

<b>COMPORTEMENT VISCOELASTIQUE D' EMULSIONS EAU DANS HUILE AVEC POLYMERE</b>			
<b>VISCOELASTIC BEHAVIOR OF POLYMER-THICKENED WATER-IN-OIL EMULSIONS</b>			
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### RÉSUMÉ

Le comportement viscoélastique des émulsions d'eau dispersées dans une huile et stabilisées avec un surfactant anionique (SPAN 80, 5 % mass.) a été déterminé à partir de mesures en cisaillement régulier et en mode oscillatoire sinusoïdal. Pour chaque concentration d'eau, des émulsions avec et sans polyisobutylène (PIB,  $M_w = 2.1 \pm 0.2 \times 10^6$  Da) ajouté dans l'huile jusqu'au recouvrement (0,5 % mass.), ont été testées. La distribution en taille des gouttes dans les émulsions a été déterminée par RMN. La viscosité augmente de façon notable avec la concentration d'eau, et augmente mais moins significativement en présence du polymère.  $G'$ ,  $G''$  et les autres propriétés viscoélastiques sont dictées par la quantité de la phase dispersée et non par la concentration de PIB dans l'huile. De plus, les émulsions composées de 60 % mass. d'eau présentent des maxima locaux dans la viscosité de cisaillement régulier et dans le module d'atténuation. Ces maxima, qui n'ont pas été observés dans des émulsions plus diluées, semblent être liés à des phénomènes de floculation et à une transition de phase dans la configuration des gouttes d'une phase diluée vers une phase compressée.

### ABSTRACT

The viscoelastic behavior of emulsions of water dispersed in a lubricant oil base and stabilized with a nonionic surfactant (SPAN 80, 5 wt.%) was determined in steady shear and sinusoidal oscillatory tests. For each water concentration, emulsions with and without polyisobutylene (PIB,  $M_w = 2.1 \pm 0.2 \times 10^6$  Da) added to the oil phase at its overlap concentration (0.5 wt. %) were tested, and the distribution of drop sizes of each emulsion was determined via nuclear magnetic resonance. It was found that the steady shear viscosity increased noticeably with the water content, and to a significantly less extent with the presence of polymer. Similarly,  $G'$ ,  $G''$  and other related viscoelastic properties were dictated mainly by the dispersed phase content, and not by the PIB present in the oil. Also, emulsions with water content of 60 wt.% exhibited local maxima in shear viscosity and loss modulus. These maxima, which were not observed in more diluted emulsions, seem to be related to flocculation and to a structural transition in the configuration of drops from diluted to compressed.

**Mots clés 5 maximum :** Emulsions avec polymère , émulsions eau dans huile , PIB  
**Key words maximum 5 :** Polymer-thickened emulsions, water-in-oil emulsions, PIB

# VISCOELASTIC BEHAVIOR OF POLYMER-THICKENED WATER-IN-OIL EMULSIONS

## 1. INTRODUCTION

Experimental studies on the viscous and elastic properties of emulsions are commonly referred to dispersions of oil in water (o/w) (1, 2). The case in which polymers are added to the aqueous phase has also been considered (3). Viscosity data are scarce for polymer-thickened water-in-oil dispersions (4), and probably nothing has been said about the elastic properties of such emulsions. Rheological properties of w/o dispersions containing macromolecules in the oil phase are relevant, for example, to oilfield (water-in-crude-oil) emulsions, which usually contain high-molecular-weight aggregates dissolved in the crude.

This paper reports experimental results on the viscoelastic behavior of model emulsions of water dispersed in an oil-based polymer solution, and made at several water/oil compositions. Polymer-free emulsions formulated at such compositions were also characterized to assess the relative importance of water content and presence of polymer on emulsion properties. It was found that macromolecules present in the continuous phase at the overlap concentration significantly affected the rheological properties of diluted emulsions, but not of emulsions with moderate-to-high dispersed phase content. In the latter case, the concentration of the dispersed phase was mainly responsible for the observed steady shear viscosity, and for the elastic properties of the dispersion. Data suggests that the structural transitions in the conformation of droplets that have been proposed for polymer-free emulsions as the dispersed phase content is increased (Figure 1) could also apply to polymer-thickened water-in-oil emulsions.

## 2. EXPERIMENTAL

Emulsions were stabilized with the nonionic surfactant SPAN 80 (sorbitan monooleate, Sigma), which has an average molecular weight of 428 Da. A non-commercial base for the formulation of lubricant oils (Exxon Chemicals) with density  $0.87 \text{ g/cm}^3$  was used as oil phase. Vistanex MML-140 (Exxon Chemicals), a polyisobutylene (PIB) with reported molecular weight of  $(2.11 \pm 0.23) \times 10^6 \text{ Da}$ , was previously dissolved in the oil phase at the overlap concentration (0.5 wt.%, see below) in some cases. Bi-distilled water was used as aqueous phase.

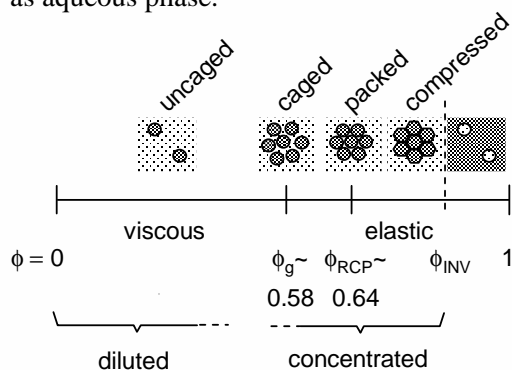


Figure 1. Structural changes and rheological behavior of emulsions as a function of the dispersed phase content.  $\phi_g$ , transition to glassy structure;  $\phi_{RCP}$ , transition to random closest packing;  $\phi_{INV}$ , inversion (adapted from Ref. 5).

Emulsions were prepared according to the formulations listed in Table 1.  $50 \text{ cm}^3$  of surfactant/oil/water mixtures were emulsified by ultrasonication during 5 minutes, followed by agitation with a two-blade paddle at 750 rpm for 10 minutes. Emulsions were placed in  $15 \text{ cm}^3$  capped test tubes and these in an orbital shaker rotating at 8 rpm to prevent sedimentation of water droplets. Experiments on emulsions were performed within the first four hours after emulsification to prevent changes in microstructure due to coalescence and Ostwald ripening.

Table 1. Formulations of emulsions characterized in this study

Emulsion	Water (wt.%)	Oil or polymer solution (wt.%)	Surfactant (wt.%)	Volume fraction of water ( $\phi$ )
10%, 10%+PIB	10	85	5	0.09
35%, 35%+PIB	35	60	5	0.32
60%, 60%+PIB	60	35	5	0.57
75%, 75%+PIB	75	20	5	0.72

Drop size distributions were determined with a 2.2-MHz NMR spectrometer (Resonance), using a technique described in Ref. 6. Steady shear viscosity measurements and small-amplitude oscillatory shear tests were performed in an ARES rheometer (Rheometrics Scientific). A cone-and-plate geometry (plate diameter = 25 mm; cone angle = 0.04) was used to study polymer solutions, and a Couette geometry (cup diameter = 17 mm; bob diameter = 16.5 mm; bob length = 13 mm) was used for emulsion samples. Tests were carried out at 25 °C.

Solutions of PIB in oil were prepared at concentrations between 0.05 and 2.4 wt.% to determine the overlap concentration via steady shear viscosity measurements as explained below. Polymer was slowly added as small particles (~ 0.5 mm) to 100 cm<sup>3</sup> of oil. The mixtures were heated at 60°C and constantly agitated with a magnetic stirrer for at least 24 hours to ensure complete dissolution of the polymer.

### 3. RESULTS AND DISCUSSION

#### 3.1. Overlap concentration

Polymer-thickened emulsions were formulated at so-called overlap concentration ( $c^*$ ) to study the effect of non-entangled polymer on their rheological behavior. Such concentration was determined from zero-shear viscosity,  $\eta_0$ , of solutions of polymer in oil, corrected by the zero-shear viscosity of the pure oil,  $\eta_{0,oil}$ , as shown in Figure 2.

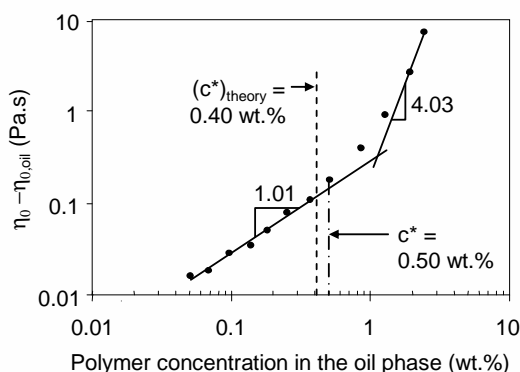


Figure 2. Effect of PIB concentration on the zero-shear viscosity of polymer solutions, and determination of the overlap concentration  $c^*$ .

Below the overlap concentration ( $c^* = 0.50$  wt.%),  $\eta_0 - \eta_{0,oil}$  grows linearly with the concentration of PIB, whereas above  $c^*$ ,  $\eta_0 - \eta_{0,oil}$  is proportional to the fourth power of concentration, which is typically observed in solutions of linear polymers (7). The overlap concentration can also be extracted from the low-concentration slope of the zero-shear viscosity vs. concentration curve (7). The overlap concentration so obtained was  $c^* = 0.40$  wt.%.

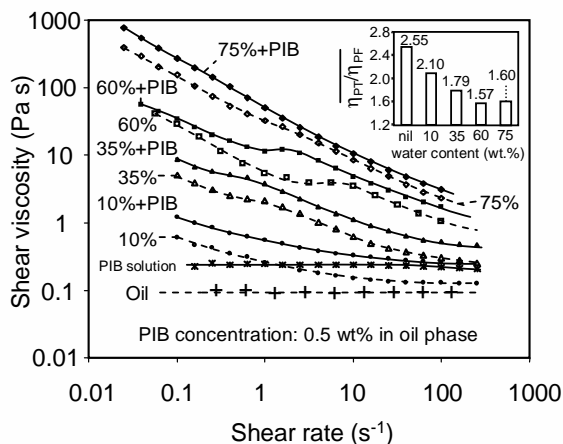


Figure 3. Shear viscosity measurements for emulsions with and without polymer added to the oil phase.

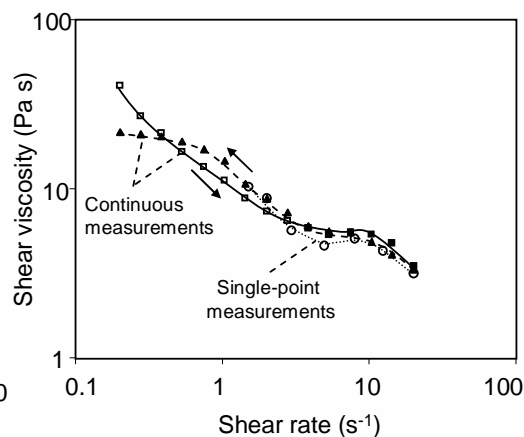


Figure 4. Characterization of the plateau in shear viscosity exhibited by polymer-free emulsions containing 60 wt.% water.

### 3.2. Drop size distributions

Emulsions exhibited drop size distributions that could be described well by a log-normal probability distribution function:

$$p(a) = \frac{1}{2a\sigma(2\pi)^{1/2}} \exp\left\{-\left[\frac{\ln(2a) - \ln(d_{gV})}{2\sigma^2}\right]^2\right\} \quad [1]$$

where  $a$  is the drop radius,  $d_{gV}$  is the geometric mean of the volume-weighted distribution and  $\sigma$  is a parameter associated to the width of the distribution. In all cases, values of  $d_{gV}$  between 11.5 and 17.0  $\mu\text{m}$  were obtained. Distributions were fairly narrow ( $\sigma \sim 0.1$  in all cases), and no trends related to water or polymer content were observed. Therefore, the microstructure of the emulsions was not expected to play a role in the differences in rheological behavior between emulsions that are discussed below.

### 3.3. Steady shear viscosity ( $\eta$ )

Figure 3 shows steady shear viscosity measurements for the pure oil, for the polymer solution at the overlap concentration and for the emulsions listed in Table 1, as a function of the shear rate ( $\dot{\gamma}$ ). The oil behaved as a Newtonian liquid with shear viscosity of 90 mPa.s. The viscosity of the polymer solution was  $\eta = 230$  mPa.s at low shear rates, and lowered when  $\dot{\gamma} > 100$  s<sup>-1</sup>. Emulsions displayed shear-thinning throughout the entire range of shear rates that were tested.

Figure 3 also shows that shear viscosity grew with water content and polymer content in the oil phase. The water content affects  $\eta$  because a higher amount of dispersed phase yields more droplets per unit volume of emulsion; at high concentrations these interact more strongly while flowing. The presence of polymer raises the viscosity of the continuous phase, and therefore of the emulsion.

Very importantly, the relative effect of PIB became less significant as the water content was increased. For example, the average value of the ratio of shear viscosities of polymer-thickened to polymer-free emulsions ( $\overline{\eta_{PT}/\eta_{PF}}$ ) diminished from 2.6 to 1.6 when the water content was increased from 0 to 75 wt.% (see inserted plot in Figure 3). In contrast, the shear viscosities of the polymer-free emulsion containing 75 wt.% of water were two to four orders of magnitude greater than those of the pure oil.



Table 2.- Maximum strain for linear viscoelastic behavior

Emulsion	Strain (%)	Emulsion	Strain (%)	Emulsion	Strain (%)	Emulsion	Strain (%)
10%	< 20	35%	< 8	60%	< 0.8	75%	< 0.2
10%+PIB	< 20	35%+PIB	< 9	60%+PIB	< 0.6	75%+PIB	< 0.4

Figure 3 shows also that emulsions containing 60 wt.% water ( $\phi = 0.57$ ) exhibited a plateau in shear viscosity at shear rates between 1 and 10  $s^{-1}$ . Figure 4 reports more detailed measurements for polymer-free emulsions at this water content, and shows that the occurrence of the plateau was independent of the previous history of the emulsion. Noticeably, at about this dispersed phase content a transition in the microstructure of the emulsion is expected (Figure 1). The formation of large aggregates in which droplets are locally caged by other droplets would be aided by the high concentration of nonionic surfactant present in the system via depletion flocculation and bridging (8). The existence of a plateau suggests that there is a critical shear rate that demarks the transition between different conformations of droplets.

### 3.4. Viscoelastic behavior

Table 2 reports the strain limit for linear viscoelastic behavior of the emulsions, as determined in small-strain oscillatory tests at constant frequency ( $\omega = 6.28 s^{-1}$ ). Below such limit, the storage,  $G'$ , and loss,  $G''$ , moduli were independent of strain. It is seen that the strain limit was strongly affected by the water content, whereas no trend related to the presence of polymer was observed.

Figure 5 shows the behavior of the phase angle [ $\delta = \tan^{-1}(G''/G')$ ] as a function of strain. A purely viscous fluid would exhibit  $\delta = \pi/2$ , whereas a purely elastic solid would show  $\delta = 0$  (9). Therefore, a transition from viscous to elastic was observed in the emulsions as the water content was increased. Again, data show little differences between the behavior of polymer-thickened and polymer-free emulsions.

Figure 6 shows the transition from linear to non-linear viscoelasticity in high-water-content emulsions as a function of shear stress  $\tau$ .  $G''$  was independent of  $\tau$  in the linear region. The transition between the linear and nonlinear domains was characterized by a maximum in the loss modulus. The stress at which this maximum is observed has been considered as a yield stress and is thought to be related to a transition in the structure of the emulsion (10, 11). The presence of polymer in the continuous phase did not affect significantly the observed behavior.

Figure 7 show (symbols) results from sinusoidal oscillatory experiments at variable frequency for polymer-free (left) and polymer-thickened (right) emulsions. Tests were performed at constant strains equal or below those listed in Table 2 to assure linear viscoelastic behavior. Results for polymer-free and polymer-thickened emulsions with water contents of 35, 60, and 75 wt. % were practically identical, and they are typical of those expected for concentrated monodisperse emulsions (1). At low frequencies, the trends in  $G'$  exhibited a plateau, whereas at high frequency a correlation of the type  $G'(\omega) \sim \omega^n$  was observed. A theory of collective slipping motion of clusters of particles predicts  $n = 1/2$  (1), which compares well with the results shown in Figure 7 ( $n \sim 0.35$ ). Also,  $G''$  shows a minimum that is indicative of slow relaxation of a glassy droplet structure (1). Again, conformational changes in the structure of these emulsions seem to dictate the viscoelastic behavior, which was influenced mainly by the dispersed phase content.

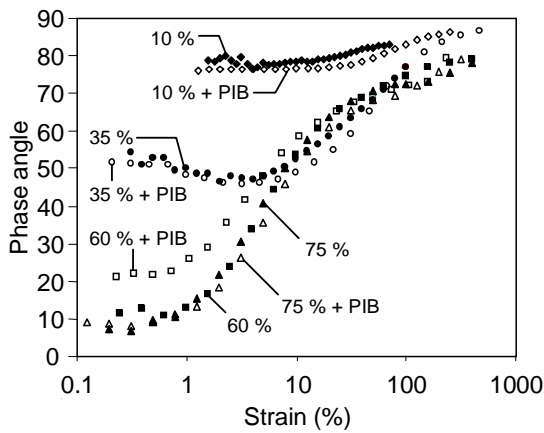


Figure 5.- Phase angle vs strain plots for emulsions with and without polymer added to the oil phase at the overlap concentration.

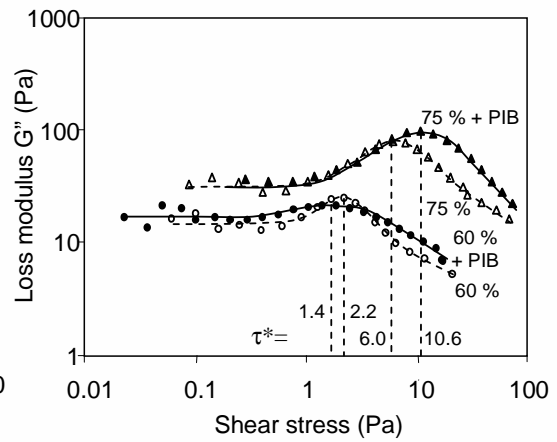


Figure 6.- Plots of loss modulus vs shear stress for concentrated polymer-thickened emulsions.

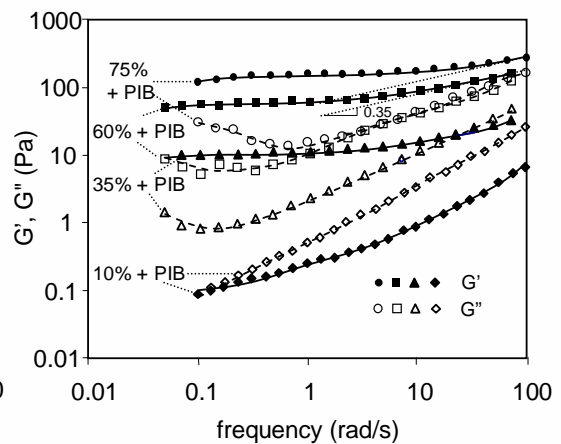
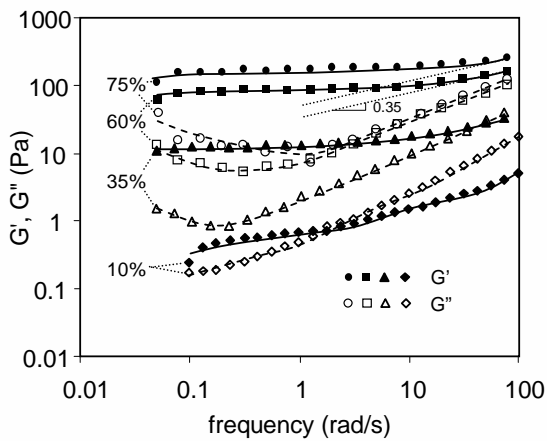


Figure 7.- Characterization of the storage ( $G'$ ) and loss ( $G''$ ) moduli for emulsions without (left) and with (right) polymer added to the oil phase at the overlap concentration.

The solid curves in Figure 7 are numerical fits of the experimental data with the linear viscoelastic model (9):

$$G(t) = \sum_k G_k e^{-t/\lambda_k} \quad \text{whence} \quad G'(\omega) = \sum_k G_k \frac{\omega^2 \lambda_k^2}{1 + \omega^2 \lambda_k^2}; \quad G''(\omega) = \sum_k G_k \frac{\omega \lambda_k}{1 + \omega^2 \lambda_k^2} \quad [2]$$

where  $G(t)$  is the shear relaxation modulus that results from the contribution of  $k$  moduli  $G_k$  with corresponding characteristic relaxation time  $\lambda_k$ .  $G_k$  and  $\lambda_k$  were determined with a least-squares procedure using  $k = 5$ .

Table 3 shows the longest characteristic relaxation time ( $\lambda_{MAX}$ ) for each emulsion. An analogous procedure was applied to data corresponding to a 0.5 wt.% PIB solution, whence  $\lambda_{MAX} = 0.11$  s was obtained with  $k = 3$ . These results clearly indicate that the elastic behavior of the emulsions was conferred mainly by the water content, and not by the presence of polymer in the continuous phase.



Table 3.- Longest relaxation time ( $\lambda_{MAX}$ ) for each of the emulsions characterized in this study

Emulsion	$\lambda_{MAX}$ (s)	Emulsion	$\lambda_{MAX}$ (s)	Emulsion	$\lambda_{MAX}$ (s)	Emulsion	$\lambda_{MAX}$ (s)
10%	90	35%	180	60%	274	75%	409
10%+PIB	99	35%+PIB	196	60%+PIB	269	75%+PIB	435

#### 4. CONCLUSIONS

The viscoelastic behavior of water-in-oil emulsions in which the oil phase is a solution of a linear polymer (PIB) at its overlap concentration was influenced by the dispersed phase content and by the presence of the polymer in the continuous phase. The effect of the polymer was more significant for emulsions with low internal phase content. Rheological properties (steady shear viscosity, maximum strain for linear viscoelastic behavior, storage,  $G'$ , and loss,  $G''$ , moduli and associated parameters such as phase angle and characteristic relaxation times) were dictated mainly by the dispersed phase content and not by the presence of polymer in moderately and highly concentrated emulsions. Results suggest that at a dispersed phase content of ca. 0.57 vol.%, the emulsion undergoes a transition in the structural arrangement of droplets, in support of recent views (5, 10, 11).

#### 5. ACKNOWLEDGEMENTS

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