
CMC 0.3%	-	CMC 0.3%	-
CMC 0.3-oil 10%	1.35c	CMC 0.3-oil 50%	4.03i
CMC 0.3-fat 10%	1.63e	CMC 0.3-fat 50%	6.69j
CMC 0.5%	-	CMC 0.5%	-
CMC 0.5-oil 10%	1.31c	CMC 0.5-oil 50%	1.06a
CMC 0.5-fat 10%	1.12b	CMC 0.5-fat 50%	2.66g

* Different letters indicate a significant difference between the treatments ($P < 0.05$).

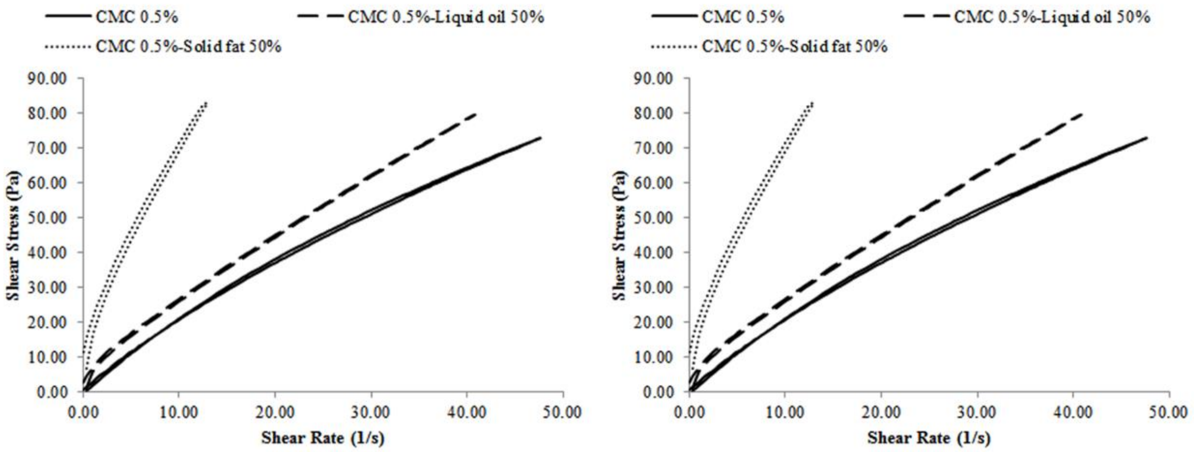

Fig. 4. Time dependency of emulsions containing 0.3% CMC (with 10% dispersed phase) and 0.5% CMC (with 50% dispersed phase).

Conclusion

The O/W emulsions containing 0.1-0.5% CMC and 10-50% dispersed phase showed a shear-thinning behavior. The viscosity of O/W emulsions increased significantly with CMC concentration (from 0.1 to 0.3%), dispersed phase concentration (from 10 to 50%) and addition of tallow fat instead of sunflower oil. The rheological behavior of emulsions was described well by Herschel-Bulkley, Power law, and Casson models. Emulsions containing 10% dispersed phase were well modeled with the Larson equation, showing that the continuous phase viscosity determines the viscosity of the emulsions. In these regimes, liquid oil droplets were supposed to be acted as soft particles which are subjected to deformation in a shear flow medium generated by continuous phase high viscosity. In concentrated emulsions with 50% dispersed phase, Dougherty and Krieger and Pal equations were fitted the best, indicating that dispersed phase viscosity remarkably affected the viscosity of the emulsions. These prospects may give the necessary information to the food industry for providing dilute or concentrated food emulsions with proper stability and rheology through the suitable selection of dispersed and continuous phases and regulation of their concentrations.

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