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Influence of carrier liquid on nanoparticle-based giant electrorheological fluid

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Abstract
The wetting characteristics of the giant electrorheological particles and the suspending fluid were investigated. In contrast to the existing electrorheological fluids, giant electrorheological particles consisting of oxalate core with urea coating are found oil sensitive. The rheological effect of oils from the family of synthetic oil, mineral oil and vegetable oil was studied. The experimental results indicated that hydrogen bonds of the oil chains are instrumental in linking the oil to the giant electrorheological particles; thus, the highest yield stress of giant electrorheological fluid was obtained when hydrogenated silicone oil was used as a suspending phase. Our investigations will provide the compatibility guiding between giant electrorheological particles and liquid phase and may broaden its application to different field, that is, microfluidics with vegetable oil as the carrier liquid.

Keywords
Giant electrorheological, wetting, oil sensitive

Introduction

Electrorheological (ER) fluid referred to a substance whose rheological behaviour can be varied by the influence of a strong electric field. The physical state of ER fluid can be changed from a liquid to a solid-like state within a millisecond and it is reversible. One significant discovery is the giant ER effect made by Wen et al. (2003). The giant electrorheological (GER) fluid consists of the nanoparticles of oxalate core with urea coating and silicone oil. Other than the breakthrough of the high yield stresses (100–200 kPa), there are other merits of such GER fluid including fast response time, much slow sedimentation rate and high breakdown voltage as shown in the application of the piezoelectric rotary motor (Qiu et al., 2014).

Even after years of intensive research, a fundamental correlation of the physicochemical properties involved in the GER effect has not been adequately developed (Chen and Wei, 2006; Shen et al., 2009; Stanway, 2004). There have been reports on the ER enhancing effect through the dispersing media and none has systematically investigated the role of the dispersing liquid (Choi and Jhon, 2009; Sheng and Wen, 2012; Wang et al., 2015). This is largely due to the conventional wisdom that the dispersing liquid plays only a passive role in providing a large mismatch between the dielectric constants of solid particles and oil (Cho et al., 2004). It is known not to be the case for the recently discovered GER effect whose mechanism is based on the alignment of molecular dipoles through the hydrogen bonding network (Chen et al., 2010; Wen et al., 2007).

In this article, we report the intensive investigation of the crucial role played by liquid phase in enhanced GER effect. We systematically studied the wetting effect of different types of oils including the synthetic oil, mineral oil and vegetable oil on its permeability travelling through the porous spaces between the GER particles (using the Washburn method), as well as the rheological data of the ER fluids.

Experiments

Synthesis of GER particles

The GER particles (urea-coated barium titanyl oxalate) were fabricated by the modification of the Kudaka method as described in our previous work (Gong et al., 2008). Initially, barium chloride was dissolved in

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distilled water at 50 °C–70 °C. Individually, titanium tetrachloride solution was slowly added to the prepared oxalic acid solution at 65 °C in an ultrasonic tank. Both the solutions were then mixed in an ultrasonic bath at 65 °C. Nanometre-sized barium titanyl oxalate particles were formed at this stage. Addition of urea to the mixed solution led to the formation of a white colloid, which was drastically cooled to room temperature. The precipitate was washed with water, filtered and then vacuum-dried at 100 °C for 1–3 h to remove all traces of water. The dried white powder consisted of the nanoparticles coated with urea, that is, $BaTiO(C_2O_4)_2$ + NH_2CONH_2. In such a core/shell structure, urea serves as an ER promoter. All the chemicals were supplied by Sigma–Aldrich Chemical Company.

ER fluids

Dimethyl terminated and hydrogenated silicone oils were supplied by Dow Corning. White mineral oil, liquid paraffin, sunflower seed oil and corn oil were supplied by Sigma–Aldrich Chemical Company. All the oils were dried at 120 °C for 2 h before the experiment to avoid the influence of moisture. The experiment samples were homogenized by mixing the GER particles with different oil samples in a high-speed grinding mill for 2 h. Some of the mixtures were not mixed well even after 2 h, therefore, consideration on longer mixing time is needed. Concentration of the ER fluids can be denoted as the amount of oil, in units of mL, mixed with each gram of particles. Hence, 0.5 means 10 g of powder mixed with 5 mL of oil.

GER particle measurement

The morphology of the GER particle was visualized on a JEOL-6700F scanning electron microscope (SEM) with a target acceleration voltage of 5 kV. SEM sample was prepared by dispersing 5 mg particle in 2 mL of ethanol by ultrasonication. A drop of the suspension sample was transferred to a wafer for volatilization. After taking away the ethanol, the sample on the wafer was then gold-coated to enhance the electrical conductivity for the SEM. The size distribution of the batch samples was confirmed by PANalytical X-ray diffractometer (X'Pert Pro).

Rheological data collection

Rheological measurements were performed on a circular-plate-type viscometer (Haake RS1) with an 8-mm diameter rotating disc and a gap of 1 mm between the rotor and stator, where the ER fluid samples were injected. A functional generator (PM 5315; Philips) was used to generate step signals for driving the DC high-voltage source (SPELLMAN SL300). Software package RHEOWIN was used to collect experimental data. A 50-s square voltage pulse was applied to the sample with each measurement repeated at least three times due to their reproducibility and repeatability. Shear stress as a function of time was measured at a very low shear rate ($0.1\ s^{-1}$). Yield point was reached when a stress–time curve changed its slope to be flat after an abrupt increase at the beginning of turning on the field. The yield stress at a given field was taken to be the maximum of the shear stress in the corresponding time span. The experiment was performed at 24 °C.

Permeability data collection

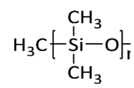
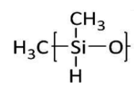
The oleophilicity of GER particles in the ER fluids was measured by the Washburn method to study the permeability of oils through the GER particles. The particles were packed in precisely selected capillary tubes with inner diameters of 0.9 mm and lengths 10 cm. The height of oil as a function of time was observed and recorded with the assistance of microscopy (Olympus SZ-CTV; PTC International Co.). Strict powder packing by a reproducible procedure is essential in this experiment. The packing process was manually operated and should be very tedious. We first weighed a certain amount of particles and introduced them into the capillary pinch by pinch, each pinch with equivalent sub-quantities. The column was dropped 20 times through a 20-cm-long tube to make the powder compact consist. The overall weight that was introduced into the tube was calculated by measuring the residual powder and it was about 0.1 g. Afterwards, we divided each portion of 0.1 g powder into 20 equivalent sub-quantities and inserted them into the tubes step by step as in the procedure stated above. The first step was to get a reference for the rest of the subsequent samples. The filled capillaries with the same powder height (observed under microscopy) were selected for the permeation process. They were vertically immersed into the same height of sample oils. Each permeation process was performed three times and the average was collected.

Result and discussion

GER particle characterization

After fabrication of the GER particles, the output product was analysed by SEM imaging in the inset of Figure 1. We observed that the particles are spherical in shape with an average size of 50 nm. The result based on size distribution by volume is given in Figure 1 with the help of X-ray diffractometer. The most frequent radius is 15 nm and the average radius is 22 nm with a relative standard deviation of 51.97%. We then confirmed our fabricated GER particles match the description from Wen et al. (2004).

Table 1. Rheological data of various oil-ER samples.

Source	Oil type	Chemical formulae	Oil viscosity (mPa s)	Mixture viscosity (mPa s)[a]	Amplifying ratio	Visual appearance
Synthetic oil	Dimethyl terminated silicone oil		12	169	14.1	Liquid-like
	Hydrogenated silicone oil		20	400	20	Liquid-like
Mineral oil	White mineral oil	$C_{25}H_{43}NO_3$	4	359	90	Clay-like
	Liquid paraffin	$[C_nH_{2n+2}\ \ n=16\sim24]$	20	477	23.85	Clay-like
Vegetable oil	Sunflower seed oil[b]	 Linoleic acid	50	336	6.7	Sol-like
	Corn oil[c]	 Oleic acid	50	336	6.7	Sol-like

ER: electrorheological.
[a]Mixture volume concentration = 0.5.
[b]Linoleic acid = 18%, Oleic acid = 60%.
[c]Linoleic acid = 65%, Oleic acid = 20%.

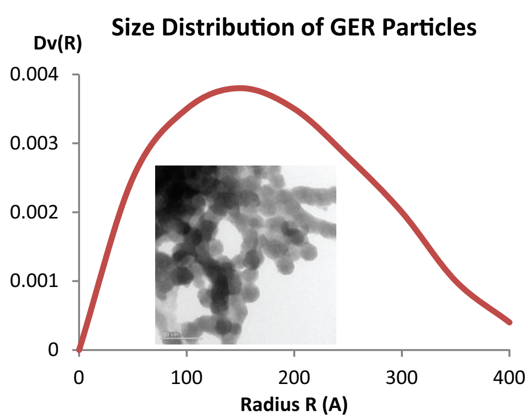


Figure 1. Size distribution of GER particles with the inset of the SEM image.

Viscosity, appearance and permeability characteristics

A total of six different oil samples from three different sources (Table 1) were investigated to give a simple physical picture of how the wetting characteristics can play a crucial role in the ER effect.

Polysiloxanes from synthetic oil are semi-organic polymers and copolymers containing an inorganic backbone of repeating silicon–oxygen units and organic side chains substituted on the silicon atom along the polymer chain. The properties may vary by selection of different substituents. Mineral oil consisted predominantly of carbon and hydrogen which is non-polar. Vegetable oil contained triglycerides or glycerine triesters of different fatty acids, accompanied by mono- and diglycerides and free fatty acids.

The oil and mixture viscosity was measured on Haake RS1. The amplifying ratio is a constant (mixture viscosity divided by oil viscosity) which represented the wetting effect of the oil with respect to the GER particles. The highest amplifying ratio was credited to white mineral oil which was meant to have the most unfavourable wetting effect among the tested samples.

With mixture concentration of 0.5, three different types of visual appearances were obtained, sol-like, gel-like and clay-like, as shown in Figure 2.

For the synthetic-oil-based ER fluid, a texture of a light cream (liquid-like) was obtained. For the mineral-oil-based ER fluid, a significant different appearance of a lumpy paste (clay-like) was obtained after mixing. The vegetable-oil-based ER fluid was in intermediate which is similar to a semi-melt butter (sol-like). Some interesting observations found that although hydrogenated silicone oil–ER fluid was having similar mixture viscosity and amplifying ratio with the paraffin oil–ER fluid, the visual appearances are in both extremes. The mixing time needed for the latter samples was two times longer than hydrogenated silicone oil–ER fluid as it appeared that the GER particles in paraffin oil did not spread out evenly. There are many examples of such systems in which non-wetting is a known factor for leading to the same texture as observed in the mineral oil–ER fluid.

The physical picture (Figure 2) is supported by the fact that different oil structure can play a significant role in the initial viscosity as well as in the visual appearances of the sample mixtures. The latter is suggestive of a strong interaction between the solid particles and oils.

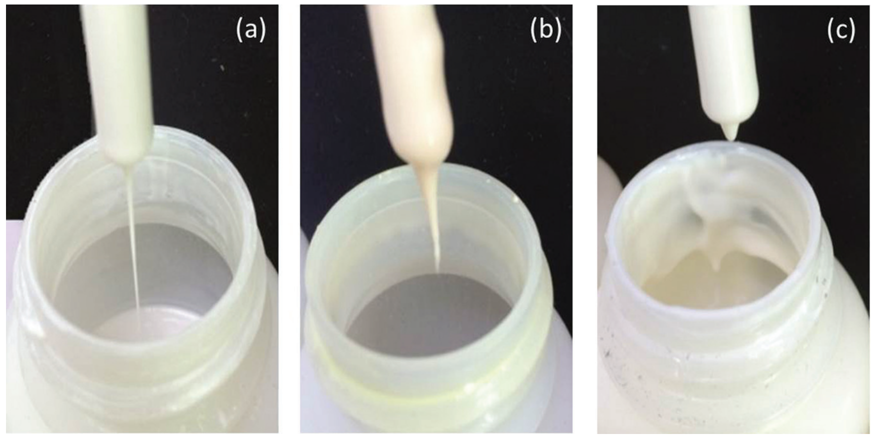


Figure 2. Visual appearances of the ER fluids: (a) liquid-like, (b) sol-like and (c) clay-like.

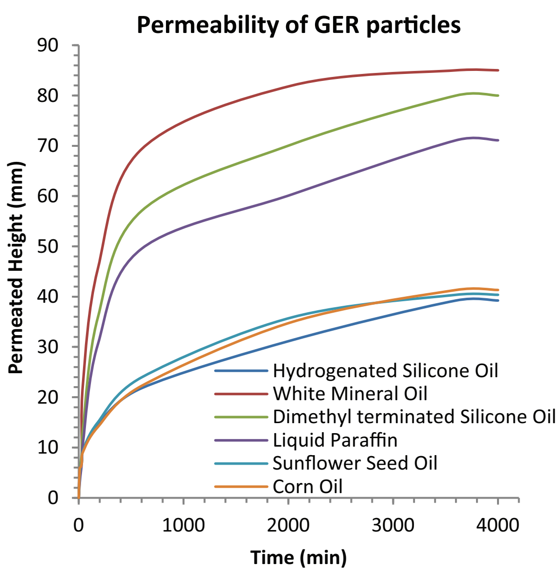


Figure 3. Permeability data of various oil samples in the GER particle columns at volume concentration of 0.5.

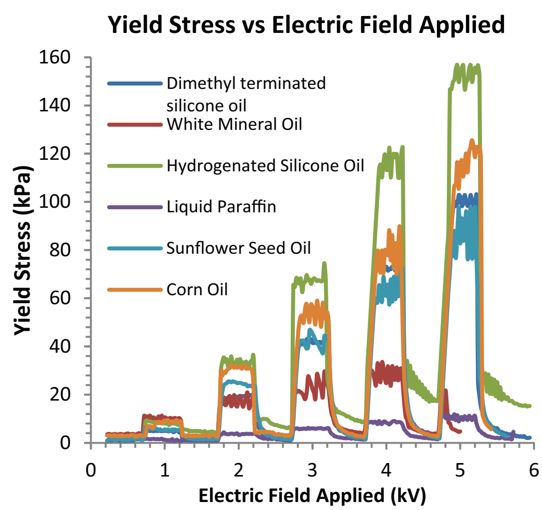


Figure 4. Yield stress of various oil-based ER fluids with volume concentration of 0.5.

The permeability of different oils through columns of solid particles was studied by the Washburn method (Figure 3). The initial motive was to measure the wetting effect; however, the result seems to be unpromising. There was a trend that higher oil viscosity led to lower permeability except for the case of hydrogenated silicone oil–ER fluid. After 3500 min, a relatively saturated height can be reached as presented in the graph. Lower oil viscosities, this means to shorten chain lengths, allowed better permeability of oils through ER powders and thus higher saturation heights. Figure 3 was believed to be dominated by the capillary effect between the oil and the wall rather than the wetting effect between the oil and the GER particles as the trend matched well only with the oil viscosity in Table 1.

ER effect

The relevant yield stress values for six different types of oil are plotted as a function of applied electrical field in Figure 4. From the experimental results, we found two interesting points. First, the result violated the norm for conventional ER fluid that high zero-field viscosity is usually accompanied by high yield stress (Halsey, 1992). Second, the plotted graph is contrary to the conventional ER fluids that are only sensitive to the complex dielectric constant of the oil (Ma et al., 2003).

Figure 4 proves that GER fluids are oil sensitive in numerous ways. For example, with hydrogenated silicone oil, one can obtain a very significant ER effect, but with the same particles dispersed in liquid paraffin, the GER effect is trivial. Such dramatic contrast implies that oil plays a synergistic role in the GER effect.

Figure 5 gives a simple physical picture on this wetting-induced GER effect illustrating the non-

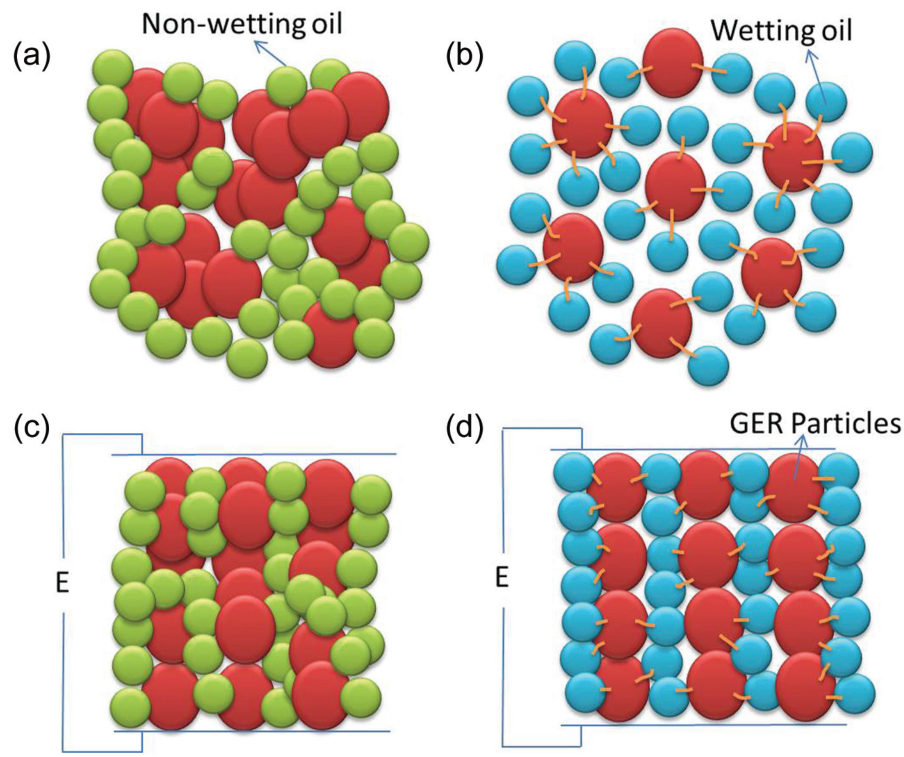


Figure 5. (a) Non-wetting effect and (b) wetting effect at zero-field suspension and (c) non-wetting effect and (d) wetting effect when electric field is applied.

wetting solid particles in mineral oil and wetting solid particles in synthetic oil. For the non-wetting case (Figure 5(a)), GER particles are phase-separated from the oil and the aggregation between two solids is large even with applied electric field. Hence, there can be no yield stress or even arcing since the solid aggregates are always separated by oil (Figure 5(c)). This phenomenon is shown (Figure 4) at the applied electric field of $5\,\mathrm{kV\,mm^{-1}}$ with white mineral oil–ER fluid. However, the surface tension between the GER particles and hydrogenated silicone oil is greatly reduced due to the mediating effect of the hydrogen atom, thus allowing the particles to disperse (Figure 5(b)) and to move close together upon the application of an electric field (Figure 5(d)).

The fact that hydrogenated silicone oil wetted particles in a perfect way was attributed to the presence of oxalate groups in the core nanoparticles and to the non-uniformity of the urea coating with the modified hydrogen atom in the oil. The formation of the filaments, with an attendant lowering of the aligning field and a finite penetration length, can be attributed to the confinement effect exerted by oil chains. Urea molecules have a strong tendency to form hydrogen bonds with one another, and this influences their interactions with hydrophobic oil chains, which are incapable of forming hydrogen bonds. In addition, the polarity of the oil chain gave a promising contribution to the ER effect as well (Shen et al., 2006).

Conclusion

In this study, we investigated whether the carrier liquid plays a crucial role in the GER effect. Our results show that GER particles are very oil sensitive. Using different dispersing media, different rheological effects (yield stress, zero-field viscosity, visual appearance and permeability) were found. A total of three different visual appearances among six different oil samples were observed. The amplifying ratio constant gives a good indication on how the oil wets the GER particles. We attribute the effect to the hydrogen bonding interaction between particles and the side chain (hydrogen molecule and oleic acid). The permeability measurements show no evidence of a possible linkage due to the domination of the capillary effect and it is non-representative to the wetting characteristics. We then confirmed the wetting effect with the rheological data. Our results indicate the hydrogen bonds are instrumental in linking the oil to GER solid particles when electric field is applied. The hydrogen groups of the oil provided a potential application as dispersing phases or additives in GER fluids. From the rheological data shown, hydrogenated silicone oil is an optimal oil structure wetting perfectly with the GER particles that gives a relatively reasonable amplifying ratio. The investigations also enhance the GER material compatibility and broaden its application to different field, that is, microfluidics.

Declaration of conflicting interests

The authors declared no potential conflicts of interest with respect to the research, authorship and/or publication of this article.

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