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Electrorheological and dielectric properties of polypyrrole dispersions

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The electrorheological (ER) response and dielectric properties of the polypyrrole (PPy) dispersions in mineral oil were investigated. Various PPy particles were synthesized controlling the amount of oxidant and surfactant to investigate the effect of these variables on the ER response. The ER response increases with the oxidant and surfactant amount, passes through a maximum, and then decreases with the oxidant and surfactant amount. However, the decrease in the ER response at large surfactant amounts is not so significant compared to that at large oxidant amounts. The increase in the ER response with the oxidant and surfactant amount arises from the enhanced particle polarization originated from the increased PPy conductivity. The decrease in the ER response at large oxidant amounts seems to arise from the increased conduction between the PPy particles, while that at large surfactant amounts arises from the decreased particle polarization.

1. Introduction

Electrorheological (ER) response is defined as the dramatic change in rheological properties of a suspension of small particles due to the application of a large electric field transverse to the direction of flow. ER suspensions are typically composed of nonconducting or semiconducting particles dispersed in a nonconducting continuous phase. A large ER effect was first reported by Winslow in 1949 [1], and has been reviewed in several publications [2–4]. The simplicity of engineering designs based on ER materials has facilitated the development of specifications for a broad range of devices, such as dampers, clutches, and adaptive structures [3]. Although many ER devices have been brought successfully to the prototype stage, and despite much industrial activity, the anticipated commercialization of these devices has yet to be realized. The main limitation of ER technology development is a lack of effective fluids [4].

Activators are often used to activate suspensions. Some suspensions display little or no ER activity unless a small amount of water or surfactant is added, while other suspensions exhibit a significantly enhanced ER response with activator present [5–8]. Enhancing ER activity with activators such as water severely limits the allowable temperature range of operation, promotes corrosion, and increases power consumption. Therefore, it is necessary to design ER suspensions which show a high ER response without the limitations imposed by introducing activators, especially water.

Recently, anhydrous ER suspensions using polymer particles [9], inorganic-organic composite particles [10], and semiconducting polymer particles [9, 11–14] were reported. The ER suspensions of semiconducting polymer (such as, polyaniline [11], copolyaniline [12], copolypyrrole [13], poly(styrene-co-divinylbenzene) [9], and acene quinone radical polymers [14], etc) particles showed good ER responses. The polarizability of these materials is high and no activator is needed. Polypyrrole (PPy) is one of the most promising semiconducting polymers, because it has higher conductivity and environmental stability in the conductive state than many other conducting polymers.

In this paper, we investigated the ER response and dielectric properties of the PPy dispersions in mineral oil. Various PPy particles were synthesized controlling the amount of oxidant and surfactant to investigate the effect of these variables on the ER response.

2. Experimental

PPy was synthesized by chemical polymerization according to the method reported by Kudoh [15]. 0.187 mol pyrrole monomer (Acros Chemical) and a surfactant were dissolved in 50×10^{-6} m^3 deionized water in a round-bottomed flask fitted with a magnetic stirrer. An oxidant dissolved in 50×10^{-6} m^3 deionized water was slowly added to the dissolved solution and polymerization was allowed to proceed at 20°C for 1 h while stirring. Pyrrole was purified by passing through a column of activated basic alumina and stored at –15°C prior to use. Sodium p-toluene sulfate (Aldrich) was used as the surfactant and ammonium persulfate (Duksan Chemical) was used as the oxidant.

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Various amounts of surfactant and oxidant were employed to investigate the effect of these variables on the ER response. The black PPy particles were filtered and washed several times with deionized water to remove by-products of the pyrrole polymerization. After being washed with ethanol several times, the particles were treated with 0.1 M aqueous NH_4OH to reduce the particle surface conductivity. The particles were dried in a vacuum oven at 50°C for 48 h.

ER dispersions were prepared by dispersing the PPy particles in mineral oil (Sunkyung Chemical, $\eta_c = 180$ cP, $\rho_c = 850$ kg/m^3) and stored in a desiccator to minimize contact with air. Dispersions were allowed to equilibrate for at least 24 h before experiments. The mineral oil was stored for more than 1 week over molecular sieves and then used for all rheological and dielectric measurements.

Rheological experiments were performed on a Brookfield viscometer DV-II fitted with parallel plates, and modified for the application of large electric fields. Potential differences were supplied by a high-voltage dc power supply. Samples were placed between the parallel plates and sheared for 1 min at a large shear rate (>30 s^{-1}) and zero field strength to ensure a uniform particle distribution. The desired electric field was then applied for 1 min with no shear prior to measurements. Rheological measurements were performed with decreasing and increasing shear rates, to obtain plots of shear stress as a function of shear rates. Values for the dynamic yield stress were determined by extrapolating the shear stress-shear rate data to zero shear rate.

Dispersion capacitance and loss were measured using a Fluke impedance analyzer (Fluke 6306A RLC meter), which probes frequencies in the range of 50 Hz to 10^6 Hz and operates with potential differences in the range of 0.05–2.0 V (rms). A three-terminal, guarded dielectric cell was employed. Suspension dielectric constants and dissipation factors were determined for decreasing and increasing field frequencies.

3. Results and discussion

PPy polymerization was confirmed by FT-IR analysis. The FT-IR spectrum of the PPy particles treated with KBr showed the characteristic peaks of PPy at 1573, 1306, 1190, 1043, 931, and 783 cm^{-1} [16]. Fig. 1 shows the scanning electron microscope (SEM) image of the PPy particles. The particle shape is irregular but almost spherical, and the particles present in aggregates. The PPy particle size is around 300 nm. The average size of the PPy aggregates dispersed in mineral oil was measured by a particle size analyzer (Malvern PSA). The average diameter of the PPy aggregates in mineral oil was 53 μm, indicating that the PPy particles in the ER dispersion were present as large aggregates.

Without an electric field, the PPy dispersions behaved like a Newtonian fluid. By applying an electric field to the dispersions, the shear stress for the PPy dispersions dramatically increased and the suspensions showed a yield stress, showing shear thinning behavior. The dependence of the dynamic yield stress on oxidant amount (ammonium persulfate) is presented in Fig. 2 for 1 wt% PPy dispersions in mineral oil. The PPy particles were synthesized using various amounts of oxidant and the surfactant amount of 0.016 mol. The yield stress increases with the oxidant amount, passes through a maximum, and then decreases with the oxidant amount. Also, the yield stress increases with the electric field strength (E) and is proportional to $E^{1.8}$. At the oxidant amount of 0.09 mol, the decrease in the ER response is very significant. Furthermore, at oxidant amounts larger than 0.09 mol, the ER measurements could not be performed because particle strands formed between the electrode gap acted as a short circuit in the applied electric field. The yield stress behavior seems to arise from the increased PPy conductivity with the increase in the oxidant amount.

The dynamic yield stress is related to polarization forces. The polarization force per pair interaction under a dc electric field is given by [17]

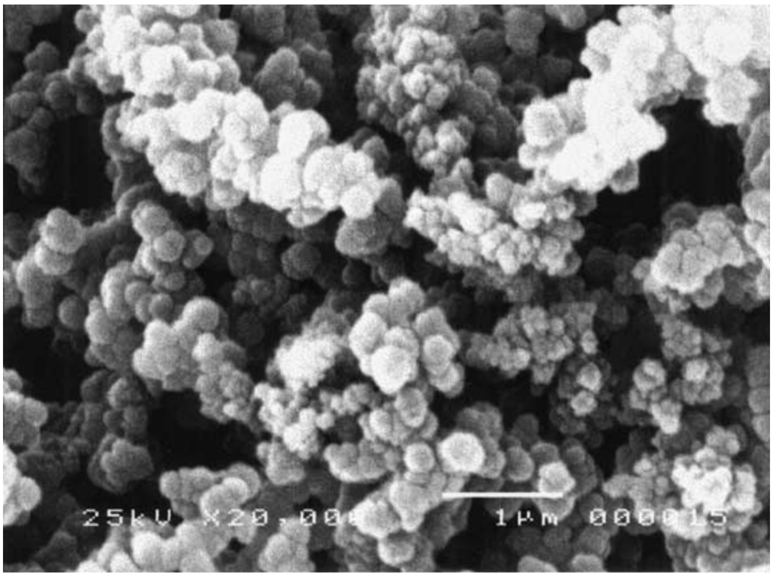


Figure 1 SEM micrograph of the PPy particles.

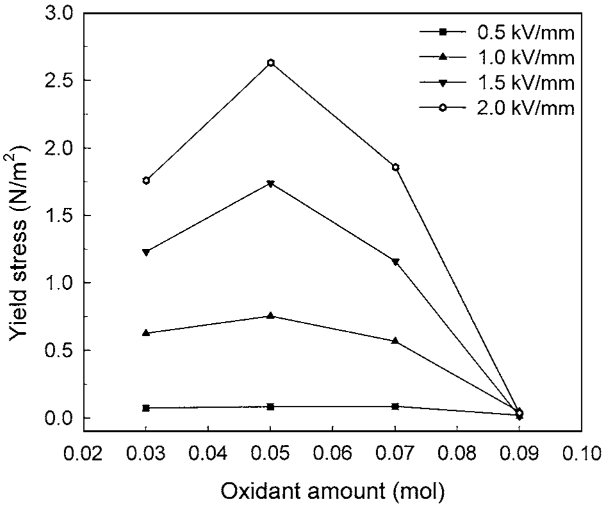
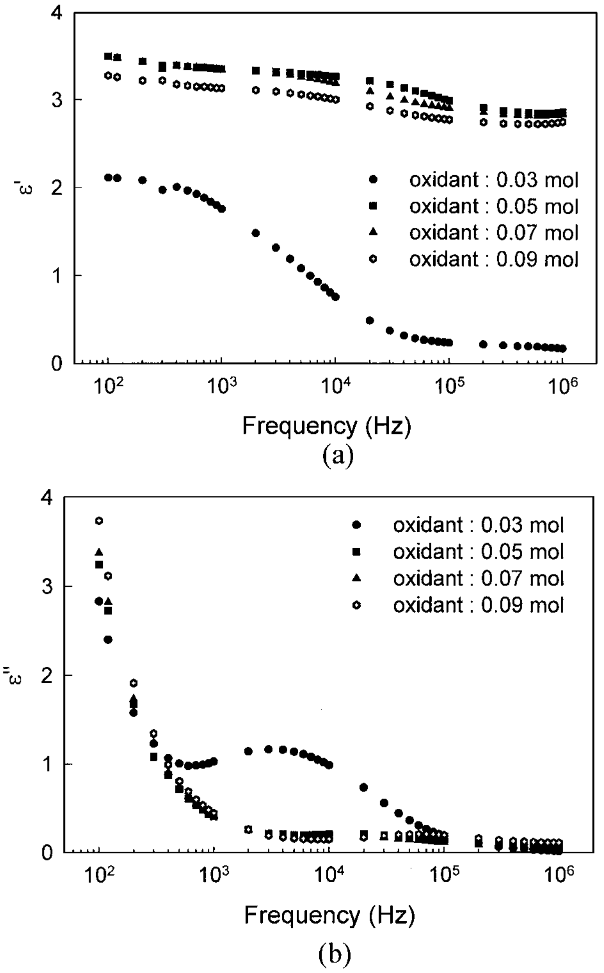


Figure 2 Dynamic yield stress as a function of oxidant amount for 1 wt% PPy dispersions of various oxidant amounts in mineral oil.

$$F = 12\pi\varepsilon_o\varepsilon_c a^2\beta^2E^2 \qquad (1)$$

where ε_o is the permittivity of free space, ε_c is the dielectric constant of the continuous phase, a is the particle radius, E is the applied electric field strength, and $\beta = (\sigma_p - \sigma_c)/(\sigma_p + 2\sigma_c)$ is the relative polarizability of the particle where σ_c is the conductivity of the continuous phase and σ_p is the particle conductivity. Therefore, the yield stress will increase by enhancing the relative polarizability β and hence particle polarization which is related to σ_p. The conductivities of the PPy particles were 2.93×10^{-6}, 3.1×10^{-6}, 3.21×10^{-6}, and 3.55×10^{-6} S/m for 0.03, 0.05, 0.07, and 0.09 mol of the oxidant amount, respectively, increasing with the oxidant amount. Therefore, the yield stress increase at low oxidant amounts arises from the enhanced particle polarization due to the increased PPy conductivity.

The particle polarization controlling the ER response depends on the dielectric properties of the dispersions. The dependence of dielectric properties on electric field frequency is presented in Fig. 3 for the same PPy dispersions in Fig. 2. As shown in Fig. 3a, the dielectric constants of the ER dispersions show similar behavior to the ER response—increasing with the oxidant amount, passing through a maximum, and decreasing with the oxidant amount. Also, the oxidant amount at the maximum dielectric constant is 0.05 mol, consistent with the ER response. Therefore, the increase in the ER response at low oxidant amounts arises from the enhanced particle polarization. However, the yield stresses of the PPy dispersion of oxidant amount of 0.03 mol are much larger than those of oxidant amount of 0.09 mol (Fig. 2), while the dielectric constant of the PPy dispersion of oxidant amount of 0.03 mol is the lowest one. Even the yield stresses of the PPy dispersion of oxidant amount of 0.03 mol are comparable to those of oxidant amount of 0.07 mol. This discrepancy can be explained by the dielectric loss (ε'') behavior (Fig. 3b).



(a)

(b)

Figure 3 Dielectric properties as a function of electric field frequency for 1 wt% PPy dispersions of various oxidant amounts in mineral oil: (a) dielectric constant and (b) dielectric loss.

The dielectric loss of the PPy dispersion of oxidant amount of 0.03 mol shows a relaxation at the frequency around 3×10^3 Hz at which the dielectric loss passes through a maximum, while those of other PPy dispersions decrease monotonically with frequency. The monotonic decrease in the dielectric loss with frequency suggests that electronic conductance in the semiconducting polymer (PPy) is significant for these dispersions, indicating that the PPy particle polarization arises from the increased PPy conductivity. However, the relaxation peak around 3×10^3 Hz for the PPy dispersion of oxidant amount of 0.03 mol indicates that there is another polarization involved in addition to the polarization due to the increased PPy conductivity. It was reported that interfacial polarization showed a relaxation in the dielectric loss in the frequency range 10^2–10^6 Hz [18]. Therefore, the PPy dispersion of oxidant amount of 0.03 shows the large ER response due to the additional interfacial polarization, despite its lowest dielectric constant.

However, the enhanced particle polarization due to the increased PPy conductivity cannot explain the decrease in the ER response at large oxidant amounts. The negligible ER response at the oxidant amount of 0.09 mol and the short circuit phenomena at large oxidant amounts seem to arise from the increased conduction between the particles originated from the increased PPy conductivity. As the conduction between the particles increases, the effective electric field strength between the particles decreases, leading to the

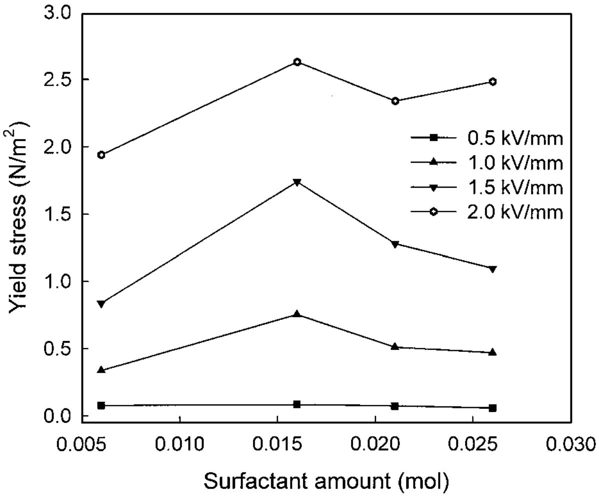
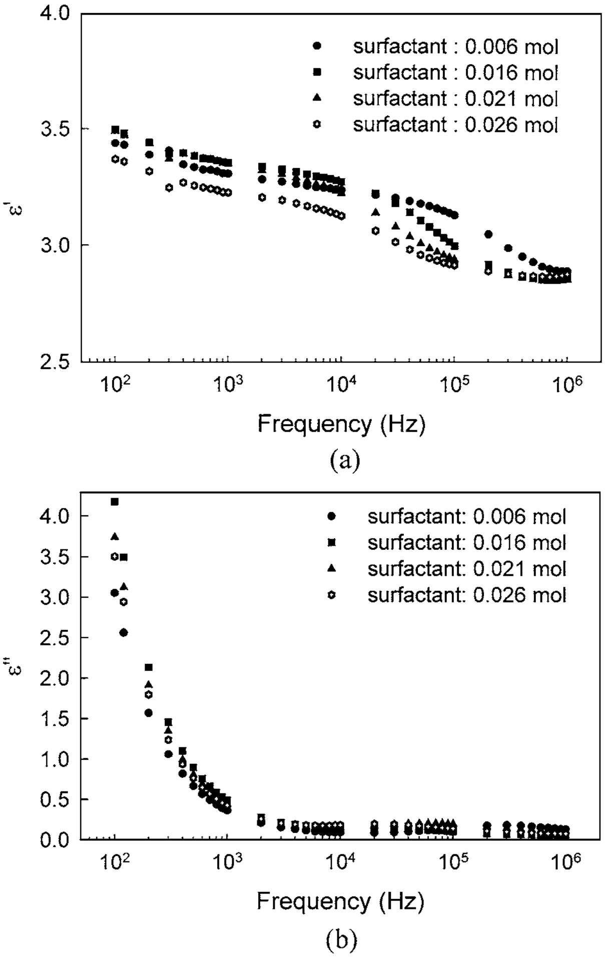


Figure 4 Dynamic yield stress as a function of surfactant amount for 1 wt% PPy dispersions of various surfactant amounts in mineral oil.

decreases in the ER response. As a result, the Er response would decrease with the increased conduction between the particles. It was also reported that the ER response deteriorated due to the nonlinear conduction between the particles due to the field dissociation of the continuous phase [19]. Therefore, the ER response of the PPy dispersions initially increases with the oxidant amount due to the enhanced particle polarization, but then decreases due to the increased conduction between the particles at large oxidant amounts.

The dependence of the yield stress on surfactant (sodium p-toluene sulfate) amount is presented in Fig. 4 for 1 wt% PPy dispersions in mineral oil. The PPy particles were synthesized using various amounts of surfactant and the oxidant amount of 0.05 mol. Again, the yield stress initially increases with the surfactant amount, passes through a maximum, and then slowly decreases with the surfactant amount. But, the decrease in the yield stress at large surfactant amounts is not so significant compared to that at large oxidant amounts. The conductivities of the PPy particles were 2.91×10^{-6}, 3.96×10^{-6}, 3.55×10^{-6}, and 3.33×10^{-6} S/m for 0.006, 0.016, 0.021, and 0.026 mol of the surfactant amount, respectively. It is notable that the PPy conductivity behavior with the surfactant amount is consistent with the yield stress behavior, showing a maximum at the surfactant amount of 0.016 mol. Kudoh [15] reported that the conductivity of PPy initially increased with the surfactant amount, showed a maximum near the maximum doping concentration, and then decreased to a constant value with the surfactant amount. The small decrease in conductivity at large surfactant amounts was explained to arise from the presence of surfactant anion adsorbed on the PPy surface. Therefore, the yield stress behavior of the PPy dispersions seems to be related to the PPy conductivity behavior, supporting that the ER response arises from the enhanced particle polarization originated from the increased PPy conductivity.

The dependence of dielectric properties on electric field frequency is presented in Fig. 5 for the same PPy dispersions in Fig. 4. As expected, the dielectric constants of the ER dispersions (Fig. 5a) show the similar behavior to the ER response—increasing with the surfactant amount, passing through a maximum, and decreasing with the surfactant amount. Also, the surfactant amount at the maximum dielectric constant is 0.016 mol, consistent with the yield stress behavior. The dielectric losses of the PPy dispersions (Fig. 5b) decrease monotonically with frequency. Therefore, the initial increase in the ER response with the surfactant amount arises from the enhanced particle polarization. Also, the slight decrease in the ER response at large surfactant amounts arises from the decreased particle polarization, originated from the decreased PPy conductivity at large surfactant amounts.



(a)

(b)

Figure 5 Dielectric properties as a function of electric field frequency for 1 wt% PPy dispersions of various surfactant amounts in mineral oil: (a) dielectric constant and (b) dielectric loss.

4. Conclusions

The yield stress increases with the oxidant and surfactant amount, passes through a maximum, and then decreases with further increase in oxidant and surfactant. However, the decrease in the ER response at large surfactant amounts is not so significant compared to that at large oxidant amounts. The increase in the ER response with the oxidant and surfactant amount arises from the enhanced particle polarization and the particle polarization is originated from the increased PPy conductivity. The decrease in the ER response at large oxidant amounts seems to arise from the increased conduction between the PPy particles, while the slight decrease in the ER response at large surfactant amounts arises from the decreased PPy conductivity at large surfactant amounts.

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