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ORIGINAL CONTRIBUTION

Synthesis of polypyrrole–polycaprolactone composites by emulsion polymerization and the electrorheological behavior of their suspensions

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Abstract Polypyrrole–polycaprolactone (PPy-PCL) composites were synthesized by emulsion polymerization to improve their mechanical and electrical properties by forming conducting polymer composites and hence enhance the electrorheological (ER) response. Various PPy-PCL composite particles were synthesized by controlling the amount of PCL. The ER response increased with increasing electric field strength and particle volume fraction. A power-law dependence, $\tau=K\phi^m E^n$, showed a good fit to the yield stresses when $m=2$ and $n=1.5$. The dependence of $E^{1.5}$ is consistent with the conduction model and the dependence of ϕ^2 appears to be related to structural changes with the electric field, which leads to many-body interactions between the particles. The ER response also increased with increasing amount of PCL, but the dielectric properties and dc conductivities of the PPy-PCL composite particles and the dielectric properties of the PPy-PCL composite suspensions were not consistent with the ER behavior. However, the particle diameter increased with the increasing amount of PCL, which is consistent with the ER behavior. The ER behavior of various amounts of PCL fits $\tau=85.12d^4E^{3/2}$ quite well. The proportionality of d^4 appears to be due to the many-body interactions between the particles.

Keywords Electrorheology · Conducting polymer composite · Conducting polymer · Suspension · Polypyrrole

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Introduction

Conducting polymers are a class of polymers that have attracted considerable interest on account of their physical and chemical properties. Among them, polypyrrole (PPy) is one of the most commonly used in commercial applications because of the long-term stability of its conductivity. However, it suffers from poor processability [1]. Many studies have focused on the preparation of conducting PPy-based composite materials in an attempt to overcome this limitation. Recently, several researchers examined conducting polymer composites with conventional polymers. In a conducting polymer composite, in which a conducting polymer is incorporated into an insulating polymer, the conducting polymer supplies the conductivity, and the insulating component supplies the necessary mechanical properties. This approach has been successful in producing conducting polymer composites with a wide range of interesting mechanical and electrical properties [2, 3].

Electrorheological (ER) fluids are suspensions of polarizable nonconducting or semiconducting particles in a nonconducting continuous phase of low relative polarizability [4–9]. In the absence of an electric field, they have the properties of a suspension of neutral solid particles. Upon the application of an electric field, an organized structure of particles is formed, and the ER fluids show remarkable changes in rheological properties, which include a significant increase in apparent viscosity and yield stress.

Because of their rapid response time and controllable shear viscosity, the engineering design based on ER fluids has facilitated the development of specifications for a broad range of applications, such as dampers, clutches, and adaptive structures [5, 6]. Most applications require fluids that possess a large field-induced yield stress, are stable to settling and irreversible aggregation, are environmentally benign, and draw a limited current [10].

Dry-based systems with anhydrous particles have been investigated in an attempt to overcome the limitations (thermal stability and corrosion) of water-based systems. Recently, anhydrous ER suspensions using polymer particles [11, 12], inorganic–organic nanocomposite particles [13–16], and semiconducting polymer particles [9, 17–20] were reported. The ER suspensions of semiconducting polymers (such as polyaniline [17, 20], pyrrole [8], copolypyrrole [19], poly(styrene-*co*-divinylbenzene) [11], and acene quinone radical polymers [21]) particles showed good ER responses.

Conducting polymer composites with conventional polymers are often prepared to improve the physical and chemical properties of the conducting polymers. This study examined the ER behavior of PPy–polycaprolactone (PCL) composite suspensions. PPy-PCL composite particles were prepared to improve the ER response by enhancing the particle properties. Various PPy-PCL composite particles were synthesized by emulsion polymerization using dodecylbenzene sulfonic acid (DBSA) as the emulsifier and controlling the amount of PCL during the synthesis. The ER response of PPy-PCL composite suspensions of various particle volume fractions was observed. The effect of the amount of PCL during synthesis on the ER behavior was also investigated using PPy-PCL composite suspensions with the same particle volume fraction.

Experimental

PPy-PCL composite particles were synthesized using DBSA (Kanto Chemical) as the emulsifier and dopant. Overall synthesis procedure of the PPy-PCL composite particles is given in Fig. 1. A series of solutions were prepared, in which 1.2, 2.4, 3.6, and 4.8 g PCL (Aldrich Chemical, M_w=10,000) were dissolved in 60 ml *p*-xylene with constant stirring. One milliliter of pyrrole (Acros Chemical) was added dropwise to each dissolved stirring solution. A 20-ml *p*-xylene solution of 2.885 g DBSA was then added slowly. After mixing with 10 ml deionized water with vigorous stirring to form an emulsion, a 10-ml aqueous solution of 1.96 g $(NH_4)_2S_2O_8$ (Kanto Chemical) was added dropwise to the emulsion with constant stirring at room temperature. Polymerization was allowed to proceed for 24 h. The pyrrole was vacuum distilled and stored at −5 °C before use. After polymerization, the PPy-PCL emulsion was precipitated by pouring into methanol. The dark green sediment was filtered and washed several times with methanol and deionized water to remove the excess DBSA and ammonium sulfate. The resulting composite particles were then dried in a vacuum for 24 h at 50 °C and sieved with a 200-mesh screen.

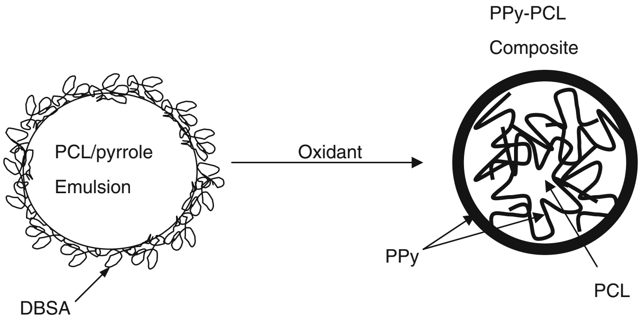

Fig. 1 Schematic diagram on PPy-PCL composite polymerization procedure

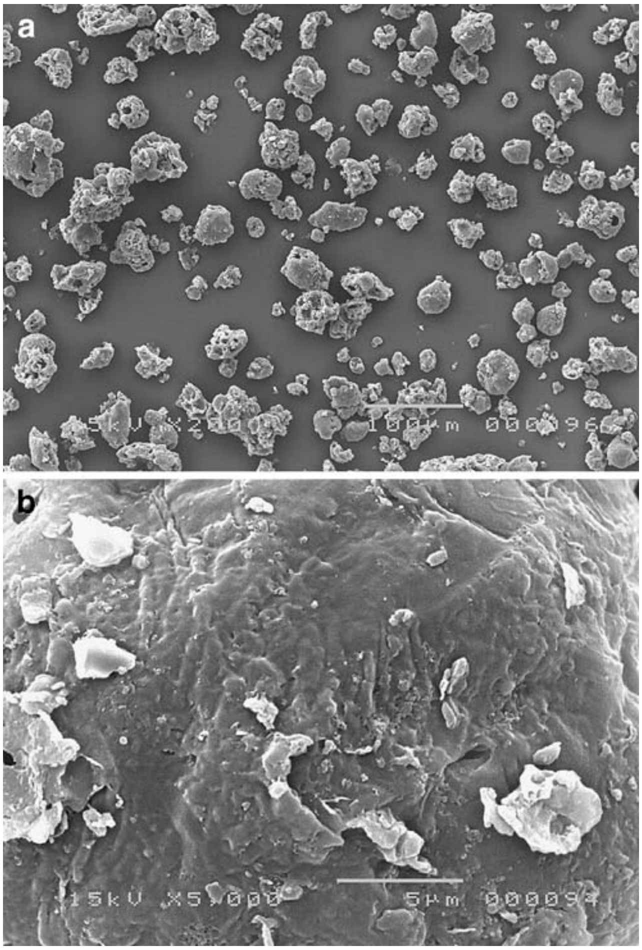

Fig. 2 Scanning electron microscopy image of the PPy-PCL composite particles **a** ×200 and **b** ×5,000

The particle size distribution of the PPy-PCL composite particles was measured using a particle size analyzer (Malvern PSA), and the average particle diameters of the PPy-PCL composites were 32.05, 40.69, 43.49, and 51.13 μm for 1.2, 2.4, 3.6, and 4.8 g PCL, respectively, increasing with increasing amount of PCL.

Figure 2 shows scanning electron microscopy images of the PPy-PCL composite particles (PCL=4.8 g). The particles had a rough surface with micropores. The micropores in the particles might be due to the PPy aggregates. Micropores in polyaniline–styrene-butadiene-styrene composites prepared by an emulsion polymerization were previously examined and attributed to polyaniline aggregates [2].

Figure 3 shows the Fourier transform infrared spectrum of the PPy-PCL composite particles. The peaks showed C–O–C stretching at 1,176 cm^{-1}, C=O stretching at 1,718 cm^{-1}, aliphatic C–H stretching at 2,924 cm^{-1}, and NH at 3,458 cm^{-1}.

PPy-PCL composite ER suspensions were prepared for the rheological and dielectric characterizations by dispersing the PPy-PCL composite particles in silicone oil (Dongyang Silicone, η_c=100 cP, ρ_c=0.96 g/cm^3). The electrorheological measurements were carried out at 25 °C using an ARES rheometer fitted with parallel plates that were modified to allow the application of high electric fields in the shear rate ranges of 0.1–100 s^{-1}. The potential differences were supplied by a high-voltage dc power supply. The suspensions were placed between the parallel plates and sheared for 1 min at a large shear rate of 100 s^{-1} and a zero field strength to ensure a uniform particle distribution. The desired electric field was then applied for 1 min with no shear before the measurements. The experiments were performed at increasing shear rates to obtain plots of the shear stress as a function of the shear rates. The values for the dynamic yield stress were determined by extrapolating the shear stress–shear rate data to a zero shear rate.

The dielectric properties were measured using a Fluke impedance analyzer (Fluke 6306A RLC meter), which probes the frequencies ranging from 50 Hz to 1,000 kHz and operates with a potential difference ranging from 0.01 to 1.0 V (rms). A three-terminal, guarded dielectric cell was used. The measured dielectric properties were corrected to eliminate the electrode polarization effects. The conductivity of the PPy-PCL composite particles was measured by a two-probe method using compressed disks with a picoammeter (Keithley 485).

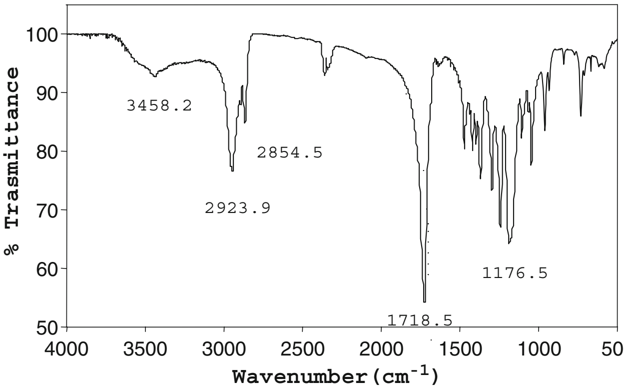

Fig. 3 FT-IR spectrum of the PPy-PCL composite particles (PCL=4.8 g)

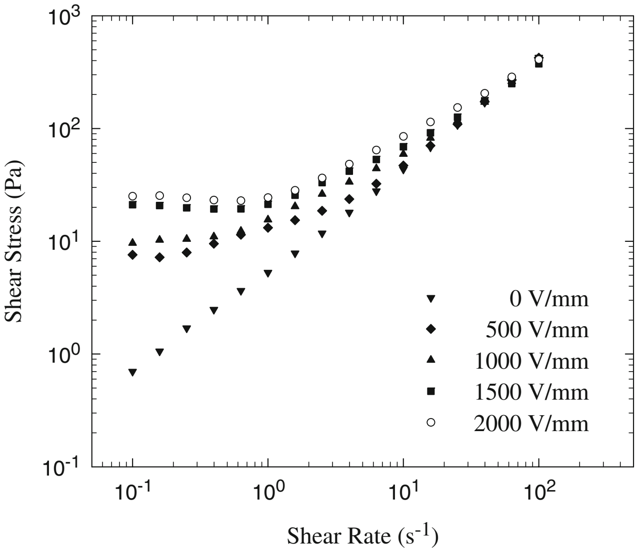

Fig. 4 Shear stress as a function of the shear rate for a 10.1-vol.% PPy-PCL composite suspension in silicone oil (PCL=3.6 g)

Results and discussion

Figure 4 shows the ER behavior for a 10.1 vol.% PPy-PCL composite suspension under various electric field strengths. The PPy-PCL composite particles were synthesized using 4.8 g PCL. Without an electric field, the suspension behaved like a Newtonian fluid with the slope of the logarithm of the shear stress to the logarithm of the shear rate equal to 1.0. When an electric field was applied to the suspension, a significant increase in the shear stress appeared, and the suspension showed a yield stress. The shear stresses and yield stress increased with increasing electric field strength. The steady-shear rheological response under an electric field can be described as that of a Bingham fluid, showing the features common to the ER response, an apparent yielding phenomenon at low shear rates and a shear thinning behavior approaching a constant viscosity at large shear rates.

An analysis of the relative magnitude of the colloidal interactions among the dispersion, thermal, electrostatic, polarization, and viscous forces revealed the polarization force for the PPy-PCL composite suspensions to be very large relative to the other colloidal forces. This suggests that the polarization and hydrodynamic forces are important for PPy-PCL composite suspensions. It was reported that the ER effect of suspensions depended on the relative influence of the polarization and hydrodynamic forces [22]. At low shear rates, the polarization force is dominant over the hydrodynamic force, and the stress is mainly determined by increases in the polarization force with increasing electric field strength. At high shear rates, the hydrodynamic force is dominant, and the shear stress is independent of the polarization force.

Figure 5 shows the dependence of the dynamic yield stress on the electric field strength for PPy-PCL composite suspensions with various particle volume fractions. The PPy-PCL composite particles were polymerized with 4.8 g PCL. The yield stress increased with increasing electric field strength and particle volume fraction. The yield stress is proportional to E^n where $n<2$ and E is the applied electric field strength. The values of n are 0.62, 0.71, 0.92, 1.55, and 1.67 for the 2.8, 4.5, 6.2, 8.1, and 10.1 vol.% suspensions, respectively, which increases with increasing particle volume fraction. A nonlinear ER behavior ($\tau \propto E^n$; $n<2$) has been reported for ER suspensions of various conducting polymer particles [9, 13, 17, 18, 23].

Figure 6 shows the dependence of the dynamic yield stress on the particle volume fraction for PPy-PCL composite suspensions at various electric field strengths. The PPy-PCL composite particles were polymerized with 4.8 g PCL. The yield stress is proportional to ϕ^m, where ϕ is the particle volume fraction. The values of m are 1.19, 1.30, 1.95, and 2.16 for E=500, 1,000, 1,500, and 2,000 V/mm, respectively. The value of m is larger than 1 and increases with increasing electric field strength, which is consistent with previous reports [13, 17]. The yield stress is proportional to the volume fraction according to the polarization model [24, 25] and the conduction model [23, 26, 27]. The value of $m>1$ is probably related to the structure changes with the electric field strength [13].

According to the polarization model, the dynamic yield stress can be represented as follows [28]:

$$\tau = 18\phi\,\varepsilon_o\varepsilon_c\beta^2E^2f_mK_m \tag{1}$$

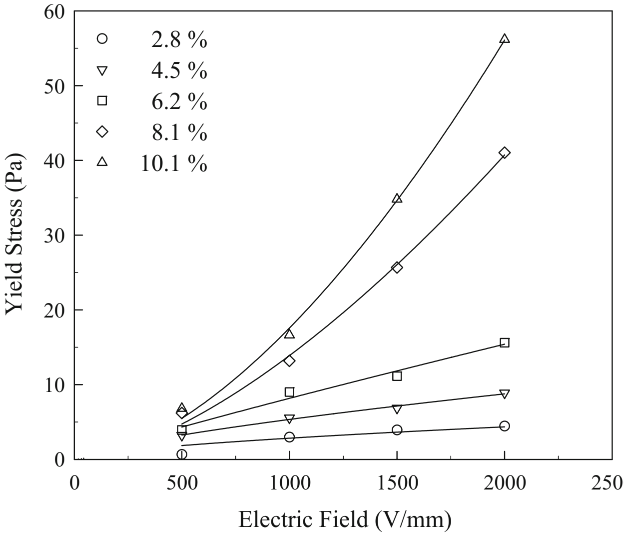

Fig. 5 Yield stress as a function of the electric field strength for PPy-PCL composite suspensions with various particle volume fractions (PCL=4.8 g)

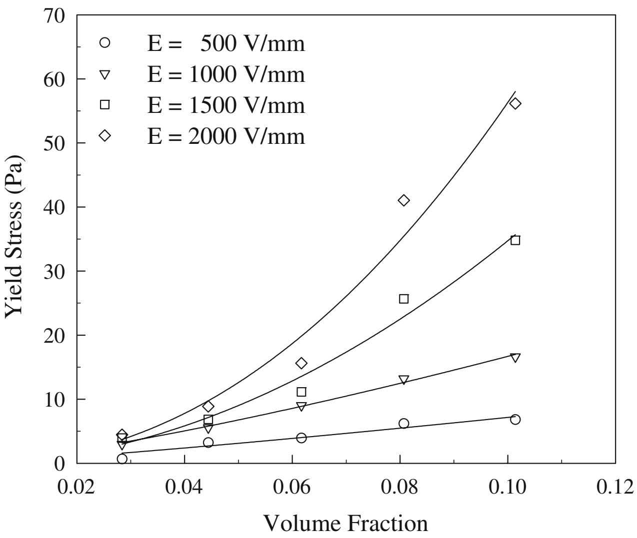

Fig. 6 Yield stress as a function of the volume fraction for PPy-PCL composite suspensions under various electric field strengths (PCL=4.8)

where ε_o is the permittivity of free space, ε_c is the dielectric constant of the continuous phase, $\beta = (\varepsilon_p - \varepsilon_c)/(\varepsilon_p + 2\varepsilon_c)$ is the relative polarizability of the particle, where ε_p is the dielectric constant of the particle, and K_m is a function of only $\varepsilon_p/\varepsilon_c$. The dynamic yield stress increases quadratically with increasing electric field strength and linearly with the particle volume fraction. The nonlinear conduction was examined by Davis and Ginder [27], who extended the conduction model of Foulc et al. [26] to determine the static yield stress. According to the conduction model, where the field strength in the interparticle gap is limited by nonlinear conduction, the yield stress can be expressed as follows [27]:

$$\tau_s = \frac{4}{\sqrt{3}}\varepsilon_0\varepsilon_c\phi E^{3/2}\sqrt{E_m} \tag{2}$$

where E_m is the maximum electric field strength in the interparticle gap, which is equivalent to the breakdown strength of the continuous phase. This model predicts that the dynamic yield stress increases with $E^{3/2}$ and linearly with the particle volume fraction.

Figures 5 and 6 shows that $\tau \propto E^n$ and $\tau \propto \phi^m$, but the values of n and m are not constant. The values of n and m appear to be a function of ϕ and E, respectively, which is not consistent with either the polarization or conduction models, where the values of n and m are constant. This inconsistency might arise because the effects of ϕ and E on the yield stress are counted separately. It would be helpful to determine the yield stress as a function of the particle volume fraction and electric field strength. A power-law dependence on both the volume fraction and the electric field strength, $\tau = K\phi^mE^n$ where K is the constant, was fitted to the dynamic yield stresses of various particle volume fractions and electric field strengths, which shows that the power-law dependence fits the yield stress adequately for values of m=2 and n=1.5.

Figure 7 shows the dependence of the dynamic yield stress on $\phi^2E^{3/2}$ for the PPy-PCL composite suspensions of various particle volume fractions. The PPy-PCL composite particles were polymerized with 4.8 g PCL. The curve, $\tau=0.06\phi^2E^{3/2}$, shows a good fit to the data. The yield stress proportionality of $E^{1.5}$ appears to be due to nonlinear conduction and is consistent with the conduction model. The yield stress proportionality of ϕ^2 is not consistent with either the polarization or conduction models. It should be noted that both the conduction and polarization models consider only the interactions between two particles, ignoring the many-body interactions between the particles. However, the many-body interactions cannot be ignored if the suspensions are not dilute. In this situation, the particles will not be subjected to a uniform external electric field but will have local fields depending on the position of all the other particles [31]. Therefore, the ϕ^2 dependence is probably related to the structural changes with the electric field strength. If ER suspensions are not dilute, the structure formed between the electrodes is more complex than an ideal chain structure, and particles would even form clusters. The effect of other particles, particularly other strands, would lead to a yield stress dependency on the higher order term of ϕ^2. For the PPy-PCL composite suspensions, ϕ^2 is dominant over the other terms, suggesting that particle aggregations is significant. During the ER experiments, it was observed that the PPy-PCL composite suspensions showed a nonuniform particle distribution of particle aggregates.

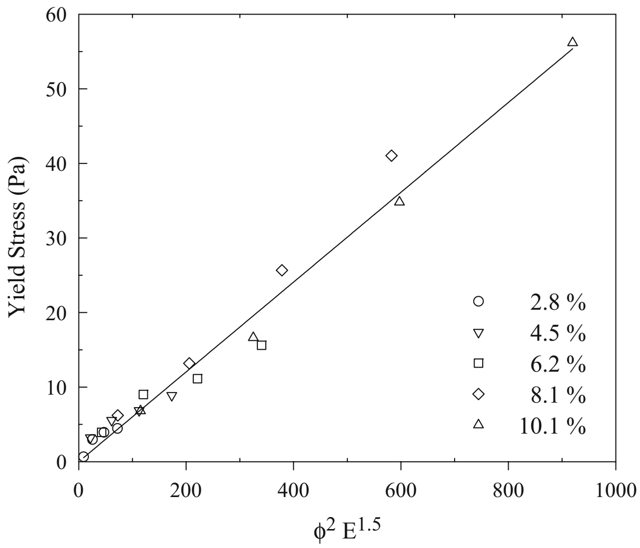

Fig. 7 Yield stress as a function of $\phi^2E^{1.5}$ for PPy-PCL composite suspensions with various electric field strengths and particle volume fractions

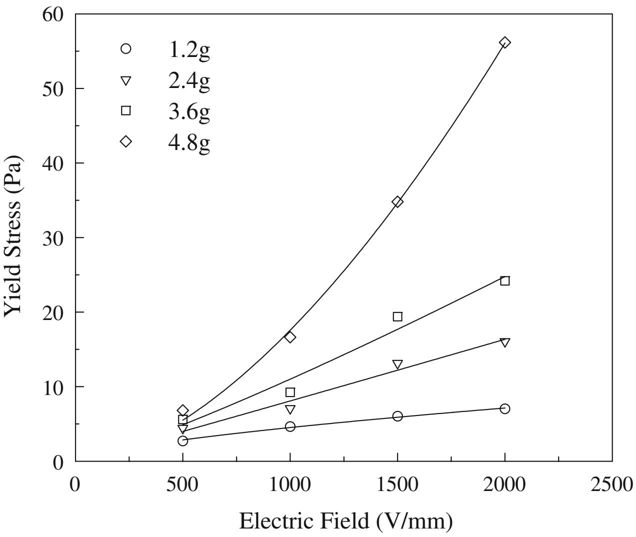

Fig. 8 Yield stress as a function of the electric field strength for 10.1 vol.% PPy-PCL composite suspensions of various amounts of PCL during synthesis

Figure 8 shows the dependence of the dynamic yield stress on the electric field strength for 10.1 vol.% PPy-PCL composite suspensions with various amounts of PCL. The yield stress increased with increasing amount of PCL and electric field strength. The yield stress is proportional to E^n where $n<2$, indicating nonlinear conduction. The value of n increases with increasing amount of PCL. The values of n are 0.66, 1.02, 1.17, and 1.67 for 1.2, 2.4, 3.6, and 4.8 g PCL, respectively. The ER response with the amount of PCL may be due to the different degrees of polarization of the PPy-PCL composite suspensions. The ER behavior is related to the polarization forces, which depend on the relative polarizability, $\beta = (\varepsilon_p - \varepsilon_c)/(\varepsilon_p + 2\varepsilon_c)$[24]. The dielectric constants of the PPy-PCL composite particles were measured at 10^5 Hz. The measured values were 9.43, 6.02, 5.17, and 5.16 for 1.2, 2.4, 3.6, and 4.8 g PCL, respectively. The dielectric constants of the PPy-PCL composite particles decreased with increasing amount of PCL, which is inconsistent with the ER behavior. However, if a dc electric field is used, the relative polarizability is based on the conductivity, $\beta_c = (\sigma_p - \sigma_c)/(\sigma_p + 2\sigma_c)$, where σ_p is the conductivity of the particle and σ_c is the conductivity of the continuous phase [28]. The effect of the particle dielectric constant is less important than that of the particle conductivity if a dc electric field is used.

It was also reported that the increased particle conductivity enhanced the particle polarization and increased the ER response [29, 30]. The dc conductivity of the PPy-PCL composite particles were measured to be 1.04×10^{-9}, 1.19×10^{-9}, 1.89×10^{-9}, and 1.38×10^{-9} S/cm for 1.2, 2.4, 3.6, and 4.8 g PCL, respectively, which is not consistent with the ER behavior. However, this inconsistency between the particle conductivity and the ER behavior does not indicate that the ER behavior is not related to polarization forces, which depend on the relative polarizability. Indeed, the values of the relative polarizabilty of the PPy-PCL composites in silicone oil are saturated, $\beta_c \sim 1$, because the particle conductivity is much higher than that of silicone oil. The conductivity of the silicone oil was 1.0×10^{-14} S/cm. The particle conductivity does not appear to influence the ER response because the polarization force is saturated. This suggests that the ER behavior of varying PCL amounts arises from other parameters.

The ER response depends on the interfacial polarization, and the dielectric properties of ER suspensions are quite useful for probing the mechanism that controls the electric properties of materials [6, 7, 28]. Figure 9 shows the suspension dielectric properties as a function of the electric field frequency for the suspensions shown in Fig. 8. The dielectric constants (Fig. 9a) and dissipation factors (=tanδ, Fig. 9b) of the suspensions decrease with increasing amount of PCL, which is inconsistent with the ER behavior. Therefore, the increasing ER response with increasing amount of PCL does not appear to be due to interfacial polarization. This suggests that the interfacial polarization is not the dominant mechanism for the ER behavior of PPy-PCL composite ER suspensions.

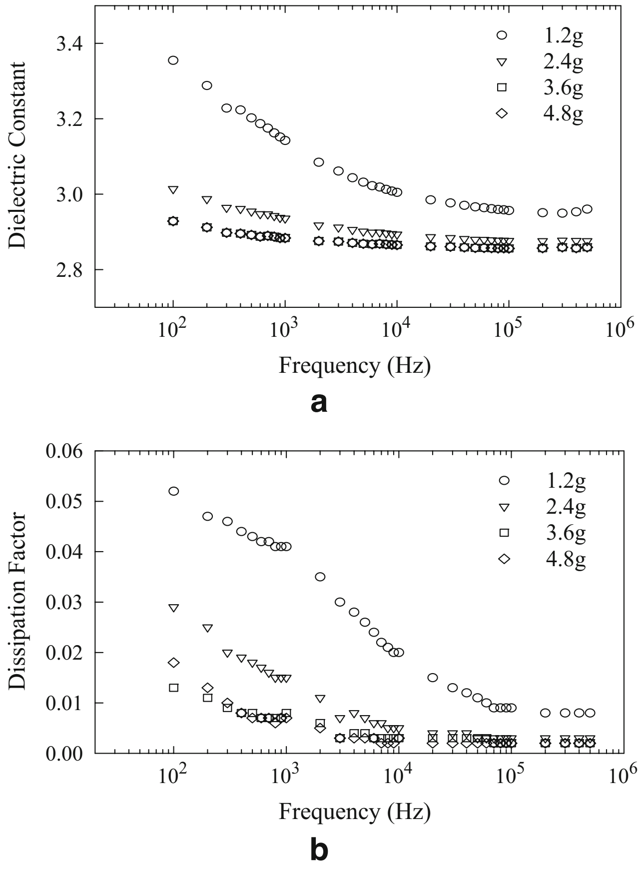

Fig. 9 Dielectric properties (**a** dielectric constant and **b** dissipation factor) as a function of the electric field frequency for 10.1 vol.% PPy-PCL composite suspensions in silicone oil with various amounts of PCL during synthesis

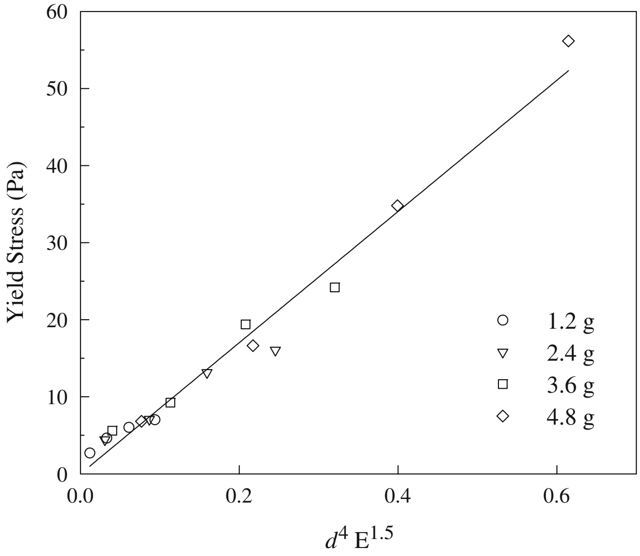

Fig. 10 Yield stress as a function of $d^4E^{1.5}$ for PPy-PCL composite suspensions with various amounts of PCL and electric field strengths

The ER response is related to the attraction force between the particles under an applied electric field. For the polarization model, the attraction force per pair interaction under an electric field is given by the following equation [25]:

$$F = 3\pi\varepsilon_o\varepsilon_c d^2\beta^2E^2 \tag{3}$$

where d is the particle diameter. The force is a function of the particle diameter, electric field strength, and β. While, the attraction force for the conduction model is given by the following equation [26, 27],

$$F = \frac{1}{2}\pi\varepsilon_o\varepsilon_c d^2E^{3/2}\sqrt{E_m} \tag{4}$$

and is a function of the particle diameter and electric field strength. Both the polarization and conduction models indicate that the particle diameter influences the ER response.

The measured average particle diameters of the PPy-PCL composite were 32.05, 40.69, 43.49, and 51.13 μm for 1.2, 2.4, 3.6, and 4.8 g PCL, respectively. The particle diameter increased with increasing amount of PCL, which is consistent with the ER behavior. It was reported that the ER response of polyaniline-coated polymethyl methacrylate ER suspensions increased with increasing particle diameter [32]. An attempt was made to model a power-law dependence of the yield stress on the relative polarizability, particle diameter, and electric field strength, $\tau=M\beta^{l}d^{m}E^{n}$, where M is the constant. The model showed a good fit to the dynamic yield stresses of the various amounts of PCL and electric field strengths. The power-law dependence shows a reasonable fit for the values of l=0, m=4, and n=1.5, showing that the relative polarizability is saturated for PPy-PCL composite suspensions, as expected from the high particle conductivity.

Figure 10 shows the dependence of the dynamic yield stress on $d^4E^{3/2}$ for 10.1 vol.% PPy-PCL composite suspensions of various electric field strengths and amounts of PCL. The curve, $\tau=85.12d^4E^{3/2}$, shows a good fit to the data. The yield stress proportionality of $E^{1.5}$ and β^0 is consistent with the conduction model. The yield stress proportionality of d^4 is not consistent with either the conduction or polarization models. This inconsistency is probably due to structural changes that occur with increasing electric field strength. If the ER suspensions are not dilute, the structure formed between the electrodes is more complex than the ideal chain structure, leading to many-body interactions. These many-body interactions would be more significant if the particles form a cluster. It was observed that during the ER experiments, the PPy-PCL composite suspensions showed a nonuniform particle distribution of particle aggregates. The formation of the particle aggregates appears to lead to the dependence on d^4. Because $\phi \propto d^2$ [25], the d^4 dependence can be reduced to a ϕ^2 proportionality, as noted previously.

Conclusion

The PPy-PCL composites were synthesized by emulsion polymerization using DBSA as the emulsifier, and the ER behavior of their suspensions in silicone oil was investigated. The PPy-PCL composites were prepared to improve the mechanical and electrical properties by forming conducting polymer composites, and thereby enhance the ER response of their suspensions. Various PPy-PCL composite particles were synthesized by controlling the amount of PCL. For ER suspensions of various particle volume fractions, the ER response increased with increasing electric field strength and particle volume fraction. The dynamic yield stress was proportional to E^n and ϕ^m, and the values of n and m were not constant but varied with the particle volume fraction and the electric field strength, respectively. A power-law dependence on the particle volume fraction and the electric field strength, $\tau=K\phi^mE^n$ shows a good fit to the dynamic yield stress of various particle volume fractions and electric field strengths. The power-law dependence was satisfied if $m=2$ and $n=1.5$. The dependence of $E^{1.5}$ is consistent with the conduction model, but the dependence of ϕ^2 is not consistent, which considers only the interactions between two particles. The yield stress proportionality to ϕ^2 appears to be related to the structure change with the electric field strength, which leads to many-body interactions between the particles such as interactions between the strands. The ER response also increases with increasing amount of PCL, but the dielectric properties and dc conductivity of the PPy-PCL composite particles and the dielectric properties of the PPy-PCL composite suspensions were not consistent with the ER behavior. It should be noted that the relative polarizability was saturated for the PPy-PCL composite suspensions. Moreover, the particle diameter increases with increasing amount of PCL, which is consistent with the ER behavior. These many-body interactions are significant. Therefore, the particle size would affect the ER behavior. The ER behavior of the ER suspensions with various amounts of PCL shows a good fit to $\tau=85.12d^4E^{3/2}$. The proportionality of $E^{1.5}$ is consistent with the conduction model, and the proportionality of d^4 can be explained by the many-body interactions.

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