Electrorheological Phenomena in Polyhedral Silsesquioxane Cage Structure/PDMS Systems

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ABSTRACT It is shown, for the first time, that mixtures of sulfonated polyhedral silsesquioxane cage structures (sPOSS) and poly(dimethyl siloxane) (PDMS) with silicone oil exhibit significant electrorheological (ER) activity. At low sPOSS concentrations, less than 10 wt %, the viscosity is enhanced by ~100, which is comparable to the viscosity enhancements exhibited by conventional ER fluids, under the influence of comparable applied electric fields, $E = 2$ kV/mm. Measurements of the shear stress, σ, dependencies on E, the conductivities, and relative permittivities reveal that the properties of these POSS/PDMS systems cannot be reconciled with theory developed to explain the behavior of conventional ER fluids.

KEYWORDS: electrorheology • POSS • rheology • dielectric • suspension • nanoparticles

INTRODUCTION

Rheological properties, such as the viscosity and the shear modulus, of electrorheological (ER) fluids undergo reversible change by orders of magnitude under the influence of an applied electric field, E (1, 2). The viscosities, η, and yield stresses, σ, of conventional ER fluids, composed of nonconducting, semiconducting, inorganic particles, with average sizes of order micrometers, suspended in a nonconducting liquid, such as silicone oil paraffin or mineral oil, increase by factors of 1×10^2 to 1×10^3 under the influence of fields $E \approx 1$ kV/mm (3−6). Other systems, suspensions of conjugated polymers, surfactants, polyelectrolytes, or liquid crystal polymers, in oil are also known to exhibit ER behavior (8−10).

The conventional ER effect is associated with the notion that the particles undergo an electric field induced polarization (6). Specifically, during the initial stage of the ER effect, which occurs in milliseconds, chains of particles are formed between the electrodes that are due to induced-dipole/induced-dipole interactions between the particles. Subsequently columns of particles develop, via a coarsening mechanism; this occurs on time-scales on the order of many seconds (7). One important characteristic of the conventional ER fluids is that, according to theory, the interaction forces between the particles, and hence the shear stresses, τ, exerted at the electrodes, scale as $\tau \propto E^2D^2$, where D is the particle diameter.

Nanoparticle-based systems have generally not been promising; they exhibit effects that are weaker than conventional ER fluids (11−13). However, in 2003, a core−shell nanoparticle system, composed of barium titanyl oxalate particles (50−70 nm) coated with urea (~10 nm) mixed with silicone oil, was found to show considerable promise. This system exhibited stresses larger than 100 kPa, approximately 2 orders of magnitude greater than that exhibited by conventional ER fluids (14). This has come to be known as the giant electrorheological (GER) effect (14, 15). Several other core−shell systems, including urea-coated TiO_2, Ca−Ti−O, and Sr−Ti−O particles, have been shown to exhibit similar behavior (16−20). A theory is based on the notion that because the particles possess permanent dipole moments, $\tau \propto E/D$, where D is the particle diameter (18). This prediction indicates that, in contrast to conventional ER fluids, the stress scales as E and the effect increases with decreasing particle size.

An important drawback for some applications would be unacceptably large viscosities in the absence of applied fields, exhibited by these solid-particle-based ER fluids. These large viscosities are associated with the significant concentrations, on the order of 30%, of the suspended particle-rich phases in ER fluids. Moreover, the GER zero-field viscosities are larger than those of the conventional ER suspensions. Consequently, it is important to identify a fluid that would exhibit a large ER effect, at least comparable to the conventional ER systems, which possess low zero shear viscosities in the absence of an electric field, and comparable to the viscosity of silicone oil. Such a system would facilitate easier processing and utilization, particularly in microfluidic applications. This article introduces a new electrorheological fluid: functionalized polyhedral silsequioxanes (POSS) in silicone oil; specifically, Tris sulfonic acid ethyl POSS (TSAE POSS) (20) (see Figure 1). The sPOSS/PDMS mixtures possess viscosities comparable to the pure silicone oil, yet experience an increase of the viscosity by a factor of 1×10^2, with only 7 wt % sulfonated POSS molecules, for $E = 2$ kV/mm. By contrast, isotropic octa-isobutyl POSS particles exhibited virtually no electrorheological behavior even at 10 wt % and under a 2 kV/mm field, which indicates that the

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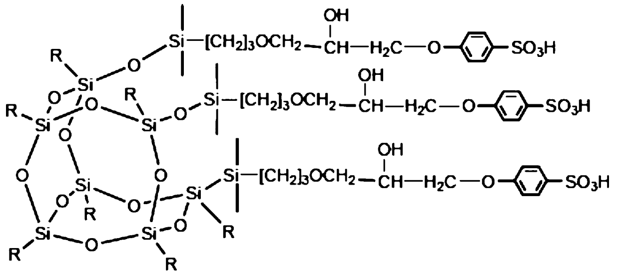

FIGURE 1. General chemical structures for TSA(R)-POSS open cage structures. R = ethyl for tris sulfonic acid ethyl (TSAE) POSS.

POSS based systems may not be generally not ER active, as discussed below.

EXPERIMENTAL SECTION

Rheological, dielectric, and conductivity measurements were performed on TSAE-POSS/silicone oil and octa-isobutyl POSS/silicone oil mixtures. The POSS molecules were purchased from Hybrid Plastics and the polydimethylsiloxane from Sigma-Aldrich. The POSS concentrations in the suspensions varied from 2 to 10 wt %. The dielectric measurements for the suspensions were performed using a dielectric spectrometer (Novocontrol GmbH) in the frequency range between 1 Hz and 1.0 MHz and at temperature T = 25 °C. The rheological measurements were performed using the TA Instruments ARES Rheometer, attached to a high voltage generator. Prior to performing the measurements, all the samples were sheared at high shear rates in the absence of an electric field in order to ensure homogeneity. Step rate and shear rate tests were performed using parallel plate (50 mm diameter plates) geometries. To ensure consistency in the measurements, we first took the shear rate sweeps at high frequencies and subsequently performed them at progressively lower frequencies.

RESULTS AND DISCUSSION

The ER response, apparent viscosities, η, obtained using constant shear rate experiments, of the sulfonated TSAE POSS/silicone oil system are shown in Figure 2a. Upon application of a DC field, η increases with increasing TSAE-POSS concentration by just over a factor of 100 for mixtures containing 7 wt %; η decreases for higher concentrations. It returns to its original value upon removal of the field. It is noteworthy that the magnitude in the increase of the viscosity at 7 wt % is comparable to that exhibited by conventional ER fluids for comparable E-fields (8). The degree of packing and orientation of the molecules along the field influences the magnitude of the ER effect. Interestingly, the timescale of the increase, seconds, is comparable to the time associated with column formation in conventional particle/oil ER fluid suspensions, despite the size of the molecules and the steric effects. The viscosities exhibited the same qualitative trends under the influence of AC fields, as they did under conditions of DC fields. The magnitude of the effect is necessarily smaller, under AC conditions. The data in Figure 2c illustrate the behavior of octa-isobutyl POSS in silicone oil; it exhibited virtually no ER response even at 10 wt % under 2 kV/mm electric field. This observation supports the notion that the effect is not ubiquitous in POSS-based systems.

To gain some insight into the response of these POSS systems dielectric spectroscopy studies were performed (3).

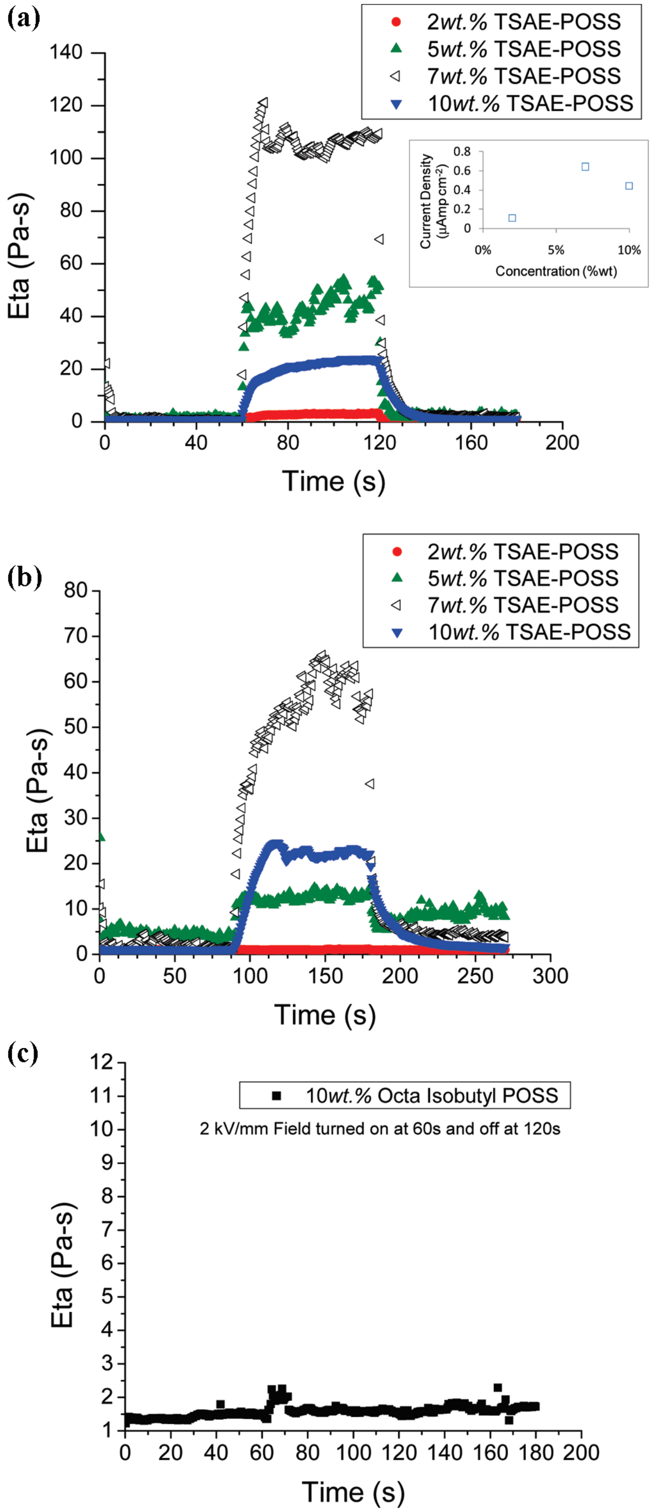

FIGURE 2. TSA(E) POSS step rate test shear rate = 0.5 s^{-1} (taken at the rim where it is maximum), voltage turned on after 60 s and then turned off after 60 s: (a) DC voltage (2 kV/mm), inset plot shows values for current density at a rate of 0.5 s^{-1} for sample sheared at a rate from 30 s^{-1} down to 0.1 s^{-1}; (b) AC voltage (1kHz, 2 kV/mm); (c) 10 wt % octa-isobutyl POSS DC voltage (2 kV/mm).

The complex permittivities and the conductivities of the suspensions increase with increasing concentration, as shown in Figure 3. For systems that possess high dielectric constants particle polarization would be enhanced; this would lead to strong and stable meso-structure formation in the

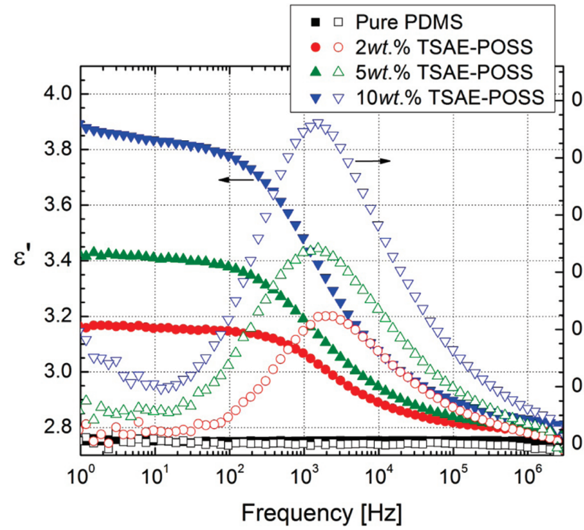

FIGURE 3. Frequency dependencies for the real and imaginative relative permittivities for the mixtures on the left and the right, respectively.

oil, spanning the electrodes. According to one assessment, particle dielectric constants should be at least four times that of the matrix fluid (21). The data in Figure 3 show that the TSAE-POSS mixture meets this criterion. Additionally, in order to achieve a strong positive electrorheological effect, the dielectric loss should be greater that 0.1 (21, 22). Finally the dielectric relaxation should fall between 1×10^2 and 1×10^5 Hz, as observed (3). We note that the octa-isobutyl POSS/silicone oil system is not dielectrically active, so it is not entirely surprising that it does not exhibit an ER effect. The presence of the sulfonated groups are evidently responsible for the dipolar behavior, and hence the ER response of the TSAE-POSS system. The results of a broader study involving a larger cross-section of POSS-based systems will be reported in a future publication.

The data in panels a and b in Figure 2 indicate that for concentrations beyond 7 wt. %, the ER effect diminishes. On the other hand, the dielectric spectroscopy data indicate that the dielectric strength increase monotonically with concentration. We also measured the current densities (leakage current), which become finite when the meso-structures span the electrodes, leading to the ER effect. The magnitudes of the current densities are comparable to, though slightly smaller than, those measured in conventional ER fluids. More important, the current densities are comparable in magnitude across the composition range. This indicates that the decrease in the ER effect for the 10% sample is not associated with a change in current densities. The decreased ER effect, beyond 7 wt.% may be associated with the inability (steric effects) of the dipoles to align within the field on sufficient time-scales during which the experiment is performed. Measurements of the shear-rate dependence of the effect under different fields support this notion.

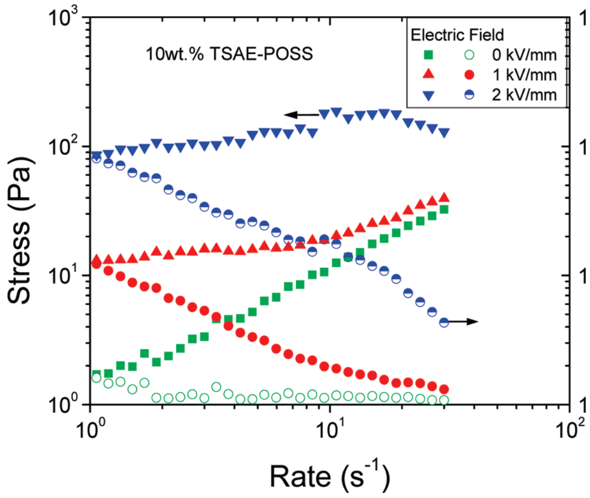

FIGURE 4. Steady rate sweep 10 wt % TSA(E) POSS in silicone oil.

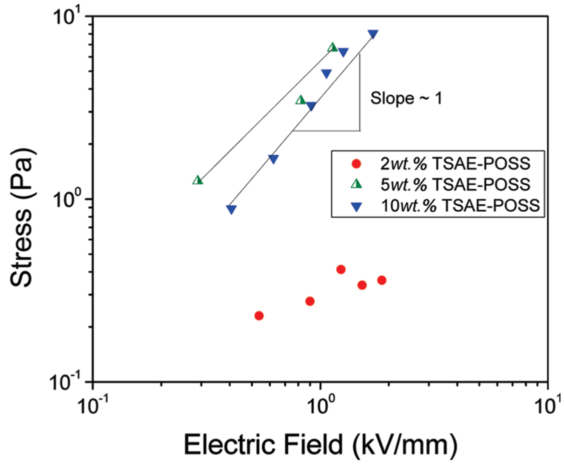

FIGURE 5. Stress as a function of electric field at low shear rate (0.1 s^{-1}) (taken at the rim where it is maximum) as the electric field is increased for sulfonated POSS/PDMS mixture at 10 wt % in order to approximate stress behavior in the pre-yield regime. Time between measurements was 45 s.

The data in Figure 4 shows the response (stress) versus shear rate behaviors of TSAE-POSS at 10 wt %, at different field strengths. In the absence of the E-field, the behavior for the TSAE-POSS suspensions is Newtonian (Figure 4). As shown in Figure 5, the electrorheological response of the TSAE POSS system increases linearly with increasing field, under conditions of low shear rates, 0.1/s. Note that at small TSAE-POSS concentrations, 2%, the ER effect is weak, and the dependence of the stress on the field is weaker than E, which may not be unexpected, because there are insufficient POSS molecules in the system to form a viable structure that spans the electrodes.

A simple way of understanding the power law dependence on the E-field in conventional ER fluids is that the induced polarization, P (number of dipoles per unit volume), is proportional to the applied field E, hence the force $F \approx PE \approx E^2$ (2, 23, 24). Notably the shear stresses of the TSAE-POSS/PDMS system exhibited a linear dependence on E. The linear dependence is readily reconciled with the fact that the functionalized POSS molecules possess permanent dipole moments. Consequently, the force between the molecules aligned between the electrodes is proportional to PE, where P, which we presume is the saturation polarization, is a constant independent of E (14).

Consequently, the stress is proportional to the field,

$$\tau \approx \phi n(E) f(m) E$$

The response of the materials should scale approximately as the volume fraction, ϕ, the number of particles per unit volume, $n(E)$, aligned with the field between the electrodes, and a function of an effective dipole moment, f of the system (18).

CONCLUSIONS

A new electrorheological system of sulfonated POSS particles in silicone oil has been identified and investigated. The stresses, τ, reflecting the response of the mixture, are comparable to the stresses exhibited by conventional ER fluids, under the influence of comparable applied electric fields, $E \approx 1$ kV/mm, at low POSS concentrations. A number of soft matter systems, polyelectrolyte/oil, polymer liquid crystal, and conjugated polymer/oil systems, where the polymer phase is able to form an extended structure, exhibit ER behavior. This linear E-field dependence is based on the notion that these POSS molecules possess permanent dipole moments and the shear stress between the electrodes is proportional to PE. It is expected that several other electrorheologically active POSS systems would be identified.

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