

Electrorheology of Polystyrene Filler/Polyhedral Silsesquioxane Suspensions

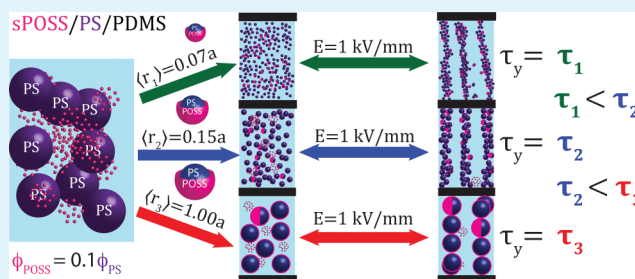
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Supporting Information

ABSTRACT: An important challenge in the field of electro-rheology is identifying low-viscosity fluids that would exhibit significant changes in viscosity, or a yield stress, upon the application of an external electric field. Our recent research showed that optimal compositions of mixtures, 10 wt % sulfonated polyhedral oligomeric silsesquioxanes (s-POSS) mixed with polydimethyl siloxane (PDMS), exhibited significant electro-rheological activity. Here we show that s-POSS/PDMS mixtures containing polystyrene (PS) fillers, of micrometer-sized dimensions, containing as little as ~1 wt % s-POSS, exhibited an increase in ER activity by an order of magnitude, beyond that of s-POSS/PDMS mixtures. The dynamic yield stress was found to scale with the particle diameter, a , as $\tau_y \propto a^{0.5}$ and with the electric field as $\tau_y \propto E^{1.5-2.5}$; this behavior is reasonably well understood within the context of dielectric electro-rheological theory.

KEYWORDS: electro-rheological fluid, polar molecule (PM) ER fluid, silsesquioxane, nanocage, polystyrene, additives,



INTRODUCTION

Electrorheological fluids (ERFs) are suspensions whose mechanical properties become solidlike in the presence of an externally applied electric field.¹⁻³ The particles in the suspension, initially randomly dispersed, self-organize to form columnar structures that span the electrodes, parallel to the direction of the applied field. These mesoscale structures are responsible for the increase in the resistance to flow and the associated increases in the apparent viscosity, η_{app} , and the yield stress, τ_y . Upon removal of the external field, the structures collapse and the suspension reverts back to its original state with randomly dispersed particles.

Diverse particle suspension systems exhibit electro-rheological behavior. A suspension of silica particles and poly dimethyl siloxane (PDMS) constitute one class of ER fluids (conventional ER fluids) whose behavior, columnar structure formation and associated enhancement of mechanical properties, is due to an electric field-induced silica particle polarization effect; the yield stress is known to depend on the external field such that $\tau_y \propto E^{2.1-3}$. In a different class of suspensions, containing particles that possess permanent dipole moments, the dipoles orient along the direction of the applied field and the $\tau_y \propto E$. Electro-rheological suspensions containing high concentrations of particles, such as urea,⁴ citric acid,⁵ 4-hydroxybutyric acid lactone,⁶ and acetic acid,⁵ that possess permanent dipoles are of great current interest. These ER fluids exhibit yield stresses approximately 2 orders of magnitude larger than conventional ER fluids that contain only dielectric (silica) particles. The use of additives to enhance the ER effect in suspensions is well-known, with publications dating back to the 1980s.^{7,8} Recently

it was demonstrated that high stresses (~200 kPa) could be achieved with large concentrations of micrometer sized strontium titanium oxalate dielectric particles, in silicone oil, in the presence of water as a polar additive.⁹ Electrolytes, acids, bases, and surfactants have previously been used as additives to enhance electro-rheological behavior.¹⁰

We recently showed that a new class of materials, PDMS mixed with a caged compound, sulfonated polyhedral oligomeric silsesquioxane (s-POSS), exhibited strong ER behavior.¹¹ The effect was largest in mixtures containing ~10 wt % s-POSS. In this paper, we show that s-POSS/PDMS mixtures containing only ~1 wt % POSS, and PS weight fractions ranging from 10 to 20 wt %, exhibit increases in viscosity of 2 orders of magnitude, with the application of an external electric field. This effect is approximately an order of magnitude larger than that of the s-POSS/PDMS system. The dynamic yield stress was found to scale with the particle diameter, a , as $\tau_y \propto a^{0.5}$ and with the electric field as $\tau_y \propto E^{1.5-2.5}$. We suggest that this enhancement in the magnitude of the ER activity is due to significant dipolar activity associated with preferential adsorption of the s-POSS molecules onto the surfaces of the polystyrene fillers. This new system has two advantages over current ER systems. Because PS is a commodity polymer the cost of processing large quantities of an ER fluid based on this system is minimized. Our findings also show that the magnitude of the effect scales as the average

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diameter of the fillers, and suggest that it would, in principle, be possible to achieve yield stresses greater than 10 kPa, without the drawbacks of high suspension concentrations, costly nanofabrication procedures and high off-state viscosities.

EXPERIMENTAL SECTION

Rheological and dielectric measurements were performed on trisulfonic acid isobutyl (TSAiB) POSS/polystyrene/silicone oil. The POSS molecules were purchased from Hybrid Plastics, the monodisperse polystyrene powders were purchased from Polymer Source; the polystyrene microspheres were purchased from Polysciences and the polydimethylsiloxane (PDMS) silicone oil from Sigma-Aldrich. The mixtures were prepared by drying both the POSS and polystyrene at 80 °C under vacuum for at least 3 h prior to adding the silicone oil which was dried at 150 °C and placed over molecular sieves. The ER fluid formulations and abbreviations are shown in Table 1 below.

Table 1. Abbreviations for Mixtures of POSS/PS/PDMS

abbrev.	formulation (wt %)					
	polystyrene ^a (<i>a</i>) (μm)			polystyrene microspheres <i>a</i> = 50 μm	TSAiB POSS	PDMS
	5.1	8.9	41.2			
s-POSS/ PDMS	0	0	0	0	10	90
s-POSS/PS/ PDMS	0	10	0	0	1	89
PS ₁	10	0	0	0	1	89
PS ₂	0	10	0	0	1	89
PS ₃ ^b	0	0	10	0	1	89
PS100	0	0	0	10	1	89

^aAverage particle Size (radius = $\langle a \rangle$). ^bPolystyrene for PS₃ was used with different compositions in Figure 5.

The dielectric measurements of the suspensions were performed using a dielectric spectrometer (Novocontrol GmbH). The liquid suspension cell used in our experiments contained two metal electrodes, connected by Teflon. Data extracted from measurements of an empty cell were used as baseline, i.e.: these data were subtracted from measurements of the fluids. All measurements were performed in the frequency range between 0.1 Hz and 1.0 MHz, at temperature of $T = 25$ °C.

The shear stress–strain rate and apparent viscosity–shear stress measurements were performed with a strain-controlled rheometer (TA Instruments ARES). The measurements were performed using 50 mm diameter parallel plate geometries. The shear rates in steady rate sweep tests spanned from 0.1 to 30 s⁻¹. The plates were attached to a DC high voltage generator (Trek Model 609 $\times 10^{-6}$) connected to a 5 MHz function generator (BK Precision 4011A) that allowed for electric fields up to 4 kV/mm. 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. To ensure consistency in the measurements and to prevent stiction,¹² we first took the shear rate sweeps at high frequencies and subsequently performed them at progressively lower frequencies.

The particle size distributions (PSD) were determined using the ImageJ software to analyze optical microscopy images of the particles. Because the particles were irregularly shaped, we used the Heywood diameter, the diameter of a circle possessing the same area of the approximately elliptical polystyrene particle, to calculate the mean particle diameter of polystyrene powders. Roughly 20 micrographs were analyzed from each PS powder, at appropriate magnifications. A potential drawback with the use of microscopic methods of particle size comparison is that the lowest number of counts is obtained for the largest particle diameter (PS₃) leading to a broader distribution. To

overcome this, in addition to the PSD, we also included the average diameters. Additionally, scanning electron microscopy measurements of the sizes and morphologies of polystyrene solid particles were performed.

RESULTS AND DISCUSSION

It is evident from the data in Figure 1 that the ER effect exhibited by the mixture containing polystyrene (PS/s-POSS/

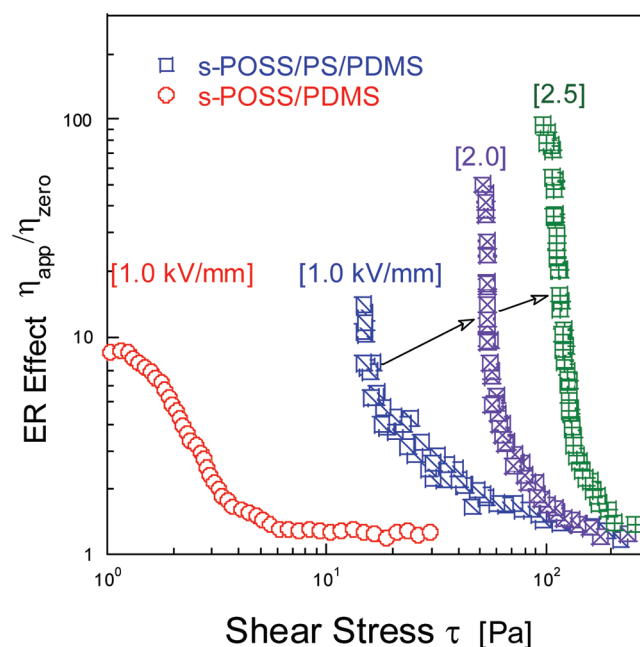


Figure 1. Electrorheological effect (apparent viscosity/viscosity at zero electric field) vs shear stress plot for 10 wt % POSS electrolytes mixed with PDMS (circles) compared to 1 wt % TSAiB-POSS mixed with 10 wt % PS/PDMS (squares). The brackets in the figure denote the electric field in units of kV/mm.

PDMS) is appreciably greater than that of the s-POSS/PDMS mixture. The yield stress, estimated from the point on the stress axis at which the curve begins to ascend, is approximately an order of magnitude larger. For the s-POSS/PDMS mixture, this $\tau_y \lesssim 10$ Pa, whereas for the PS/s-POSS/PDMS system, the stress occurs at $\tau_y \approx 30$ Pa. Additionally, experiments in our lab indicate that the reliability of the PS/s-POSS/PDMS is much better; the s-POSS/PDMS with higher concentrations of s-POSS overheats in DC electric fields of 2 kV/mm and higher.

The dependencies of the shear stress on the shear rate for mixtures, each with 1% wt. TSAiB-POSS, containing PS fillers of different sizes, labeled PS₁, PS₂, and PS₃, under an electric field are shown in Figure 2. The magnitude of the effect increased with increasing average PS filler size; the PS₃ system, containing the largest PS fillers, exhibited the largest ER effect.

An understanding of how the size of the dispersed solids affects the magnitude of the ER effect is of practical significance. A long-standing problem in electrorheology has been to understand how the size of the solid particles in suspension affects the polarization properties and ultimately the mechanical behavior of these systems.^{4,13–15} The size of the particles in suspension has been shown to affect the magnitude of the yield stress for an ER fluid under an electric field. Table 2 shows theoretical predictions for the dependence of the yield stress, τ_y , on the solid particle radius, a , and basic assumptions on which these predictions are based.

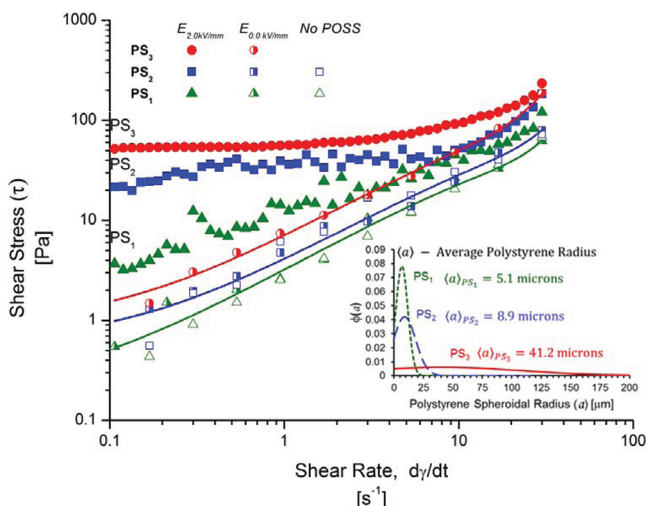


Figure 2. Shear stress is plotted as a function of shear rate for three different size polydisperse polystyrene powders mixed with 89% wt. PDMS and 1 wt % POSS electrolyte. Lines are drawn as guides to the eyes. The inset shows the normal distribution of particle sizes, measured by optical microscopy (sample size, $N = 350, 650, 3100$ for PS₃, PS₂, and PS₁, respectively).

Table 2. Size Effects in Electrorheological Models^a

model/theory	basic assumptions/ approximations	perm. dipole	$\tau_y = f(\alpha)$
electrostatic model ^{3,19}	point dipole approximation	no	$\tau_y \propto \alpha^2$
dielectric theory ¹⁶	$(\epsilon_p/\epsilon_f \rightarrow \infty)$	no	$\tau_{y,max} \propto (a/\delta)^{1/2}$
simulation ²⁰	single component identical spherical particles	no	$\tau_y \propto \alpha^3$
finite element models ¹⁴	aligned dipole layers; hertz model	yes	$\tau_y \propto \alpha^{-1}$

^a a = solid particle radius.

It is evident from Table 2 that the magnitude of the ER effect may be tailored through control of the particle size. It is known that in conventional ER fluids, which contain dielectric particles, increasing the particle size leads to increases in the yield stress; upper limits of $\tau_y \approx 10$ kPa may be achieved through increases in particle size.¹⁶ The primary limitation of this effect is that beyond a critical particle size, sedimentation occurs; this leads to diminishing ER behavior. With regard to suspensions that contain particles (of sizes less than $0.5 \mu\text{m}$) that possess permanent dipole moments, the ER effect increases with decreasing particle size. Yield stresses possessing an upper limit of $\tau_y \approx 30$ MPa can theoretically be achieved.^{17,18}

The shear stresses are plotted as a function of shear rate in Figure 2 for suspensions containing PS fillers of three very different average sizes: $\sim 5 \mu\text{m}$ (PS₁), $\sim 9 \mu\text{m}$ (PS₂), and $\sim 40 \mu\text{m}$ (PS₃). The SEM images of the polystyrene fillers are shown in the inset in Figure 4. It is noteworthy from the data in Figure 2 that in the absence of the E-field, adding the POSS electrolyte had only a nominal effect on the mechanical behavior for the suspensions containing smallest particle sizes. The effect is significant for the suspensions containing the larger fillers. In Derjaguin–Landau–Verwey–Overbeek (DLVO) theory, the electrostatic repulsion is responsible for the energy barrier that keeps particles separated. Adding an electrolyte to a suspension would have the effect of screening the electrostatic repulsion.

When the electrostatic repulsion barrier is sufficiently lowered (screened), the solid particles in suspension are free to approach each other, resulting in aggregation (floculation). A floculated suspension may exhibit a yield stress, which has its origins in the Van Der Waals attractions between the solid particles. This yield stress, due to floculation, exists even in the absence of the applied electric field. The data in Figure 3 reveal that in the absence of an applied field, the yield stress is comparable with or without the addition of POSS.

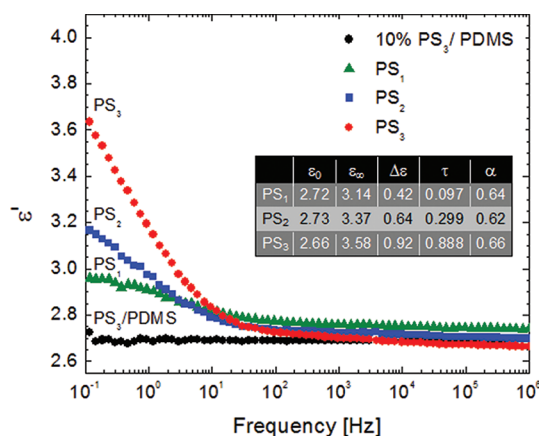


Figure 3. Real dielectric constants for 1% TSAiB POSS/10 wt % polystyrene/PDMS. The inset table provides the best fit parameters for the Cole–Cole equation based on least squares analysis.

To gain further insight into the differences in the magnitudes of the suspensions containing the PS fillers of different sizes, the dielectric properties was measured. Of particular interest is the low-frequency relaxation process, which manifests the polarization in the PS/s-POSS/PDMS system due to the permittivity mismatch across the PS/PDMS interfaces. The connection between the low frequency relaxation and the ER effect is that the ER effect is controlled by slow ($< 1 \times 10^5$ Hz) polarization processes.²¹ As shown in Figures 3 and 4, of the real ϵ' and imaginary ϵ'' parts of the relative permittivity, the two-component PS/PDMS mixture is dielectrically inactive. The data in Figure 3 show that at low frequencies, PS₃

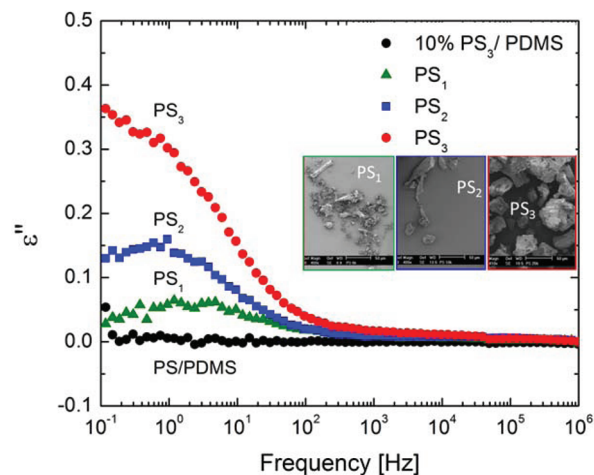


Figure 4. Imaginary dielectric constants for 1 wt % TSAiB POSS/10 wt % polystyrene/PDMS. Inset is SEM images of the PS powder with $50 \mu\text{m}$ scale bar.

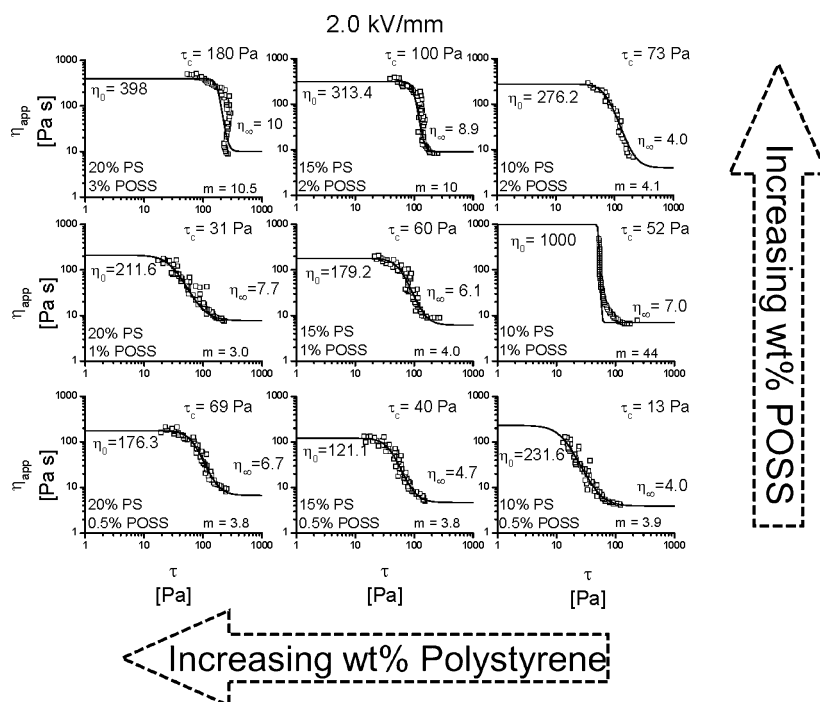


Figure 5. Apparent viscosity (η_{app}) vs shear stress (τ) for different compositions of TSAiB POSS/PS/PDMS prepared with average radius $\langle a \rangle = 41.3 \mu\text{m}$ PS. The electric field is kept at 2.0 kV/mm. The lines are fits to the Ellis model, eq 4.

exhibited the highest permittivity, followed by PS₂ and PS₁. The incremental dielectric quantities of the suspension increase with increasing average filler size. More precisely, the height of the curve, or $\Delta\epsilon$, reflects the size of the induced dipole moment.^{22,23} Clearly, the relative dielectric properties of the three different size polystyrene electrorheological suspensions, plotted in Figure 3, are consistent with the magnitudes of the stresses plotted in Figure 2.

The consistency of the connection between the dielectric activity and the average particle sizes appears to be independent of the polydispersity in the sizes and significant irregularity in their shapes.

We note moreover that the effect of the size of the polystyrene fillers is consistent with the behavior of the conventional ER size effect, i.e., suspensions containing dielectric particles. It is, however, not consistent with that of ER suspensions containing particles with permanent dipoles (see Table 2). Increasing the average PS filler size leads to enhancements of the ER effect. Sulfonic acids, which are present in TSAiB POSS, possess a strong dipole moment. Therefore, the conventional ER size effect is unexpected, because TSAiB POSS, due to the attached sulfonic acids, likely possesses a strong permanent dipole moment.

In the foregoing, we have clearly shown that adding polystyrene to the s-POSS/PDMS suspension has the effect of increasing the ER effect by over an order of magnitude. Determination of the concentration of polystyrene at which the largest yield stress is achieved requires evaluating the effects of the relative concentrations of the POSS electrolyte and polystyrene within the suspension. In order to quantify the effects of composition on the yielding behavior, the Ellis model, modified by Barnes will be employed.²⁴ The model suggests that the apparent viscosity ($\eta_{app} = \tau_{stress} / [d\gamma/dt]_{strain\ rate}$) decreases from a large asymptotic value, η_0 , to a low viscosity, η_∞ .

$$\frac{\eta_{app} - \eta_\infty}{\eta_0 - \eta_\infty} = \frac{1}{1 + (\tau/\tau_c)^m} \quad (4)$$

The transition is denoted by a critical stress, τ_c at which shear thinning occurs; the magnitude exponent m , used as a fitting parameter, is sensitive to the sharpness of the transition between the two viscosities. Large values of m are associated with increasingly sharp yielding transitions; the largest values of m are associated with “extreme” shear thinning. The physical mechanism for the yield stress of the suspension would be due to the formation of a solidlike network structure that sustains the stresses within the fluid. The suspension reverts to its liquidlike state when the stress is transferred from its solidlike network structure to the surrounding fluid. This point is referred to as the critical stress or yield stress. At higher stresses the fluid flows with a reduced apparent viscosity, η_∞ . Because the system of interest in our study exhibits a change in viscosity in response to an external field, it is useful to use the Ellis model instead of other models, such as a Bingham model. The Bingham model considers the behavior of a system with an infinite viscosity, at stresses below the yield stress ($\tau < \tau_y$), and a Newtonian viscosity at stresses $\tau > \tau_y$. The Bingham model was useful for understanding the behavior of our system (see the Supporting Information).

Shown in Figure 5 are a series of plots of the apparent viscosity as a function of shear stress, for various compositions of PS and s-POSS of the fluid. The Ellis model is used to describe the data for each composition; the fitting parameters are identified with each plot. First consider the bottom row in that figure; the magnitude of the effect increases with decreasing PS weight fraction, while the s-POSS remains constant at 0.5 wt %. The largest effect, largest m and a two-order of magnitude change in the viscosity, is exhibited by the samples: PS(20%)/s-POSS(3%), PS(15%)/s-POSS(2%), and PS(10%)/s-POSS(1%). The magnitude of the effects exhibited

by PS(20%)/s-POSS(1%) and PS(10%)/s-POSS(0.5%) are comparable. These data indicate the existence of an optimal composition which exhibits the largest effect: large ratio of PS to s-POSS, and a sufficiently large fraction of PS. There should be a sufficient fraction of filler particles to create structures, spanning the electrodes, of sufficient mechanical integrity in order to sustain a stress. Only a small quantity s-POSS would have to be available to segregate form interfacial layers on all the filler particles; so the ratio of PS to s-POSS is expected to be large. The exact amount would be determined by an optimal particle size and particle volume fraction. We examine this thesis in further detail below.

The magnitude of the ER effect exhibited by a 2-component fluid is influenced by the spatial distribution of a third component within the mixture.²⁵ With regard to our system, two extreme cases might be relevant. For Case 1, the s-POSS is located (dispersed and aggregated) entirely within the carrier fluid (Figure 6). For Case 2, the s-POSS forms an interfacial

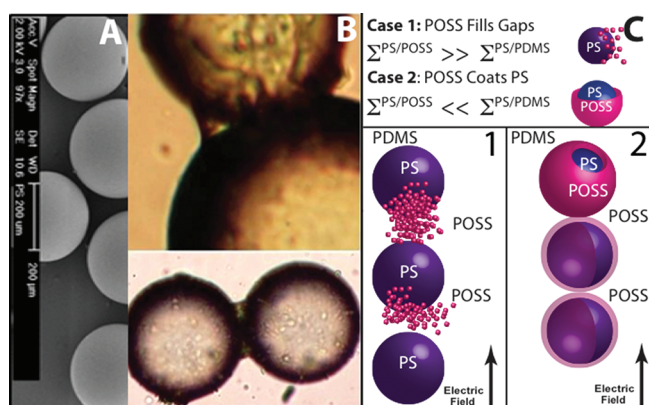


Figure 6. (A) SEM images of different size polystyrene microspheres. (B) Optical microscope images of PS spheres after removal from the TSAiB POSS/PS/PDMS suspension following electrorheological testing. (C) Cartoon showing POSS additive with PS microspheres. Lower right: Case 1 POSS fills gaps; case 2 POSS coats PS. (Σ) Interfacial tension.

layer between the PS and the PDMS; excess fluid would presumably form a separate phase. We examined a model system, monodisperse spherical polystyrene particles mixed with s-POSS/PDMS. Optical images of polystyrene microspheres in s-POSS/PS/PDMS suspensions reveal that the s-POSS coats and induces aggregation of PS spheres in the PS/s-POSS/PDMS system. Notably, these PS microspheres do not otherwise aggregate in PDMS.

That POSS coats the surface of the polystyrene is not unexpected. To begin with, PS and PDMS are immiscible and the interfacial tension between them is large 6.1 mJ/m^2 for 150°C .²⁶ We note further that the interfacial tension between PS and poly (methyl methacrylate) (PMMA) at the same temperature is 1.6 mJ/m^2 , yet it has been shown that POSS grafts have the effect of reducing the interfacial tension between PS and PMMA to 1.1 mJ/m^2 ; this is due to favorable interactions between the PS and the POSS grafts.²⁷ Therefore, the favorable POSS/PS interactions are therefore important for the existence of this effect.

The formally inert filler particles, now coated with dipolar s-POSS molecules, behave as fillers possessing effective dipole moments. We also examined the ER behavior of micrometer-sized model monodisperse spherical PS fillers (dry form

microspheres were used to minimize the effect of water) and measured an appreciable ER effect.

The presence of adsorbed polar molecules on the PS fillers suggests that the properties of our system would bear similarities to polar molecule (PM) ER fluids. The notable difference, of course, is that the particles in the PM-ER fluids are generally of nanoscale dimensions. For polar molecule dominated ER fluids the yield stress $\tau_y \propto E$. In contrast, for conventional dielectric ER fluids, the yield stress varies as: $\tau_y \propto E^2$. We examined the dependence of the yield stress of the PS/s-POSS/PDMS system on the applied field.

In Figure 7, the data reveal that the dynamic yield stress increases with increasing PS filler radius. The dynamic yield

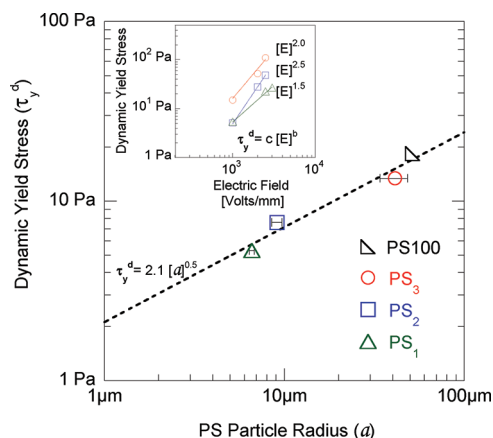


Figure 7. Dynamic yield stress (Bingham model) as a function of particle radius (a) for 1 wt % TSAiB POSS/10 wt % PS/PDMS Suspensions at $E = 1 \text{ kV/mm}$. Least-squared error linear fits for each electric field are shown. Horizontal bars are for 95% confidence intervals on size based on the PSD from optical microscopy.

stress, τ_y^d , was calculated from our data, using the Bingham model. Here the stress, τ , is expressed in terms of the dynamic yield stress, the viscosity, η_p , and the strain rate, $\dot{\gamma}$: $\tau = \tau_y^d + \eta_p \dot{\gamma}$. The yield stress increases with the radius of the polystyrene filler such that τ_y is proportional to $a^{0.5}$. The largest particles we studied were of radius $50 \mu\text{m}$. This trend in fact is consistent with predictions developed for dielectric electrorheological materials (Table 2). The inset of Figure 7 indicates an electric field dependence of $\tau_y \propto E^{1.5-2.5}$. This too is consistent with the predictions for the yield stress, using conduction theory, for the dielectric ER fluids.²⁸

CONCLUSION

We showed that a suspension composed of PDMS, PS fillers and small concentrations, $\sim 1 \text{ wt.}\%$ s-POSS, exhibited a significant ER effect under the presence of an external field. The viscosity changed by 2 orders of magnitude with the application of a field. This increase is an order of magnitude larger than that exhibited by that of a 10 wt % s-POSS/90 wt % PDMS ER mixture. The ER yield stress increased with filler size a such that $\tau_y^d \approx a^{0.5}$, where a is the radius of the microsphere. This behavior is associated with the interfacial adsorption between the PS surfaces and PDMS environment. The phenomenon occurs regardless of PS filler size and shape.

■ ASSOCIATED CONTENT

● Supporting Information

More detailed particle size analysis, the figures showing shear stress shear rate behavior, and additional experiments demonstrating the role of POSS in the ER effect (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org/>.

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Notes

The authors declare no competing financial interest.

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