Electrorheological properties of hematite/silicone oil suspensions under DC fields

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Abstract

Electrorheological (ER) fluids composed of \( \alpha-Fe_2O_3 \) (hematite) particles suspended in silicone oil are studied in this work. The rheological response has been characterized as a function of field strength, shear rate and volume fraction. Rheological tests under DC electric fields elucidated the influence of the electric field strength, \( E \), and volume fraction, \( \phi \), on the field-dependent yield stress, \( \tau_y \). It was found that this quantity scales with \( E \) and \( \phi \) with a linear and parabolic dependence, respectively. The viscosities of electrified suspensions were found to increase by several orders of magnitude as compared to the unelectrified suspension at low shear rates, although at high-shear rates hydrodynamic effects become dominant and no effects of the electric field on the viscosity are observed. The work is completed with the analysis of microscopic observations of the structure acquired by the ER fluid upon application of a constant electric field. Electrohydrodynamic convection is found to be the origin of the ER response rather than the commonly admitted particle fibrillation. This fact can provide an explanation to the relationship between yield stress and electric field strength as well as the pattern of periodic structures observed in the measurement geometries.

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1. Introduction

The increase in the viscosity of suspensions upon application of an electric field is commonly referred to as the electrorheological or Winslow effect [1], and such fluids have come to be known as electrorheological (ER) fluids. Most of them are made of a solid (highly conductive or polarizable particles) or liquid (liquid crystal material) phase dispersed in an insulating oil. Sometimes, they also contain small amounts of additives such as water and other polar compounds, to increase their response [2,3].

ER fluids constitute nowadays a very promising area of research and development because of their potential technological applications. These materials have been used as ideal mechanical-electrical interfaces (for transferring and controlling mechanical movement) because of their very fast response time [4–7] and their reversible rheological properties (high increment in viscosity and yield stress). Some ER-based devices include brakes, clutches, robotic controlling systems, human muscle simulators, . . .

It has long been known that rheological changes in ER fluids are associated with field-induced structures [1,8–10] of particles between the electrodes so that the enhancement of viscosity is due to the mechanical work required to break such structures in order to make the suspension flow. This explains that ER fluids shift from newtonian to Bingham fluids upon application of electric fields. The field-induced structures in the suspensions can accumulate elastic energy unless the applied strain exceeds some critical value [11,12], and hence ER fluids behave as solids at very low strains. When they flow at low shear rates, rupture and reformation of the field-induced structure are constantly occurring. This process generates a constant shear stress, which corresponds to the
Stress) are often found to vary as shear rate (Newtonian liquid behavior).

Not many ER devices have been commercialized because of a number of problems that must be solved: their yield stress is not high enough; they have a limited working temperature range; they present problems of suspension stability against sedimentation, and of malfunctions once contaminated, may provoke abrasion of pipes and containers, and others.

The limited understanding of the ER activity has also hindered the development of ER suspensions optimized for particular applications, although since the pioneering work of Widnall [1] in 1949, several mechanisms have been proposed as the origin of the ER response. These include degradation of the fibrous structure formed by polarization forces between particles [1,13,14], distortion and overlap of the electrical double layers of colloidal particles resulting in increased energy dissipation [15,16], and existance of water bridges between particles [17]. Many of these models are qualitative in nature and do not predict links between rheological behavior and the physical properties of the suspending medium and particles, such as permittivity and conductivity of both, shape and size of the particles, and viscosity of the medium.

Another interesting aspect that needs further understanding is the ER response for DC excitation. Elevated suspension conductivities result in prohibitive power requirements to achieve a useful enhancement in viscosity. As a result, many systems are optimized to minimize suspension conductivity, and consequently, the effects of mobile charge carriers are expected to be small. Under these conditions, particle interaction potentials are dominated by the conductivity mismatch between the solid and liquid phases and the interpretation of the rheological properties might be carried out in terms of the electrostatic polarization model [9,18–20]. This assumes that particles in an electric field will polarize (due to an interfacial or Maxwell-Wagner mechanism involving mobile charge carriers mostly present on the particles) and appear to leading order as electric dipoles. These dipoles attract head-to-tail in the direction of the electric field, forming the fibrous structures commonly observed.

However, experimental data cannot be always explained by the polarization model just described, particularly at high electric field strengths, where responses become non-linear. For example, electrostatic forces (as manifested by, e.g., yield stress) are often found to vary as $P^1 \times E^n$ where $n < 2$ in contrast to the $E^2$ dependence predicted by the polarization model [21,22]. One explanation for this phenomenon is non-linear conduction [23,24]: the electric field strength between closely spaced particles can be much larger than the nominal one. At such large field strengths, the fluid conductivity begins to increase with $E$ due to field-enhanced dissociation of solute in the fluid. This causes the field between the particles to increase more slowly with $E$, eventually saturating at large field strengths, and results in electrostatic forces and stresses scaling as $E^n$ where $n < 2$. However, the interpretation of non-linear conduction as a field-enhanced dissociation in the bulk liquid phase has come into question. Felici [25] argued that field-enhanced dissociation is likely limited and cannot account for the properties observed experimentally. Charge injection at the electrode/liquid or particle/liquid interfaces has been proposed as another plausible mechanism [26] which can explain the inter-particle interactions.

From this, it is clear that several kinds of phenomena may appear as ER response under DC fields. This paper tries to shed light on these facts. We examine the rheological behavior of iron oxide/silicone oil suspensions under DC excitation. The mechanisms accounting for the ER response will be elucidated considering yield stress and viscosity analyses, as well as direct structural observations.

2. Experimental

2.1. Materials

The iron oxide ($α$-Fe$_2$O$_3$ or hematite, density 5.24 g/cm$^3$) powder was purchased from Aldrich, USA, and was used as received. Fig. 1 is a SEM picture of the particles: they are irregular polyhedra, with an average size of $105 \pm 25$ nm. This was determined by fitting a log-normal distribution to the size determinations on about 200 particles on TEM micrographs. The conductivity of the particles is $\sigma_p = (2.6 \pm 0.2) \times 10^{-7}$ S/m [27] and their relative permittivity is $\varepsilon_r = 12$ [28]. In all cases, the continuous phase consisted of poly(dimethylsiloxane) or silicone oil with nominal viscosity $\eta_0 = 1$ Pa s, manufactured by General Electric (USA).

The conductivity of the oil is $\sigma_o = 10^{-14}$ S/m, and its relative electric permittivity is $\varepsilon_r = 2.6$ [29].

Fig. 1. SEM micrograph of iron(III) oxide particles used in the preparation of the ER suspensions. Bar length: 1 μm.
2.2. Methods

2.2.1. Preparation of the ER fluids
Different volume fractions (2, 4, 6, 8 and 10%) were prepared by blending of a stock sample with silicone oil in an internal mixer (Cowles type) at 2500 rpm and room temperature during 3 min. The ER suspensions were placed in a vacuum chamber to extract the air bubbles for 2 min previously to any measurements. After that time, the suspensions obtained were completely uniform and no additives appeared necessary.

2.2.2. Rheological measurements
Rheological properties were determined with a Rheometrics Ares 2KFRTN1 (USA) rheometer using a parallel plate geometry with a plate diameter of 50 mm and an electrode gap of 1 mm. The DC field applied was supplied by a GW GFG-89159 wave generator (USA), after rectification and 1000× amplification with a Trek High Voltage Amplifier 609E-6 (USA). The electric field strength ranged from 0.5 to 2.5 kV/mm.

All rheological tests were conducted at 25°C, and consisted of the following steps: (i) preshear the sample during 60 s at 100 s⁻¹ in order to set the same initial conditions in all experiments; (ii) let the sample equilibrate for 40 s, with the electric field applied, so that particle structures can eventually form; (iii) apply a shear rate sweep between 0.059 and 300 s⁻¹.

2.2.3. Structure observations
The type of sample cell used to observe the suspensions during application of different strengths of the electric field is shown schematically in Fig. 2. The electrodes were cooper foils, 100μm thick, glued on the glass plates. The electrode spacing was set for this work at a nominal 1 mm gap. The sample cell was placed on the stage of a Nikon SMZ2T stereoscopic microscope equipped with a video camera connected to an image acquisition card controlled by a software tailored for these experiments. The magnification used was 50-60×. The amount of ER fluid used to fill up the sample cell was of the order of 500μl, and the electric field strengths ranged from 0.5 to 2.5kV/mm, supplied by a HV Dipotonic (USA) power source.

3. Results and discussion

3.1. Electrorheological properties

3.1.1. Response time
Prior to rheological measurements, the response time, τR, of the suspensions was determined. This is the time that the suspension takes to go from a quiescent state to its final, field-induced structured state. In order to estimate τR, a step-rate test was performed: firstly, the ER fluid was sheared at 100 s⁻¹ for 60 s. This pre-shear step destroyed any previous structure of the suspensions, so that initial conditions were the same in all cases. After that time, an electric field strength of 0.5 kV/mm was instantaneously applied for 120 s while the viscosity was measured at a constant shear rate of 0.03 s⁻¹. At such small rate, one can consider that the structures induced by the field are evaluated in approximately quiescent suspensions.

Fig. 3 shows the transient response (shear viscosity, η, versus elapsed time), for suspensions of several volume fractions. Note that in the zero-field condition, a minimum flow resistance (a constant shear viscosity), due to dissipative loss from the solid phase, is experienced. When the external electric field is applied, the field-induced interactions cause particles to have an effective motion relative to the liquid phase. This increases the dissipative losses so that a dramatic enhancement in shear viscosity can be observed.

Let us note that all the suspensions tested required a relatively long time (of the order of several seconds) to reach a steady state after the electric field was applied. Although the time required for typical ER suspensions to respond to a step increase of electric fields is reported [4–7] to be of the order of 10⁻³ s, it is also found that a fully stable structure in a static suspension may be formed on a time scale of seconds, particularly at small shear rates when slow reaction times are often observed [30,31].

We will consider that τR is the time between the application of the field and the instant at which η reaches a maximum.

![Fig. 3. Response time test of iron oxide suspensions at different concentrations. The suspensions were subjected to shear rates γ = 100 s⁻¹ during 120 s, followed by γ = 0.03 s⁻¹ during 120 further s. After the first 120 s the 0.5 kV/mm was applied and kept during the second 120 s period. The field was switched off at t = 240 s.](image-url)
Results are shown in Fig. 4, where it is demonstrated that $\tau_R$ decreases with volume fraction, and a plateau is suggested at high particle concentration. A similar dependence between reaction time and volume fraction has been described by other authors [32,33].

According to these results, the longest response time is about 30 s for a volume fraction of 2% and 0.5 kV/mm field strength. Since $\tau_R$ decreases with volume fraction and electric field [10], a time of 40 s was considered long enough for structuring the suspensions and was set as equilibration time for shear rate sweeps in all cases.

3.1.2. ER response and field strength

Fig. 5 shows the apparent viscosity $\eta$ of hematite suspensions with 8% volume fraction as a function of shear rate for several field strengths. Similar plots for constant field (1.5 kV/mm) and several volume fractions are given in Fig. 6. Let us first of all note that when no field is applied the suspensions were approximately newtonian. Figs. 5 and 6 indicate that the samples are shear-thinning, and their viscosity decreases more rapidly with shear rate the higher the field strengths. On the other hand, the effect of the applied field is more pronounced at low shear rates, when hydrodynamic interactions are weaker. Finally, at high-shear rates, curves corresponding to different field strengths tend to merge and reach the values in absence of field, showing that the electric field ceases to have an effect on the measured viscosity.

Furthermore, Fig. 7 demonstrates that the electrified suspensions display a plastic behavior, with a finite yield stress, $\tau_y$, more significant the higher the field strength. Similar plots, not shown for brevity, indicate the $\tau_y$ also increases with $\phi$. Since the suspensions are newtonian fluids when no field is applied, the yield stress observed in this suspensions must be an ER effect.

The yield stress, $\tau_y$, is plotted as a function of the field strength $E$ and volume fraction in Fig. 8: whatever the volume fraction, $\tau_y$ increases with $E$, and a roughly linear dependence of $\tau_y$ on the field strength is observed in all cases. This is an indication that other phenomena (such as the above mentioned non-linear conduction effects or ion injection) will prevail over the interfacial (Maxwell–Wagner) polarization mechanism in the overall explanation of the observed ER behavior of iron oxide in silicone oil suspensions. We will return to this point below.

3.1.3. Effect of volume fraction on the ER response

Fig. 9 shows that a parabolic dependence, $\tau_y \propto \phi^2$, describes adequately the variation of the yield stress with the
volume fraction of solids. Such dependence is a result also found by other authors [34,35], but disagrees with the commonly admitted linear relationship between \( \tau_y \) and \( \phi \). In fact, according to the polarization and conduction theories of the ER response, the yield stress should be proportional to the volume fraction. Such dependence has been found particularly when the results are averaged over a wide concentration range [36], but other exponents are possible in a \( \tau_y \propto \phi^n \) relationship: \( n \) is believed to be less than one at low and high concentrations, and >1 at intermediate \( \phi \) values [18,27,34]. This spread is probably related to changes in structure with the concentration of particles [37].

3.1.4. Phenomenological description

As mentioned in the introduction, ER fluids become Bingham bodies when the electric field is applied. This behavior is due to the constant rupture and reformation of the field-induced structures in the suspension at low shear rates. Such a process gives rise to a finite yield stress, \( \tau_y \). From this, the data should be reasonably well fitted by the Bingham equation:

\[
\tau = \tau_y + \eta(\infty)\dot{\gamma}.
\]

Here \( \tau \) is the shear stress, \( \dot{\gamma} \) the shear rate and \( \eta(\infty) \) is the plastic viscosity. At high-shear rates the viscosity of the suspension approaches that of a simple sterically stabilized dispersion, as hydrodynamic forces dominate over other interactions. The high-shear limiting viscosity can then be fitted to the Dougherty–Krieger [38] equation:

\[
\frac{\eta(\infty)}{\eta_c} = \left(1 - \frac{\phi}{\phi_m}\right)^{-1/(\alpha+1)},
\]

where \( \eta_c \) is the viscosity of the continuous medium, \( [\eta] \) the intrinsic viscosity and \( \phi_m \) the maximum packing volume fraction. For a random suspension of hard spherical particles, \( [\eta] \) and \( \phi_m \) are 2.5 and 0.605, respectively. However, for particles of different geometries and sizes the intrinsic viscosity and maximum packing volume fraction can reach significantly different values. In order to get information about these parameters for the hematite/silicone oil suspensions, the high-shear rate limiting viscosity of the unelectrified suspensions was fitted to the Dougherty–Krieger equation (Fig. 10) resulting \( [\eta] = 7.0 \pm 0.1 \) and \( \phi_m = 0.3 \pm 0.1 \). The value obtained for \( [\eta] \) is higher than that of suspensions of spherical particles. However, it must be taken into account that intrinsic viscosity is very sensitive to the shape of particles and small changes in the aspect ratio of solids (such as shown by our polyhedral hematite) may give rise to much higher values of this parameter [39].

Eq. (1) combined with Eq. (2) gives a new constitutive equation for our ER fluids [40]:

\[
\tau = \tau_y + \eta(\infty)\dot{\gamma} - \eta \dot{\gamma} + \tau_y.
\]

Fig. 11 shows shear stress as a function of shear rate at different field strengths. The predictions of Eq. (3) for different yield stresses are also shown. Over the whole experimental range of the variables investigated, the Bingham–Dougherty–Krieger model provides an adequate description of the experimental data.

3.2. Experimental observation of suspension structures

The ER effect due to DC fields is much more complex than under AC excitation. Fibrillated arrangements, non-linear
Fig. 11. Data in Fig. 7 together with fittings to the Bingham–Dougherty–Krieger model.

Conduction, charge injection and/or electrophoretic migration and deposition are some of the possible phenomena which can occur under this condition. For these reasons, a structural analysis is required to elucidate which mechanisms are mainly responsible for the ER response of our hematite/silicone oil suspensions.

Fig. 12. Photographs of an iron oxide/silicone oil suspension of 0.1% volume fraction for a field strength of 2.5 kV/mm at different times. (a) t = 0 s, suspension in quiescent state; (b) t = 2.7 s, motion of particles from electrodes; (c) t = 4.5 s, formation of convection cells; (d) t = 7.2 s, fully developed EHD convection (or Bénard) cells.

Fig. 13. Photograph of rings in a bob geometry observed after a simultaneous application of a DC electric field and a shear rate field. The volume fraction was 10% hematite in silicone oil.
Fig. 12a–d show photographs of a suspension with a 0.1% volume fraction, taken at different times after application of a constant electric field of 2.5 kV/mm. From a quiescent state (a), particles start to move from the electrodes to the center of the cell (b). This movement is caused by the surface charge of the particles, and if the particles reach the opposite electrode, an injection of charge from the latter will occur until the potential of both particle and electrode are equal; the solids will then be repelled towards the other electrode and so on. This situation collapses into the formation of convection cells where an inter-electrode circulation of particles can be observed (c and d).

These phenomena are jointly called the electrohydrodynamic (EHD) instability [13,41]; the process is continuously repeated if the dipole-dipole interactions between particles are not very strong [13]. Although some aggregation between particles can be observed (because of the Maxwell–Wagner polarization), a pattern of chain or columns between the electrodes was not observed. According to our structural observations, the first step of the ER response arises in these suspensions mainly from this mechanism and not because polarization of particles, as it has been reported by other authors with other systems [41,42].

Recently, Cho et al. [43] compared the ER behavior of polyaniline and polyaniline-covered PMMA particles. They found that only in the latter case both fibrillation and electrophoresis were responsible for the observed effects. These authors suggest that the latter mechanism may be dominant when electrostatic interactions between the particles are not sufficiently strong to overcome the ever present electrophoretic migration.

Otsubo and Edamura [41] and Filisko et al. [44,45] also found that in concentrated suspensions the electrophoretic movement of the charged particles between the electrodes (EHD convection) and the action of shear fields collapse in the formation of deposits, lamellae or rings of solids. Fig. 13 shows our observations of such periodic particle deposits in a bob and cup geometry, for our concentrated suspensions.

Fig. 14. Photographs of an iron oxide/silicone oil suspension of 0.1% volume fraction at different electric field strengths (1.5 and 2.5 kV/mm), taken at the times, t, indicated after application of the DC field. (a) t = 0.45 s; (b) t = 2.70 s; (c) t = 4.50 s; (d) t = 7.20 s; (e) t = 22.50 s; (f) t = 45.00 s.
These findings can explain the increase in viscosity shown by the suspensions, particularly at low shear rates; viscous dissipation occurs by the tendency of these structures to maintain their integrity and by their friction between each other or with the electrodes [44]. Similarly, the observed yield stress must be a consequence of the electrophoretic deposition of particles in rings or lamellae on the electrodes and the formation of slippage planes between these particle layers in the two plates of the rheometer [44,45]. The linear dependence between the yield stress and the field strength (Fig. 8) reflects the shear force required to balance and overcome the tendency of these rings to maintain their integrity which is due to the linear electrical attraction force between the charged particles and the electrodes.

3.2.1. Response times

Finally, let us note that the structural observations also show the dependence of the response time with the electric field strength. Fig. 14a-f show photographs of a suspension with 0.1% volume fraction at two different electric field strengths (1.5 and 2.5 kV/mm), taken at different times (t = 0.45, 2.70, 4.50, 7.20, 22.50 and 45 s). It can be observed how for the highest applied field, the EHD convection cells are completely formed at 7.2 s while for 1.5 kV/mm these structures do not appear until 45 s. These observations show the decrease in reaction time with electric field strength commonly observed in electrorheological measurements.

4. Conclusions

The rheological properties of ER fluids consisting of iron(III) oxide particles dispersed in silicone oil under DC electric fields have been determined. A plastic behavior has been observed, adequately described by a combination of the Bingham and Dougherty–Krieger equations. It is worth to mention that the ER response and, consequently, the yield stress, increase linearly and in an approximately parabolic
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