

# Rheological Characterization of Polyoxyethylene (POE) and Carboxymethyl Cellulose (CMC) Suspensions with Added Solids

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**Abstract** The rheological properties of high molecular weight POE and CMC suspensions by adding micro-metric solid particles such as fibers or spheres were studied. The volume fraction,  $\Phi$ , was varied between 0 and 0.4. Their rheological properties were obtained after fitting a Cross model. For POE suspending fluid with spherical particle, the behavior of the normalized steady shear viscosity,  $\mu/\mu_0$ , as function of the fraction volume followed a Thomas model. However, for CMC suspensions,  $\mu/\mu_0$  seems to be lineal with  $\Phi$ . For a pure fluid or a suspension with  $\Phi = 0$ ; 2, the suspension presented an elastic behavior whereas it was observed a viscous behavior when the volume fraction was increased.

## 1. Introduction

Suspensions are a class of complex fluids (and dispersed system) in which a finely divided solid is dispersed uniformly in a liquid dispersion medium [1]. Suspensions of solid particles in polymeric fluids are present in many industrial applications, including: food engineering, pharmaceutical production, material engineering [1-4]. Knowledge of the rheological behavior of these viscoelastic fluids is fundamental to understand their processing behavior and relations between structure and property. Indeed, the addition of solid particles to polymeric fluids does not simply change the magnitude of the viscosity, it can modify strongly the rheological properties of the fluid. Rheological properties of polymeric fluids with solid particles are strongly related to chemical formulation, molecular weight and polymer concentration, solvent properties, volume fraction and particle geometry. Moreover, external variables such as temperature and pressure can also influenced the rheological behavior. Thus, understanding the relationship between the microstructure of the polymer solutions and their macroscopic properties is of fundamental importance.

Considerable attention in the literature is given to the rheology of suspensions of particles in Newtonian fluids. Due to their technological importance, most studies are focused on highly filled systems (typically, volume fractions greater than 10%), with polydisperse particles of irregular shapes. In contrast, even if the rheology of suspensions in non Newtonian media is, from a technological point of view, more important than its counterpart in Newtonian media, relatively few studies are conducted on the rheology of dilute or semi-dilute suspensions of solid particles in no-newtonian fluids. If both theoretical and experimental studies for dilute and semi-dilute suspensions in Newtonian matrices are relatively scarce and somewhat contradictory, the situation is even worse for suspensions in viscoelastic fluids.

In engineering, pseudo-plasticity or shear-thinning fluids as Polyoxyethylene (POE) or Carboxymethyl cellulose (CMC) are the most common type of time-independent non-Newtonian fluid



[5]. These fluids are characterized by an apparent viscosity  $\eta$  (defined as shear stress  $\sigma$  / shear rate  $\dot{\gamma}$ ), which decreases with increasing shear rate. The rheological properties of polymer solutions are strongly related to the chemical formulation, the molecular weight and the concentration of the polymer and external variables such as temperature and pressure [6].

Polyoxyethylene (POE) is a polymer of ethylene oxide, flexible and non-ionic water-soluble used in many applications from industrial manufacturing to medicine [7]. The shear rheology of POE solutions has been characterized by several authors. Effects of concentrations, molecular weights, salt and anionic surfactants on the viscoelastic character of POE in aqueous solution were commented by [8]. Carboxymethyl cellulose (CMC) is derived from cellulose, it is used as a viscosity modifier or thickener, and to stabilize emulsions in various products including ice cream; it is known for its excellent water retaining capacity [7]. Moreover, this is the sodium salt of CMC ( $\text{CH}_2\text{COONa}$ ) that promotes water solubility, which is not affected by the temperature of the water itself. The rheological properties of CMC solutions at high concentrations have both non-Newtonian and viscoelastic properties. The aim of this article is to present the changes in apparent viscosity of high molecular weight POE and CMC suspensions by adding micro-metric solid particles such as fibers or spheres. Steady shear flow tests were done to measure the steady-state viscosity of the suspension. Linear oscillatory tests (upon verification of the linearity limit) were also performed to determine the viscoelastic frequency response.

## 2. Materials and methods

### 2.1. Suspending fluids

Two different types of suspending fluids were used. Poly(ethylene oxide) (POE) is used as shear-thinning fluid whereas sodium carboxymethyl cellulose (CMC) are, instead, used as viscoelastic carrier fluid. Both fluids have a density  $\rho = 1000 \text{ kg}\cdot\text{m}^{-3}$  at  $20^\circ \text{C}$ . POE and CMC were provided by Sigma-Aldrich. POE has a nominal molecular weight  $M_w$  of  $4 \times 10^6 \text{ g}\cdot\text{mol}^{-1}$  whereas CMC had  $M_w \approx 7 \times 10^5 \text{ g}\cdot\text{mol}^{-1}$  with a degree of substitution of 0.80 – 0.95. Aqueous solutions of POE and CMC were prepared by dissolving the appropriate amount of POE and CMC in distilled water at room temperature. Sufficient time ( $> 24\text{h}$ ) of continuous magnetic stirring was allowed to achieve complete homogenization. POE concentration varied from 1% to 1.5% w/w whereas CMC varied from 1.5% to 2.2% w/w.

### 2.2. Solid particles

Glass bead spheres (Sigmund Lindner, Germany) with a particle diameter of 0 - 50  $\mu\text{m}$  and 40 - 70  $\mu\text{m}$  and carbon fibers (Panex 35, Zoltek, USA) were used as solid suspensions. In Table 1, physical and geometry properties of the solid particles are presented. Solid particle concentrations varied

Table 1: Properties of solid particles

Particle	$\rho \text{ (kg}\cdot\text{m}^{-3})$	$l_p(\mu\text{m})$	$d_p(\mu\text{m})$	$r_p = l_p/d_p$
sphere (0 – 50 $\mu\text{m}$ )	2550			1
sphere (40 – 70 $\mu\text{m}$ )	2550			1
fiber	1810	100	7.2	13.88

between 0 and 40% for each range and geometry.

### 2.3. Preparation of the suspensions

Preparation of the suspensions was done with care as homogeneous dispersion of non agglomerated particles are difficult to obtain especially for low solid concentrations. The solid particles were dried to remove moisture. The polymer solution and solid particles were then weighted and gently stirred (to not introduce air) in a beaker for XXX minutes in the desired proportion. Optical observation

$$t_{\text{settling}} = \frac{0.45\mu_0 h}{R^2 g(\rho_p - \rho_f)} \quad (1)$$

confirmed that the particles were well dispersed and did not form aggregates. It was checked that in all cases the time scale associated with sedimentation was much larger than the time scale of both sample preparation and experiment. For a sphere, the settling time required to migrate 10% of the rheometer gap,  $h$ , under the influence of gravity,  $g$ , acting perpendicular to the gap is:

From the settling vertical velocity of the fiber:

$$V_z = \frac{d_p^2 g (\rho_p - \rho_l)}{16\mu} [2 \ln 2r_p - 1.614 - 0.355(\ln 2r_p)^{-1} + O(\ln 2r_p)^{-2}] \quad (2)$$

it was also able to calculate a settling time.

#### 2.4. Rheological measurements

All the rheological measurements were performed on a rheometer (Carri Med, CSL2 100, TA Instruments, England) using a 40 mm diameter parallel plate fixture with a gap  $h = 400 \mu\text{m}$ . The lower plate is equipped with a Peltier temperature control system; all tests were conducted at  $20^\circ\text{C}$  with 3 repetitions. The samples were carefully loaded to the measuring plate of the rheometer using a spatula and then the measuring plate was lowered at a very slow speed, in order to prevent the disruption of the solution structure. The flow curves were obtained by applying an increasing shear stress ramp at a constant stress rate of  $\text{XXPa}\cdot\text{s}^{-1}$ . Storage  $G'(\omega)$  and loss  $G''(\omega)$  moduli were measured at frequencies ranging from 0.01 to 20 Hz and, by applying a chosen stress value, allowing measurements within the linear viscoelastic region. Rheological behavior of the suspensions was modeled using the Cross model:

$$\frac{\mu - \mu_\infty}{\mu_0 - \mu_\infty} = \frac{1}{1 + (\lambda\dot{\gamma})^m} \quad (3)$$

where  $\mu$  is the dynamic viscosity at any given shear rate  $\dot{\gamma}$ ,  $\mu_0$ , and  $\mu_\infty$  are the asymptotic values of viscosity at zero-shear rate and infinity shear rate, respectively.  $\lambda$  is a time constant with the dimensions of time and  $m$  is a dimensionless rate constant indicating the degree of dependence of the viscosity on shear rate in the shear-thinning region. This model was chosen because it can describe both monotonic and non-monotonic flow curves.

### 3. Results and discussion

For four suspending fluids, the viscosity as function of the shear rate is presented in Figure 1. Their rheological properties obtained after fitting the Eq. 3 are reported in Table 2. All pure solutions are shear-thinning since  $m > 1$ ; however, when the polymer concentration increase  $m$  was close to 1. For POE and CMC polymers, the viscous interactions between polymers chains are higher when the concentration increase since the viscosity at zero shear rate and infinity shear rate increase. When the concentration was fixed to 1.5%, the viscosity at zero shear rate of CMC is higher than POE. The time constant,  $\lambda$ , also increases with the polymer concentration therefore the entanglement-disentanglement process with shear rate is longer.

In Figure 2 and 3, the normalized steady shear viscosity as function of volume fraction is presented for POE and CMC solutions. As it is generally observed, the additive of solid particles increased the viscosity over those of the pure polymeric solutions. Moreover, it is possible to express the normalized viscosity in terms of third order polynomials in the volume fraction. Indeed, for volume fraction slightly higher than 30%, for Newtonian fluid with

Table 2: Cross model constants of pure suspending solutions

Fluid	$\mu_\infty$ (Pa.s)	$\mu_0$ (Pa.s)	$\lambda$ (s)	$m$
POE 1%	0.04	1.49	0.439	0.741
POE 1.5%	0.11	11.25	2.187	0.757
CMC 1.5%	0.24	14.25	0.318	0.773
CMC 2.2%	0.58	62.69	0.514	0.827

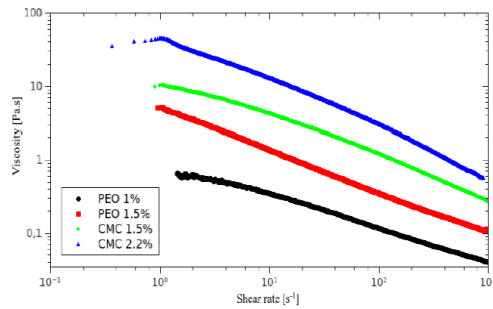


Figure 1: Viscosity as a function of shear rate of suspending fluids.

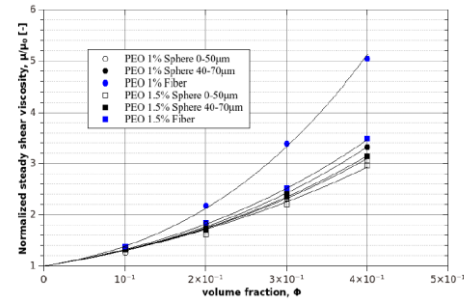


Figure 2: For PEO suspensions normalized steady shear viscosity as function of volume fraction.

spherical particles [9], considered a third term in the polynomial expansion that take into account hydrodynamic interactions of an arbitrary number of spherical spheres:

The polynomial fits of the experimental data are shown as solid lines in Figure 2 and 3. For POE

$$\frac{\mu}{\mu_0} = 1 + 2.5\Phi + 4.83\Phi^2 + 6.4\Phi^3 \quad (4)$$

solutions with particles (spheres or fibers), it can be noticed that the fit on the first order coefficient is quite robust and always in good agreement with Einstein's prediction since  $a_1 \approx 0.25$ . The maximum deviation from the theoretical value of 2.5 is 3%. The 2.5 value confirmed for non Newtonian suspensions by our results, as theoretical reported by [10]. When spherical particles were added to POE solutions, the coefficient  $a_2$  is close to 4.83 and the hydrodynamic interaction between particles was well described by the Thomas's model. However, as expected, in case of fiber particles, the model (Ec. 4) was not correct. The normalized steady shear viscosity as function of volume fraction seems to be linear. Four linear lines (guides to the eyes) are shown as dot lines in Figure 3. More experimental results are necessary to confirm these results but clearly the Thomas model was not correct to model the rheological behavior. In particular, it will be interesting to work with low concentration of solid particles. However, for CMC and POE suspensions, it can be observed that the addition of fibers in the suspending fluid allow to increase more the viscosity of the solution than the addition of the spherical particles.

Table 3: Fit values of the polynomial coefficients of  $\frac{\mu}{\mu_0} = 1 + a_1\Phi + a_2\Phi^2$ . Standard deviations are also shown.

Fluid	Suspensions	$a_1$	$a_2$	$a_3$
POE 1%	sphere (0 – 50 $\mu\text{m}$ )	$2.47 \pm 0.27$	$4.79 \pm 0.31$	$5.34 \pm 0.20$
	sphere (40 – 70 $\mu\text{m}$ )	$2.53 \pm 0.41$	$4.83 \pm 0.23$	$6.87 \pm 0.017$
	Fiber	$2.48 \pm 0.09$	$11.83 \pm 0.94$	$19.29 \pm 0.20$
POE 1.5%	sphere (0 – 50 $\mu\text{m}$ )	$2.49 \pm 0.17$	$4.90 \pm 0.31$	$2.32 \pm 0.01$
	sphere (40 – 70 $\mu\text{m}$ )	$2.51 \pm 0.14$	$4.82 \pm 0.72$	$5.84 \pm 0.74$
	Fiber	$2.53 \pm 0.12$	$6.37 \pm 0.58$	$6.64 \pm 1.03$

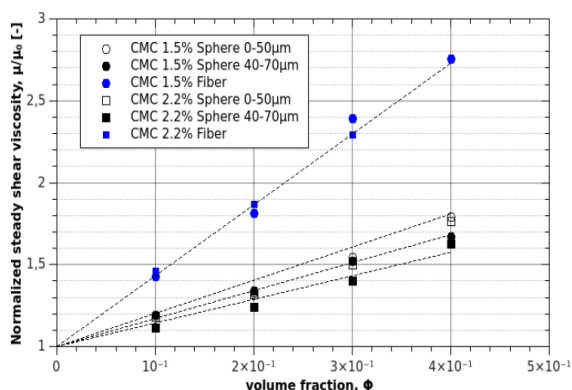
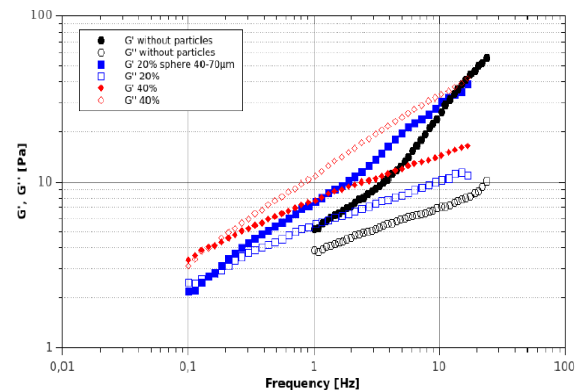


Figure 3: For CMC suspensions normalized steady shear viscosity as function of volume fraction.

Figure 4: For 1.5% of PEO, elastic modulus,  $G'$ , and loss modulus,  $G''$ , as function as function of volume fraction.

To observe and explain more the influence of the spherical particles concentrations on the rheological behavior, for POE at 1.5%, the linear viscoelastic response of the pure fluids and fluids with added solid particles are presented in Figure 4. The elastic modulus,  $G'$ , of the pure suspending fluid shows an erratic behavior at frequencies lower than 1 Hz; in particular, values for  $G'$  were negative, indicating that the elastic modulus was non measurable, within the sensitivity limits of the rheometer. For a pure fluid or a suspension with  $\Phi = 0.2$ ,  $G''$  was smaller than  $G'$  indicating an elastic behavior. However, when the volume fraction was increased it was observed a viscous behavior since  $G'' > G'$ . It would be very interesting to study the transition between both behaviors. This phenomenon was also observed for POE at 1% is (results not show).

#### 4. Conclusion

As it is generally observed, the addition of solid particles increased the viscosity over those of the pure polymeric solutions. The increase of viscosity was more notorious when using fiber. For POE suspending fluid with spherical particles, the behavior of the normalized steady shear viscosity,  $\mu/\mu_0$ , as function of the fraction volume followed a Thomas model. These results are consistent with those reported theoretically by [10]. For CMC suspensions,  $\mu/\mu_0$  seems to be lineal with  $\Phi$ . However, more experimental are necessary especially for low volume fraction. For a pure fluid or a suspension with  $\Phi = 0.2$ ,  $G'' < G'$  whereas  $G'' > G'$  when the volume fraction was increased.

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