Particle size scaling of the giant electrorheological effect

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This letter shows that by decreasing the size of the barium titanyl oxalate nanoparticles coated with urea, achieved through Rb doping, the giant electrorheological (GER) effect can attain a yield stress of >250 kPa. The shear thinning effect observed in parallel-plate sandwich configuration is also reported, and attributed to the centrifugal sedimentation effect of the inhomogeneous structures induced by applied electric field. In addition, it is found from experiments that the ER effect is very sensitive to the solid particles volume fraction. © *2004 American Institute of Physics*. [DOI: 10.1063/1.1772859]

Electrorheological (ER) fluids are a class of colloids whose viscosity increases under the application of an electric field.[1–4] For certain ER fluids the application of a strong field (>1000 V/mm) can lead to an anisotropic solid, with a yield stress characterizing its strength.[5–10] As the change of the rheological properties is usually accomplished in less than 10 ms and is reversible, ER fluids can potentially function as an interface which translates electrical signals into mechanical signals, opening the possibility of actively controllable clutches, dampers, valves, locks, etc.[11] Although a wide variety of ER fluids applications have been identified, and a number of ER fluids are already produced on a commercial scale, they have not yet enjoyed widespread commercialization mainly because of the low yield stress (a few kPa) achieved up to now. In our previous publication[12] we reported the discovery of the giant electrorheological (GER) effect in nanoparticle-based suspensions. In this letter, it is shown that reducing the particle size can significantly enhance the GER yield stress and also reduce the current density.

Our GER fluids comprise nanometer-sized particles with a hard core enclosed by a relative soft shell (core@shell structure) suspended in an electrically insulating silicone oil, wherein the hard core is made of inorganic materials such as metal salts of the form $M1_xM2_{2-2x}TiO(C_2O_4)_2$, where M1 can be selected from the group consisting of Ba or Sr and M2 is selected from the group consisting of Rb, Cs, or Li. The coating shell is composed of urea molecules, with a molecular dipole moment of 4.6 D.[13] In this work the ER fluid sample is composed of $Ba_{0.8}(Rb)_{0.4}TiO(C_2O_4)_2$@urea dispersed in silicone oil, noted to differ slightly from that reported previously.[12] The particles were fabricated by first dissolving barium chloride and rubidium chloride in distilled water at 50–70 °C. Separately, oxalic acid was dissolved in water at 65 °C in an ultrasonic tank, with titanium tetrachloride slowly added. The two solutions were mixed in an ultrasonic bath at 65 °C. Nano-sized barium titanium oxalato particles with addition of Rb element were formed at this stage. Here the addition of Rb to the core materials has the effect of increasing structural defects, thereby reducing the particle size. Inset to Fig. 1 shows the TEM images wherein the nanoparticles in (a) were made without the addition of Rb, while those in (b) were obtained by adding Rb during the fabrication. A difference in particle size is clearly visible. The GER suspension is made by mixing the nanoparticles powder with silicone oil to form a milk-like colloid. The powder was weighed and then added to the silicone oil to produce the desired concentration of the GER fluid suspensions. The concentration of the GER fluid suspensions is denoted by its volume of oil, e.g., 10 g of the powder mixed with 3 ml of silicone oil is denoted by 0.3.

The rheological properties were measured by a circular-plate type (8 mm in diameter) viscometer (Haake RS1) with a gap width of 1 mm. We used PM5134 (Philips) functional generator to generate linear and step signals for driving the dc high voltage source (SPELLMAN SL300). Experimental data were collected with the help of the software package RHEOWIN. The electric field was applied to the GER colloid

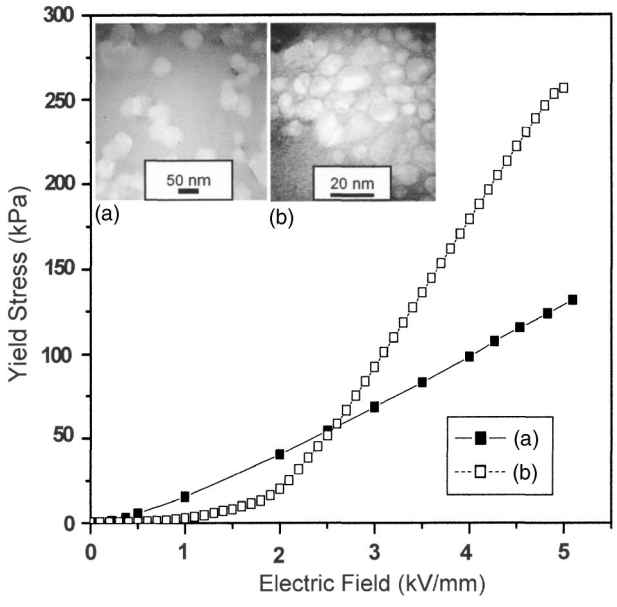

FIG. 1. A comparison of the ER effect variation with the electric field for GER fluids with different particle sizes. Both GER fluids have concentration of 0.3. Inset: TEM images of coated nanoparticles. In (a) the nanoparticles were fabricated without Rb addition, and in (b) the nanoparticles were fabricated with Rb addition to the core materials. A clear difference in particle size is seen, with the smaller particle GER fluid attaining a larger maximum yield stress at 5 kV/mm electric field.

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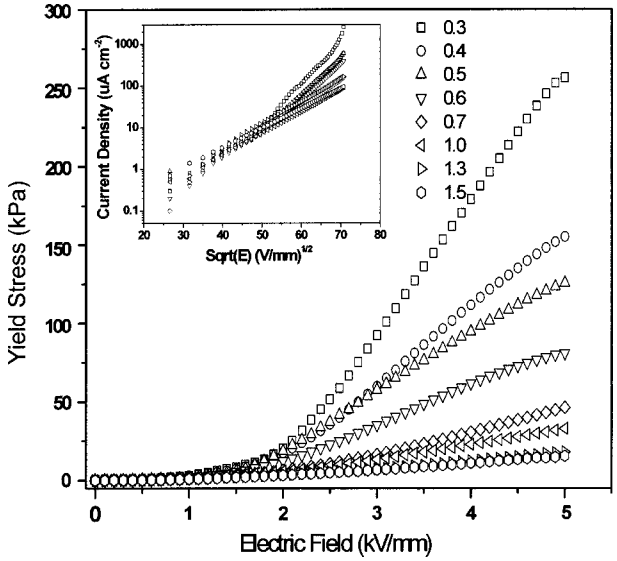

FIG. 2. Measured yield stress plotted as a function of electric field, for GER fluids with different solid particle concentrations. The measured current densities corresponding to those samples are shown in the inset.

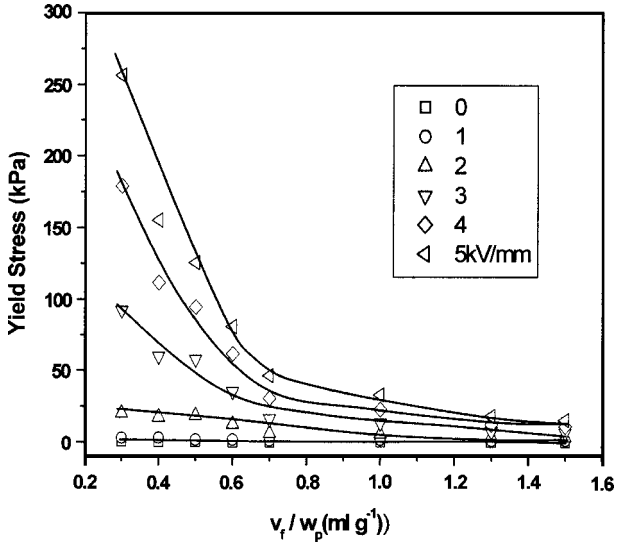

FIG. 3. Variation of the yield stress vs the volume fraction, measured at different electric fields.

sandwiched between two parallel plates. The static yield stress was determined by the maximum shear stress value at which a kink occurs in the strain–stress curve, beyond which the strain increases almost vertically. All measurements were carried out at room temperature.

Figure 1 shows a comparison of the measured yield stress for two samples consisting of two particle sizes with the same concentration (0.3). We observe that the (Rb-doped) GER fluids exhibit very strong yield stress—up to 250 kPa at 5 kV/mm. Thus particles $\sim 1/2$ the size led to a doubling of the maximum attainable yield stress. However, we note that at the lower field range, the ER fluid with the larger particle size has a stronger ER effect than that for the smaller particles.

The observed size dependence is noted to be opposite to that for the traditional ER fluids, based on the mechanism of linear induced polarization. In that case, the ER effect increases with the size of the particles. Here the opposite trend can be understood on the basis of the proposed surface saturation polarization mechanism,[12] in which the GER effect originates from the two saturated polarization layers at the contact region of two coated nanoparticles. As the contact region can be regarded as a tiny parallel-plate capacitor, its energy density is approximately given by εwA, where ε denotes the (roughly constant) average energy density inside the contact region, w the gap width, and A the contact area. From numerical simulations carried in the manner described in Ref. 12 (by varying the particle radius), it is found that $A \propto R^2$, where R is the radius of the coated particle. Hence the overall energy density is proportional to $1/R$. This is in reasonable accord with the observed correlation between the yield stress, which is proportional to the overall energy density, and the particle size.

The measured electric field dependencies of yield stress and solid particle concentration are shown in Figs. 2 and 3. The corresponding current densities are plotted in the inset to Fig. 2. We note from Fig. 2 that the ER effect is weak when the electric field is below 2 kV/mm. However, above 2 kV/mm the effect increases very rapidly. We found from experiments that the ER effect is sensitive to the solid particles volume fraction. This can be seen in Fig. 3, where the yield stress of GER fluids is seen to drop significantly with a small volume fraction decrease.

The ER effects shown above were measured at the fixed shear rate of 1.0 s^{-1}. Shown in Figs. 4(a) and 4(b) are the results obtained with two samples (concentrations are 0.7 and 0.3, respectively) by using step-function voltage pulses, in which the time t(40 s) of each pulse acting on the ER fluid is fixed while the height of the voltage pulse was varied, leading to applied electric varying from 1 to 5 kV/mm.

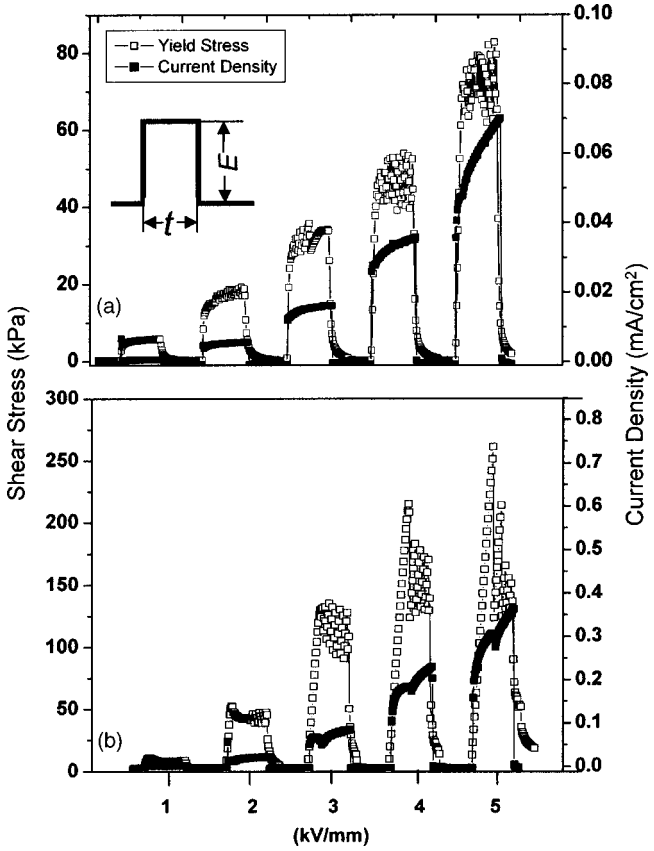

FIG. 4. Measured shear stress variation under pulsed electric field, carried out with different solid particles concentrations of (a) 0.7 and (b) 0.3.

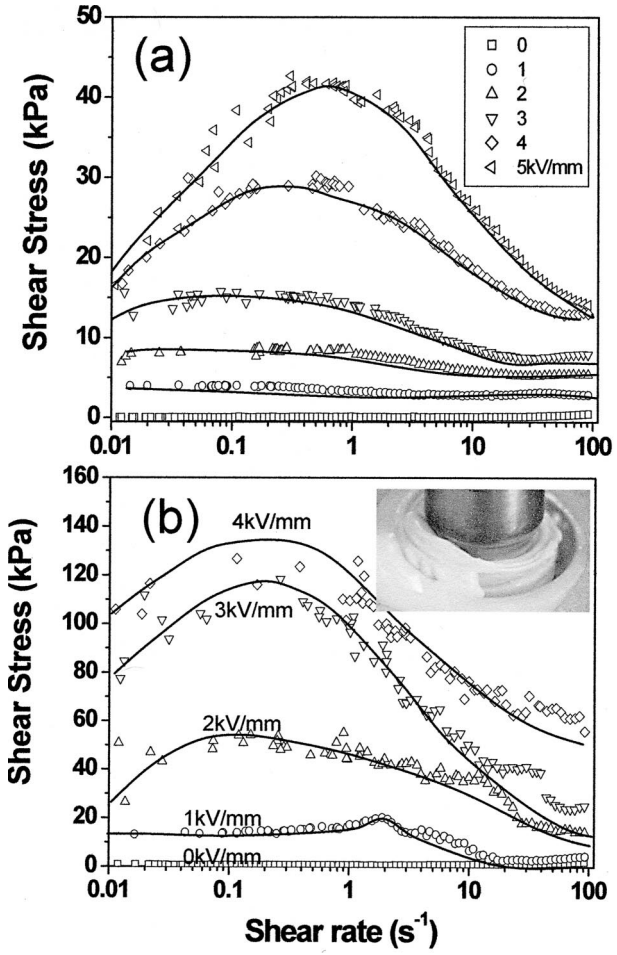

FIG. 5. Shear stress variation as a function of the shear rate, measured at different field strengths. Here the concentrations for (a) and (b) are 1.0 and 0.3, respectively. Inset to (b) clearly shows the problem of suspension material being expelled from the high field region.

From Fig. 4(a), we note that stable shear stress could be observed when the electric field varied from 1 to 5 kV/mm, while obvious fluctuations in the measured shear stress were seen in (b) when the electric field was more than 4 kV/mm. At 5 kV/mm, the shear stress in (b) was seen to first reach 250 kPa at the pulse onset, and then to drop to 150 kPa. The rate of the drop was seen to vary as a function of the rotation rate of the plate. Moreover, when the GER sample was rearranged (mixed and smoothed) with a spatula, the original high yield stress was restored. Hence the effect is spurious. In order to investigate the cause of this spurious effect, we have measured the shear stress under shear rate increasing from 0.1 to 100 s^{-1}. The results are shown in Fig. 5 for two samples [1.0 in 5(a) and 0.3 in 5(b)] at different field strengths. It is observed that whereas the shear stress increased with the shear rate initially, reaching a maximum at , it decreased beyond that. Close observations found that for the higher volume fraction GER suspensions and/or at high electric fields, the suspension materials were actually expelled from the central region of the testing apparatus [inset to Fig. 5(b)], leading to a net decrease in the measured shear stress. We found this to be a generic problem encountered in all the parallel-plate type of measurement apparatus or clutches. The physical reason underlying this phenomenon is that when an electric field is applied across the GER suspension, particles tend to aggregate into columns and structures that are much larger than the nanoscale. Since the solid particles have densities higher than that of the fluid, the rotating motion of the fluid leads to a net centrifugal force acting outward on the meso-scale structures formed from the solid particles, for which the Brownian motion has negligible effect. Over a time period measured in minutes, the higher density materials would migrate to the outer edges of the plate where the electric field is weak, leaving mainly oil in the middle region where the field is large. As a result, the measured shear stress decreases.

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