Journal of
MATERIALS RESEARCH

Electrorheological fluids using bidispersed particles

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(Received 8 July 1997; accepted 15 May 1998)

We report very large enhancement of static yield stress for electrorheological fluids by adding ferroelectric nanoparticles of lead zirconate titanate (PZT) or lead titanate ($PbTiO_3$) to ER fluids consisting of 50 μm glass spheres. It is found that the enhancement peaks at certain nanoparticle/microparticle ratios for fixed solid/liquid volume fractions. The results are explained by calculations using an effective medium approach, based on the physical picture that the nanoparticles modify the properties of the liquid and solid components.

Electrorheological (ER) fluids constitute a class of materials whose rheological properties are controllable through the application of an electric field.[1] The most common type of electrorheological fluids is a dispersion of micron-sized particles in a dielectric fluid. It is a common practice that particles of the same size are purposely selected for use in ER fluids, and multidispersity in particle size is avoided partly because of factors whose effects are not well understood. In this communication, we report a study of ER fluids using bidispersed particles with one size much larger than the other. The large particles are micron-sized glass spheres and the small ones are nanoparticles of ferroelectric materials.[2] The bidispersed ER fluids show drastic improvement in yield stress over the bare-glass ER system as the nanoparticle concentration increases, with fixed total solid/liquid volume fractions. The enhancement peaks at different nanoparticle/microparticle ratios for different solid/liquid volume fractions. The effects are captured qualitatively by calculations based on a model where the nanoparticles modify the effective dielectric constants of both the microparticles and the liquid. Below we describe the fabrication of the ferroelectric nanoparticles and the measurements of ER static yield stress. We then compare the experimental results with the predictions of the theory. Good agreement is obtained.

To fabricate the PZT nanoparticles, stock solutions were first formed by dissolving 12 g of lead acetate $[Pb(CH_3CO_2)_2 \cdot 3H_2O]$ in 5 ml of acetic acid which had been preheated over 100 °C to remove any trace water. After cooling the resulting stock solution to below 80 °C, 6.55 g of zirconium propoxide $[Zr(C_3H_7O)_4]$ and 2.18 g of titanium isopropoxide $\{Ti[(CH_3)_2CHO]_4\}$ were added sequentially. The solution was agitated by an ultrasonic cleaner at 60 °C until all solids were dissolved. 50 g of sugar and 50 ml of distilled water were added to form the final solution, which was heated to 250 °C until the sugar started to carbonate and form a foam structure,[3] providing the surface areas necessary for the formation of nanoparticles. The carbonated foam was then heated in an oven at 550 °C and annealed for few hours. Nanoparticles of PZT were collected as ashes after the heat treatment. The same procedure was used to fabricate the lead titanate nanoparticles using stock solution with the same formula as in the PZT solution but without the zirconium propoxide.

Figure 1 shows a TEM micrograph of the PZT nanoparticles. The particles are about 0.1–0.2 μm in size, nested with 10–20 nm-sized islands. These islands were particles formed during the sol-gel process and fused together during annealing to form the larger particles. The inset in Fig. 1 shows the x-ray diffraction picture where the crystalline structures of the particles were evident. Similar results were obtained for the lead titanate nanoparticles.

The "bare" ER fluids used in our experiments consisted of 50 μm glass spheres dispersed in silicon oil (DOW Corning #705). Nanoparticles were added to the bare ER fluids to form the bidispersed ER fluids. All the particles and the oil were heated to 100 °C for 5 h to remove any trace water. A parallel plate viscometer was used to measure the yield stress of the bidispersed ER fluids. The yield stress was measured with a 50 Hz ac electric field applied between the parallel plates. To start the measurement, the lower plate was rotated very slowly, dragging the top plate, which was attached to a torque meter. The static yield stress was determined as the point where slipping just occurred between the two plates.

Figure 2 shows the static yield stress versus the applied electric field for different solid/liquid volume fractions ϕ with the ratio of nanoparticle to glass spheres fixed at the ratio θ, defined as (volume of glass spheres $-$ volume of nanoparticles)/(volume of glass spheres $+$ volume of nanoparticles), equal to 0.22. For small volume fractions ϕ, the static yield stress increases roughly as E^2 while it is linear for high volume fractions. Furthermore, the static yield stress saturates at fields

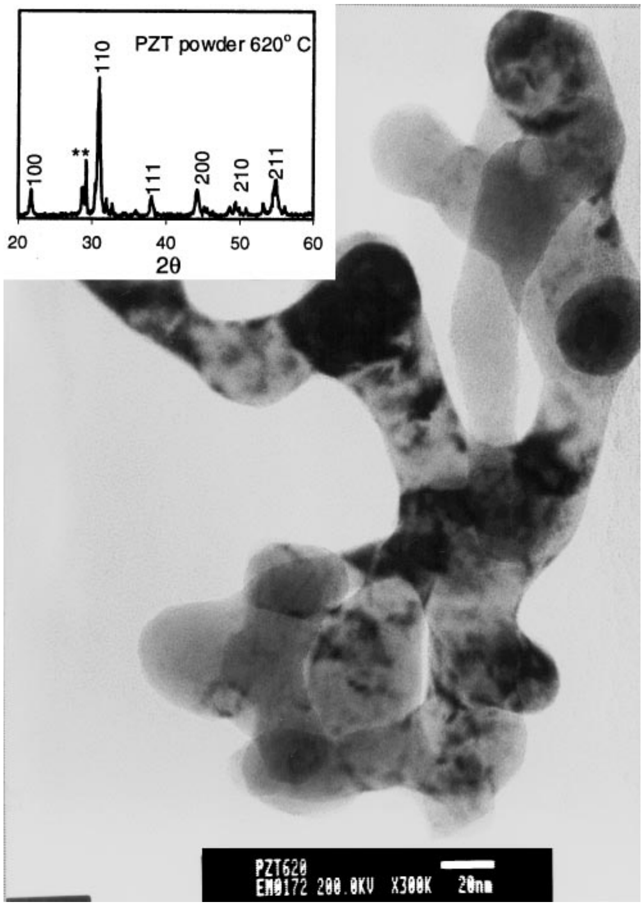

FIG. 1. TEM micrograph of PZT nanoparticles. Inset is the corresponding XDR result. The particles were annealed at 620 °C and the "**" indicates the PbO_3 residue.

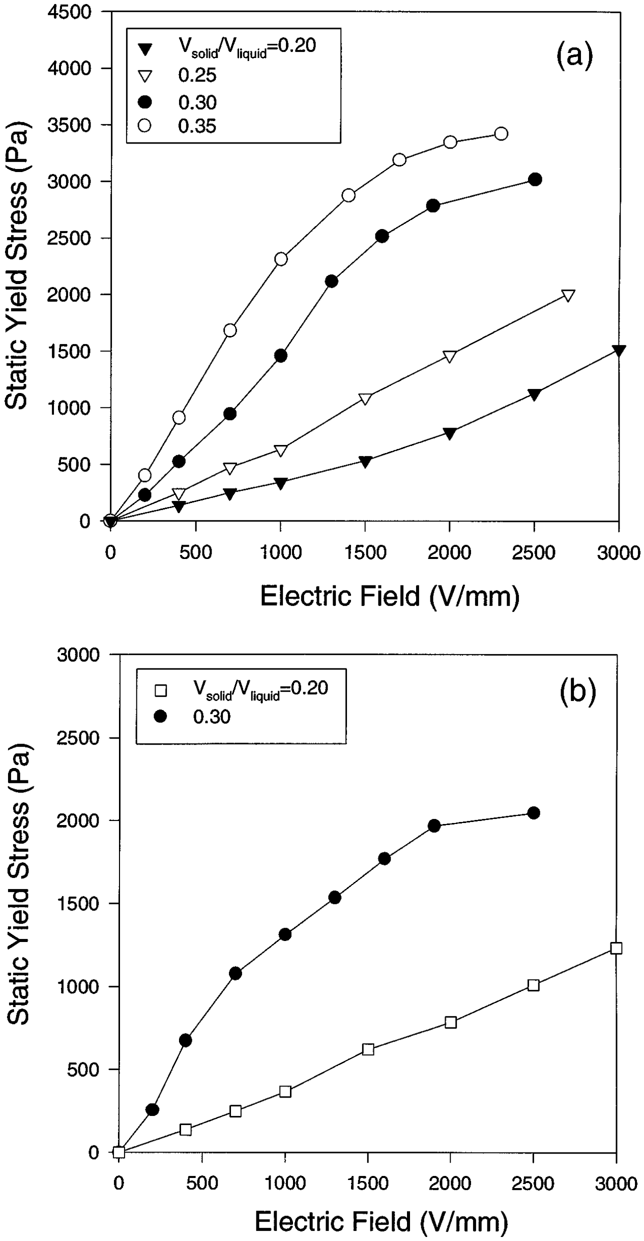

FIG. 2. Static yield stress of (a) PZT glass and (b) $PbTiO_3$ glass bidispersed ER fluids versus the electric field, for the ratio θ fixed at 0.22, and different solid/liquid volume fractions ϕ.

over 2 kV/mm for high volume fractions. This may be explained by the fact that the origin of yield stress lies in the interaction between the polarizations P of the particles. As a result, it is expected that the yield stress should be $\propto P^2$. In the usual case, $P \propto E$, so that yield stress $\propto E^2$. However, in the present case since the effect is from adding the nanoparticles which are ferroelectric, $P \propto E^{1/2}$, for ferroelectric materials at low fields.[3] Consequently the yield stress $\propto E$ for $E \leqslant 1$ kV/mm. Saturation of the yield stress is reached when the increase in P slows down at higher field strengths. Thus, an increase in ϕ is seen to lead to ferroelectric behavior. Figure 3 shows the static yield stress versus θ for different solid/liquid volume fractions at 1 kV/mm applied field. At $\theta = 1$, corresponding to only glass spheres, the yield stress is negligible. The yield stress increases as the nanoparticle concentration increases (decreasing values of θ), and peaks at different θ for different solid/liquid volume fractions. The location of the peak is noted to depend monotonically on the solid/liquid volume fraction. At the peak, the static yield stress is about 10 to 20% higher than that of pure nanoparticle ER fluids. It should be emphasized here that the present results are for fixed total solid (glass spheres + nanoparticles) volume fractions, so the usual solid fraction effects are discounted. The observed results suggest that the ferroelectric nanoparticles not only modify the dielectric constant of the liquid, but also "coat" the large glass spheres and, as a consequence, lead to a nonmonotonic ER fluid stress behavior, as explained below.

It is difficult to perform an exact calculation for the bidispersed ER fluids without detailed knowledge for the structure formed by the nano- and microparticles under

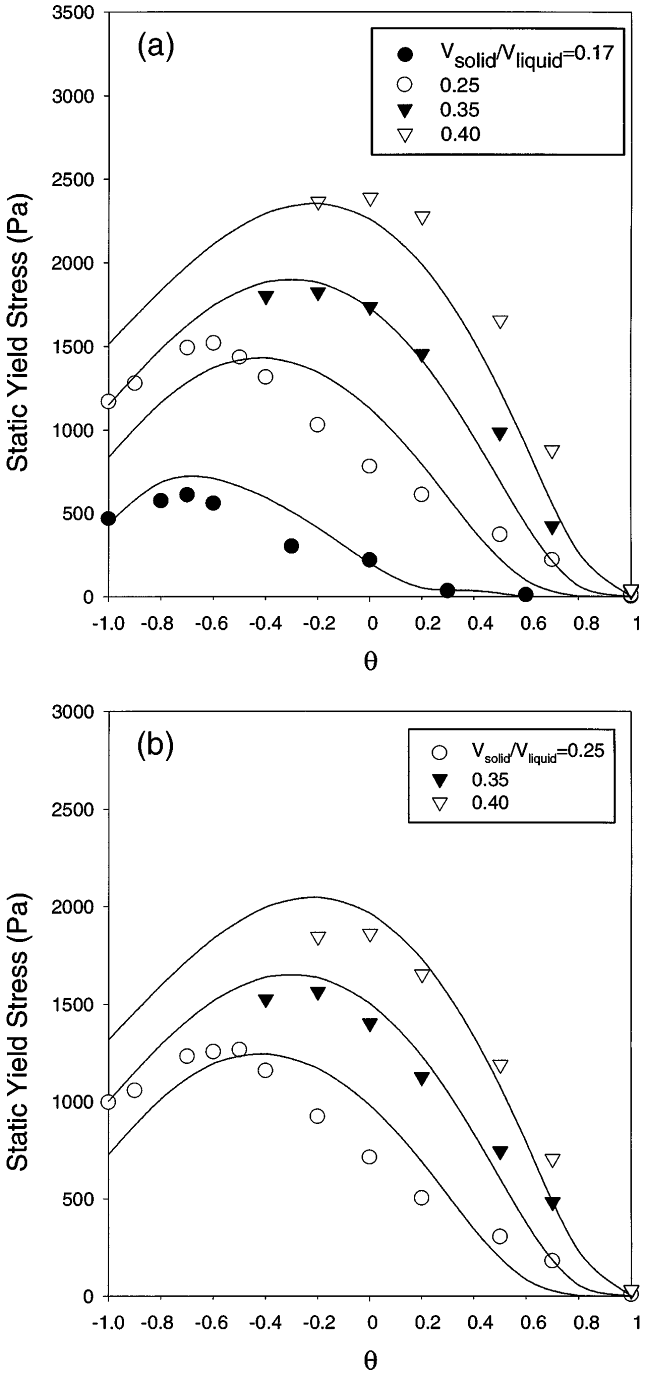

FIG. 3. Static yield stress of (a) PZT glass and (b) $PbTiO_3$ glass bidispersed ER fluids versus the nanoparticle-glass spheres ratio θ, at $E = 1$ kV/mm and different solid/liquid volume fractions ϕ. The solid lines are theoretical predictions explained in the text.

an electric field. Thus, we take an empirical approach and assume the nanoparticles as passive components which modify the dielectric constants of the liquid and the glass spheres. The problem is then reduced to solving an ER system with only one solid component in a liquid characterized by an effective dielectric constant. This is done by assuming that some nanoparticles are attached to the glass spheres and the rest are dispersed in the fluid. The fraction of nanoparticles ψ attached to glass spheres is assumed to be a function of the solid ratio θ and the solid/liquid volume fraction ϕ given by the expression

$$\psi = A\chi^{b} \exp\left[\frac{b(1-\chi)}{B}\right], \tag{1}$$

where $\chi = (1 - \theta)/2$ and $b = 1/(2\phi)^2$. A and B are fitting parameters in this model. The function, shown in Fig. 4 for the PZT nanoparticles and glass spheres, increases monotonically from zero to a maximum value of 0.84 as χ changes from 0 to 1 for different values of ϕ. Since the dielectric constant for crystallized PZT is much higher than that of the glass spheres, the effective dielectric constant for the "dressed" glass spheres can be approximated by the functional form of Eq. (1), scaled between the bare glass dielectric constant, 5, and the PZT value of about 5000. The effective dielectric constant for the liquid, on the other hand, is calculated by assuming the nanoparticles predominantly fill the interstitial spaces between the microspheres, so that the relevant liquid effective dielectric constant for the static yield stress calculation may be obtained by using the Maxwell–Garnett formula for randomly dispersed dielectric particles.[5] With the effective dielectric constants for the liquid and the "dressed" glass spheres thus determined, we used the same first principles calculation for the bidispersed ER fluids as that in Ref. 4. However, in this calculation the fact that the nanoparticles dispersed in liquid also

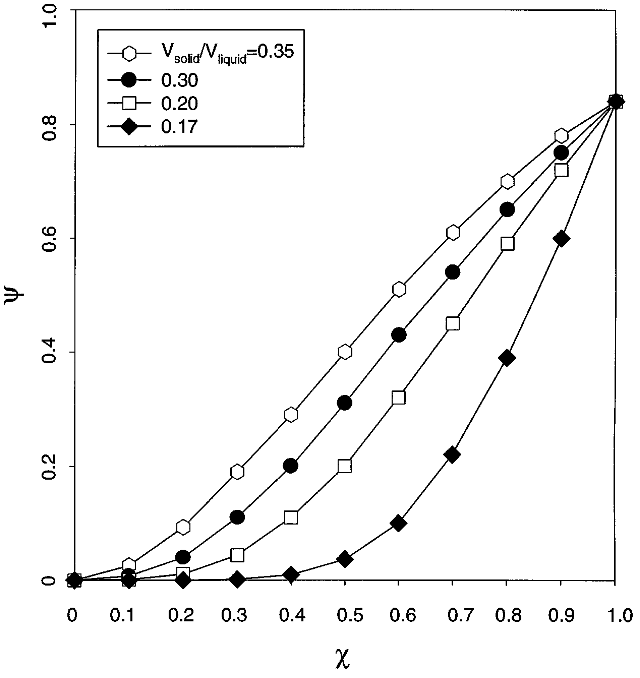

FIG. 4. χ vs ψ for PZT-glass ER system with $A = 0.84$ and $B = 1.5$ in Eq. (1) for different solid/liquid volume fractions.

has a nonzero ER effect was ignored. To take that into account, we used the same first-principles calculation of the static yield stress for the nanoparticle-liquid system, at the limit of $\theta = -1$ (no glass spheres). We then added a linear interpolation of the static yield stress results between $\theta = -1$ and 1 to the prior calculation where the nanoparticles in liquid were treated only as an effective liquid. The combined results are shown as solid lines in Figs. 3(a) and 3(b) for the PZT-glass sphere and $PbTiO_3$-glass sphere ER systems, respectively. The fits are obtained using the same values of A and B as shown in Fig. 4 (i.e., only two fitting parameters were used for all fits). It can be seen that the model not only reproduces qualitatively the experimental results, but also captures the monotonic shift of the peak projects.

In conclusion, we have demonstrated large enhancement of static yield stress using bidispersed nano- and microparticles in ER fluids. We explain the enhancement by a physical pictures where the ferroelectric nanoparticles not only modify the dielectric constant of the liquid, but also coat the micron glass spheres to form, effectively, particles with higher dielectric constant. The increased yield stress was captured by a first principles calculation using effective dielectric constants for the fluid and the coated glass spheres, obtained using an empirical approach.

ACKNOWLEDGMENTS

We acknowledge useful discussions with Michael Loy, and wish to thank Keding Xia for technical support and running the codes for the first principles calculation. This work was supported by HKUST Research Infrastructure Grant RI 93/94, SC09, and the William Mong Solid State Cluster Laboratory.

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