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Rheological behavior of electrorheological fluids: effect of the dielectric properties of liquid phase

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Abstract

Electrorheological (ER) fluids composed of non-colloidal silica gel particles of irregular shape and liquids with different dielectric properties are studied in this work. The rheological behavior of the suspensions is analyzed in the diluted and semiconcentrated regimes under different constant dc electric fields. Primarily, the dielectric properties of the suspensions are studied with particular attention to the dependence of the dielectric relaxation process on particle concentration and their relation with the conductive behavior. Rheological tests under applied electric fields elucidate the influence of the electric field strength and dielectric properties of the solid and liquid phases on the yield stress. It was found that the yield stress scales as $(\phi E^2)^{\alpha}$, where *E* is the electric field, ϕ is the particle volume concentration and α is a constant which depends on the spatial arrangement of the particles and dielectric properties of the suspensions. For high particle concentrations in liquids with high permittivity (or conductivity), the relative viscosity of the suspension in the presence of an electric field is lower than that observed in liquids with low permittivity, presumably due to an electrohydrodynamic (EHD) instability. © 2001 Published by Elsevier Science B.V. All rights reserved.

Keywords: Electrorheology; Dielectric relaxation; Impedance, conductivity; Electrohydrodynamic instability

1. Introduction

During the last decade, particular attention has been given to materials with strong response to an electric field, such as the so-called electrorheological (ER) fluids. These fluids are suspensions composed of polarizable particles dispersed in weakly conducting liquids. Rheological properties are dramatically altered when an electric field is applied, showing reversible liquid-to-solid transitions in time scales of the order of milliseconds. Generally, it is accepted that the origin of the ER response is due to the aggregation (fibrous structure) of the particles in the suspensions. The formation of these aggregates is ascribed to polarization of the materials due to the permittivity mismatch between suspending liquid and solid particle.

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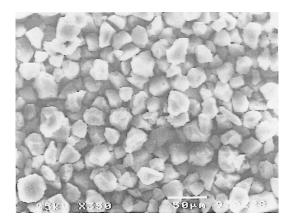


Fig. 1. SEM micrograph of silica particles (Merck 60, 0.015–0.040 mm).

However, in some situations this explanation is not complete, particularly in the case when arbitrary, low frequency ac or dc electric fields are applied to liquids with various particle and liquid conductivities. Several authors [1–3] have illustrated the role of conduction on the ER effect, and have pointed out that the formation of fibrous structures is only possible if the conductivity of solid phase (σ_p) is larger than the conductivity of the liquid phase (σ_L). On the other hand, when σ_p presents very high values, the ER effect may disappear [4], presumably because two particles coming into contact can exchange charges very quickly and separate.

Recently Otsubo, Y and K. Edamura [5] have shown that in flowing dilute suspensions under a constant external electric field, periodic structures may form in electrified suspensions. When a dielectric liquid is subjected to a strong electric field, a secondary motion of fluid may be produced by Coulombic forces acting on the free charges within the liquid, inducing electrohydrodynamic (EHD) instabilities. Nevertheless, there are interesting aspects that need further understanding, such as the influence of the dielectric behavior of the solid and liquid phases on the resulting ER response. Taking this into account, in this work a detailed description of the dielectric behavior of suspensions as a function of frequency is given, and this behavior is related to the resulting ER response for various dc electric field strengths. Particular attention is given to the influence of the permittivity and conductivity of the liquid phase, the particle concentration, and structural arrangement of the suspension on the resulting ER response.

2. Experimental procedure

2.1. Preparation of ERF's

The ERF employed in this study were prepared using suspensions of silica particles of irregular form (Merck 60, 0.015-0.040 mm) of approximately 22.1 µm in average size (Fig. 1) in silicon oil, dioctyl phthalate and tricresyl phosphate. Solid volume fraction were 0.03 and 0.16. The blend was prepared in a Cowles-type mixer during 10 min at 3000 rpm. Table 1 contains a summary of the corresponding viscosity and dielectric properties of the particles and fluids. The ERF was placed in a vacuum chamber to extract the air bubbles previously to dielectric and rheological measurements

2.2. Dielectric characterization

Dielectric measurements were performed in a Dupont (DEA 2970) dielectric analyzer. Experi-

Table 1					
Characteristics	of	solid	and	liquid	phases

Materials	Permittivity 60 Hz	Conductivity (S cm ⁻¹)	Viscosity (mPa s)
Silica (Merck 60, 0.015–0.040 mm)	10.9	2.0×10^{-9}	-
Silicon oil (S100)	2.40	6.8×10^{-16}	95
Dioctyl phatalate (DOP)	4.60	2.3×10^{-11}	50
Tricresyl phosphate (TCP)	6.10	1.4×10^{-9}	50

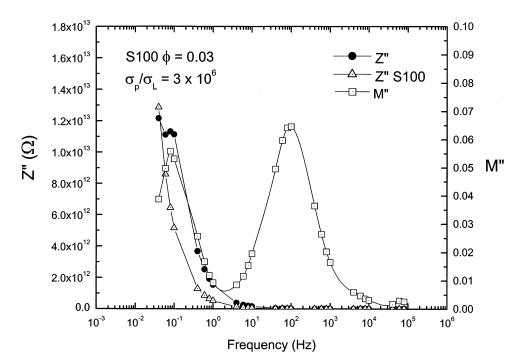


Fig. 2. Dielectric relaxation spectrum for dilute ER suspensions for S100 at $\phi = 0.03$, showing the spectrum of the pure silicon oil. The solid lines are aids to the eye.

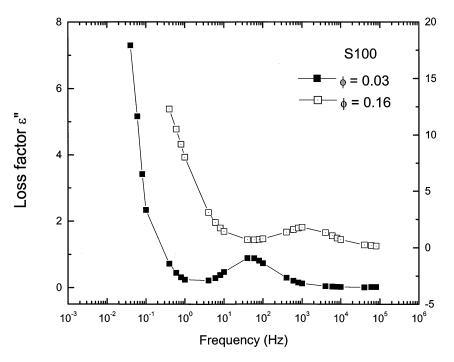


Fig. 3. Imaginary dielectric part of S100 for $\phi = 0.03$ and $\phi = 0.16$.

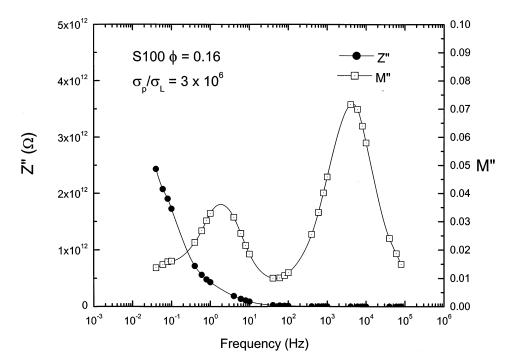


Fig. 4. Dielectric relaxation spectrum for semiconcentrated ER suspensions for S100, $\phi = 0.16$. The solid lines are aids to the eye.

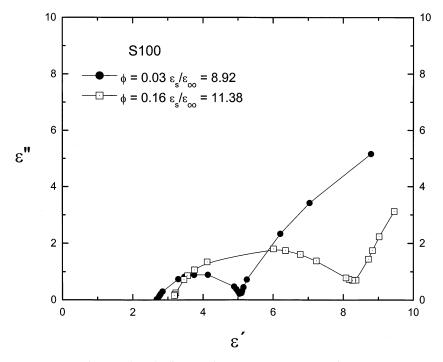


Fig. 5. Cole-Cole diagrams for S100 at two concentrations.

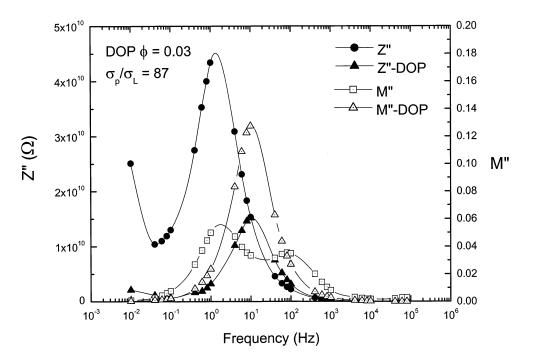


Fig. 6. Dielectric relaxation spectrum for dilute ER suspensions based in DOP at $\phi = 0.03$, showing the spectrum of the pure DOP. The solid lines are aids to the eye.

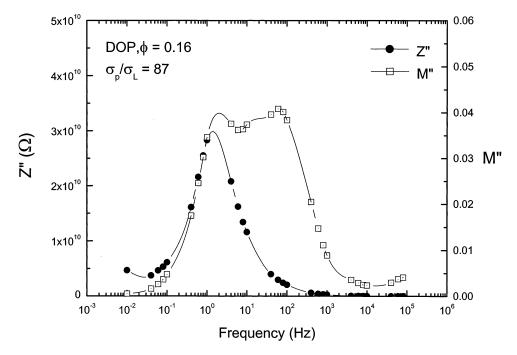


Fig. 7. Dielectric relaxation spectrum for dilute ER suspensions based in DOP at $\phi = 0.16$. The solid lines are aids to the eye.

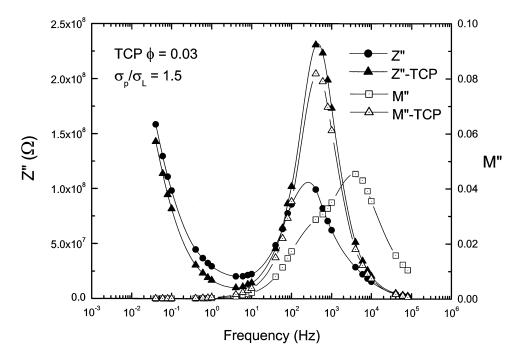


Fig. 8. Dielectric relaxation spectrum for dilute ER suspensions based in TCP at $\phi = 0.03$, showing the spectrum of the pure TCF. The solid lines are aids to the eye.

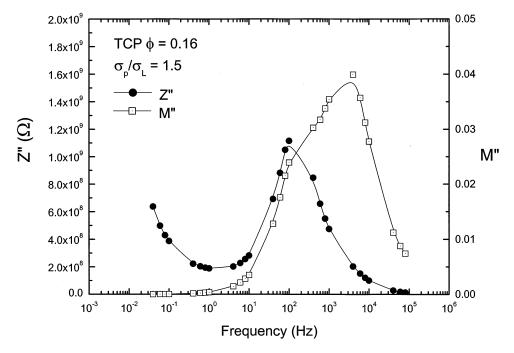


Fig. 9. Dielectric relaxation spectrum for dilute ER suspensions based in TCP at $\phi = 0.16$. The solid lines are aids to the eye.

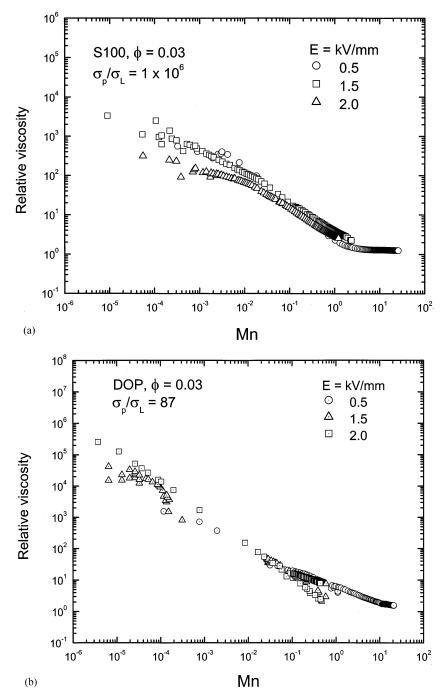


Fig. 10. Relative viscosity vs. Mn for ER suspensions with different liquid phase, (a) S100, (b) DOP and (c) TCP, for $\phi = 0.03$.

mental conditions covered a frequency range of 0.02–100 000 Hz, 1 V amplitude and at 30°C. The permittivity of the silica particle ε_p was

esti-mated from that of the suspension by a volume average calculation [6] given by the equation

 $\varepsilon = \varepsilon_{\rm p}\phi + (1-\phi)\varepsilon_{\rm L}$

where ε and ϕ are the permittivity and volume fraction of the suspension and $\varepsilon_{\rm L}$ is the permittivity of the fluid.

2.3. Rheological measurements

The rheological properties of the suspensions were evaluated in a Carri-med CLS 500 controlled stress rheometer, adapted with a polarizable cell. The measuring cell was a parallel plate geometry, with a diameter of 4 cm. In each test, the separation of the electrodes was fixed at 0.750 mm. Voltage (dc) was supplied by a Bertan high voltage power source (Model 205B-10R). Electric fields applied covered from 0.5 to 2 kV mm⁻¹. The temperature of test was 30°C. The yielding behavior shown by the suspensions is characteristic of a Bingham fluid. Following the usual procedure, field-dependent dynamic yield stresses were obtained either by extrapolating the curves at zero shear rates or by creep flow measurements.

2.4. Spatial arrangements observation

The sample cell and procedure used to observe

the change of the spatial arrangements of the silica particles at different intensities of the electric field reported previously [7].

3. Results

3.1. Dielectric properties

The dielectric spectrum reflects the collective response of microscopic polarization processes under an external electric field. The presence of any dielectric relaxation corresponds to one or more of the possible polarization mechanisms that occur in a microscopic scale.

In Fig. 2, the impedance (Z'') and the modulus spectra (M'') for conducting silica particles in the non-conducting silicon oil are shown. Suspension concentration corresponds to a dilute regime ($\phi = 0.03$). The impedance of the suspension follows closely that of pure silicon oil (also shown in Fig. 2), which means that particle contribution to the overall resistance is negligible at this concentration. According to data shown in Table 1, the resistance (inverse conductivity) of the silicon oil is 1.4×10^{15}

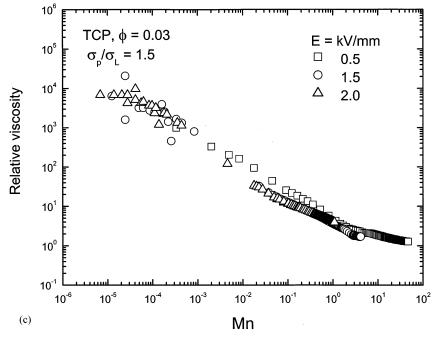


Fig. 10. (Continued)

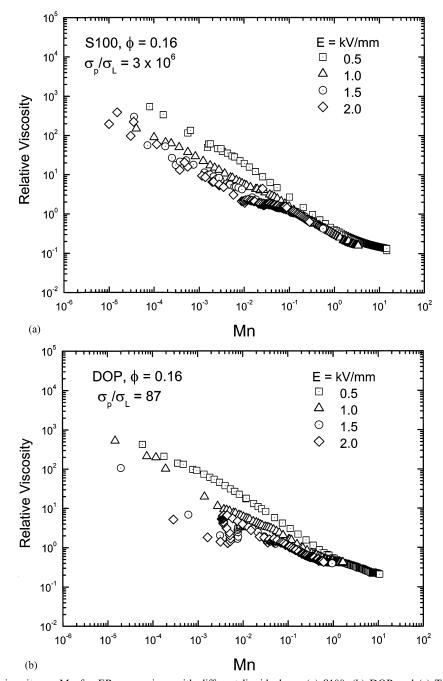
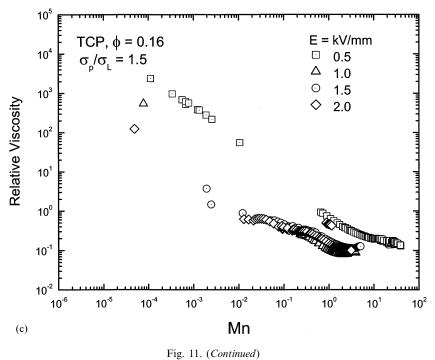


Fig. 11. Relative viscosity vs. Mn for ER suspensions with different liquid phase, (a) S100, (b) DOP and (c) TCP, for $\phi = 0.16$.

 Ω cm, and the frequency of the maximum may be given by:

where ε_{o} is the permittivity of free space. This gives, with data of Table 1, $f_{max} = 0.0005$ Hz. Thus, it is clear that the Z" spectrum describes a large peak located at very low frequencies, and indeed dominates the particle resistance.

$$f_{\max} = \frac{\sigma}{2\pi\varepsilon_o\varepsilon}$$





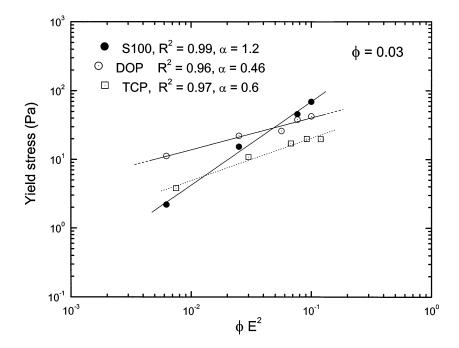


Fig. 12. Yield stress as a function of ϕE^2 for suspensions with $\phi = 0.03$.

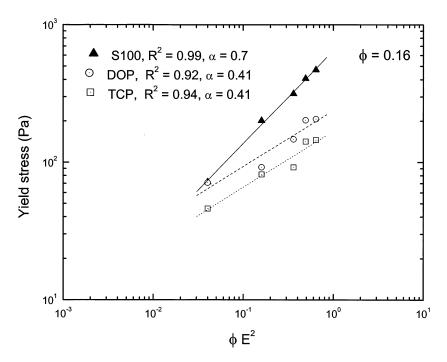


Fig. 13. Yield stress as a function of ϕE^2 for suspensions with $\phi = 0.16$.

The M" spectrum of the dilute suspension, also shown in Fig. 2, describes two peaks, the one at low frequencies is located at around 0.08 Hz with magnitude of 0.056 and the high frequency peak is located at 100 Hz with magnitude of 0.065. The M" spectrum of silicon oil corresponds to a peak located at the same frequency of the impedance peak (0.0005 Hz), with a maximum of 0.21, as calculated from the asymptotic value of M' at high frequencies (not shown). Upon addition of particles, the decrease in magnitude of the M" peak of the liquid from 0.21 to 0.056 means that the permittivity of the system has grown 4-fold due to the presence of the particles.

A very interesting feature of the dilute suspension is the presence of a relaxation peak in the variation of the dielectric loss (ε'') versus frequency shown in Fig. 3. Its magnitude is 0.88 located at around 40–60 Hz, of the same order of the high-frequency modulus peak. In a Debye-type relaxation, the permittivity and modulus relaxation times are related by the following equation:

$$\tau_{M''} = \left(\frac{\varepsilon_{\infty}}{\varepsilon_{\rm s}}\right) \tau_{\varepsilon'}$$

where $\tau_{M''}$ and $\tau_{\varepsilon''}$ are the inverse peak frequencies of the M'' and ε'' spectrum and $(\varepsilon_{\infty}/\varepsilon_s)$ is the relaxation ratio (dielectric constants at infinite and zero frequency). Similar peak frequencies imply a relaxation ratio close to unity. In a Debye process, the particles act as independent polarizable entities with localized oscillation in an inert (non-conducting) material. However, in the low frequency range, the imaginary part of the complex permittivity increases as the frequency is decreased, following a conductivity-type response. Usually, the conductive part of ε'' is modeled by the following expression:

$$\varepsilon'' = \frac{\varepsilon_s}{(\tau_{\varepsilon''}\omega)}$$

corresponding to an ionic conductor. In the modulus representation, this conductive region appears as a low frequency peak, as shown in Fig. 2. Notice that this peak is located at a frequency of 0.08 Hz, which is the same frequency of the largest increase in ε'' shown in Fig. 3. At higher particle concentration (0.16), the relaxation peak shifted to higher frequency (~1000 Hz) and its magnitude has grown 2-fold, as compared with the peak at low particle concentration. As in the dilute solution, the conductive part is also apparent at frequencies below 0.1 Hz, i.e. an increasing ε'' with decreasing frequency is observed. In the modulus representation, the relaxation peak in Fig. 3 corresponds to the peak shifted to higher frequencies (~4000 Hz) shown in Fig. 4. Differences in the relaxation times corresponding to each peak are due to increasing relaxation ratio ($\varepsilon_{\infty}/\varepsilon_s$) with increasing concentration. The peak at low frequency in Fig. 4 corresponds to the conductivity part of the dielectric loss in Fig. 3. In addition, at high concentration ($\phi = 0.16$), Fig. 4 shows the rise of Z" at low frequencies, whose magnitude indicates that the impedance of the suspension in lower than that of the pure liquid.

The behavior of the dielectric loss with frequency presents two different manifestations, the bulk response (corresponding to the particle itself) located in the high frequency part of the spectrum, and the interfacial response, located at low frequencies. The interfacial response arises from the high difference in conductivity between the particle and the silicon oil. Interfacial polariza-

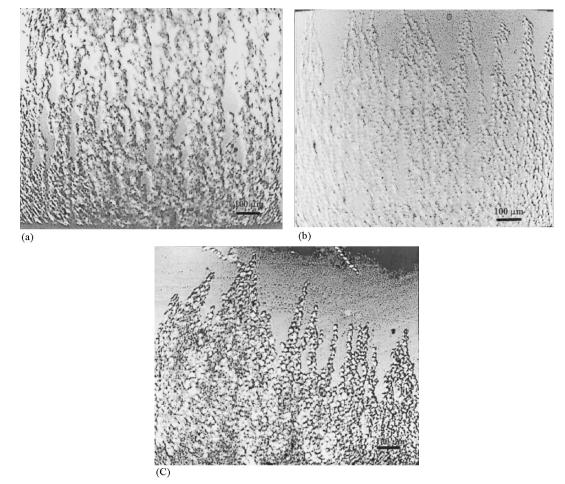


Fig. 14. Structural arrangement of ER suspension with different liquid phases, (a) S100, (b) DOP and (c) TCP, for $\phi = 0.03$ and an intensity of electric field of 0.5 kV mm⁻¹.

tion, the so-called Maxwell-Wagner polarization, may also depend on the presence of water residues that strongly affect the dielectric loss at low frequencies. The reason of this behavior lies on the space charge build-up due to either residues or wide differences in conductivity occurring at the particle-oil interface, which leads to field distortions and a dielectric loss that is similar in behavior to that arising with ionic or dipole relaxation phenomena. In dc or low frequency ac fields, mobile charges accumulating at the interface 'screen' the field within the particle and hence particle polarization is completely determined by conductivity. As will be mentioned later, this type of polarization mechanism strongly influences the viscosity behavior under a constant electric field.

The conductive part appears as a spike in the semicircle representation shown in Fig. 5 (ε'' vs. ε' plot). Notice that the semicircles shown in Fig. 5 are of the Cole–Cole type with a center located below the ε' axis, which indicates deviations from the pure Debye response.

To sum up, in the silicon oil/silica particle system, the Debye response is observed at high frequencies, in both permittivity or modulus representation (Figs. 2–4). Interfacial polarization leads to a conductive contribution to the dielectric loss spectrum at low frequency, manifested either by a rising in ε'' for decreasing frequency (Fig. 3) or as a peak in the low frequency region in M''(Figs. 2 and 4). In both representations the bulk relaxation contribution due to the particle shifts to larger frequency as the concentration increases.

In Figs. 6 and 7 results of the suspension with DOP are presented. In this case the liquid conductivity is about two decades smaller than the particle conductivity, and therefore, the continuum phase may not be considered as a dielectric medium itself. Qualitative differences to the system with silicon oil are observed in the impedance behavior. As in the silicon oil systems, interfacial polarization is present at both concentrations (0.03 and 0.16) and hence the low frequency peak in the modulus spectrum is due to interfacial effects and the high frequency peak corresponds to the bulk particle response. The impedance peak is located at the same frequency of the modulus peak assigned to the interfacial polarization and

the effect of increasing particle concentration is just to decrease the magnitude of the impedance peak. The behavior of the dielectric loss with frequency is purely conductive, since the relaxation region is almost absent. It should be remarked that in systems where both the impedance and modulus relaxation times are equal the conduction process is of the non-localized ideal type.

In systems where the fluid and particle conductivity are almost equal. as the silica particle/TCP systems shown in Figs. 8 and 9, characteristic responses are similar to the case of the DOP/silica systems, except for a few distinctive features. For example, the appearance of a dominant electrode contribution at the lower end of the frequency range (seen as spikes rising as frequency lowers) and the presence of the relaxation peak in M'' of the bulk particle contribution shifted to higher frequencies (4000 Hz). In addition, in this case the interfacial polarization peak for $\phi = 0.03$ is located at similar frequency than that of pure TCP (seen as a small shoulder in the M'' spectrum in Fig. 8) so that the splitting observed in the silicon oil and in DOP does not occur here. On the other hand, as in the DOP system, the modulus peak corresponding to the bulk particle response does not change in magnitude nor in position on the frequency axis as the particle concentration increases.

The spikes shown in the impedance spectra in Figs. 8 and 9 correspond to the high impedance due to the generation of charge carriers at the electrode-liquid interface, resulting from electrochemical reaction [8]. These effects are invisible in the modulus spectrum, since the electrode permittivity attains very high values. In the modulus spectrum, the height of each peak is proportional to inverse permittivity, and so information about electrode/suspension double layer will tend to be suppressed.

3.2. Rheological behavior

The origin of the ER response is attributed to the polarization of the dispersed particles relative to the continuous phase induced by the applied constant electric field. Upon application of the electric field, neighboring particles are attracted to each other and form fibrous structures perpendicular to the electrodes. The formation of these structures induce dramatic changes on the rheological behavior of the suspension, manifested as large increases in the shear viscosity which arise from the work required to overcome the attractive dipolar particle interactions [9,10]. The rheological properties of the suspension thus depend on the balance between the electric forces that tend to form the fibrous structures and the flow forces, which tend to deform and break such structures. For this reason, experimental results of the variation of the shear viscosity of the suspension with either the applied electric field or the shear rate are usually plotted in terms of the relative viscosity (ratio of the suspension viscosity at different electric fields to that of the Newtonian viscosity of the suspension in the absence of electric field) as a function of the Mason number (Mn). This characteristic number is defined as the ratio of viscous forces to electrical forces, in such a way that for low Mn, electric forces dominate and for high Mn, the viscous response dominates.

In Fig. 10(a-c) and Fig. 11(a-c) the relative viscosity is plotted with the Mason number for several values of the electric field, in the low concentration ($\phi = 0.03$) and high concentration $(\phi = 0.16)$ regimes, respectively. In all cases, the effect of the electric field vanishes when the Mason number is larger than one. The effect of the electric field increases as the Mason number decreases, although the viscosity attained in this region is not a simple function of the particle concentration or electric field. In most cases an increase in the electric field has the effect of diminishing the shear viscosity, with exception of Fig. 10(b and c), i.e. with DOP or TCP at low particle concentration. As a general observation, the increase in the particle concentration leads to a diminishing ER effect, and this is more accentuated at high electric fields Fig. 11(b and c). This latter observation is in agreement with other studies [3] in systems where the liquid and particle conductivities are similar or when the particle conductivity possesses very high values. The mechanism proposed to account for these observations considers that two particles coming in contact can exchange charges quickly and separate, preventing the formation of structured fibrils. Furthermore, high electric fields are known to induce motion of the fluid due to Coulombic forces exerted by the electric field on any charge present in the liquid. As mentioned above, the spikes shown in the impedance relaxation spectrum in TCP suggest the presence of charge carriers generated at the metallic-liquid interface (electrode-suspension interface). This process has been named ion injection, and has been associated to EHD instabilities [5,8]. Of course, this process is enhanced at high particle concentration, as shown in Fig. 11(c).

Results presented in Figs. 12 and 13 show the yield stress plotted against ϕE^2 for suspensions in the dilute ($\phi = 0.03$) and high concentration regimes ($\phi = 0.16$), respectively. In all the cases, the yield stresses scale as $(\phi E^2)^{\alpha}$, and the value of the exponent α is a function of the dielectric properties of the liquid phase. For low conductivity or low permittivity of the fluid, α has a value of 1.2 for low concentrations, but for high conductivities, representative values tend to 0.46 for DOP and 0.6 for TCP. On the other hand, in more concentrated regimes, for low conductivity of the liquid phase the value is 0.7. At high conductivity of the liquid phase, $\alpha = 0.41$ (DOP and TCP). Otsubo et al. [11], assign a value of $\alpha = 1$ to linear structures and $\alpha > 1$ to cross-linked structures. In our case, a value of $\alpha < 1$ indicates the formation of non-fibrous structure, representative of low yield stress values. This behavior is more accentuated at high field intensities and large concentrations.

The microstructure changes as functions of the dielectric properties of the liquid phase are illustrated in Fig. 14(a-c), for 0.5 kV mm⁻¹. High field levels induce fluid motions, and no photographs can be taken. For low conductivity of the liquid phase, fibrous structures are observed. As the conductivity increases, complete fibrous structures are not formed. In liquids with high conductivity in dc field, the charge generation by ion injection [8], is likely to be responsible of structural arrangements in DOP and TCP suspensions. The EHD instabilities produce fluid motions, which tend to break the fibrous structure formed by polarization of the particles. In our case, EHD instabilities are observed under high electric fields in the ERF suspensions with DOP and TCF, respectively.

4. Conclusions

Rheological properties and microstructure investigations of ERF fluids consisting of silica gel particles with irregular form and various fluids were determined. The following is a summary of the results obtained.

- The observed ER effect depends strongly on the ratio of conductivities of both phases when a dc electric field is induced. The suspension with the fluid of high conductivity shows a small ER effect. This effect is more evident when the concentration of solid and electric field increases.
- 2. The yield stress varies as $(\phi E^2)^{\alpha}$ for low concentrations and in the case where $\sigma_{\rm p} > \sigma_{\rm L}$, a value of α close to 1 is obtained, which supports the model of linear chains of single particle width. For $\sigma_{\rm p} \approx \sigma_{\rm L}$, α attains values between 0.46 and 0.6, indicating the presence of electrophoresis. At high concentration and when $\sigma_{\rm p} \approx \sigma_{\rm L}$, the exponent α decreases steeply to 0.4, indicating a substantial electrode contribution and interfacial polarization. Interfacial polarization is observed as the concentration increases, either as a conductive region in the ε'' at low frequencies or as a peak in the modulus spectrum at low frequencies. Consequently, the yield stress decreases. In the latter case, the observed ER behavior cannot be explained on the basis of the chain formation mechanism.
- 3. The impedance behavior of the suspension with high conductive fluid reveals the generation of charge carriers, at the metallic-liquid interface, known as ion injection. This mechanism is responsible of the EHD instabilities, which leads to a decrease in the relative viscosity and yield stresses.
- 4. The discontinuity shown in the variation of the relative viscosity with Mn number, in the systems with either DOP or TCP, may be attributed to the periodic distribution of parti-

cle concentration induced by the mentioned EHD instabilities.

Acknowledgements

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