# Evaluation the rheological properties of a stabilizer in corresponding solutions and emulsions

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***Abstract*—In this study, it was aimed to compare the rheological properties of Carboxymethylcellulose (CMC) in aqueous solutions and their corresponding emulsions containing 0.05, 0.1, 0.25 and 0.5% CMC in the aqueous phase. Samples with 0.05 and 0.1% CMC showed Newtonian behavior but shear-thinning behavior was observed in CMC solutions and emulsions with increasing CMC concentrations to 0.25 and 0.5%. Rheological behavior of all samples were modeled by Power law ($R^2$= 0.986–197) and Casson models ($R^2$= 0.968–1). According to ''Ostwald–de Waele'' model, the consistency index of all samples was increased and the flow behavior index decreased with increasing CMC concentration. Addition of CMC increased the emulsion stability of O/W emulsions. This stability was increased with increasing CMC concentrations.**

***Keywords- rheology; stabilize; CMC; emulsion; stability***

## I. INTRODUCTION

Imagine of today's life without emulsions is impractical, as a great group of foods such as milk, mayonnaise, numerous creams, pastes, musses are considered in emulsion categories [1]. Oil-in-water emulsions are very applicable systems in the food industry. An important problem of these systems is their low stability as emulsions are thermodynamically unstable systems [2]. By using emulsifiers and stabilizers, the stability of these systems can be increased. The stabilizers' mechanism for improving the stability of emulsions is increasing the viscosity of the medium.[2] The high molecular weight of gums or other carbohydrate thickeners and the interactions between polymer chains are the reason of changing in viscosity [3]. Carboxymethylcellulose (CMC) is a linear anionic water-soluble cellulose derivative with carboxylic acid groups which is produced from natural cellulose [4, 5]. CMC is used as a thickener, binder, stabilizer, suspending and water-retaining agent in pharmaceutical and food industries [4]. The objectives of this research were: 1) To evaluate and compare the rheological characteristics of CMC solutions and their corresponding emulsions. 2) To compare the experimental results with different models which are commonly used for calculating the viscosity of emulsions. 3) To evaluate CMC ability for stabilizing a formulated O/W emulsion.

## II. MATERIALS AND METHODS

### *A. Materials*

Commercial CMC (carboxymethylcellulose) was obtained from Sigma–Aldrich (USA). Sun flower oil was purchased from a local market. Soybean lecithin was commercial grade.

### *B. Preparation of Gum Solutions*

Water solutions of CMC with 0.05, 0.1, 0.25 and 0.5% concentration (in the range usually used in the food systems) were prepared. For this purpose, the proper amounts of CMC were dissolved in deionized water, while a magnetic stirrer was dispersing the solution at ambient temperature. For prevention of coalescence, CMC powder should be added to the stirring water gradually, while giving time to CMC to be dissolved during adding. The solutions were kept at refrigerator overnight for completion of hydration, before the experiments were carried out.

### *C. Preparation of Emulsions*

O/W emulsion was prepared using sun flower oil and water with the ratio of 1/1. For this purpose, lecithin was dissolved in the oil phase to give a final concentration of 0.5% in the emulsion, and then water was added. For emulsions containing CMC, CMC solutions with concentrations of 0.05, 0.1, 0.25 and 0.5% were added instead of water. Then the premixes were homogenized by an ULTRA-TURRAX high speed homogenizer (IKA, model T25 basic equipped with S18N-19G dispersing tool, Germany) for 1 min at 3500 rpm and then 30 sec at 7000 rpm at ambient temperature. Immediately after preparation the experiments were carried out.

### *D. Rheological Experiments*

The viscosity of the prepared emulsions (immediately after preparations) and also CMC solutions was measured as a function of shear rate at ambient temperature using a Brookfield LV-DVIII Ultra rotational rheometer (Brookfield

Engineering Laboratories, Stoughton, MA, USA), equipped with co-cylinder assemblies (UL or SS Adaptor). For determining zero-shear viscosities, log apparent viscosity vs. log shear rate was constructed.

*E. Emulsion Stability Measurements*

Emulsion stability measurement is essential for indicating the stability of emulsion during storage. For measuring emulsion stability, 10 cc of the prepared emulsions were centrifuged at 5000 rpm for 5 min. After centrifuging, the separated phases of water and oil at the bottom and top of the emulsions were observed. The volume of stable phase was determined as the tubes were graduated. The emulsion stability was reported as the ratio of emulsion phase volume to total liquid volume (as percent) [6].

## III. RESULTS AND DISCUSSION

*A. Flow Behavior of CMC Aqueous Dispersions and O/W Emulsions Stabilized with CMC*

By plotting shear stress as a function of shear rate, two types of curves, linear and nonlinear, were detected for different CMC concentrations in both CMC solutions and O/W emulsions stabilized with CMC, indicating presence of two types of flow behaviors (Fig. 1). Presence of a linear relation between shear stress and shear rate in 0.05 and 0.1% CMC solutions shows that CMC solutions exhibited a Newtonian behavior in the dilute regimes. On the other hand, the nonlinear relation at higher CMC concentrations of 0.25 and 0.5% represents a non-Newtonian behavior.

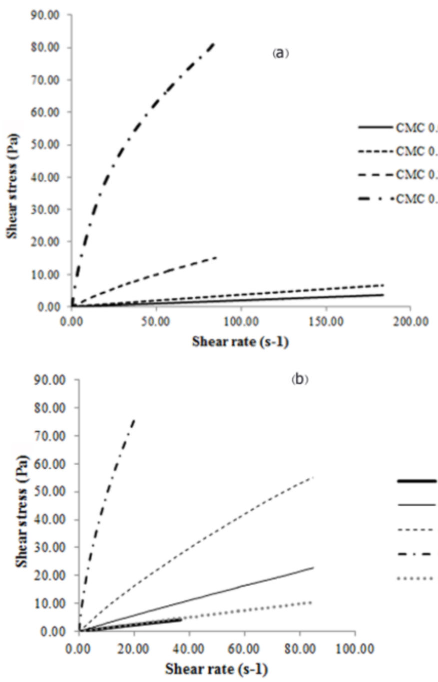


Figure 1. Shear stress-shear rate relation in different CMC concentrations of a) CMC solutions and b) emulsions containing CMC.

Fig. 2 shows the viscosity of different concentrations of CMC in the solutions and emulsions vs. shear rate. According to Figure 1a the viscosity of CMC solutions increases with the CMC concentrations. CMC solutions showed constant viscosity with increasing the shear rate at low concentrations of 0.05% and 0.1%. Therefore, a Newtonian behavior is observed for CMC at lower concentrations, while at higher concentrations, viscosity decreased with increasing shear rate. This shear thinning behavior increased with CMC concentration from 0.25% to 0.5% (Fig. 2a). Generally, the range of shear rate over which the apparent viscosity is constant increases as polymer concentration (in solution) drops [7].

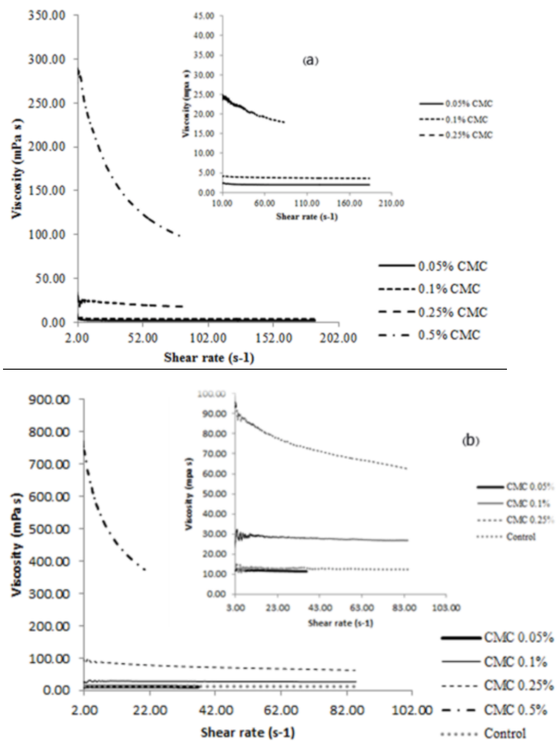


Figure 2. Effect of shear rate on the apparent viscosity of different concentrations of a) CMC solutions and b) emulsions stabilized with CMC.

In emulsions, when the concentration of hydrocolloids increased, the viscosity (resistance to shearing forces) was also increased (Fig. 2b). In all cases (except 0.05%) the viscosity of the emulsions was higher than that of control (Fig. 2). Addition of 0.05% CMC didn't have any influence on emulsion viscosity. Samples with lower polymer concentrations (0.05% and 0.1%) as well as control showed constant viscosity with shear rate increasing, while with increasing in CMC concentration to 0.25% and 0.5%, emulsions presented a shear thinning behavior, as viscosity decreased with shear rate. This pseudoplastic behavior of emulsions was due to CMC flow behavior, as similar behaviors were observed from CMC solutions, too. CMC like other high-molecular-weight polymers such as beta-lactoglobulin and xanthan showed pseudoplastic behavior [8]. The systems contain highly entangled long chain polymeric molecules in solutions like CMC, are oriented randomly corresponding to their minimum energy state. At low levels of externally applied stress, the system resists any deformation and strives to retain its structure, thereby offering a very high resistance by exhibiting either a very large value of the apparent viscosity [7]. As the level of shearing stress is gradually increased, the structural units respond to the applied stress either by aligning themselves in the direction of flow, or by deforming to orient along the streamlines, or by way of decomposition of the aggregates into primary particles. Similarly, coiled and entangled polymeric molecules may become disentangled and finally, may fully straighten out. All these micro-structural changes facilitate bulk flow in the system. This can be seen as the lowering of the effective viscosity with increasing rate of shear, as seen in viscoplastic and shear-thinning substances [7].

The critical shear rate ($\gamma_c$), representing transition from Newtonian behavior to viscoelastic behavior, decreased with increasing concentration from 0.25% to 0.5%. This result is in good agreement with Xu et al. [9] in studying Aeromonas gum and Yaseen et al. [3] in studying CMC, λ-carrageenan, ι-carrageenan and xanthan. Therefore, the flow behavior of CMC solutions depends on CMC concentration as other common polymers [9].

Consequently, at higher shear rates viscosity decreased in both CMC solutions and emulsions (at higher concentrations); according to dependence of power law to shear rate:

$\tau = k(\dot{\gamma})^n$ Ostwald–de Waele model [8]

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

TABLE 1. *k* and *n* coefficients of Ostwald–de Waele equation for CMC solutions and emulsions with different CMC concentrations

| Concentration (%) | *n* | | *k* (mpa.s$^n$) | |
|---|---|---|---|---|
| | *solutions* | *emulsions* | *solutions* | *emulsions* |
| 0.05 | 1.00 | 0.97 | 0.019 | 0.12 |
| 0.1 | 0.95 | 0.94 | 0.046 | 0.33 |
| 0.25 | 0.79 | 0.86 | 0.43 | 1.19 |
| 0.5 | 0.60 | 0.70 | 5.78 | 9.36 |
| Control | - | 0.96 | - | 0.14 |

*n* values are depicted versus CMC concentration in Figure 3. According to this figure, *n* values decreases with increasing concentration. It has been reported that the lower *n* values confirms the presence of interchain association in the semi- and concentrated solutions [9].

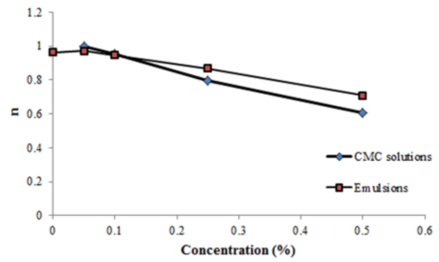


Figure 3. Dependence of n on the concentration of CMC at ambient temperature in CMC solutions and emulsions containing CMC.

Therefore, with increasing *n* value to 1, the flow behavior of the solution would be more like a Newtonian fluid and on the other hand, with decreasing the *n* value towards zero (Fig. 3), CMC solution would have more shear thinning behavior. According to Ostwald–de Waele constants, the consistency index of CMC solutions (*k*) were increased with CMC concentration, while the flow behavior index (*n*); decreased linearly with increase in CMC concentration (Table 1), resulting in highly pseudoplastic samples (Table 1). Such behavior was also observed in emulsions. Hence, addition of CMC increased the emulsion consistency. The effect of CMC, at higher concentrations was more pronounced.

As it was illustrated, the shear stress vs. shear rate data obtained for CMC solutions and emulsions were fitted well to Power Law model with high coefficient of determination values ($R^2$= 0.986–1). The Power Law model constants are shown in Table 1.

Another model which was evaluated is the Casson equation which is:

$\tau^{0.5} = \tau_0 + k_c (\dot{\gamma})^{0.5}$ *Casson equation* [10]

where $\tau$ is shear stress (Pa), $\tau_0$ the yield stress (Pa), $k_c$ consistency coefficient (mPa s)$^{1/2}$ and $\dot{\gamma}$, the shear rate ($s^{-1}$). Casson yield stress ($\tau_0$) and consistency coefficient ($k_c$) was determined from linear regression of the square roots of shear rate–shear stress data [11].

Casson model was also a proper model for explaining the rheological characteristics of CMC solutions or CMC containing emulsions as high determination coefficient values ($R^2$= 0.968–1) were obtained (Table 2). Turabi et al. [11] found Casson model a good model for rice cake batter. This model was also used in cooked rice flour dispersions, rice starch dispersions and glutinous rice flour dispersions [11].

TABLE 2. Casson model constants for CMC solutions and emulsions with different CMC concentrations

| **Concentration (%)** | **$\tau_0$ (mPa)** | | **$k_c$ (mPa s)$^{1/2}$** | |
|---|---|---|---|---|
| | ***solutions*** | ***emulsions*** | ***solutions*** | ***emulsions*** |
| 0.05 | 0.0004 | 0.0024 | 0.1390 | 0.3301 |
| 0.1 | 0.0070 | 0.0410 | 0.1843 | 0.4955 |
| 0.25 | 0.4563 | 0.5017 | 0.3496 | 0.7428 |
| 0.5 | 7.6862 | 3.4943 | 0.7135 | 1.5697 |
| Control | - | 0.0121 | - | 0.3390 |

Comparison of consistency index ratios ($k_{emulsion}/k_{solution}$) of the CMC solutions and their corresponding emulsions also shows a significant reduction of this ratio at the critical concentration point from 7.25 to 2.74 which indicate reduction of consistency difference between CMC solutions and their corresponding emulsions. This indicates that the higher viscosity of the continuous phase after this point reduces the effect of dispersed phase in CMC containing emulsions and causes the viscosity of system to be closed to the viscosity of continuous phase.

There are a number of fluids in which their shear stress is a function of both the shear rate and the time (time dependency) when subjected to shearing forces [10]. CMC solution of 0.5% showed a thixotropic shear thinning behavior, but CMC in the solutions (with lower concentrations) and in the emulsions showed non-thixothropic behavior (time-independent behavior). It seems that CMC containing formulations exhibit a time-independent behavior. This result was well in accordance with batter cake containing xanthan studied by Turabi et al [11].

*B. Emulsion Stability*

Fig. 4 shows the emulsion stability of O/W emulsions containing different concentrations of CMC. Addition of CMC was significantly effective in increasing the stability of emulsions. This stability was improved by increasing CMC concentration. In these samples separation of the aqueous upper phase was much higher than that of the oil phase. Addition of CMC at low concentration of 0.05% didn't increase the stability of the formulated emulsion.

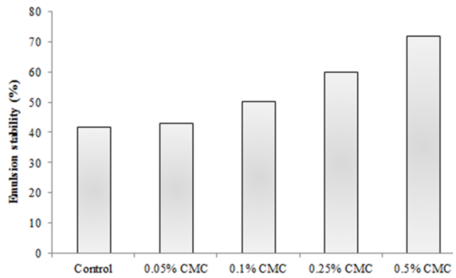

Fig. 4. The emulsion stability of emulsions containing different concentrations of CMC.

## IV. CONCLUSIONS

Viscosity was affected by addition of CMC and was increased with increasing CMC concentration in the solutions and emulsions. The stability of emulsions was improved with increasing CMC concentration. Solutions and emulsions containing CMC showed Newtonian behavior at low concentrations while shear-thinning behavior was observed at higher concentrations. Rheological behavior of CMC solutions and emulsions was well explained by both Power law and Casson model.

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