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ORIGINAL CONTRIBUTION

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Differences in the electrorheological response of a particle suspension under direct current and alternating current electric fields

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Abstract We have observed an unusual reduction of shear stress with increasing shear rate under direct current electric fields, for an electrorheological fluid composed of sulfonated poly(styrene-*co*-divinylbenzene) particles dispersed in silicone oil. At all shear rates, the shear stress under the electric field is larger than that in the absence of the field, indicating that there is still some field-induced agglomeration of the particles. In contrast, the behavior under alternating current electric fields is the Bingham-fluid-type response commonly observed with electrorheological fluids. It is suggested that the conventional dipole–dipole interaction approach based on simplified microstructural models would be unable to explain these phenomena.

Keywords Electrorheological fluid · Flow curve · Electric current

Introduction

An electrorheological fluid (ERF) is typically a suspension of solid micron-sized particles dispersed in a nearly insulating solvent. Under an electric field, there is a dramatic and reversible increase in shear viscosity, an effect sometimes called the Winslow effect after the discoverer [1]. Because of these tunable rheological properties, ERFs have been the subject of much attention in recent years from both the academic and the industrial communities, with possible applications including adjustable vibration isolation dampers and fluid clutch systems. The basic mechanism behind the electrorheological response is thought to be that the external field electrically polarizes each particle, and the resulting dipole–dipole interactions lead to the formation of elongated particle aggregates which increase the resistance to flow. Extensive review articles are now available [2–8] as well as detailed proceedings of international conferences [9, 10].

In many experimental investigations of the response of an ERF under steady shear flow, it is observed that the shear stress, τ, under a shear rate, $\dot{\gamma}$, and an electric field, E, can be modeled approximately by the Bingham fluid equation:

$$\tau = \tau_y + \eta\dot{\gamma} \qquad (1)$$

Here τ_y is the yield stress, which has been found to be proportional to E^α, with $\alpha \approx 2$, and η (>0) is the plastic viscosity. This type of response has been reported extensively in the literature [7, 11–13]. Note that Eq. (1) implies that the shear stress increases monotonically with shear rate.

In this article, we report a distinctive shear stress versus shear rate curve (hereafter called the "flow curve") of a suspension of sulfonated poly(styrene-*co*-divinylbenzene) particles dispersed in silicone oil. Under direct current (dc) electric fields of various magnitudes, it is found that τ decreases with increasing shear rate; however, at all shear rates, the field-induced shear stress is observed to be larger than the shear stress in the absence of the electric field, showing that the electric field still induces an increment in the shear stress. On the other hand, under alternating current (ac) electric fields, the sample shows the often-observed behavior with the shear stress increasing as both the shear rate and the electric field are raised (reflecting Eq. 1). From a rheological viewpoint, materials where the shear stress decreases as the shear rate is raised are of great interest, since most non-Newtonian fluids (including complex fluids such as polymer melts and solutions) show an increase in τ with $\dot{\gamma}$ – indeed it can be shown that this is a condition for the stability of the shear flow of a macroscopically uniform fluid [14, 15].

A survey of the literature on ERFs reveals that in a few of the experimental studies the shear stress has indeed been observed to decrease with shear rate; however, this phenomenon and the differing behavior under dc and ac fields have yet to be discussed in any detail, despite the interest such a decreasing flow curve presents from the theoretical rheological perspective. Using a similar ERF system to the present study, Kawakami et al. [16] and Aizawa et al. [17] reported distinctly decreasing flow curves under dc electric fields. Schubring and Filisko [18] also reported decreasing flow curves with systems of amorphous aluminosilicate particles in paraffin oil under dc fields. Other systems with decreasing flow curves that have appeared in the literature include zeoilte particles in paraffin oil [19], chitosan derivative particles in silicone oil [20], silica-based mesoporous particles in silicone oil [42], and copolyaniline-based particles in silicone oil [21, 22]. It should be noted that all of these decreasing flow curves appear under dc electric fields, and to the authors' knowledge, there are no such reports of the behavior under ac electric fields. In this article we present a comparison of the flow curve behavior under dc and ac electric fields. Further, we discuss this phenomenon in the context of the stability of such flow behavior, as mentioned previously. This is an issue which does not seem to have been addressed by previous investigators, despite its importance from a fundamental rheological viewpoint.

This article is organized as follows. The materials used and the experimental setup and procedure are discussed in the following section. Then, we present the results of the rheological tests, where the magnitude of the shear stress is plotted as a function of shear rate and electric field for dc and ac fields. The variation of the electric current with the shear rate as well as the dielectric properties of the sample are also presented. A discussion of the rheological significance is given and possible mechanisms for the decreasing flow curves under dc fields are presented. In the final section we make some concluding remarks.

Experimental

The ERF used was a 10% weight suspension of sulfonated poly(styrene-*co*-divinylbenzene) particles dispersed in silicone oil of viscosity 0.1 Pas, received from Nihon Shokubai Co. Ltd., Japan. The particles were spherical, 15 μm in diameter and highly monodisperse. The water content was 2.9%, measured at Nihon Shokubai using the Karl-Fischer technique. This general type of ERF suspension has been investigated extensively and there are several reports in the literature [16, 17, 23, 24]. The sample was measured on several separate runs with a shear rate sweep program that increased the shear rate in a stepwise fashion, remaining at each shear rate for 1 min to allow the shear stress value to settle. The values reported here are the final values reached at each shear rate step, and they were found to be quite reproducible.

The rheometer was a Haake VT550 Viscotester in the concentric cylinder configuration. The inner bob had a diameter of 20.2 mm and a wetted height of 19.6 mm, with a 1-mm gap between the bob and the outer cup. The inner bob was rotated at constant velocity to give a steady-shear flow, and the torque acting on it was converted to a shear stress. The rheometer was electrified so that a voltage (dc or ac) could be applied across the gap. The ac field was applied at a frequency of 50 Hz. The power source was a model 9051 instrument from Zentech Technology (Taiwan), which also enabled determination of the instantaneous electric current. The electric current values quoted here are averages of the final values at the end of each shear rate step, and these did not show significant fluctuations.

Dielectric measurements were performed with a Hewlett-Packard 4284A precision LCR meter, covering a frequency range of 20 Hz–1 MHz, using a weak electric field. The dielectric test cell was manufactured by Ando Electric Co., Japan.

Results

The flow curves for the case of the ERF under dc electric fields of different magnitudes are shown in Fig. 1 and the flow curves under ac electric fields (the field values are root-mean-square values) are shown in Fig. 2. A difference is clearly observed in the slopes of the two sets of curves when an electric field is applied. The variation of electric current with shear rate is plotted in Fig. 3.

The electrical properties of the ERF are characterized by dielectric measurements, and the curves for the relative permittivities ε' and ε'' as a function of frequency are shown in Fig. 4.

It should be noted that at the time of these experiments, the rheometer and power supply were also being used to test other electrorheological materials which did show their expected behavior. Hence it can be said with reasonable certainty that the behavior seen in Figs. 1 and 2 is a genuine response from the material and not an artefact arising from the equipment or setup.

Discussion

The curves for the dielectric properties in Fig. 4 show a peak in ε'' at 2,840 Hz and the change in ε' was 1.1 over the frequency range measured. These values lie in the

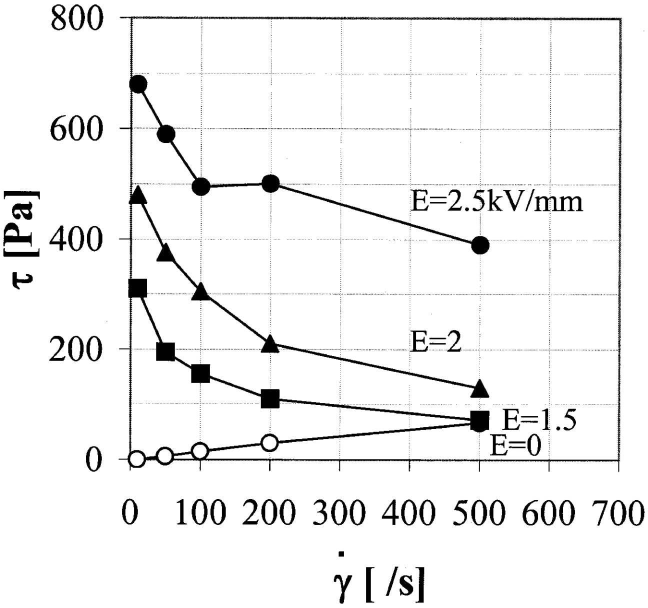

Fig. 1 Variation of shear stress, τ, with shear rate, $\dot{\gamma}$, under different direct current (*dc*) electric field strengths, *E* (magnitudes indicated on the curves)

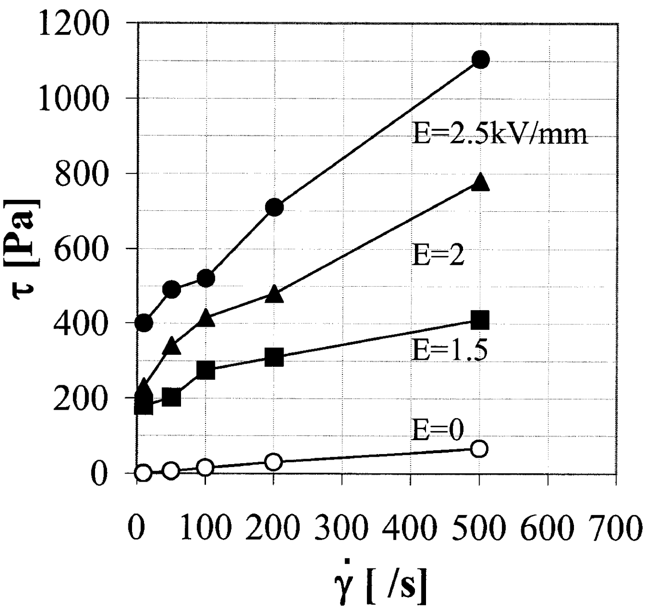

Fig. 2 Similar to Fig. 1, but now under different alternating current (*ac*) electric field strengths (root-mean-square, *rms*, magnitudes are indicated on the curves)

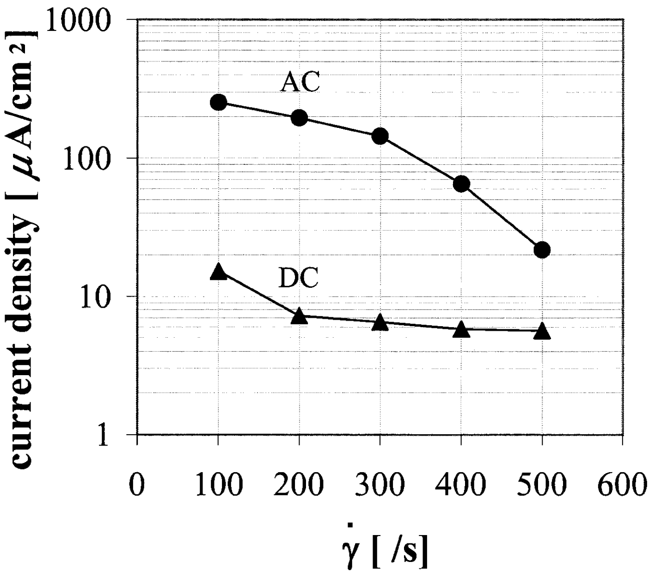

Fig. 3 Electric current density versus $\dot{\gamma}$, under 2kV/ mm dc and ac electric fields (rms values for ac)

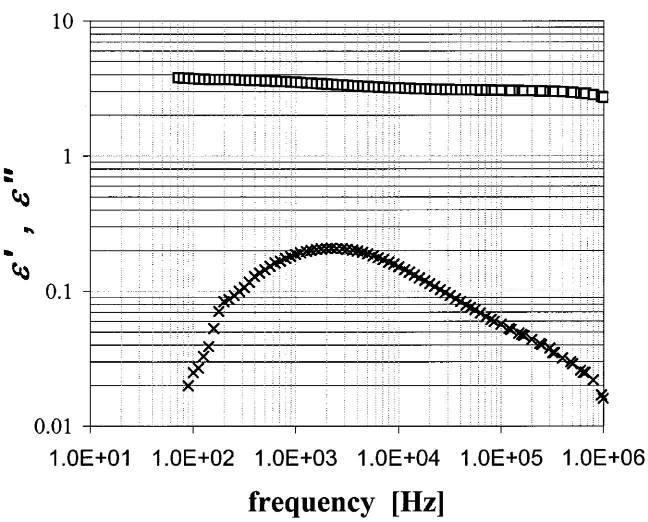

Fig. 4 Relative permittivities ε' (*squares*) and ε'' (*crosses*) versus frequency

ranges that have been proposed by Ikazaki et al. [24] as leading to a reasonable electrorheological response. The reduction in electric current with increasing shear rate shown in Fig. 3 has been widely reported for various ERFs [25–27]. Thus, the dielectric properties and electric current behavior (under both dc and ac fields) are similar to those observed for other ERF systems.

The unusual behavior of the ERF system used in this study is apparent when we look at the flow curves (Figs. 1, 2). Under the dc electric field, we see that the shear stress decreases with increasing shear rate, but at all shear rates it is always above the zero-field shear stress. This indicates that there must still be some electrically induced agglomeration of the particles in the flow field, causing the enhanced flow resistance. On the other hand, the response under the ac field resembles the often observed response for ERFs (cf. Eq. 1).

From a fundamental rheological viewpoint, a reduction in shear stress with increasing shear rate is an unusual phenomenon, since the majority of non-Newtonian fluids (including complex fluids, such as polymer melts and solutions, hard sphere suspensions, etc) show an increase in τ with $\dot{\gamma}$ – indeed this result can be derived from quite general continuum mechanics stability considerations [14]. It should be emphasized that this does not preclude the material from showing so-called "shear-thinning" behavior – the stability analysis reveals that the viscosity ($=\tau/\dot{\gamma}$) may decrease with shear rate as $\dot{\gamma}^{-\beta}$, with β being at most 1. For example, the low-shear-rate behavior of materials with a yield stress corresponds to $\beta=1$, a fact which can be appreciated from the Bingham fluid equation (Eq. 1) since the viscosity will approach $\tau_y/\dot{\gamma}$ for small $\dot{\gamma}$. In the present study we found $\beta \approx 1.4$ for the ERF under dc electric fields. Other reports of $\beta > 1$ have appeared in the general rheological literature for various materials, but the explanations presented introduce some concept of macroscopic non-uniformity of the material: the $\beta > 1$ predicted by the Doi–Edwards reptation model for concentrated polymer solutions under high shear rates has been explained in terms of the formation of stratified layers of low- and high-viscosity fluid [28–30]; and Orihara et al. [31] found $\beta > 1$ for a range of shear rates in their rheological study of immiscible polymer blends under an electric field, which was also explained by macroscopic layer formation.

To explain the behavior of the ERF observed in this study, a natural first step would be to consider the "dipole–dipole interaction model", which assumes that the particles interact through dipoles (magnitude, p) proportional to the external electric field, E. Generally, three microstructural models have been presented for the mechanism of an ERF under steady shear based on the dipole–dipole interaction model: breaking and reformation of chains or columns of particles which span the electrodes [32, 33]; (ii) chains of particles which are suspended in and translate with the flow field [34–37]; and layers of particle chains adhering to the electrodes accompanied by a dilute free-flowing layer where the shearing is concentrated [38, 39]. Interestingly, these models all predict that the particle-contributed stress, τ^p, is proportional to E^2, with no explicit dependence on the shear rate. Hence these models predict the Bingham fluid behavior (no doubt one reason for their continued popularity) with τ_y given by τ^p, which means that β in the viscosity–shear rate relation is predicted to be at most 1. Indeed, this fact can be appreciated by the following general scaling argument without detailed consideration of the microstructure of the particle aggregates. Ignoring hydrodynamic interactions the contribution to the stress tensor from interparticle forces, τ^p, is given by $\tau^p = -1/V \sum \mathbf{r}_i \mathbf{F}_{i\mathrm{TOT}}$, where V is the system volume, $\mathbf{r}_\mathrm{i}$ is the position of particle i, $\mathbf{F}_{\mathrm{iTOT}}$ is the sum of all nonhydrodynamic forces on particle i, and the summation is over all particles [40]. Since the dipole–dipole interaction force, F^{electro} ($\propto p^2 \propto E^2$), is short-ranged (decaying as the inverse fourth power of interparticle distance), from the stress formula we can estimate the particle-contributed shear stress by $\tau^p \sim nF^{\mathrm{electro}}/a^2$, where n is the number concentration of contacting particle pairs, a is the particle radius, and for simplicity the orientational dependence of the dipole–dipole interaction has been ignored. This result indicates that τ^p has no direct dependence on the shear rate. It thus seems rather difficult to explain the $\beta \approx 1.4$ result seen in this study (the distinct decreasing flow curves under a dc field), using the simple dipole–dipole interaction model, regardless of the type of microstructural model adopted.

Thus, while the dipole–dipole interaction model can explain the essential features of many ERF systems [7, 11–13], it seems that modifications to the existing basic framework should be explored in order to explain decreasing flow curves obtained in the present study under dc (but not ac) fields, as seen in Figs. 1 and 2. One possibility is to modify the assumption that the interparticle forces are determined only by the instantaneous particle configurations and the magnitude of the external electric field, which is a key assumption of the conventional dipole–dipole interaction model. Instead of assuming a dependence on only the (fixed) external electric field, it could be assumed that the interparticle forces are also strongly determined by the magnitude of the local electric current flowing in the vicinity of each particle. This basic idea is supported by the series of experiments performed by Atten et al. [41], who measured the electric current and force acting on a pair of two 7-mm half-spheres under different electrostatic conditions. If this is the case, since the overall electric current decreases significantly with shear rate as seen in Fig. 3, owing possibly to changes in the system's overall microstructure, the local electric current and, hence, the interaction force between particles would be reduced, leading to less particle-contributed shear stress. On the other hand, for the case of ac fields, it would be the local alternating electric current within the particle aggregates which determines the interaction strength, and this is not expected to depend so significantly on the overall microstructure. Although speculative, it is felt that these concepts can explain many of the essential features of the phenomenon observed in this study.

Conclusions

We have found a significant difference in the field-induced response of an ERF under dc and ac electric fields. The reduction in shear stress with shear rate observed under dc fields is an interesting rheological phenomenon. Calculations based on simple microstructures and the dipole–dipole interaction model (where the interparticle force is proportional to the square of the external electric field) typically predict a Bingham-type response and seem unable to straightforwardly explain the flow curves obtained. It is suggested that a possible mechanism for the behavior observed under dc fields is that the interparticle forces are also influenced by the local electric current flowing through neighboring particles, in addition to the magnitude of the external field. The magnitude of this current is determined by the overall system microstructure, which is expected to change significantly with shear rate.

The fact that these decreasing flow curves have appeared in other experimental reports suggests that this is possibly not an uncommon phenomenon in electrorheology, although up to now there have been no studies focusing on the differing behavior under dc and ac fields. Our understanding of this phenomenon is still very rudimentary, and we are unable to predict whether this behavior will occur for given types of particulate and carrier fluid materials. Further characterization of the behavior will be the focus of future investigations.

ERFs are still the subject of much academic and industrial attention, and there are ongoing efforts to develop ERF devices based on dc as well as ac fields; therefore, an understanding of the fundamental features of the ac and dc responses is very important. It is hoped this work has helped to highlight one possible significant difference in ERF behavior under dc and ac fields.

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