Influence of liquid phase on nanoparticle-based giant electrorheological fluid

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Abstract
We show that the chemical structures of silicone oils can have an important role in the giant
electrorheological (GER) effect. The interaction between silicone oils and solid nanoparticles is
found to significantly influence the ER effect. By increasing the kinematic viscosity of silicone
oils, which is a function of siloxane chain length, sol-like, gel-like and clay-like appearances of
the constituted ER fluids were observed. Different functional-group-terminated silicone oils
were also employed as the dispersing media. Significant differences of yield stress were found.
We systematically study the effect of siloxane chain lengths on the permeability of oils traveling
through the porous spaces between the particles (using the Washburn method), oils adsorbed on
the particles' surface (using FT-IR spectra), as well as their particle size distribution (using
dynamic light scattering). Our results indicate the hydrogen bonds are instrumental in linking
the silicone oil to GER solid particles, and long chain lengths can enhance the agglomeration of
the GER nanoparticles to form large clusters. An optimal oil structure, with
hydroxyl-terminated silicone oil and a suitable viscosity, was chosen which can create the
highest yield stress of $\sim$300 kPa under a 5 kV mm^{-1} DC electric field.

1. Introduction

The rheology of polymer composites consisting of particulates dispersed in a polymer matrix is complicated. The flow characteristic of this two-phase system depends on both the properties of the dispersed particles and the polymer matrix, such as the particle size and shape, molecular weight, viscosity of polymer, interfacial interaction between particle and polymer, etc [1–3]. It was reported that the chain length of the polymer and the functional groups in the chain can influence the interfacial adhesion strength between the two phases and consequently the viscoelastic properties [1]. Such an effect can favor the agglomeration of particles into large clusters by interparticle electrostatic and van der Waal's forces [4, 5]. Although there have been many reports about the relationship between viscoelasticity and polymer–particle interactions, most of them were based on the alkane matrix and inorganic particles [6, 7].

Electrorheological (ER) fluids are a type of smart material composed of dielectric particles suspended in insulating oil and can be treated as a two-phase system. The viscosity can vary by a few orders of magnitude under the application of an external electric field. If the field is strong enough, some of the ER fluids can 'solidify' into an anisotropic solid, with a yield stress to characterize its strength. The change in the rheological characteristics is usually accomplished within 10 ms and is reversible; thus, the ER fluid can serve as an electrical–mechanical interface [8–10] with potential applications in actively controllable clutches, dampers, valves, etc [11–14]—hence the 'smart' denotation. Considerable efforts have gone into the preparation of different suspended particles with the aim of improving the ER yield stress. These include semiconductive polymers [15–18], metal- or metal-oxide-doped titania or titanate [19–22], intercalated clay composites [23, 24], organic layers modifying titania or silica [25–27], mesoporous composites and nanocomposites, etc [28–32]. Although there have been reports on the ER-

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enhancing effect through the dispersing media [33–36], none has systematically investigated the role of the dispersing liquid. 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. While this might indeed be the case for the conventional ER mechanism based on induced polarization, it is known not to be the case for the recently discovered giant electrorheological (GER) [37, 38] effect whose particle size is nanoscale and whose mechanism is based on the alignment of molecular dipoles through the hydrogen bonding network [39].

ER fluids can be considered as a matrix–particle system with dispersing liquid as the matrix and ER particles as the inclusion. In particular, we investigate the chain lengths and molecular structures dependences of the dispersing oils (silicone oil). By correlating the molecular structures of oils with the corresponding ER effect, an optimal molecular structure for the silicone oil is identified, leading to a GER yield stress value up to 300 kPa—the strongest ER effect tested to date [29, 37, 38].

2. Experimental details

2.1. Materials

BTRU nanoparticles (urea-coated barium titanyl oxalate) were synthesized by modifying the method of Kudaka and mainly described as in our previous work [29, 40]. In the presence of a saturated urea solution, solutions of barium chloride, titanium tetrachloride and oxalic acid were co-precipitated at 65 °C to form colloidal sols. The mixture was washed using de-ionized water to remove aqueous acid. The BTRU particles were subsequently dried. Another type of solid particles are the 3A 1/16 type molecular sieves supplied by Nacalai Tesque Inc. Silicone oils with different kinematic viscosities, 1, 5, 10, 20, 50, 100 and 200 cSt, were obtained from Clearco Chemical Co. The hydroxyl group and diglycidyl group-terminated silicone oils were supplied by the Sigma Aldrich Chemical Co. All the oils were dried at 120 °C for 2 h before the experiment to avoid the influence of moisture. ER fluids were formed by mixing the BTRU particles or molecular sieves with silicone oils. Concentration of the ER fluids can be denoted as the amount of silicone oil, in units of ml, mixed with each gram of particles. Hence 0.6 means 10 g of powder mixed with 6 ml of oil.

2.2. Sample preparation and characterization

The morphology of the BTRU particle was visualized on a JEOL-6700F SEM with a target acceleration voltage of 5 kV. To prepare the SEM sample, 1 mg BTRU was dispersed in 2 ml ethanol by ultrasonics. Then one drop of the suspension was transferred to a wafer. After volatilization of the ethanol, the sample was then gold-coated to increase its electrical conductivity before conducting SEM. The inset of figure 2 shows the SEM picture of the BTRU particles. They are spherical in shape with sizes between 80 and 100 nm. The size distribution was also confirmed by a particle size analyzer (90Plus/BI-MAS, Brookhaven Instruments Corporation). For

each sample, 5 mg particles were dispersed in 50 ml ethanol. The average diameter of 90.6 nm and the polydispersity of 0.12 were recorded by particle sizing software (Brookhaven Instruments Corporation).

The Fourier transform IR (FT-IR) transmission spectrum was recorded on a Bio-Rad FTS6000 spectrometer with a DTGS detector. The number of scans is 32 with a spectral resolution of 4 cm^{-1}. The samples were prepared by dispersing 1 g BTRU particles in a mixture of 20 ml toluene and 0.1 ml silicone oil. After stirring for 30 min, the particles were filtrated. The residua were repeatedly washed in 20 ml toluene by 5 ultrasonic redispersions/filtrations and the washing process was applied to all the FT-IR samples. The filtered particles were dried at 80 °C overnight in a dry oven. The final powders were prepared as slices using spectroscopic-grade KBr to identify the absorbed groups on ER particles.

The size distribution of the particles wetted with oils was measured by a dynamic light scattering (DLS) system. It was equipped with a COHERENT INNOVA 300 laser system, a BI-200SM goniometer and an EMI 9863/350B04 type PMT (Brookhaven Instruments Co.). The goniometer arm was rotated to an angle of 90°. The wavelength of the laser is 514 nm and the temperature is set at 22 °C. A unimodal fitting of the measured correlation function to the autocorrelation function $C(t)$ is processed by a BI-900AT correlator (Brookhaven Instruments Co.). The average diameter was obtained by the relationship between diffusion coefficient D and particle size. For the sample preparation, the key step is to establish a suitable concentration which allows the sample to acquire a relatively monodisperse state and a suitable average count rate (ACR) between 10 and 100 kcps while the laser power and pinhole were fixed. The cumulative time is 4 min. In our approach, one drop of ER fluid was continuously diluted with 20 ml toluene five times and ultrasonics were applied for better dispersion. A standard control sample polystyrene polymer of 204 ± 6 nm diameter (Duke Scientific Corp.) was measured first to verify the set-up. The average diameter obtained is 204.4 nm with an ACR 69.8 kcps and polydispersity 0.005.

2.3. Rheological data collection

Rheological measurements were performed on a circular-plate type viscometer (Haake RS1, 8 mm diameter rotating disc, with a gap of 1 mm between rotor and stator). A PM 5134 (Philips) functional generator was used to generate step signals for driving the dc high-voltage source (SPELLMAN SL300). The software package Rheowin was used to collect experimental data. The ER fluid was spread in the 1 mm gap between the rotor and stator. A 50 s square voltage pulse was applied to the sample. For reproducibility and repeatability of the measurements, ER fluids were re-dispersed before each measurement, and each measurement was repeated at least three times. For dynamic measurements, the stress versus shear rate curve for each ER fluid was recorded for shear rates varying from 0 to 400 s^{-1}. To obtain the static yield stress, a stress–strain measurement was carried out at a very low shear rate, and the stress value at which the viscosity decreases abruptly is defined to be the yield stress.

2.4. Permeability experiment

The Washburn method [41] which had been used to measure the oleophilicity of nanoparticles in ER fluids [42] was employed to study the permeability of silicone oils through the BTRU powder. The BTRU powder was packed in precisely selected capillary tubes with diameters 0.16 cm and lengths 10 cm. The raised floor of oils was observed by the assistance of microscopy (Olympus SZ-CTV, PTC International Co). The height of oil as a function of time was recorded. In this method, strict powder packing by a reproducible procedure is essential. The packing process was mainly manually operated [43]. First, we weighed a certain amount of particles and introduced them into the capillary step by step, each step with equivalent subquantities. The column was dropped from a height of 10 cm ten times to make the powder compact. The overall weight that was introduced into the tube was calculated by weighing the residual powder and it was about 0.1 g. Afterwards we divided each portion of 0.1 g powder into 20 equivalent subquantities and inserted them into the tubes step by step as in the procedure stated above. 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 silicone oils. Each permeation process was performed three times. Figure 5 is the average result of this procedure. The approximate saturated heights were obtained by laying the capillary tubes in the oils for 24 h.

3. Results and discussion

3.1. Structure of the silicone oils

The methyl-terminated silicone oils with seven kinematic viscosities of 1, 5, 10, 20, 50, 100, and 200 cSt were chosen to study the effect of chain length on the ER effect. The oil viscosity depends directly on the degree of polymerization n and hence the polymer chain length. Here n varies from 3 to 400. The bond length of Si–O is about 0.164 nm and the bond angle of Si–O–Si in linear silicone oils is approximately 140° [44–46].

3.2. Rheological measurement

When the ER fluid concentration is 1, i.e. 10 g BTRU particles mixed with 10 ml of the different silicone oils, there will be three different types of visual appearance: sol-like, gel-like and clay-like, as shown in figure 1.

The relevant yield stress values are plotted in figure 2. It was found that the ER fluids prepared with higher viscosity oils have larger yield stress values. In order to make a comparison between the GER fluid and ER fluid constituted with larger-sized particles, a conventional micron-sized molecular sieve was selected which shows good wetting characteristics with silicone oils, and the mixture also displays a relatively large ER effect [47, 48]. The measured yield stresses are less varied than that of the GER fluids when the concentration is the same and the oil structures are not changed. The zero-field viscosity does not vary as significantly with the oil structure as in the case of GER particles (see table 2). All the mixtures have sol-like
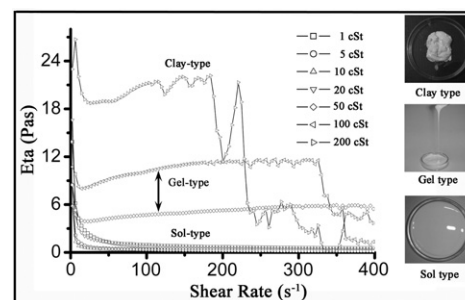

Figure 1. Left panel: Zero-field viscosity plotted as a function of shear rate varying from 0 to 400 s^{-1}, for 1, 5, 10, 20, 50, 100 and 200 cSt silicone oils. Signs of the curves indicate the different viscosities, shown in the middle. The right panel shows three different types of visual appearances for the ER fluids constituted by using different oils. All sample concentrations are set at 1.
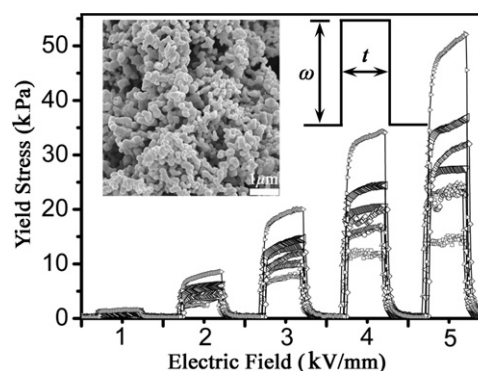
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Figure 2. ER effect comparing between seven GER fluids constituted using different silicone oils. Yield stresses are plotted as a function of applied electrical field. A square voltage pulse ($t = 50$ s duration) was applied to the sample across a 1 mm gap. Upper left inset is an SEM photograph of the as-prepared BTRU particles which are around 100 nm in diameter. Signs corresponds to the different oils used, specified in the middle of figure 1.

appearance as shown by the viscosity values in figure 3. It was reported that chain lengths have an effect on the agglomeration of the filled particles and consequently influence the fluid viscoelasticity and flow characteristics [1]. This mechanism may also be applied here. We deduce that the longer chain lengths of silicone oils can lead to the large agglomeration of ER particles, especially when the particles are nanoscale. The long chain polymers essentially act as the agent of linkage between the particles [2] (since the oxygens in the chain can 'stick' to the nanoparticles by forming hydrogen bonds). As a result, the higher yield stress of the GER fluids composed of higher viscosity oils (and hence the longer siloxane chain length) may be attributed to the agglomeration effect. In GER fluids, the relationship between yield stress and oil chain length, oil viscosity and particle concentration is simply shown in figure 4 [29, 37, 38].

This physical picture is supported by the fact that, as the concentration decreases, the effect of higher viscosity oil becomes much less pronounced when compared with
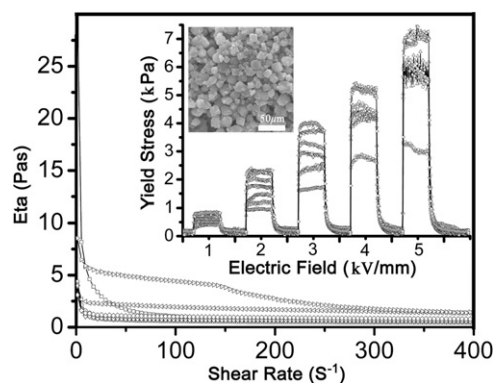
Figure 3. Comparison between seven different ER fluids constituted by using a micron-sized molecular sieve as solid particles and different silicone oils (signs have the same meaning as in figure 2). Zero-field viscosity (denoted Eta) is plotted as a function of shear rate. Yield stress versus applied electric field is given in the inset. The picture inset is an SEM image of the micron-sized molecular sieve particles. The particle size is about 3–5 μm.
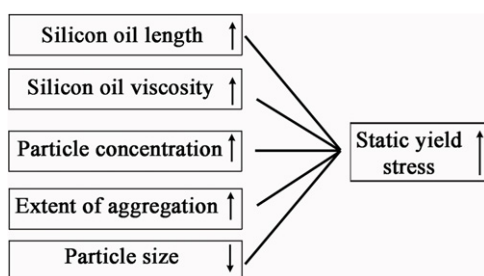

Figure 4. Schematic diagram indicating the yield stress increase with the increase or decrease of silicone oil length, viscosity, particle size and concentration, and extent of agglomeration.

those GER fluids constituted by lower viscosity silicone oils. Likewise, the clay-like appearance of the GER fluid composed of higher viscosity oils can be understood as the formation of an agglomeration. When the molecular sieves act as the solid particles, the effect of higher viscosity oils is not significant, since in that case the particle size is much larger (micron-sized). Even the longest chain length can no longer be effective in favoring agglomeration. Hence all the ER fluids have sol-like appearance. We thus speculate that long chain silicone oils are especially effective in inducing agglomeration of the nanoparticles. This phenomenon accounts for the higher ER yield stress and the higher zero-field viscosity, with the trend being more pronounced when the particles are smaller in size.

3.3. Permeability and adsorption characteristics

Rheological measurements have shown that the chain length of silicone oils can play a significant role in the ER effect as well as in the visual appearances of the mixtures. The latter is suggestive of a strong interaction between the solid particles and oils [38]. To better quantify such an effect, we study the permeability of different oils through columns of solid particles by the Washburn method [33], as well as the adsorption of different oils on the solid particles' surface through FT-IR spectra.
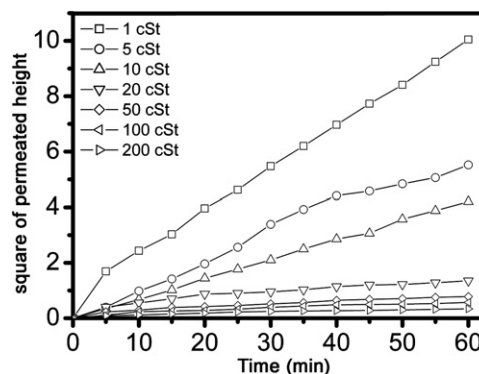

Figure 5. Square of the permeated height (in cm^2) plotted as a function of time (in min).

Permeability can be simply compared by the slopes in the plot of the square of the height H^2 (permeated oil in the capillary tube) as a function of time t, shown in figure 5. It is clear that higher viscosity of oil leads to lower permeability. After 24 h, a relatively saturated height can be reached as presented in table 3. To lower oil viscosities, which means to shorten chain lengths, allowed better permeability of oils through ER powders and thus higher saturation heights. In figure 5, it is found that low viscosity oils (1, 5 and 10 cSt) can lead to a better linear relationship between H^2 and t, although there are some bad points which may be caused by the packing effect of powders. The difference between their slopes is mainly affected by the variance of viscosities. A direct confirmation is if we put the capillaries in the silicone oils for long enough time (about 2 days), then the saturation heights of the three oils are almost the same. But for the 20 cSt oil or other more viscous oils, things are different. The H^2 plotted as a function of t is not a straight line. That means the Washburn equation needs to be modified to add other elements [43]. Indirect evidence is that, no matter how long you put them together, the saturation height will not change with time. From this point, there must be other factors ascribed to the permeation of oil when the viscosity is high. We deduce these factors may contain the chain length impact because these silicone oils have similar chemical and physical characteristics except for their viscosities which are decided by the chain lengths. If the chain length is long enough, for example several tens of nanometers, the small pore size will impede the permeation of oils and thus the capillary flow is not the only effect in the Washburn method [49, 50]. Whether or not, during the ER effect measurement, from the point that you mix the particles and the oils together to the point that you start to measure the ER effect, this time interval is limited. Consequently, the oils will not distribute everywhere inside the powders. This is another reason we deduce the ER effect increase is attributed to the cluster formation.

The adsorption of oils on the surface of solid particles was studied by FT-IR spectroscopy. The results are shown in figure 6. There is a small (absorption) dip at 1150 cm^{-1}, which appears in all oil spectra and is attributed to the asymmetric stretching vibration frequency of Si–O–Si [51] of the attached silicone oils. For 5 cSt silicone oil, the Si–O–Si stretching
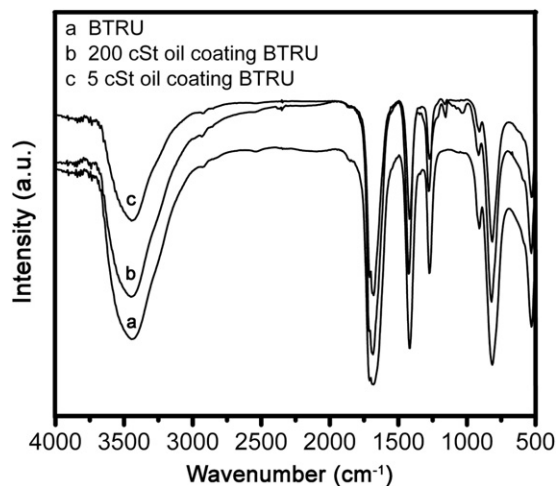
Figure 6. FT-IR spectra of the BTRU particles (a), with 200 cSt silicone oil coating (b) and with 5 cSt silicone oil coating (c). The small dip centered at 1150 cm^{-1} wavenumber is indicative of the Si–O stretching vibration.

Figure 7. Schematic illustration of ER fluid structures: (a) BTRU particles, (b) dispersed in short chain length oil, (c) dispersed in long chain length oil, (d) dispersed in hydroxyl-group-terminated silicone oil. (e) and (f) are chemical structures of methyl-terminated silicone oil and hydroxyl-terminated silicone oil.

vibration at 1050 cm^{-1} also appears [52, 53]. This result implies that the silicone oils can be 'caught' by the BTRU particles, even after the particles were vigorously washed many times. If so, two factors might contribute to this strong adsorption. The first is the hydrogen bonding interaction between BTRU and oxygen atoms in silicone oil chains. It has been proved that silicone oil chains can form hydrogen bonds with surface silanol groups on the silica wafer [54]. In our study, the BTRU particle produced by the Kudaka method has 4 mol of crystalline water [40, 55], which allows the formation of hydrogen bonds between Si–O and H–O or N–H in urea [1, 39]. The second is the low surface tension of silicone oils and the flexible siloxane backbone, which enable them to be good wetting agents on the surface of solids [44]. According to the measurements of permeability and adsorption, the effect of different chain lengths on the structures of the corresponding ER fluids can be conceived and schematically illustrated as shown in figures 7(b) and (c). Better permeability of short chain oils can efficiently segregate the BTRU particles (figure 7(b)). In contrast, when the oil chain is long, e.g. 200 cSt oil with $n \sim 400$ and chain length $\sim$65 nm, the oil becomes an effective agent to agglomerate the nanoparticles into clusters (figure 7(c)). These clusters can greatly increase the zero-field viscosities of ER fluids as shown in figure 1.

3.4. Size distribution

The measured size distribution of ER particles with and without oils as a function of oil viscosity is shown in figure 8. (For oils with different chain lengths, the dissolving ability of toluene is different [56], but when the concentration of silicone oils is low and the mixing time is long enough, such an influence of solvent can be neglected. In addition, there is no chemical interaction between toluene and silicone oils as seen from the FT-IR results.) Comparison between the effective particle diameters indicates that the cluster sizes in
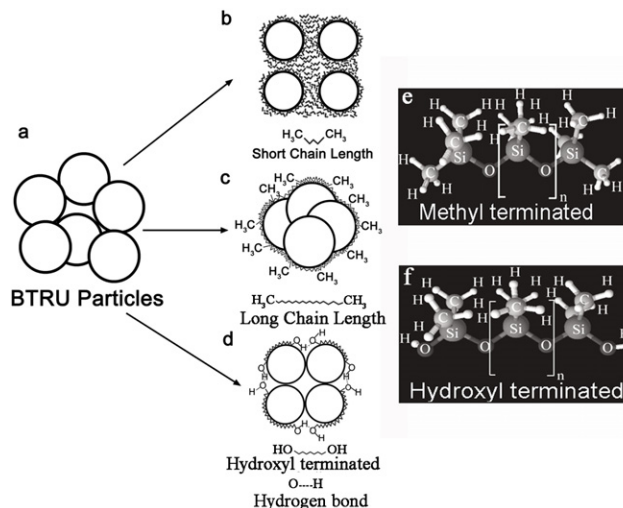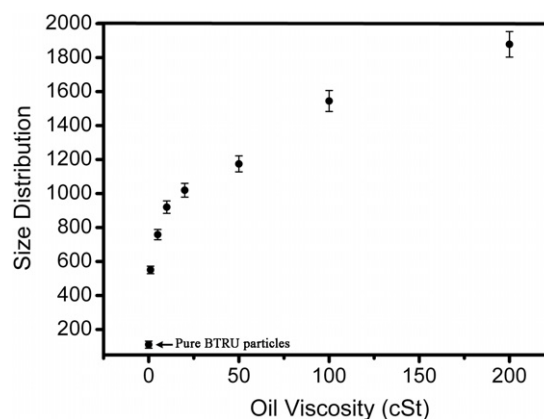

Figure 8. Particle size distribution in GER fluids prepared by different viscosity oils. The error bar is obtained by multiplying the effective particle dimension by the corresponding polydispersity index. The arrow shows the average diameter of pure BTRU particles which is 110 nm with a polydispersity 0.1. All the samples experience the same washing steps.

different oils are very different. The particles with long chain oils favor the formation of large-sized clusters, consistent with the schematic picture presented in figure 7.

3.5. Oils with different terminal functional groups

It was found that high zero-field viscosity is usually accompanied by high yield stress. However, it is not always the case. When 25 cSt diglycidyl-terminated silicone oil was used as the dispersing medium, the measured zero-field viscosity—2.87 Pa (figure 9(b))—is higher than the viscosity of 20 cSt methyl-terminated silicone oil, which has a zero field viscosity of 0.76 Pa (table 1). But the yield stress of the former is lower (figure 9(a)). The reason is that, when the terminal methyl group is substituted by other groups, the ER effect can change
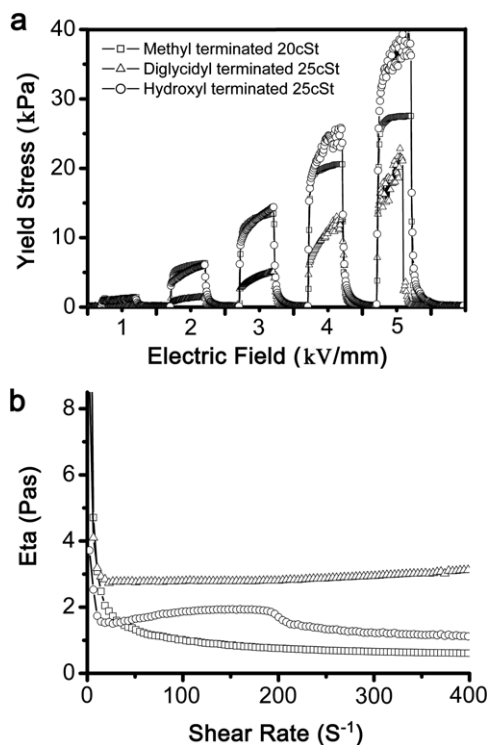
Figure 10. Yield stress variation of GER fluid constituted by using hydroxyl-group-terminated silicone oil, measured as a function of applied electric field. The concentration is 0.25. Inset is the limiting yield stress value—300 kPa—obtained by directly applying a 5 kV mm^{-1} electric field.

Figure 9. (a) Yield stresses measured as a function of applied electric field of GER fluids constituted of hydroxyl-, methyl- and diglycidyl-group-terminated silicone oils, (b) dependence of the zero-field viscosity (Eta) on the shear rate. The sample concentrations are set at 1.

Table 3. Saturation heights of different oils.

Silicone oil viscosity (cSt)	Saturation height (cm)
1	Exceeds 10 cm
5	Exceeds 10 cm
10	6.98 cm
20	5.60 cm
50	3.41 cm
100	2.57 cm
200	1.60 cm

Table 1. The strongest yield stress values in the past 5 years achieved by different types of GER fluids.

Type of GER fluids in different years	The highest static yield stress at 5 kV mm^{-1}
Nanoscale GER fluids, 2003	130 kPa
Rb-doped GER fluids, 2004	250 kPa
Wetting-induced GER fluids, 2006	250 kPa

Table 2. Zero-field viscosity and the corresponding visual appearances of the constituted GER fluids.

Viscosity of the silicone oils (cSt)	Zero-field viscosity (in Pa) and visual appearance at concentration 1	
	BTRU particles	Molecular sieves
1	0.51 (Sol)	0.75 (Sol)
5	0.24 (Sol)	0.56 (Sol)
10	0.43 (Sol)	0.49 (Sol)
20	0.76 (Sol)	0.64 (Sol)
50	5.34 (Gel)	0.92 (Sol)
100	9.37 (Gel)	1.67 (Sol)
200	11.56 (Clay)	2.82 (Sol)

owing to the fact that the protruding end groups may have an adverse effect on the formation of ER particle chains under an applied electric field.
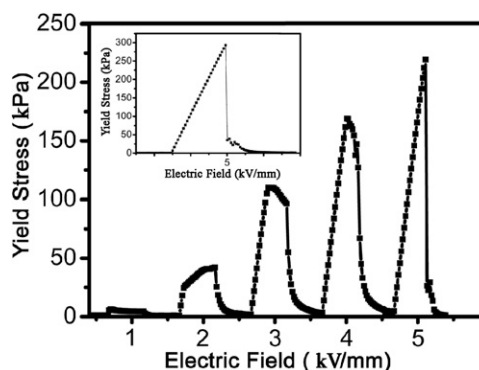
From the point of view of steric hindrance, small end groups should be beneficial to high yield stress. In order to acquire a high yield stress and relatively low zero field viscosity, suitable chain lengths and end groups should be considered together. Hence a small hydroxyl-group-terminated silicone oil, with 25 cSt kinematic viscosity, has been selected as the optimal oil. By comparing the ER yield stresses and zero viscosities of hydroxyl-, methyl- and diglycidyl-group-terminated oils (see figure 9), it could be found that the GER fluid with the hydroxyl-group terminated oil has the highest yield stress while the zero-field viscosity is not similarly increased. The interaction between the hydroxyl-group-terminated silicone oil and the BTRU particles is shown in figure 7(c). Being a strong hydrogen bond donor, the hydroxyl group can achieve inter-polymer hydrogen bonding interaction [1, 57, 58]. It can effectively link the ER particles together and create high yield stress while the zero-field viscosity is not greatly enhanced. If we increase the concentration of hydroxyl-terminated ER fluid to 0.25, the limiting yield stress is ∼300 kPa at 5 kV mm^{-1} (see the inset to figure 10), the highest achieved so far.

4. Conclusion

We have studied the role of silicone oil structure, in particular the backbone chain length and the end groups, on the GER effect. The results suggest a significant interaction between the solid particles and the oils, and this interaction can be tuned by varying either the oil chain lengths or the end groups.

5. Summary

The chemical structure of the dispersing phase (silicone oil) can have a direct effect on the resultant ER effect. By continuously increasing the chain lengths or changing the terminating functional groups, different values of zero-field viscosity (Eta) and yield stress could be achieved. Therefore, three different visual appearances of the constituted ER fluids were observed. The absorption and permeability measurements show that the silicone oils have affinity on the surface of particles. We attribute this to the hydrogen bonding interaction between particles and the siloxane skeleton. Dynamic light scattering discloses that the flexible siloxane chain could effectively agglomerate the nanoparticles, which in turn greatly increases the zero-field viscosity. If the siloxane chain is extended, the agglomerates could be even greater. A schematic diagram was presented to interpret the structures between silicone oils and ER particles. From this point on, an optimal oil structure, a hydroxyl-terminated silicone oil with suitable chain length, was employed which can increase the degree of hydrogen bonding interaction by the terminal hydroxyl group while not greatly enhancing the zero-field viscosity. With this kind of oil, the highest yield stress of $\sim$300 kPa under a 5 kV mm^{-1} dc electric field could be obtained. These oils with terminating functional groups provide a potential application as dispersing phases or additives in ER fluids.

Acknowledgment

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