

## Wetting-induced electrorheological effect

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We demonstrate the role of particle-fluid wetting in inducing the electrorheological (ER) effect. Nanoparticles of barium titanyl oxalate coated with urea (BTRU) were suspended in either silicone oil or hydrocarbon oil. In the former, a high yield stress of more than 250 kPa can be attained at an electric field of 5 kV/mm, while for the latter no measurable ER effect can be obtained. The two suspensions exhibit completely different appearances. Whereas the silicone oil suspension has the consistency of light cream, in the case of hydrocarbon oil with the same solid concentration the appearance is that of a lumpy paste. This clear visual distinction is attributed to the wetting characteristic between the solid BTRU particles and the suspending oil. We found that by adding a controlled, small amount of surfactant additive to the hydrocarbon oil suspension (oleic acid), the consistency can change drastically to resemble that of the silicone oil suspension, with a yield stress of 260 kPa attained at an electric field of 3 kV/mm. We give a simple physical picture of wetting-induced giant electrorheological effect. © 2006 American Institute of Physics.

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Electrorheological (ER) fluids are a class of colloids whose viscosity increases under the application of an electric field. For certain ER fluids the application of a strong field ( $>1000$  V/mm) can lead to an anisotropic solid. 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.<sup>1-10</sup> The dispersing phase of an ER fluid is generally an insulating oil with low volatility and high chemical stability. An ideal dispersing liquid material should have a high boiling point, low viscosity (below 1 Pa s), a high breakdown strength (greater than 7 kV/mm), and good lubricating characteristics. Commonly used oils include polydimethylsiloxane oil (silicone oil), mineral oil, paraffin, kerosene, chlorinated hydrocarbons, transformer oil, etc. Generally, the dispersing phase has a low dielectric constant and does not have much impact on the ER activity, apart from an influence on the response time of the ER fluid due to its viscosity. Particulate materials should display similar ER responses regardless whether dispersed in silicone oil or mineral oil.<sup>3,5</sup>

Here we show that in the case of the recently discovered giant electrorheological effect, the conventional wisdom no longer applies. In particular, the wetting characteristic between the solid particulates and the suspending fluid plays a crucial role in the giant electrorheological (GER) effect. In this regard it should be noted that it has been observed previously if water exists in the system or intentionally added, the ER effect can be enhanced. The particulate materials can also be dispersed in a liquid mixture comprising two different solutions in order to improve the stability and ER effect.<sup>5</sup> Some ER additives have also been discussed in the literature. Water, acid (inorganic and organic), alkali, salt, and surfactants are the most common. Surfactants were observed to improve particles' sedimentation properties and/or to enhance the ER effect<sup>11,12</sup> such as in the case of water.

While additives to ER fluids can serve a variety of purposes, there is still a lack of understanding for their functionalities. In this work, we show that for the recently discovered GER effect,<sup>13</sup> an additive to induce wetting between the solid particles and the suspending fluid can induce yield stress, from practically no yield stress to 260 kPa at 3 kV/mm. The role of the additive in inducing wetting is made obvious by comparison with a reference sample in which the same particles are suspended in a fluid which wets the solid particles, and which exhibits a yield stress of 250 kPa at 5 kV/mm.

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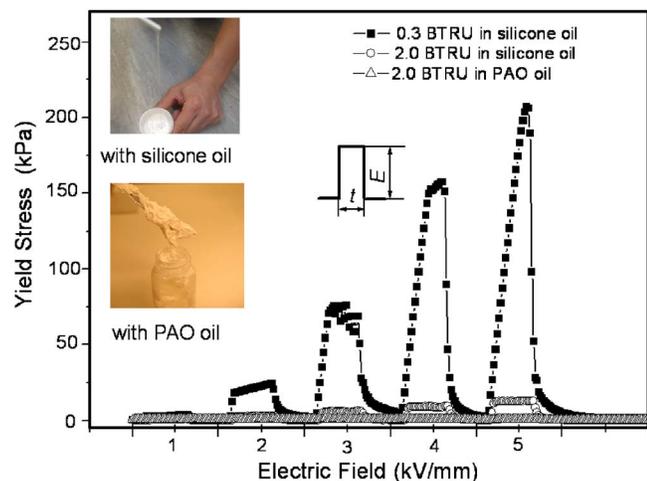


FIG. 1. (Color online) A comparison between silicone oil-based GER fluid (left upper inset), which has excellent yield stress characteristic (red and green symbols), and hydrocarbon oil-based mixture (left lower inset) which exhibits no yield stress (blue symbols). The square voltage pulse applied to the sample is shown in the figure. The height of the pulse corresponds to the voltage denoted on the horizontal axis across a 1 mm gap. Duration of the pulse is  $t=25$  s. Here the concentration is denoted by the amount of suspending fluid, in unit of ml, mixed with each gram of powder. Hence 0.3 means each gram of powder is mixed with 0.3 ml of oil.

We give a simple physical picture of how the wetting characteristic can play a crucial role in the GER effect.

BaTiO(C<sub>2</sub>O<sub>4</sub>)<sub>2</sub> nanoparticles coated with urea (NH<sub>2</sub>CONH<sub>2</sub>), BTRU for short, were prepared as described in Refs. 13 and 14. The powders were divided into two equal portions, each (10 g) mixed with the same volume of silicone oil (3 ml) and hydrocarbon oil (3 ml). The latter is poly- $\alpha$  olefin (PAO), with 99% [-CH<sub>2</sub>CH[(CH<sub>2</sub>)<sub>7</sub>CH<sub>3</sub>]-]<sub>2</sub> and 1% [-CH<sub>2</sub>CH[(CH<sub>2</sub>)<sub>7</sub>CH<sub>3</sub>]-]<sub>3</sub>. After the same mixing process of shaking for 30 min in a SPEX 8000 mixer/mill, two different mixtures were obtained, shown in the insets of Fig. 1. For the silicone oil-based GER fluid, a consistency like that of light cream can be obtained (upper inset in Fig. 1). When measured by a circular plate-type (8 mm in diameter) viscometer (Haake RS1) with a gap width of 1 mm at a shear rate of 0.1 s<sup>-1</sup>, a yield stress of 250 kPa was obtained at 5 kV/mm. While the zero field viscosity, 6.0 Pa s, is not particularly low, yet the electroviscous component is dominant. For the hydrocarbon oil-based GER fluid, a completely different appearance of a lumpy paste is obtained after mixing (lower inset in Fig. 1), and the same measuring condition yields practically no yield stress.

The clear difference in appearance of the two mixtures is attributed to the wetting characteristic between the solid particles and the suspending fluid. Whereas in the silicone oil case the nice consistency is a clear indication of wetting, in the hydrocarbon oil case the lumpy paste is a visual evidence for nonwetting between the solid particles and the hydrocarbon oil.<sup>15,16</sup> There are many examples of such systems in which nonwetting is a known factor for leading to the same texture as observed in the BTRU-hydrocarbon oil mixture.<sup>17</sup>

After diluting both mixtures with additional amount of oil (20 ml total), the silicone oil-based GER fluid still exhibits a yield stress of >10 kPa at 5 kV/mm (with a zero field viscosity of 0.07 Pa s). For the hydrocarbon oil-based ER

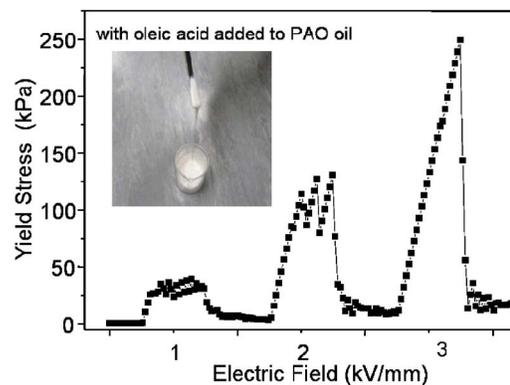


FIG. 2. (Color online) Yield stress as a function of applied electric field for the hydrocarbon oil-based GER fluid (with the oleic acid additive). Here 0.3 means each gram of solid powder is mixed with 0.3 ml of hydrocarbon oil. Inset shows the changed appearance of the mixture after adding a very small amount of oleic acid. For comparison, see the lower left inset of Fig. 1. Measurement conditions are the same as those data shown in Fig. 1. The jagged tops of the yield stress curves are due to the stick-slip phenomenon when the sample is “solidified” across the measuring gap.

fluid, on the other hand, a somewhat smoother but claylike mixture was obtained, which still shows no yield stress (with a zero field viscosity of 0.11 Pa s).

After trying different additives, such as dimethylsulfoxide or aniline with no effect, it is found that if a small drop (0.03 Vol %) of oleic acid [CH<sub>3</sub>(CH<sub>2</sub>)<sub>7</sub>CHCH(CH<sub>2</sub>)<sub>7</sub>COOH] was added into the hydrocarbon oil before mixing with the BTRU powder, there results a totally different mixture with the consistency of light cream (see inset to Fig. 2). When this new mixture was measured at 3 kV/mm, we obtained 260 kPa, which is almost four times greater than the silicone oil-based GER fluid (~70 kPa at 3 kV/mm) at the same concentration (with a zero field viscosity of 9.4 Pa s). However, the current density in this case is higher: 0.35 mA/cm<sup>2</sup>.

We give a simple physical picture on this wetting-induced GER effect. Figure 3 gives cartoons of nonwetting solid particles in hydrocarbon oil and additive-induced wetting solid particles in the same hydrocarbon oil. For the nonwetting case, particles are phase separated from the oil and the distance between two solid aggregates is large even at high electric field. Hence there can be no yield stress since the solid aggregates are always separated by oil [Fig. 3(a)]. For the oleic acid additive-induced wetting case, the surface tension between the particles and oil is greatly reduced due to the mediating effect of the oleic acid molecules, thus allowing the particles to disperse [Fig. 3(b)] and to move close together upon the application of an electric field. The scanning electron microscopy images shown in Figs. 3(c) and 3(d) are evidence for the above description. Since close contact is a necessity for the GER effect, it follows that wetting between the solid particles and the suspending fluid is a necessary precondition for the high yield stress. As the small amount of oleic acid is not enough to cover all the BTRU particles' surfaces, the adsorbed oleic acid molecules would not prevent the close contact of the BTRU particles under an electric field. Hence the amount of added oleic acid has to be well controlled.

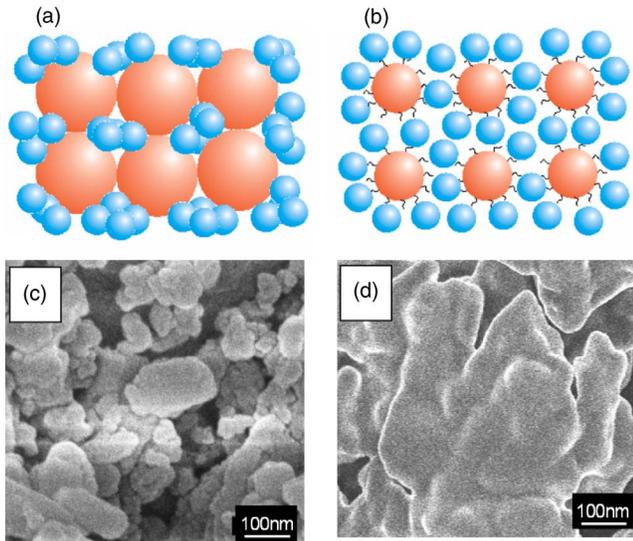


FIG. 3. (Color online) Pictorial cartoons of the wetting effect. (a) shows that when the fluid does not wet the solid particles, the two phases tend to phase separate, and the solid particles would form aggregates. (b) shows that with the addition of oleic acid, wetting is mediated by the surfactant, and dispersion of the nanoparticles becomes possible. Here red denotes oil, blue denotes the solid particles, and the wiggly lines denote the surfactant (oleic acid in this case). (c) and (d) are SEM images that correspond the cases (a) and (b), respectively.

It should be mentioned that while the addition of oleic acid solves the wetting problem with enhanced GER effect, the low density of the hydrocarbon oil (compared to silicone oil) means that sedimentation of the solid particles can be

more serious. However, at the same time the low viscosity of the hydrocarbon oil, plus its better lubrication properties, offer some advantages in that the mixture can have lower zero field viscosity (0.6 times lower than the silicone oil-based mixture), suitable for high shear-rate applications.

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