

## Electrorheological properties of polypyrrole-silica nanocomposite suspensions

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**Abstract**—The electrorheological (ER) and dielectric properties of PPy-silica nanocomposite suspensions in silicone oil were investigated. Various PPy-silica nanocomposite particles were synthesized by suspension polymerization in the presence of silica nanoparticles controlling the ratio of silica/pyrrole during the polymerization. The ER response and the particle conductivity increased with the increase in the silica/pyrrole ratio, indicating that the increased particle polarization plays a role in enhancing the ER response. The dielectric properties of PPy-silica nanocomposite particles and their suspensions support that the enhanced ER response with the increase in the silica/pyrrole ratio arises from the enhanced polarization, which originates from the increased particle polarization.

Key words: Electrorheology, Polypyrrole-silica Particles, Conducting Polymer, Nanocomposite, Suspension

### INTRODUCTION

Electrorheological (ER) fluids are prepared by dispersing polarizable nonconducting or semiconducting particles in a nonconducting continuous phase of low relative polarizability [1-6]. In the absence of an electric field, they have the properties of suspensions of neutral solid particles. Upon the application of an electric field, an organized structure of particles is formed. Consequently, when an ER structure is destroyed and a flow starts by a shear stress, the dissipation energy results in a much higher viscosity than in the absence of the electric field, showing a yield stress.

A large ER effect was first reported by Winslow in 1949 [1] and has been reviewed in several publications [2-4]. The ER effects can be potentially suitable for various engineering applications, such as dampers, clutches, and adaptive structures [2,3]. Although many ER devices have been brought successfully to the prototype stage, the anticipated commercialization of these devices has yet to be realized. The main limitation of ER technology development is a lack of effective fluids [7]. Most applications require fluids that possess a large field-induced yield stress, are stable to settling and irreversible aggregation, are environmentally benign, and draw limited current.

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 [9-13]. 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.

Anhydrous ER suspensions using polymer particles [14], inorganic-organic composite particles [15], and semiconducting polymer particles [14,16-21] have been reported. The ER 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.

Often, conducting polymer-inorganic composites are prepared to improve the physical and chemical properties of conducting polymers by coating conducting polymers on inert core inorganic particles or forming polymeric nanocomposites by carrying out the polymerization in the presence of inorganic nanoparticles. In conducting polymer-inorganic nanocomposites, the nanoparticles generally provide the system with improved colloidal stability and mechanical strength. Recently, conducting polymer coated inorganic-organic composites particles (polyaniline-coated inorganic particles [22,23]) and conducting polymer-inorganic nanocomposites (polyaniline-montmorillonite particles [23]) were used for ER suspensions and they showed promising ER responses.

In this paper, we investigated the ER response and dielectric properties of polypyrrole (PPy)-silica nanocomposite suspensions. PPy is one of the most promising conducting polymers, because it has higher conductivity and environmental stability in the conductive state than many other conducting polymers. PPy-silica nanocomposite particles were prepared to improve the ER response by enhancing the particle properties by forming nanocomposite of silica and PPy. For this purpose, various PPy-silica nanocomposite particles were synthesized by suspension polymerization, controlling the silica/pyrrole ratio during the polymerization, and the ER response of the corresponding ER suspensions in silicone oil was observed. To investigate the ER behavior, the dielectric properties of the PPy-silica nanocomposite particles and suspensions and dc conductivity of the PPy-silica nanocomposite particles were observed.

### EXPERIMENTAL

PPy-silica nanocomposite particles were synthesized by the procedure reported by Flitton et al. [24] 4.55 g  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  (Kanio Chemical) was dissolved in deionized water at room temperature. 1.4-5.4 g silica (Ace Hightech, average diameter of 20 nm, provided as 31 wt% aqueous dispersion at pH 10) was added to the solution (total solvent volume=200 ml). 0.5 ml of pyrrole (Acros Chemical) was then in-

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jected via syringe to this stirred solution and the polymerization allowed to proceed for 24 h. Pyrrole was vacuum-distilled and stored at  $-5^{\circ}\text{C}$  prior to use. The polymerization product was centrifuged for 6,000 rpm for 30 min and the black sediment was dispersed in deionized water by mechanical stirring. The centrifugation-dispersion cycle was repeated three times to completely remove the excess 20 nm silica particles from the larger PPy-silica nanocomposite particles. The resulting PPy-silica nanocomposite particles were then treated with excess 0.5 N NaOH solution. The dedoped PPy-silica nanocomposite particles were then washed twice with deionized water and dried at  $50^{\circ}\text{C}$  in a vacuum oven for 24 h. The density of PPy-silica nanocomposite measured by a pycnometer was around  $1.6\text{ g/cm}^3$ .

A scanning electron microscopy (SEM) image of the PPy-silica nanocomposite particles is shown in Fig. 1. The PPy-silica nanocomposite particles of 200 to 300 nm diameters are agglomerated. It shows that small silica particles are glued together with PPy in the PPy-silica nanocomposite particles. It was reported that colloidal raspberries consisted of micro-aggregates of silica glued together by the chain of PPy [25]. The particle size distribution of the PPy-silica nanocomposite particles was measured with a particle size

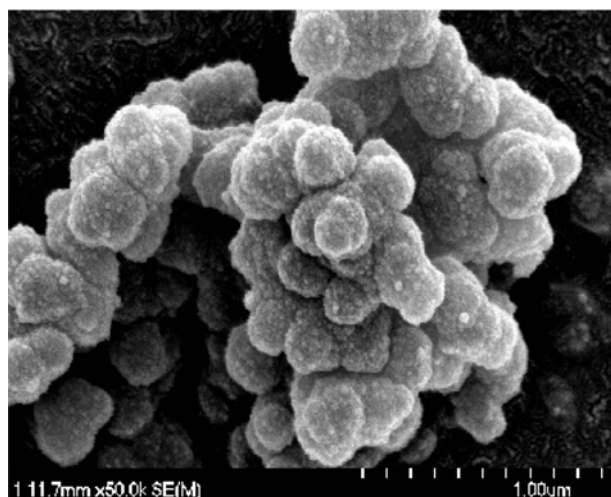


Fig. 1. Scanning electron microscopy image of the PPy-silica nanocomposite particles ( $\times 50,000$ ).

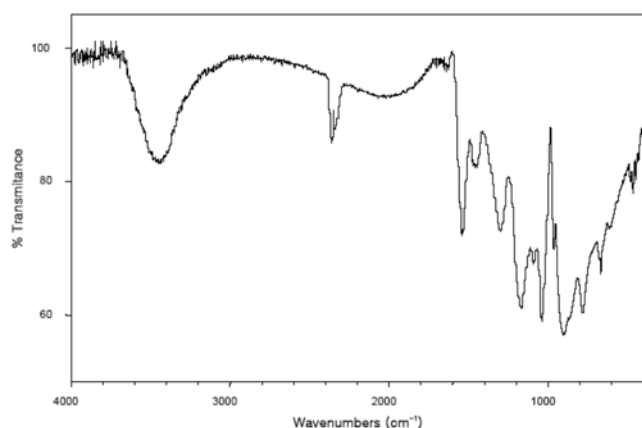


Fig. 2. FT-IR spectrum obtained from the PPy-silica nanocomposite particles.

analyzer (Microtrac, UPA-150). The particle sizes of the various PPy-silica nanocomposite particles synthesized by controlling the ratios of silica/pyrrole were almost the same and the average particle diameter of PPy-silica nanocomposite particles is 255 nm.

Fig. 2 shows the FT-IR spectrum of the PPy-silica nanocomposite particles. The peaks observed the NH at  $3,000\text{--}3,500\text{ cm}^{-1}$ , the C=C at  $1,542\text{ cm}^{-1}$ , the symmetric Si-O-Si stretching at  $480\text{ cm}^{-1}$ , and the asymmetric Si-O-Si stretching at  $1,039\text{ cm}^{-1}$ .

PPy-silica nanocomposite ER suspensions were prepared for rheological and dielectric characterizations by dispersing PPy-silica nanocomposite particles in silicone oil (Dongyang Silicone,  $\eta_c=100\text{ cP}$ ,  $\rho_c=0.96\text{ g/cm}^3$ ) and allowed to equilibrate for at least 24 h before experiments in a desiccator to minimize contact with air.

Electrorheological measurements were performed at  $25^{\circ}\text{C}$  with an ARES rheometer fitted with parallel plates modified for the application of high electric fields in the shear rate ranges of  $0.1\text{--}100\text{ s}^{-1}$ . Potential differences were supplied by a high-voltage dc power supply. Suspensions were placed between the parallel plates and sheared for 1 min at a large shear rate of  $100\text{ s}^{-1}$  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. 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.

Dielectric properties were measured by using a Fluke impedance analyzer (Fluke 6306A RLC meter), which probes frequencies in the range of 50 Hz to 1,000 kHz, and operates with potential differences in the range of 0.01–1.0 V (rms). A three-terminal, guarded dielectric cell was employed. The conductivity of the PPy-silica nanocomposite particles was measured by the two-probe method using compressed disks with a picoammeter (Keithley 485).

## RESULTS AND DISCUSSION

Fig. 3 shows the ER behavior as a function of shear rates for 2.0

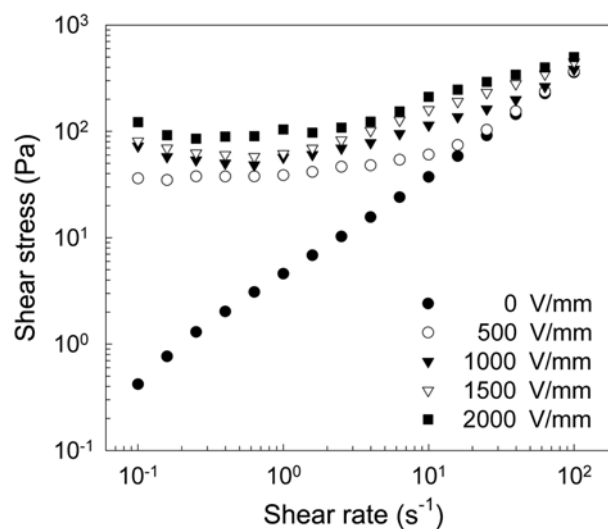


Fig. 3. Shear stress as a function of shear rate for 2.0 vol% PPy-silica nanocomposite suspension in silicone oil (silica/pyrrole weight ratio during the polymerization=7.0).

vol% PPy-silica nanocomposite suspension under various electric field strengths. Without an electric field, the suspension shows Newtonian behavior. When an electric field is applied to the suspension, a marked increase in the shear stress appears and even the suspension shows a yield stress. The flow properties under an electric field can be described as a Bingham model [25].

$$\tau = \tau_0 + \eta \dot{\gamma} \quad (1)$$

where  $\tau$  is the shear stress,  $\tau_0$  is the yield stress,  $\eta$  is the effective viscosity, and  $\dot{\gamma}$  is the shear rate. The shear stress (or yield stress) increases as the applied electric field strength on the suspension is increased. From the analysis of the relative magnitude of colloidal interactions among dispersion, thermal, electrostatic, polarization and viscous forces, the polarization force is very large relative to other colloidal forces for PPy-silica nanocomposite suspensions. Marshall et al. [26] also showed that the ER effect of suspensions depended on both the electric field strength and the shear rate, i.e., depended on the relative influences of polarization force and hydrodynamic force. At low shear rates, polarization force is dominant over hydrodynamic force. At high shear rates, hydrodynamic force is dominant and the shear stress is independent of polarization force.

The dependence of the dynamic yield stress on the electric field strength is presented in Fig. 4 for PPy-silica nanocomposite suspensions of various particle volume fractions. The PPy-silica nanocomposite particles were polymerized with the silica/pyrrole weight ratio of 7.0. The yield stress increases with the increase in the electric field strength and the particle volume fraction. The yield stress is proportional to  $E^n$  where  $n \approx 1$ . The nonlinear ER behavior ( $\tau \propto E^n$ ;  $n < 2$ ) has been reported for the ER suspensions of various conducting polymer particles [5,6,14,16-18]. The nonlinear behavior arises from the increased conduction between the PPy-silica nanocomposite particles owing to their high particle surface conductivity [5,6].

A power-law dependence on the volume fraction  $\tau_0 = K(E) \phi^m$  adequately fits the dependence of the yield stress on the particle volume fraction, where  $\phi$  is the particle volume fraction and  $K(E)$

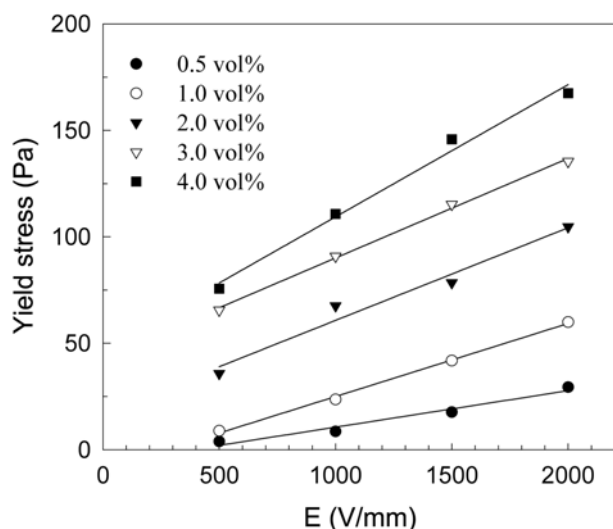


Fig. 4. Yield stress as a function of electric field strength for PPy-silica nanocomposite suspensions of various particle volume fractions (silica/pyrrole weight ratio during the polymerization=7.0).

Table 1. Parameters of the power law fit,  $\tau_0 = K(E) \phi^m$

E (kV/mm)	K(E) (Pa)	m
0.5	150±30	1.2±0.12
1.0	255±28	1.08±0.04
1.5	408±18	0.93±0.09
2.0	589±25	0.76±0.04

is an electric field strength dependent proportional constant. The values of the parameters are summarized in Table 1. The value of  $K(E)$  increases with the increase in the electric field strength, while the value of  $m$  decreases. The value of  $m$  is around 1. According to the polarization model and the conduction model, the yield stress is proportional to the volume fraction [25]. Variation of the value of  $m$  is probably related to the structure change with the electric field strength. It was observed by using a charge-coupled-device camera that the ER response was related to the electric field-induced alteration of the suspension structure. The structure of strands of particles formed spanning the electrode gap depended on the applied electric field strength, forming more particle clusters with the increase in the electric field strength.

The dependence of the dynamic yield stress on the silica/pyrrole weight ratio during the polymerization is presented in Fig. 5 for 2.0 vol% PPy-silica nanocomposite suspensions. The yield stress increases with the increase in the silica/pyrrole ratio and electric field strength. The ER response increase with the silica/pyrrole ratio may arise from the different degrees of polarization of the PPy-silica nanocomposite particles of different silica/pyrrole ratios. The ER behavior is related to polarization forces. The polarization force per pair interaction is given by [9]

$$F = 12\pi\epsilon_0\epsilon_r a^2 \beta^2 E^2 \quad (2)$$

where  $a$  is the particle radius,  $\epsilon_0$  is the permittivity of free space,  $\epsilon_r$  is the dielectric constant of the continuous phase, and  $E$  is the applied electric field strength. When the applied electric field is dc, the relative polarizability  $\beta = (\sigma_p - \sigma_c) / (\sigma_p + 2\sigma_c)$  where  $\sigma_c$  is the conductivity

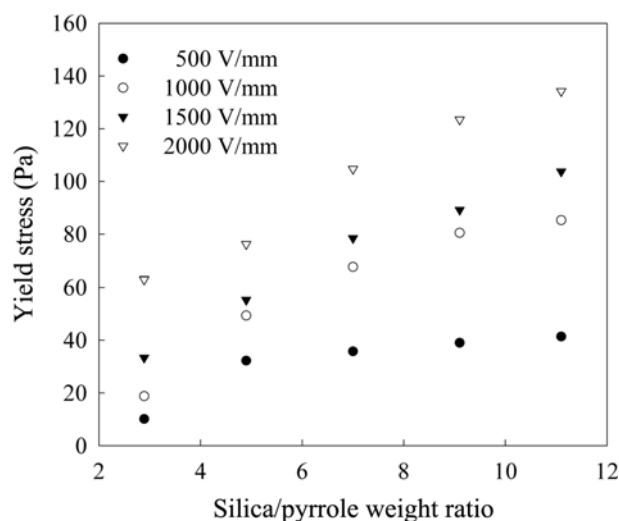


Fig. 5. Yield stress as a function of silica/pyrrole weight ratio during the polymerization for 2.0 vol% PPy-silica nanocomposite suspensions.

of the continuous phase and  $\sigma_p$  is the particle conductivity. Therefore, the ER response would increase by enhancing the relative polarizability  $\beta$  and hence increasing the particle conductivity,  $\sigma_p$ .

It was reported that the increased particle conductivity enhanced the particle polarization and hence increased ER responses [12,13]. The dc conductivity of the PPy-silica nanocomposite particles was measured as  $2.62 \times 10^{-8}$ ,  $7.83 \times 10^{-8}$ ,  $1.19 \times 10^{-7}$ ,  $1.79 \times 10^{-7}$ ,  $2.23 \times 10^{-7}$  S/cm for 2.9, 4.9, 7.0, 9.0, and 11.0 silica/ppyro weight ratios, respectively, increasing with the increase in the silica/ppyro ratio. It is an interesting result considering that PPy has higher conductivity than silica does. However, it has been reported that the conductivity of conducting polymer-inorganic composite increases with the increase in the inorganic particle/conducting polymer ratio (polyaniline-inorganic nanocomposite [28] and polyaniline-iron oxide nanocomposite [29]), consistent with our result. Furthermore, the conductivity of the PPy-silica nanocomposite increased with the increase in the silica/ppyro ratio in a certain range [25]. Thus, the increasing dc conductivity of the PPy-silica nanocomposite particles with the increase in the silica/ppyro ratio would increase the particle polarization. As a result, the increased particle polarization seems to contribute to the increasing ER behavior with the increase in the silica/ppyro ratio.

The particle polarization controlling the ER behavior depends

on the dielectric properties. The dependence of the particle dielectric properties on the electric field frequency is presented in Fig. 6 for various silica/ppyro ratios. The dielectric constants (Fig. 6(a)) of the PPy-silica nanocomposite particles increase with the increase in the silica/ppyro ratio, as expected from the dc conductivity data. But, the dissipation factors (Fig. 6(b)) do not show any notable relaxation. The dielectric constants keep increasing due to the increasing particle conductivity with the increase in the silica/ppyro ratio, which would increase the particle polarization and therefore, increase the ER response. Also, since the dissipation factors show no relaxation over  $10^2$ - $10^6$  Hz, the particle polarization does not arise from interfacial polarization but from the increased dielectric constant originating from the increased particle conductivity.

The dependence of the suspension dielectric properties on the electric field frequency is presented in Fig. 7 for the suspensions in Fig. 5. The dielectric constants (Fig. 7(a)) of the suspensions increase with the increase in the silica/ppyro ratio, but the dissipation factors (Fig. 7(b)) do not show any notable differences regardless of the silica/ppyro ratio. It is generally accepted that interfacial polarization plays a role in the ER response, which shows a relaxation in the dissipation factor in the frequency range  $10^2$ - $10^6$  Hz [4]. The dissipation factors (Fig. 7(b)) show relaxation frequencies around

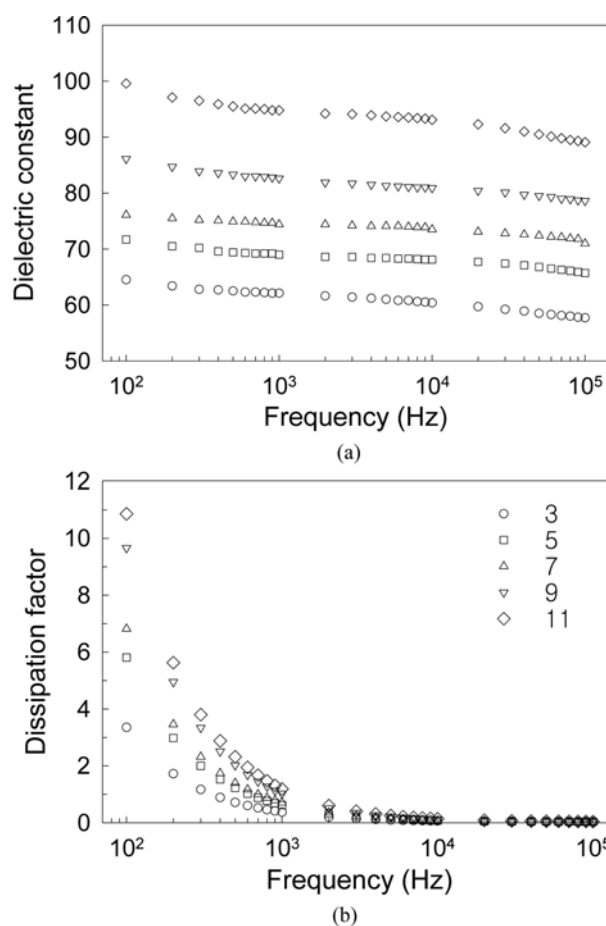


Fig. 6. Dielectric properties as a function of electric field frequency for PPy-silica nanocomposite particles of various silica/ppyro ratios during the polymerization.

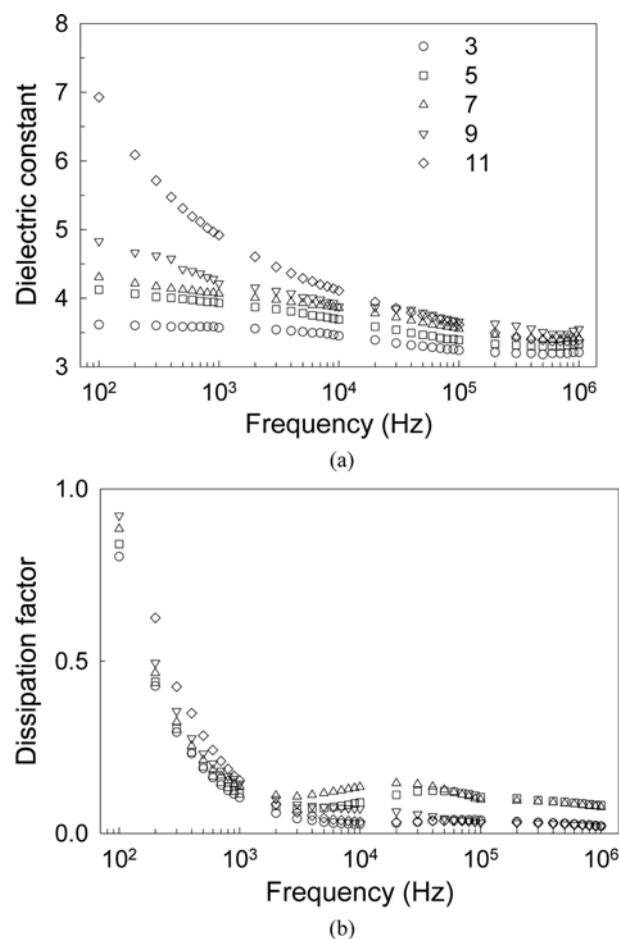


Fig. 7. Dielectric properties as a function of electric field frequency for 2.0 vol% PPy-silica nanocomposite suspensions in silicone oil for various silica/ppyro ratios during the polymerization.

$2 \times 10^4$  Hz, but the relaxation is quite small and is not consistent with the ER response. The suspension polarizability, proportional to the slope of the frequency spectra of the dielectric constant, increases with the increase in the silica/pyrrole ratio, indicating that the polarization increases with the increase in the silica/pyrrole ratio. Therefore, the enhanced ER response with the increase in the silica/pyrrole ratio arises from the enhanced polarization.

## CONCLUSION

The ER and dielectric behaviors of PPy-silica nanocomposite suspensions in silicone oil were investigated. PPy-silica nanocomposite particles were prepared to enhance the ER response by improving particle properties by forming conducting polymer-inorganic nanocomposites. Various PPy-silica nanocomposite particles were synthesized by suspension polymerization in the presence of silica nanoparticles controlling the ratio of silica/pyrrole during the polymerization. The ER response increases with the increase in the silica/pyrrole ratio. The dielectric properties and dc conductivities of PPy-silica nanocomposite particles indicate that the increased particle polarization arises from the increased particle dielectric constant, which originates from the increased particle conductivity. The dielectric properties of PPy-silica nanocomposite suspensions support that the enhanced ER response with the increase in the silica/pyrrole ratio arises from the enhanced polarization.

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