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# Rheological and dielectric behavior of electrorheological emulsions

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## Abstract

The rheological and dielectric behavior of electrorheological (ER) emulsions composed of silicone oil (continuous phase) and two chlorinated paraffins (dispersed phase) are studied in this work. The chlorinated paraffins have different permittivity and conductivity values, and both are more conducting than the silicone oil. The rheological behavior of the emulsions is analyzed under constant dc electric fields, for two chlorinated paraffin concentrations. Results reveal that the magnitude of the ER response in the emulsions increases with the applied voltage but is affected negatively by the concentration of the chlorinated paraffin. The growth of viscosity in the presence of the electric field is less significant in the system with the largest conductivity at high electric fields. At low concentration, a Maxwell–Wagner polarization mechanism (interfacial polarization) is observed. A relationship between the dielectric and ER behavior is established, and also between the microstructural changes in the emulsions and their rheological and dielectric properties.
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## 1. Introduction

Electrorheological fluids (ERF) are very interesting materials for scientific research due to the drastic rheological changes (such as reversible increments in viscosity) occurring when they are influenced by external electric fields [1–3]. Their main applications are in dampers, shock absorbers, electrorheological (ER) valves and mechanical and electrical interfaces. Generally, the ERF are composed of polarizable particles suspended in an insulating medium. Novel fluids that have shown important electrorheological effects are immiscible polymer blends [4]. In general, these blends are composed of liquid crystalline polymers (LCP) suspended in polydimethylsiloxane (DMS), where the LCP are characterized by large values of viscosity, conductivity and permittivity [5]. Also, the ER effect has been reported in immiscible blends and emulsions based on silicone or castor oils and chlorinated paraffins [6,7]. These systems have been shown to serve as a basis to obtain formulations of ER suspensions with high ER response, as has been shown else-

where [8,9]. Although the ER response in emulsions is not as high as that observed in conventional ER suspensions (such as those used for applications in damping devices), they are homogeneous ER fluids since the dispersed phase is in the liquid state. However, the analysis and interpretation of the phenomena becomes more complicated due to the deformation, break-up and coalescence of the dispersed drops.

The polarizations that occur in an ER fluid induced by an external electric field are believed to play a crucial role in the ER effect. Among the polarization processes existing in dispersed systems, is the interfacial polarization (the Maxwell–Wagner polarization), the dominant process that contributes substantially to the ER effect. Materials having large dielectric loss could give a large interfacial polarization once they are dispersed into a liquid. This type of polarization mechanism together with the Debye polarization, appear at low frequency fields.

The objective of the present work is the analysis of the ER and dielectrical properties of two emulsions composed of silicone oil and two chlorinated paraffins with different permittivity and conductivity values. Particular attention is given to the relation between the dielectric and ER behavior to elucidate the type of polarization mechanism present in the ER response in emulsion systems.

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Table 1
Properties of the liquids

| Oil | Permittivity (at 10 Hz) | Conductivity (S/cm) | Viscosity (Pa s) |
|---|---|---|---|
| Silicone | 2.45 | $7.6 \times 10^{-15}$ | 0.95 |
| Paraffin S52 | 7.80 | $1.1 \times 10^{-11}$ | 1.70 |
| Paraffin PC40 | 6.80 | $7.4 \times 10^{-12}$ | 1.45 |

## 2. Experimental

The emulsions were prepared using silicone oil (GE) and two chlorinated paraffins (Paraclor S52 and PC40, Charlotte Chemicals Inc.) of different conductivity values at two concentrations (10 and 40 wt.%). Blend A was prepared with silicone oil and Paraclor S52, and blend B included silicone oil and Paraclor PC40. Properties of the blends are shown in the Table 1. The blends were prepared using an internal mixer (Cowles type) at 150000 Hz and at room temperature during 10 min. The rheological properties of the emulsions were measured using an ARES rheometer (Rheometric Scientific) with parallel plates (diameter 50 mm). The gap between two plates was set at 1 mm. The method used was steady shear-rate sweep. A Trek High Voltage Amplifier model 609E-6 was connected to these plates. The ER response was measured at 25 °C using various dc electric field strengths. Dielectric measurements were performed in a dielectric analyzer (Dupont DEA 2970). Experimental conditions covered a frequency range from 0.02 to 100 kHz, with 1 V amplitude using a single surface sensor. Micrographs of the structural arrangements of the emulsions for various electric fields were carried out using the set up reported elsewhere [10].

## 3. Results and discussion

Fig. 1a and b show the reduced viscosity (ratio of the viscosity of the blend to the viscosity of silicone oil) as a function of the shear rate for blend A at two concentrations (10 and 40 wt.%, respectively). In this case, the conductivity ratio ($\lambda$) of the dispersed phase and medium is close to 1500. The reduced viscosity decreases with the shear rate in both cases and approaches the viscosity of the silicone oil at high shear rates. This behavior has been observed in emulsions and was attributed to the increasing breaking of elongated liquid structures of the dispersed phase due to the flow. These structures were formed by coalescence of drops of the dispersed phase due to the applied electric field [6,7].

When the concentration of the dispersed phase increases to 40 wt.% (Fig. 1b), the reduced viscosity shows lower values than those observed at 10 wt.% in the low shear-rate region, and this effect is more accentuated at high electric fields. Same behavior is observed in blend B ($\lambda \approx 1000$) as the concentration of the dispersed phase is increased from 10 wt.% (Fig. 2a) to 40 wt.% (Fig. 2b). In fact, in Figs. 1b
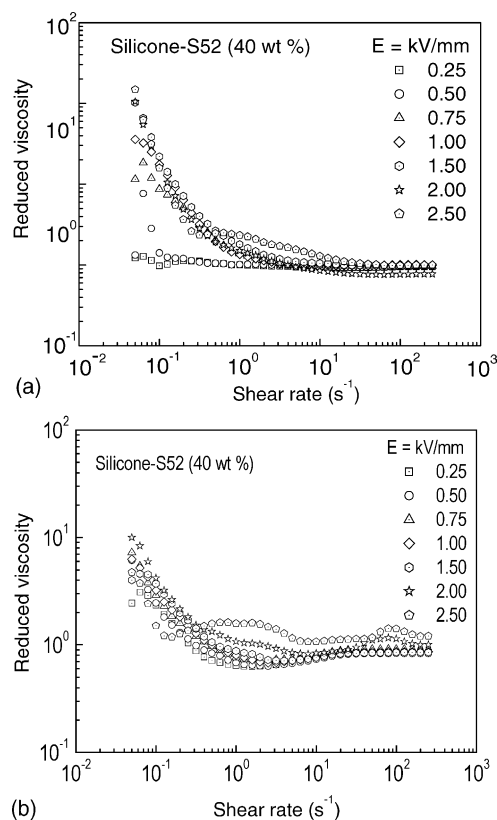


Fig. 1. Reduced viscosity, defined as the ratio of the shear viscosity of the emulsion to that of the silicone oil, vs. shear rate for blend A (silicone oil–paraffin S52). Concentration of the dispersed phase is: (a) 10 wt.%; (b) 40 wt.%.

and 2b, the flow curves display several peaks at high electric fields as the shear rate increases, suggesting some kind of instabilities in the flow. This observation together with the reduction in the reduced viscosity as the concentration of the dispersed phase is increased may be associated with electric field-induced rotations of the dispersed droplets (electro-hydrodynamic (EHD) motions). This behavior is also observed at the highest electric field in Fig. 1a, and it may be attributed to the combination of high conductivity of the emulsion and large electric field. It is noteworthy the apparent minimum in the reduced viscosity observed in Figs. 1b and 2b. This effect may be explained as a result of the kinetic process of rebuilding by the electric forces and the structure breaking due to the flow. The minimum in the viscosity is thus related with a dominant flow forces occurring at a critical shear rate. On the other hand, the ER effect observed in these emulsions is more substantial than that reported in similar immiscible blends [6] attributed to a large $\lambda$. When $\lambda$ decreases, the ER response shows a small reduction attributed to a decrease in the electrical polarization, which inhibits the coalescence of drops.

The yield stress ($\tau_y$) of ER suspensions increases with the field strength primarily due to an increase in dipole–dipole interaction between two particles [11]. Generally, $\tau_y$ varies as $E_0^\alpha$ ($E_0$ is the applied electric field), where $\alpha \approx 2$ for low
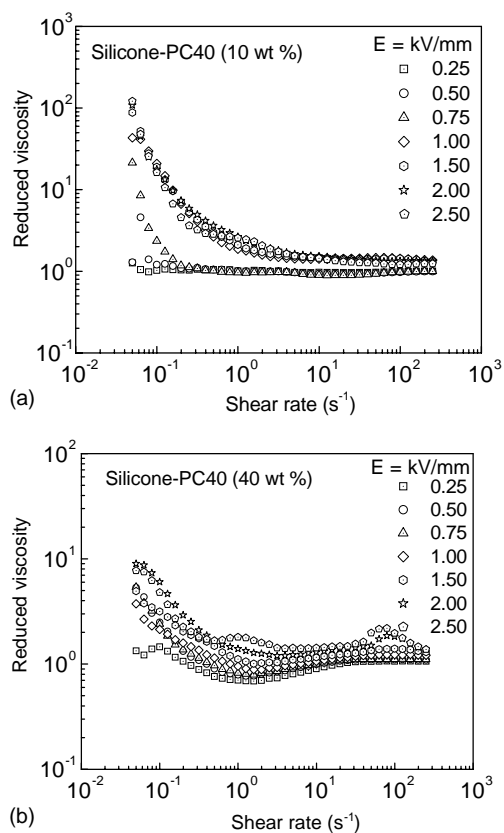
Fig. 2. Reduced viscosity vs. shear rate for blend B (silicone oil–paraffin PC40). Concentration of the dispersed phase is: (a) 10 wt.%; (b) 40 wt.%.
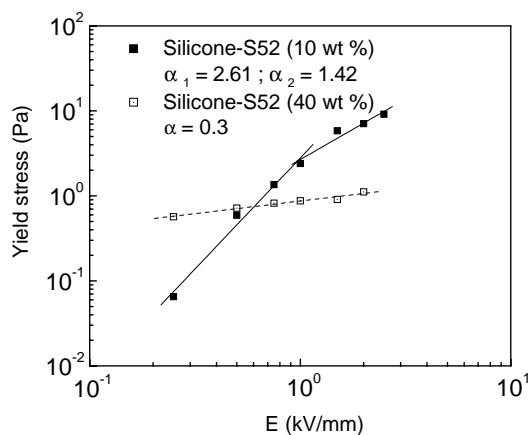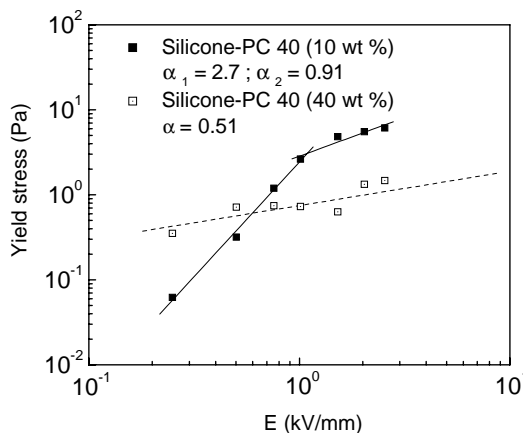


Fig. 4. Yield stress vs. electric field for blend B at 10 and 40 wt.% concentration of the dispersed phase.

and moderate electric fields. At large electric fields $\alpha$ may decrease below 2 [1,12]. For values of $\alpha > 2$, the structure formed by electrical polarization of particles, is cross-linked [13]. In the case of suspensions of solid particles, a $\alpha$-value smaller than 2 has been attributed to the formation of incomplete chains of particles due to electro-hydrodynamic instabilities [12].

In Figs. 3 and 4, the yield stress is plotted as a function of the electric field strength for emulsions A and B at two

concentrations. In the low concentration regime, the presence of a critical electric field ($E_c$) is apparent, where the slope of $\tau_y$ changes. The first zone at low electric fields has a $\alpha$-value near to 2.6. At high electric fields ($>1$ kV/mm), the $\alpha$-value depends on the conductivity of the dispersed phase.

When the concentration of the dispersed phase increases (40 wt.%), the absence of the critical electric field is apparent, and $\alpha$ shows values between 0.3 and 0.5. In this case, the yield stress approaches a constant value, close to saturation as the electric field increases. This very low value indicates the lack structure formation in the systems. The critical electric field ($E_c$) has been qualitatively related to dispersed phase properties and conductivity mismatch [14].

The dielectric properties largely determine the mechanism responsible for the ER response. Fig. 5 shows the behavior of the loss factor ($\varepsilon''$) as a function of frequency for systems A and B at 10 wt.%. A decrement in $\varepsilon''$ within the low-frequency region is followed by a maximum in the moderate frequency range. This behavior corresponds to a Maxwell–Wagner mechanism of interfacial polarization



Fig. 3. Yield stress vs. electric field for blend A at 10 and 40 wt.% concentration of the dispersed phase.
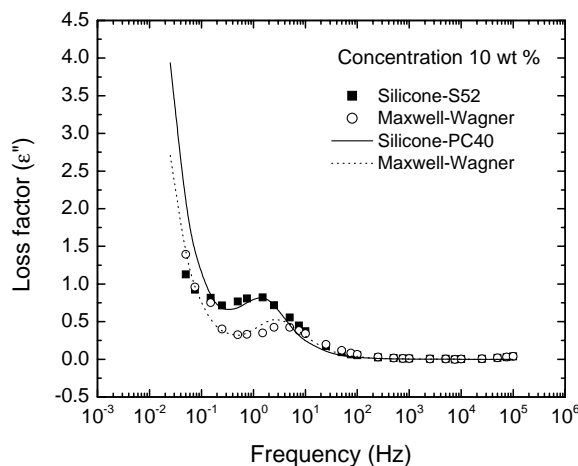


Fig. 5. Loss factor vs. frequency for blends A and B. Concentration of the dispersed phase is 10 wt.%.

[15]. This model is characterized by the following equations

$$\varepsilon' = \varepsilon_\infty \left[ 1 + \frac{K}{1 + \omega^2 \tau^2} \right] \tag{1}$$

$$\varepsilon'' = \varepsilon_\infty \left[ \frac{\tau}{\omega \tau_1 \tau_2} + \frac{K \omega \tau}{1 + \omega^2 \tau^2} \right] \tag{2}$$

where $\varepsilon'$ is the blend permittivity, $\varepsilon''$ the loss factor, $\omega$ the angular frequency ($2\pi f$) and $K$ the absorption factor defined in terms of the static and high frequency permittivities as $K = (\varepsilon_s - \varepsilon_\infty)/\varepsilon_\infty$. The characteristic times $\tau$, $\tau_1$, $\tau_2$ are the relaxation times of the blend (systems A and B), continuum phase (silicone) and dispersed phase (S52, PC40), respectively, and they are calculated using the following relations

$$\tau = \frac{1}{2\pi f_{\max}} \tag{3}$$

$$\tau_1 = R_1 C_1 \tag{4}$$

$$\tau_2 = R_2 C_2 \tag{5}$$

where $f_{\max}$ is the frequency of the maximum, and $R$ and $C$ the resistance and capacitance of the silicone oil (1) and paraffin (2). The values obtain are: for the system A, $\tau = 0.08\,\text{s}$ and for system B, $\tau = 0.06\,\text{s}$; $\tau_1 = 34.80\,\text{s}$, $\tau_{S52} = 0.03\,\text{s}$, $\tau_{PC40} = 0.02\,\text{s}$.

It is clear that interfacial polarization may result from a number of causes. It is possible that the contiguous dielectric layers (oil–paraffin) may, for example, differ only in conductivities but have equal permittivities. Alternatively, only the latter quantities may differ, or both the conductivities and permittivities may differ (as in this case). Furthermore, both conductivities and permittivities of the respective strata may be complex functions of the temperature, electric field, and frequency, with the result that the interfacial polarization losses may exhibit a very intricate behavior, since $K$ would then be a multivariable function. In Fig. 5, the experimental data at 10 wt.% dispersed phase concentration for blends A and B is modeled using Eqs. (2)–(5) and data from Table 1.

The absorption region resulting from the interfacial polarization (second term in the RHS of Eq. (2)) displays the maximum in $\varepsilon''$ and the conductive term (first term in the RHS. of Eq. (2)) gives rise to the increasing loss with decreasing frequency in the low-frequency regime. Thus, the dielectric behavior of the emulsions at low paraffin concentrations is in agreement with the Maxwell–Wagner model. In Fig. 5, the different magnitudes of the maximal in blends A and B reflect different values of the static dielectric constant of the
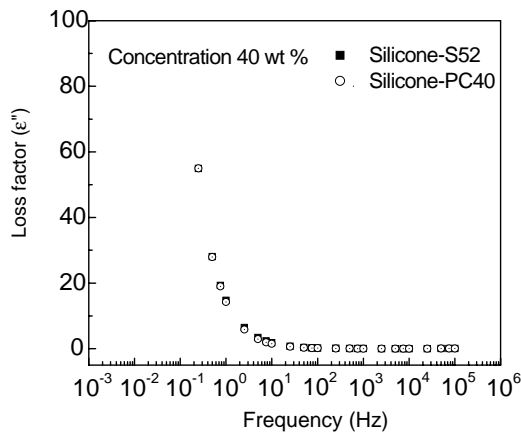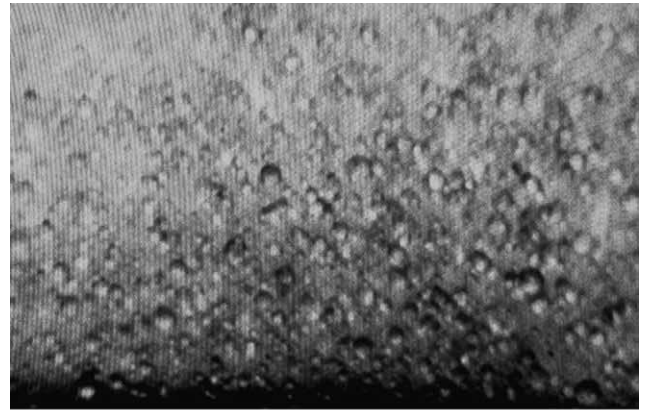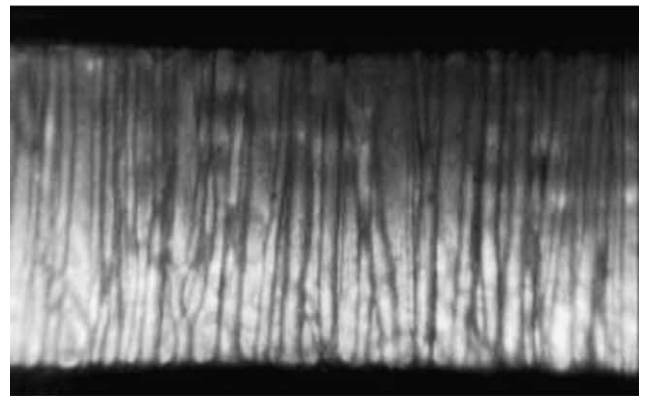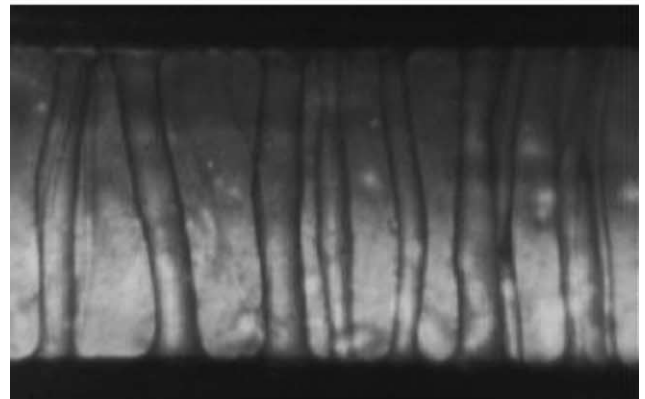
(a)

(b)

(c)

Fig. 6. Loss factor vs. frequency for blends A and B. Concentration of the dispersed phase is 40 wt.%.

Fig. 7. Micrographs showing the structure of blend A: (a) $E = 0\,\text{kV/mm}$; (b) $E = 1.0\,\text{kV/mm}$; (c) $E = 2.0\,\text{kV/mm}$.

dispersed phase. Furthermore, the maximum in blend A is shifted to lower frequency, indicating that the characteristic relaxation time of the absorption peak is larger, which implies a larger response time. These results are similar to those found by Hao et al. [16] in electrorheological suspensions.

When the concentration of the dispersed phase increases (40 wt.%) the relaxation process is not observed along the

frequency range of the experiments (Fig. 6). The increase in the loss factor as the frequency is lowered indicates a dominating conductivity contribution. Since the increase in concentration of the blends brings about a dominant conductivity behavior, the polarization of the dispersed phase is then inhibited and hence the structural arrangements in the blend are sufficiently weak to present a substantial resistance to the flow. This behavior clearly explains why the reduced viscosity decreases with the concentration of the dispersed phase increases in the low shear-rate region of the flow curve.

## 4. Structural properties

Microscopic observations were carried out under an external electric field (dc) in quiescent conditions. Figs. 7a and 8a show the structural arrangement of the drops for emulsions A and B (at 10 wt.% concentration), respectively. When the electric field is applied, the drops in the emulsion coalesce to form elongated structures that spanned the electrodes [6]. As soon as electric field is removed, the emulsion goes back to the initial state of well-dispersed droplets under flow.
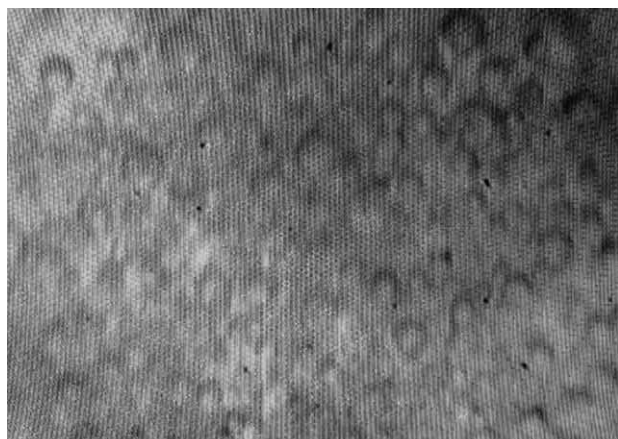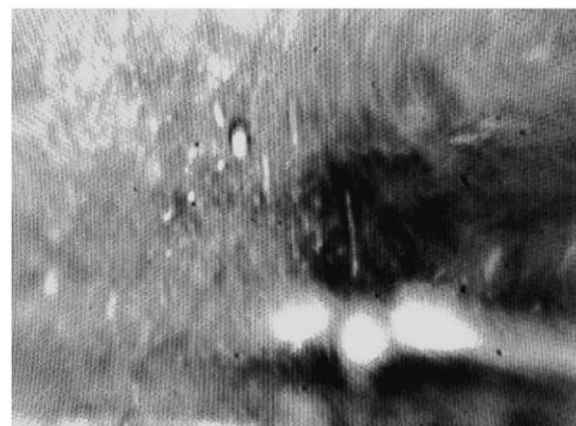


(a)
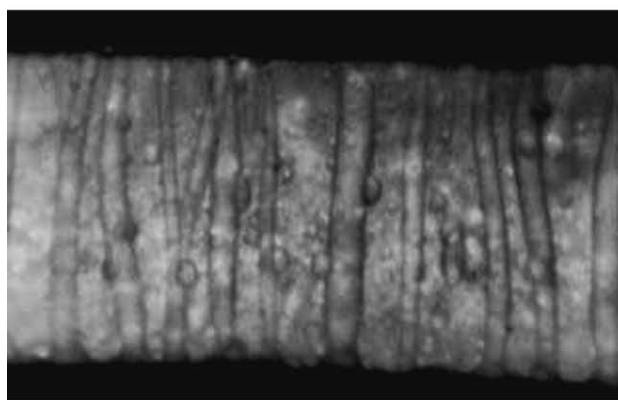


(b)
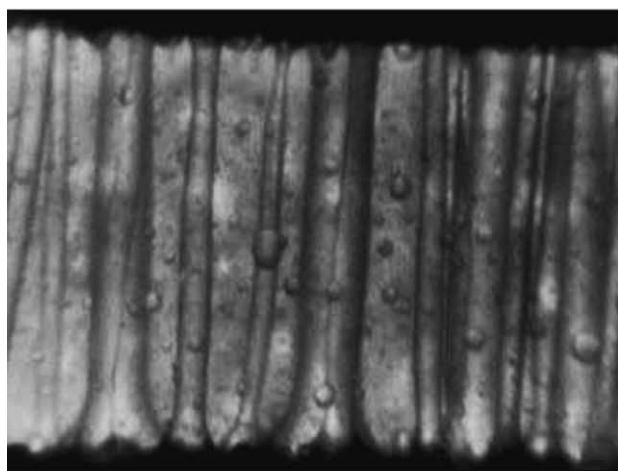


(c)

Fig. 8. Micrographs showing the structure of blend B: (a) $E = 0$ kV/mm; (b) $E = 1.0$ kV/mm; (c) $E = 2.0$ kV/mm.



(a)



(b)

Fig. 9. Micrographs showing the structure of blends A (a) and B (b). Concentration of the dispersed phase is 40 wt.%; $E = 1.5$ kV/mm.

Similar behavior is observed in both emulsion A (Fig. 7b) and B (Fig. 8b) at 1.0 kV/mm. For increasing electric fields (2.0 kV/mm) some fiber-like structures depict an angle of inclination (Fig. 7c). A dielectrophoretic effect resulting from a non-uniform distribution of the electric field around the structure is a possible reason for this behavior. However, in emulsion B this effect is not as apparent as in blend A. In this case, the higher conductivity of the dispersed phase in blend A may be the cause of the instabilities observed. When the concentration of the paraffin is increased, the elongated structures are not formed (see Fig. 9a and b for blends A and B, respectively). Incomplete elongated structures are only observed with fast motions similar to electro-hydrodynamic instabilities, which are the cause of the viscosity reduction with increasing dispersed phase concentration. Therefore, the conductivity ratio of the fluids is an important parameter that governs the shape and stability of the structures.

## 5. Conclusions

The rheological and dielectric properties of ER emulsions are influenced by the conductivity and concentration of the dispersed phase. The dielectric response of the systems examined in this work suggests the presence of a relaxation process occurring in the interfacial region of the drops. This process depends of the concentration of the dispersed phase. The Maxwell–Wagner polarization model is able to describe the dielectric properties of the blends when the dispersed phase concentration is low (10 wt.%).

The yield stress and reduced viscosity show a strong dependence on conductivity of the emulsion when the electric field is high (>1 kV/mm).

Microscopic observations suggest that the presence of polarizable drops promote the formation of elongated structures that represent a flow resistance, observed as increasing viscosity with the electric field strength. However, the increase in the dispersed phase concentration induces higher conductivity in the dispersed phase, which restricts the polarization of drops giving rise to a substantial reduction in the ER response.

The relation found between the dielectric and ER behavior presents direct evidence that the Maxwell–Wagner mechanism (interfacial polarization) dominates and also shed light on the ER mechanism in emulsions.

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