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The Electrorheological and Dielectric Behaviors of Conducting Polymer-coated Poly(ethyl methacrylate) Suspensions

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Abstract : The electrorheological (ER) and dielectric behaviors of the polypyrrole(PPy)-coated poly(ethyl methacrylate)(PEMA) suspensions in mineral oil were investigated. PPy was coated on PEMA particles to enhance the particle polarization, which would lead to the enhanced ER response. Various PPy-coated PEMA particles were synthesized by controlling the oxidant amount during the pyrrole polymerization, and the ER responses of their suspensions were investigated. The ER response initially increases with the oxidant amount, passes through a maximum, and then decreases with the oxidant amount. The initial increase in the ER response with oxidant amounts is due to the enhanced particle polarization with the increased particle surface conductivity. The dielectric properties of the corresponding suspensions support that the ER enhancement arises from the enhanced particle polarization. The decrease in the ER response at large oxidant amounts seems to arise from the increased conduction between the PPy-coated PEMA particles.

Keywords : electrorheology, conducting polymer-coated particle, polypyrrole, suspension.

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.[2-5] 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 suspensions.[5]

Various mechanisms have been proposed to explain the ER response. The electro-osmosis suggests that the ER response arise from the formation of a water bridge between the particles.[6] The inter-electrode circulation proposes that the inter-electrode circulation of particles between the electrodes, due to the particle charge change by electrochemical reactions at the electrode surface, lead to the ER response.[2] The electric double layer proposes that the origin of the ER response is the overlap of electric double layers.[7] The electrostatic polarization model explains that the ER response arises from the electrostatic interactions between the particles due to the field induced polarization of the particles.[8,9] Among these mechanisms, the electrostatic polarization model seems to be the most suitable explanation for the ER phenomena.

Some suspensions display little or no ER activity unless small amount of water or surfactant is added, while other suspensions exhibit a significantly enhanced ER response with activator present.[6,10-13] 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.

Recently, anhydrous ER suspensions using polymer particles,[14] inorganic-organic composite particles,[15] and semiconducting polymer particles[14,16-19] were reported. The ER

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suspensions of semiconducting polymer (such as, polyaniline,[16] copolyaniline,[17] copolypyrrole,[18] poly(styrene-*co*-divinylbenzene),[14] and acene quinone radical polymers,[19] etc) particles showed good ER responses.

In this paper, we investigated the ER response and dielectric properties of the suspensions of polypyrrole(PPy)-coated poly(ethyl methacrylate) (PEMA) particles. PPy was coated on PEMA particles to enhance the particle polarization by increasing the particle surface conductivity, which would lead to the enhanced ER response. It was reported that the increased particle surface conductivity enhanced the particle polarization and hence increased the ER response.[12,13] PPy-coated PEMA particles were synthesized by the pyrrole polymerization on PEMA particles. Various PPy-coated PEMA particles were synthesized by controlling the oxidant amount during the pyrrole polymerization, and the ER responses and dielectric properties of their suspensions were investigated.

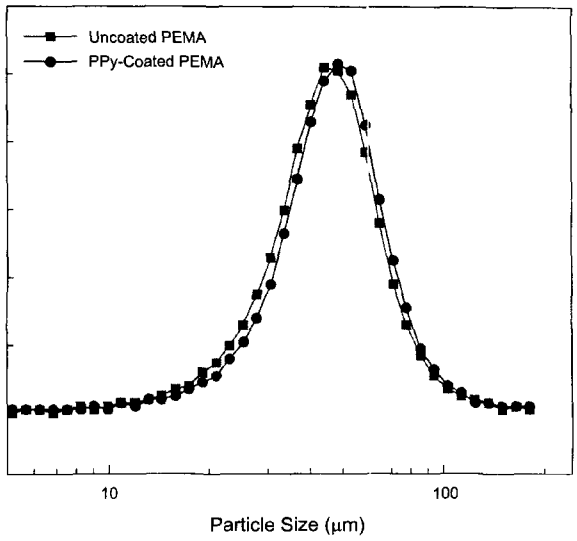

Figure 1. Particle size distributions of the PEMA particles and the PPy-coated PEMA particles.

Experimental

2.5 g PEMA particles (Aldrich) were dispersed in 200 mL deionized water containing 1.0 g methylcellulose (Showa chemical) in a round-bottomed flask fitted with a magnetic stirrer. The oxidant, $FeCl_3 \cdot 6H_2O$ (Kanio Chemical), dissolved in 50 mL deionized water was slowly added to the PEMA particle dispersed solution. Pyrrole (Acros Chemical) was added and polymerization was allowed to proceed at 25 °C for 24 h while stirring. Pyrrole was purified by passing through a column of activated basic alumina and stored at -5 °C prior to use. The black PPy-coated PEMA particles were filtered and washed several times by deionized water to remove by-products of the pyrrole polymerization. The particles were dried in a vacuum oven at 50 °C for 24 h.

Particle sizes of PEMA and PPy-coated PEMA particles were measured by a particle size analyzer (Malvern PSA) and presented in Figure 1. The average diameters of PEMA particles and PPy-coated PEMA particles were 40 μm and 43 μm, respectively. Figure 2 shows the SEM images of the PEMA (Figure 2(a)) and PPy-coated PEMA particles (Figure 2(b)). Compared to the PEMA particles, the PPy-coated PEMA particles show PPy coverage on the particle surfaces.

ER suspensions were prepared by dispersing PPy-coated PEMA particles in mineral oil (Sunkyung Chemical, η_c = 180 cP, ρ_c = 0.85 g/cm^3, SAE 5 W/50, channel point = -45 °C) and stored in a desiccator to minimize contact with air. Suspensions 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 at 25 °C on a Rheometric ARES rheometer fitted with parallel plates, and modified for the application of large electric fields. Potential

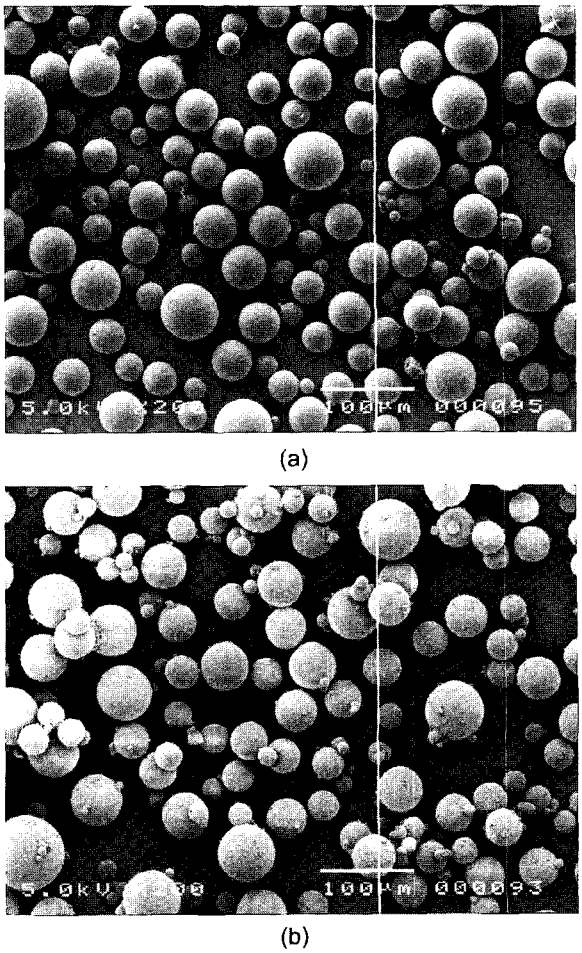

Figure 2. SEM micrographs of (a) the PEMA particles (× 200) and (b) PPy-coated PEMA particles (× 200).

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 by shearing the suspension at a constant shear rate under the applied electric field, and recording the shear stress transmitted by the suspension. Experiments were performed with 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.

Suspension capacitance and loss were measured using a Fluke impedance analyzer (Fluke 6306A RLC meter), which probes frequencies in the range of 50 Hz to 100 kHz, and operates with potential differences in the range of 0.01~1.0 V(rms). A three-terminal, guarded dielectric cell was employed. Suspension dielectric constants and dissipation factors were determined for decreasing and increasing field frequencies. The conductivities of the PPy-coated PEMA particles were measured by the two-probe method using compressed disks with a picoammeter (Keithley 485).

Results and Discussion

The ER behaviors under various electric field strengths are presented in Figure 3 for a 10 wt% PPy-coated PEMA suspension in mineral oil. The PPy-coated PEMA particles were synthesized by using 0.1 g of pyrrole and 1.5 g of $FeCl_3 \cdot 6H_2O$. Without an electric field, the suspension behaves like a Newtonian fluid with the slope of log (shear stress) to log (shear rate) of 1.0. By applying an electric field to the suspension, the shear stresses for the ER suspension dramatically increase and even the suspension shows a yield stress, showing shear thinning behavior. The shear stresses and yield stress increase with the increase in the electric field strength. The steady-shear rheological response can be described as that of Bingham fluid, showing the prevalent features of the ER response–an apparent yielding phenomenon at low shear rates and shear thinning behavior approaching a constant viscosity at large shear rates. At intermediate shear rates (5-20 s^{-1}), however, anomalous behaviors where the shear stress decreases with shear rate are observed. The anomalous behavior might arise from a negative synergistic interaction between hydrodynamic and polarization forces. The change in the shear stress at the intermediate shear rates was referred as forming small strand-like aggregates[9] or swirling motion.[16,19]

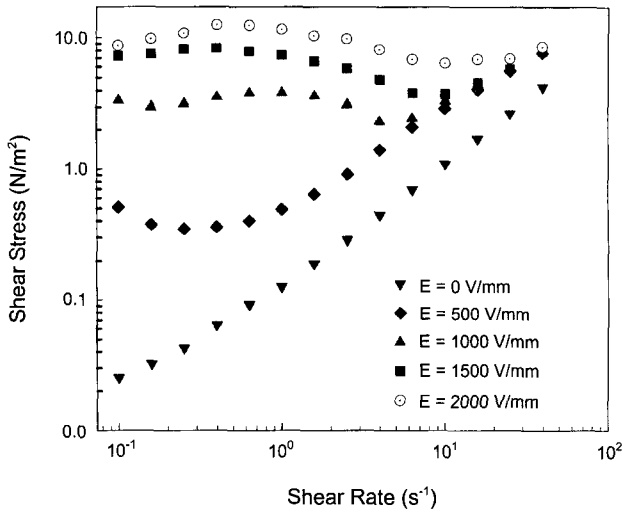

Figure 3. Shear stress as a function of shear rate for 10 wt% PPy-coated PEMA suspension in mineral oil (pyrrole = 0.1 g and $FeCl_3 \cdot 6H_2O$ = 1.5 g).

It was also observed that the ER response was related to the electric field-induced alteration of the suspension structure, where strands of particles formed spanning the electrode gap under the applied electric field. The electric field-induced alteration of the suspension structure is presented in Figure 4. Without applied electric fields, the suspension shows random particle configuration (Figure 4(a)). When an electric field is applied, particles are polarized due to the imposed electric field and form particle strands spanning between the electrodes due to the dipole interactions between the particles (Figure 4(b) and (c)). Compared to the particle strands under E = 500 V/mm (Figure 4(b)), the particle strands under E = 1,000 V/mm are more uniform and completely spanning between the electrodes, indicating that the ER response will increase with the increase in the electric field strength.

The shear stress as a function of shear rate at E = 1,000 V/mm is plotted in Figure 5 for 10 wt% PPy-coated PEMA suspensions of various PPy-coated particles. The PPy-coated PEMA particles were synthesized by using 0.1 g of pyrrole and various amounts of $FeCl_3 \cdot 6H_2O$. It was reported that 2.33 mol of ferric chloride was needed for the oxidation of 1 mol of pyrrole.[23] The PPy contents in the PPy-coated PEMA particles were estimated as 2.13 and 3.2 wt% for 0.5 and 0.75 g of $FeCl_3 \cdot 6H_2O$ and reached 4 wt% at large $FeCl_3 \cdot 6H_2O$ amounts. Therefore, the PPy content in the PPy-coated PEMA particles increases with the increase in the $FeCl_3 \cdot 6H_2O$ amount, but reaches the maximum PPy content of 4 wt% for the $FeCl_3 \cdot 6H_2O$ amounts larger than 0.9 g. At low shear rates, the shear stresses are enhanced with the increase in the $FeCl_3 \cdot 6H_2O$ amount, but the ER enhancement rate at large $FeCl_3 \cdot 6H_2O$ amount is not so significant. The shear stresses increase with the $FeCl_3 \cdot 6H_2O$ amount because the PPy-coated PEMA particle polarization increases due to the increased particle surface conductivity. At high shear rates, the shear stress enhancement with the increase in the $FeCl_3 \cdot 6H_2O$ amount is not so significant and the shear stress is independent of the $FeCl_3 \cdot 6H_2O$ amount

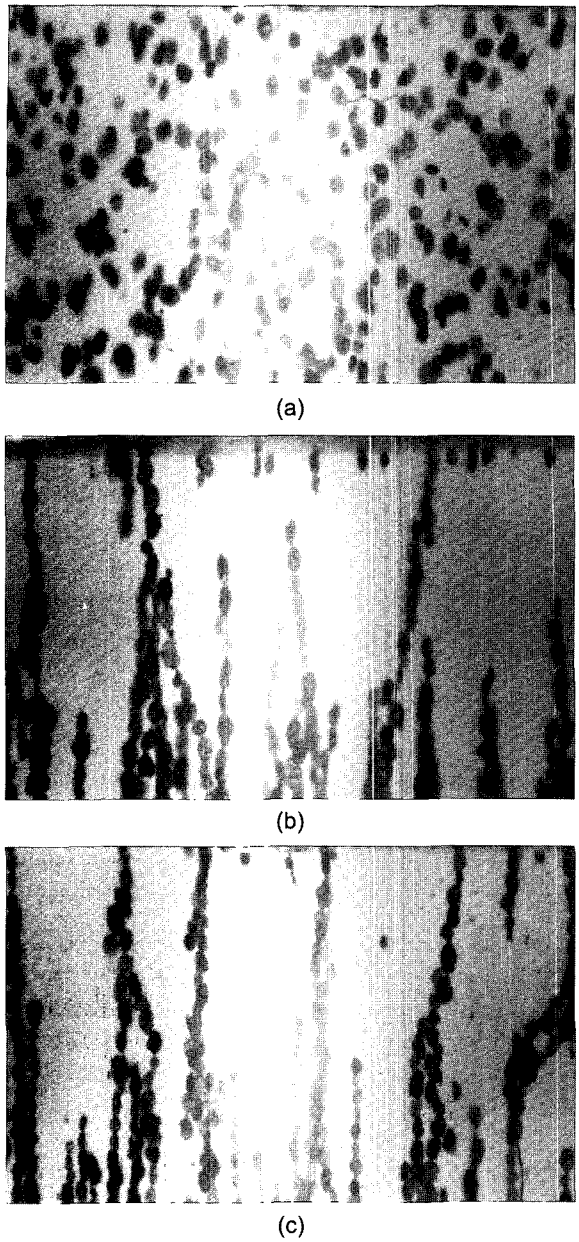

Figure 4. Configurations of 1 wt% PPy-coated PEMA particles in mineral oil at (a) E = 0 V/mm, (b) E = 500 V/mm, and (c) E = 1,000 V/mm.

at very large shear rates.

The dependence of the suspension dielectric properties on electric field frequency is presented in Figure 6 for the suspensions in Figure 5. The dielectric constants of the suspensions increase with the increase in the $FeCl_3 \cdot 6H_2O$ amount, but the dissipation factors do not show any notable differences. The dielectric constants keep increasing due to the increasing particle surface conductivity with the $FeCl_3 \cdot 6H_2O$ amount, which leads to the enhanced ER response. The dynamic yield stress is related to polarization forces.

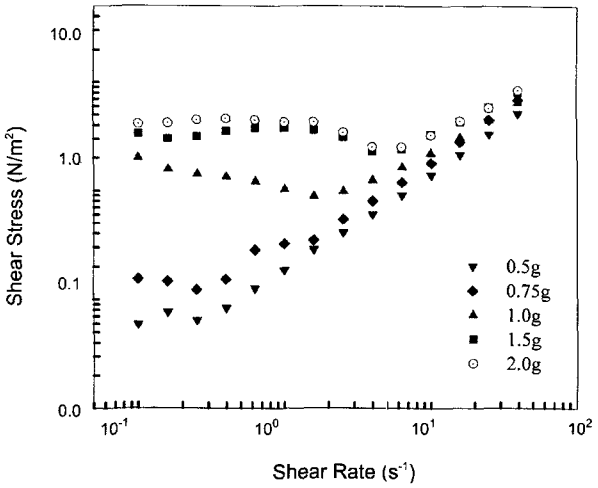

Figure 5. Shear stress as a function of shear rate at E = 1,000 V/mm for 10 wt% various PPy-coated PEMA suspensions in mineral oil (pyrrole = 1.0 g, symbol: $FeCl_3 \cdot 6H_2O$ amount).

The polarization force per pair interaction is given by[9]

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

where a is the particle radius, ε_o is the permittivity of free space, ε_c is the dielectric constant of the continuous phase, and E is the applied electric field strength. The term $\beta = (\varepsilon_p - \varepsilon_c)/(\varepsilon_p + 2\varepsilon_c)$ is the relative polarizability of the particle where ε_p is the particle dielectric constant. Therefore, the ER response will increase by enhancing the relative polarizability β and hence particle polarization which is related to ε_p.

The particle polarization will increase with the coating of a conducting polymer (e.g., PPy) on the particles, since the particle surface conductivity increases due to the high conductivity of the coated conducting polymer. It was reported that the particle polarization was enhanced by the increased particle surface conductivity.[12,13] However, it was observed that the ER response decreased rapidly when the amount of $FeCl_3 \cdot 6H_2O$ was larger than a critical amount.

The dependence of the dynamic yield stress on $FeCl_3 \cdot 6H_2O$ amount is presented in Figure 7 for 10 wt% PPy-coated PEMA suspensions of various PPy-coated particles. The yield stress initially increases with the $FeCl_3 \cdot 6H_2O$ amount, passes through a maximum, and then decreases with the $FeCl_3 \cdot 6H_2O$ amount. The increase in the ER response with $FeCl_3 \cdot 6H_2O$ amounts is due to the enhanced particle polarization with the increased particle surface conductivity. The $FeCl_3 \cdot 6H_2O$ amount at the maximum seems to depend on the applied electric field strength, shifting to lower at higher electric field strengths.

The decrease in the ER response at large $FeCl_3 \cdot 6H_2O$ amounts arises from the increased particle surface conductivity at large $FeCl_3 \cdot 6H_2O$ amounts. However, this phenom-

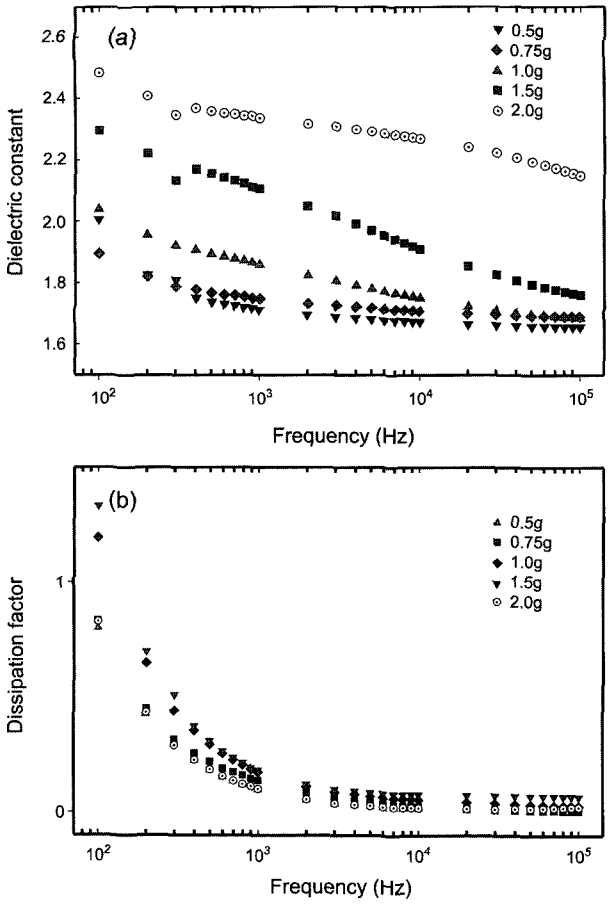

Figure 6. Dielectric properties as a function of electric field frequency for 10 wt% various PPy-coated PEMA suspensions in mineral oil (pyrrole = 1.0 g, symbol: $FeCl_3 \cdot 6H_2O$ amount): (a) dielectric constant and (b) dissipation factor.

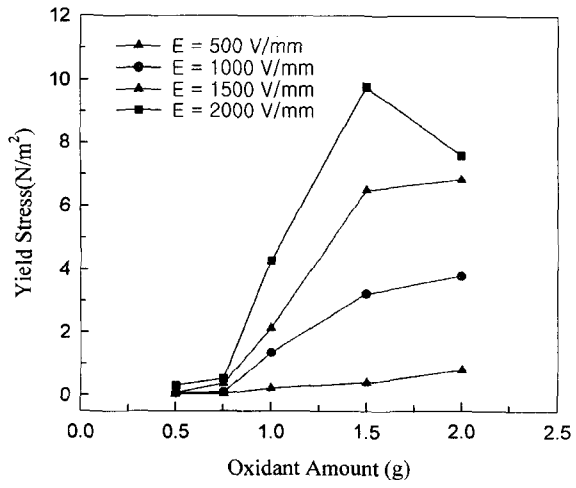

Figure 7. Yield stress as a function of $FeCl_3 \cdot 6H_2O$ amount for 10 wt% various PPy-coated PEMA suspensions in mineral oil (pyrrole = 1.0 g).

enon is different from the nonlinear conduction[20,21] in that the increased conduction arises from the high particle surface conductivity, not from the field dissociation of the continuous phase.[20,21] The conductivities of the PPy-coated PEMA particles were mea-sured as 1.46×10^{-10}, 1.94×10^{-10}, 2.14×10^{-10}, 2.52×10^{-10}, and 2.89×10^{-10} S/cm for 0.5, 0.75, 1.0, 1.5, and 2.0 g of $FeCl_3 \cdot 6H_2O$, respectively, increasing with the $FeCl_3 \cdot 6H_2O$ amount. It was also reported that PPy conductivity increased with the increase in the $FeCl_3 \cdot 6H_2O$ amount.[22]

With the increase in the $FeCl_3 \cdot 6H_2O$ amount, the particle surface conductivity of PPy-coated PEMA particles increases, leading to the increased conduction. It is also notable that the yield stress is proportional to E^2 at lower $FeCl_3 \cdot 6H_2O$ amounts (less than 1.0 g), but the yield stress is proportional to E^n ($n < 2$) at higher $FeCl_3 \cdot 6H_2O$ amounts (higher than 2.0 g). As the conduction between the particles increases, the effective electric field between the particles decreases, leading to the decreased ER response. As a result, the ER response and the value of n decrease as the conduction between the particles increases.

Conclusions

PPy-coated PEMA particles were prepared by the pyrrole polymerization on PEMA particles. It was found that the ER response increased with the coating of PPy on the PEMA particles. The ER response initially increases with the $FeCl_3 \cdot 6H_2O$ amount, passes through a maximum, and then decreases with the $FeCl_3 \cdot 6H_2O$ amount. The increase in the ER response with $FeCl_3 \cdot 6H_2O$ amounts is due to the enhanced particle polarization with the increased particle surface conductivity. The ER responses were consistent with the dielectric properties of the corresponding suspensions, supporting that the enhanced ER response arose from the enhanced particle polarization due to the coating of PPy on PEMA particles. The decrease in the ER response at large $FeCl_3 \cdot 6H_2O$ amounts seems to arise from the increased conduction between the PPy-coated PEMA particles.

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