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Electrorheology of suspensions of elongated goethite particles

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ABSTRACT

We describe the rheology of moderately concentrated suspensions of elongated goethite (β-FeOOH) particles with axial ratio around 8, both in the absence and presence of high-strength DC electric fields (up to 4.3 kV/mm). The selected liquid medium was a silicone oil with 1 Pa s nominal viscosity. The aim of this work is the evaluation of the electrorheological (ER) effect of suspensions containing highly anisotropic particles and the comparison with that exhibited by samples made of less anisotropic particles of similar chemical composition (hematite, α-Fe_2O_3). Under the application of large electric fields, goethite suspensions changed their rheological behavior, as expected, from Newtonian – at zero field – to shear thinning, thus displaying electrorheological response. A well defined yield stress (σ_y) was observed in the electrified suspensions, that increases with both the field strength and particle concentration ϕ, although following different trends to those predicted by the classical chain models. σ_y was found to depend on ϕ in a parabolic fashion, as a consequence of the fact that field-induced structures in the suspensions do not consist of individual chains as the classical models consider, but of much more complex particle aggregates. The yield stress was found to be almost linearly dependent on the field strength, contrary to the predictions of the polarization model ($\sigma_y \propto E^2$). The field-induced enhancement of the conductivity of the host oil, leading to saturation of the electrical forces among polarized particles, is required to explain this deviation. The goethite suspensions were also analyzed under oscillating shear stresses for investigation of their viscoelastic properties as well. The results indicate that the ER effect was only noticeable for sufficiently high field strength and particle concentrations, typically >1 kV/mm and >4% in volume fraction, respectively. In such conditions the elastic modulus G' was independent of the shear frequency as corresponds to an elastic solid-like structure. Suspensions of goethite particles display an ER effect with the same characteristics as hematite dispersions (same tendencies of σ_y with both E and ϕ^2), indicating that the physical mechanism responsible of such effects is the same in both cases. However, suspensions containing elongated particles produce a more efficient response to the electric field than those made of irregularly shaped solids, since the former give rise to higher yield stress for the same field strength, and exhibit a lower viscosity in absence of external excitation.

1. Introduction

The name "intelligent materials" encloses a wide group of materials whose properties can be controlled to a certain extent by external stimuli. The so-called electrorheological (ER) fluids belong to this group [1–3]. Their main characteristic is a dramatic change (in a rapid and reversible fashion) in their rheological properties under the application of sufficient large electric fields. ER fluids usually show a liquid (close to Newtonian) behavior in the absence of the field, while becoming viscoelastic (or even solid-like) materials, with a significant yield stress and elastic modulus, under the application of an external electric excitation. Understanding the mechanisms by which such changes take place is an interesting and difficult challenge since the ER response is controlled not only by the magnitude and characteristics of the applied field [4] but also by a wide range of properties of the system itself. For ER fluids consisting of particles dispersed in a fluid (heterogeneous ER fluids), this effect is controlled by a number of parameters, including the volume fraction of solids, the electrical conductivities and permittivities of the solid and liquid phases, the particle size and shape and the contents of water and other additives in the samples [1,5,6].

The rapid and reversible control on the flow properties of the ER fluids suggests a large number of potential technological applications, with various degrees of feasibility. Some currently available devices are hydraulic valves on dampers, clutches or brakes [1–3,7]. However, the industrial production and extended commercialization of these prototypes is still limited because of a number

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of unsolved problems, including the sometimes irreproducible behavior of the ER fluids, their low settling stability, the requirement of higher yield stresses (although recent formulations display giant ER effect [8]), or abrasion of pipes and valves, to mention a few.

All these problems reflect that we still have a limited understanding of the parameters responsible for the ER effect, and their relative roles in it. For example, it is still not clear the effect of the particle shape on the ER response. Kawai et al. [9] reported differences in the ER effect of fluids based on ZnO or hydroxyzinc complexes containing particles differing in size and shape. They suggested, however, that such differences could be ascribed to changes in the electric permittivity of the fluids and not specifically to size or shape effects. On the other hand, Lengálová et al. [10] suggested that, in addition to permittivity, the geometry of the particles also affects the ER response, since the particle size and shape should influence the hydrodynamics of the polarized structures and thus their elasticity or capability to withstand applied stresses. Another explanation for the increase in the ER effect could be that, as it is well known, needle-shaped or very elongated particles lead to large zero-field viscosities of their suspensions [11–13] and expectedly to large viscosities when the electric field is applied, as well. Furthermore, it is also likely that non-spherical particles produce a more intense ER effect because of the large-induced dipole moments, as compared to that of spheres of similar size and polarizability. This was experimentally shown by Kanu and Shaw [14,15], working with a liquid crystalline polymer with fiber-like structure, and two different axial ratios. These authors found that the ER response is indeed increased by raising the aspect ratio of the particles, a phenomenon explained by the more intense dipolar interactions between longer fibers. Summarizing, we can say that many factors may affect the magnitude of ER effect of suspensions containing non-spherical particles and more experimental results are necessary.

This is the aim of this paper, as we intend to contribute new data from steady state viscous flow and oscillatory shear on the electrorheology of concentrated suspensions of elongated particles. The system selected for study is goethite/silicone oil. There are several reasons for this choice. Goethite is commercially available with the desired characteristics (mainly, elongated shape). No recent works – to the authors' knowledge – can be found about this material, and, finally (and most important), we can analyze the effect of the shape on the ER response by comparing our results with those obtained from less anisometric particles of similar chemical composition (hematite, α-Fe_2O_3) which have been extensively studied in recent years [16–18].

2. Experimental

2.1. Materials

The goethite particles used in this investigation were purchased from Bayer (Germany) under the trademark BayFerrox 920. According to the manufacturer, the mass density of the particles is 4.1 g/cm^3 and their average semi-axes are 50 and 400 nm. Fig. 1 is a scanning electron microscope picture of the particles. Hematite particles of approximately the same volume (mean diameter 105 nm), but of polyhedral shape, were used to study the effect of shape. A complete description of their characteristics can be found in previous works [5,19].

The dispersing fluid was in both cases a silicone oil (Aldrich, USA, Ref DC200) with nominal viscosity η_m = 1 Pa s and density 0.97 g/cm^3.

2.2. Methods

Suspensions with different volume fractions of solids (ϕ = 2–15% by volume) were prepared by slow addition of the goethite powder to the oil under mechanical stirring (about 400 rpm). At the end of the process, the suspensions were further homogenized in an ultrasonic bath. Samples were left to stay overnight before measurement and homogenized again by stirring and ultrasonics.

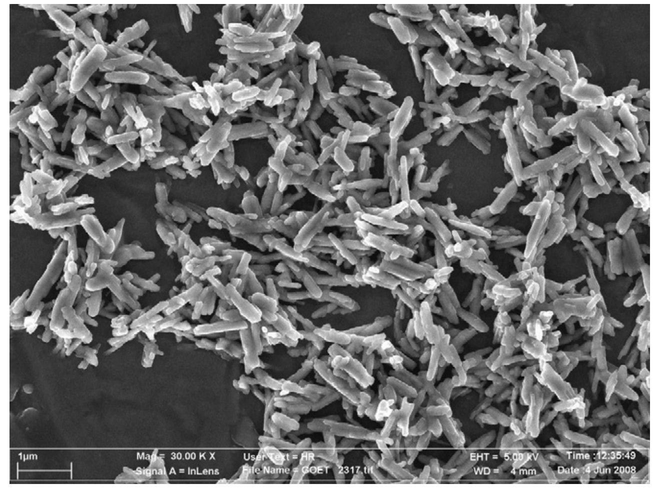

Fig. 1. Scanning electron microscope picture of the goethite particles.

ER experiments were performed (at 25.0 ± 0.2 °C) in a Bohlin CS-10 rheometer (Malvern Instruments, Malvern, England) using the ER cell designed by the manufacturer (a parallel-plate system, 40 mm in diameter with a gap of 0.7 mm between them). A copper wire (0.1 mm in diameter) was used to electrify the upper plate while the lower one was grounded. To avoid the passage of the electric current through the rheometer, the upper plate of this ER cell was fixed by means of a plastic piece.

The electric field (ranging between 0 and 4.3 kV/mm) was generated by a DC power supply (LD Didactic 521–535, Germany) connected to a Trek Model 606E6 High Voltage Amplifier (Trek, USA).

All samples were subjected to a 30 s pre-shear and then allowed to equilibrate with the electric field applied (in absence of shear) during 45 s. Two kinds of experiments were then performed. Steady state viscous flow measurements consisted of shear stress (σ) ramps in which shear rate ($\dot{\gamma}$) and viscosity η data were collected while the electric field was kept at a different strength for each test. In the oscillatory shear measurements, the elastic moduli of the systems were measured as a function of the frequency (between 3×10^{-2} and 10 Hz) of the applied oscillating shear stress for different magnitudes of the electric field.

3. Results and discussion

3.1. Zero-field rheology of goethite suspensions

As shown in Fig. 2, unelectrified goethite suspensions behave nearly as Newtonian fluids without yield stress. The slope of the σ vs. $\dot{\gamma}$ curves, that is, the Newtonian viscosity, showed a significant increase with the particle concentration. In order to analyze such dependence, we computed the Newtonian viscosity as the viscosity corresponding to high shear rates, η_∞, and we observed that it could be adequately described by Krieger–Dougherty equation [20,21]:

$$\frac{\eta_\infty}{\eta_m} = \left(1 - \frac{\phi}{\phi_m}\right)^{-[\eta]\phi_m} \quad (1)$$

where ϕ_m is the maximum packing volume fraction and $[\eta]$ is the intrinsic viscosity. As observed in Fig. 3, the values of η_∞ for goethite suspensions could be well fitted by Eq. (1) when the parameters mentioned are $[\eta]$ = 3.7 ± 0.5 and ϕ_c = 0.22 ± 0.04 (in good agree-