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# Electrorheological properties of polypyrrole–$SnO_2$–methylcellulose nanocomposite suspensions

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**Abstract** Inorganic-conducting polymer particles were prepared to enhance physical and chemical properties by forming hybrid nanocomposites, which would improve the electrorheological (ER) effect of their suspensions. Polypyrrole (PPy)–$SnO_2$–methylcellulose nanocomposite particles were synthesized by controlling the ratio of pyrrole, $SnO_2$, and methylcellulose during the polymerization. The ER and dielectric properties of the PPy–$SnO_2$–methylcellulose nanocomposite suspensions were investigated. The ER response increases with the increase in the $SnO_2$/pyrrole ratio and also depends on the amount of methylcellulose amount during the polymerization, showing a maximum ER behavior.

## Introduction

The development of nanocomposites is a topic of great current interest. Nanocomposites are ultrafine particles of nanometer dimensions located in the transition region between atoms and bulk solids. Conducting polymers constitute a class of polymers with particular interest owing to their physical and chemical properties. PPy is one of the most studied conducting polymers due to its relative stability. Heterogeneous-conducting polymer nanocomposites, especially organic–inorganic nanocomposites, have drawn the attention of scientist over last few years, giving rise to a host of nanocomposites with interesting physical properties and important application potential [1, 2].

ER fluids are suspensions of polarizable nonconducting or semiconducting particles in a nonconducting continuous phase of low relative polarizability [3–9]. 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 and the ER fluids exhibit a remarkable change in rheological properties, including a drastic increase in apparent viscosity as well as a yield stress. Due to their fast response time and controllable shear viscosity, the ER fluids have been widely used for various engineering applications, such as dampers, clutches, and adaptive structures [2, 3].

To overcome the limitations (thermal stability and corrosion) of water-based systems, anhydrous ER suspensions using polymer particles [10], inorganic–organic composite particles [11], and semiconducting polymer particles [10, 12–15] were reported. Often conducting polymer–inorganic nanocomposites are prepared to improve the physical and chemical properties of conducting polymers [1, 2]. In conducting polymer–inorganic nanocomposites, the nanoparticles generally provide the system with improved colloidal stability and mechanical strength [16]. Conducting polymer coated inorganic–organic composites particles (polyaniline-coated inorganic particles [17, 18]) and conducting polymer–inorganic nanocomposites (polyaniline–montmorillonite particles [19] and polypyrrole/$Na^+$-montmorillonite particles [20]) were used for ER suspensions and they showed promising ER responses.

In this study, we investigated the ER behavior of the PPy–$SnO_2$–methylcellulose nanocomposite suspensions. The PPy–$SnO_2$–methylcellulose nanocomposite particles were prepared to improve the ER response by enhancing

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the particle properties by forming inorganic-conducting polymer hybrid nanocomposites. Conducting polymer–inorganic nanocomposites generally provide the system with improved colloidal stability and mechanical strength, which would lead to the enhanced ER response. For this purpose, various PPy–$SnO_2$–methylcellulose nanocomposite particles were synthesized by suspension polymerization controlling $SnO_2$, pyrrole, and methylcellulose amounts during the polymerization. The ER response of the corresponding ER suspensions in silicone oil was observed. Also, the dielectric properties of the PPy–$SnO_2$–methylcellulose nanocomposite suspensions were investigated.

## Experimental

PPy–$SnO_2$–methylcellulose nanocomposite particles were synthesized using methylcellulose (Showa Chemical, $\eta$ = 4,000 cP (2 w/w% aqueous solution)) as a polymeric stabilizer. 4.55 g $FeCl_3 \cdot 6H_2O$ (Kanio Chemical) were dissolved in deionized water containing 0.3 g methylcellulose at room temperature. A series of syntheses were performed in which 1.4, 2.4, 3.4, 4.4, and 5.4 g $SnO_2$ nanoparticles (NYACOL, average diameter of 20 nm, provided as 31 wt% aqueous dispersion at pH 10) were added to the solution (total solvent volume = 200 ml). 0.5 ml of pyrrole (Acros Chemical) was then injected via syringe to each stirred solution and the polymerization was allowed to proceed for 24 h. Also, the various amounts of methylcellulose (0.1, 0.2, 0.3, and 0.4 g) were employed to observe the effect. Pyrrole was vacuum distilled and stored at –5 °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 using mechanical stirring. The centrifugation-dispersion cycle was repeated three times in order to completely remove the excess 20 nm $SnO_2$ particles and by-products from the PPy–$SnO_2$–methylcellulose nanocomposite particles. The nanocomposite particles were then washed twice with deionized water and dried at 50 °C in a vacuum oven for 24 h.

ER suspensions were prepared for rheological and dielectric characterizations by dispersing PPy–$SnO_2$–methylcellulose nanocomposite particles in silicone oil (Dongyang Silicone, $\eta_c$ = 100 cP, $\rho_c$ = 0.96 g/cm$^3$) and allowed to equilibrate for at least 24 h before the experiments in a desiccator to minimize contact with air.

Electrorheological measurements were carried out at 25 °C using ARES rheometer fitted with parallel plates modified for the application of high electric fields in the shear rate ranges of 0.1–100 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 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 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–$SnO_2$–methylcellulose nanocomposite particles was measured by the two-probe method using compressed disks with a picoammeter (Keithley 485).

## Results and discussion

A scanning electron microscopy image showed that small $SnO_2$ particles were glued together with PPy in the PPy–$SnO_2$–methylcellulose nanocomposite particles of 80–200 nm diameters and that the PPy–$SnO_2$–methylcellulose nanocomposite particles were agglomerated. It was reported that colloidal raspberries consisted of micro-aggregates of silica glued together by the chain of PPy [21]. The particle size distribution of the PPy–$SnO_2$–methylcellulose nanocomposite particles was measured using a particle size analyzer (Microtrac, UPA-150) and the average particle diameter is 118 nm. The surface area is 203.6 m$^2$/g.

Without an electric field, the PPy–$SnO_2$–methylcellulose nanocomposite suspensions showed Newtonian behavior. When an electric field was applied to the suspension, a marked increase in the shear stress appeared and the suspension showed a yield stress, showing shear thinning behavior. The shear stresses and yield stress increased with the increase in the electric field strength. The dynamic yield stress as a function of electric field strength is presented in Fig. 1 for PPy–$SnO_2$–methylcellulose nanocomposite suspensions of various particle volume fractions. The PPy–$SnO_2$–methylcellulose nanocomposite particles were synthesized with the $SnO_2$/pyrrole weight ratio of 7.0 and 0.3 g methylcellulose. 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 $n < 2$ and the value of $n$ decreases with the particle volume fraction. The values of $n$ are 1.48, 1.41, 1.0, and 1.0 for 1.5, 4.5, 7.0, and 10.0 vol% suspensions, respectively. The nonlinearity of the ER behavior ($\tau \propto E^n; n < 2$) has been reported for the ER suspensions of various conducting polymer particles [7, 8, 10, 12–14].

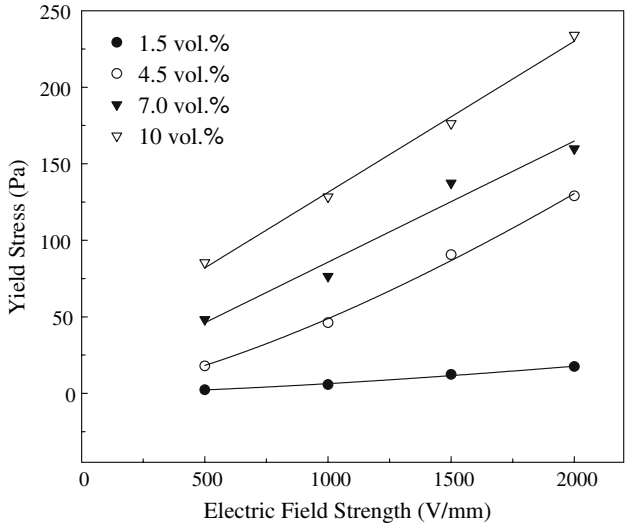


**Fig. 1** Yield stress as a function of electric field strengths for PPy–$SnO_2$–methylcellulose nanocomposite suspensions of various particle volume fractions ($SnO_2$/pyrrole weight ratio during the polymerization = 7.0)

The dynamic yield stress as a function of particle volume fraction is presented in Fig. 2 for PPy–$SnO_2$–methylcellulose nanocomposite suspensions under various electric field strengths. The PPy–$SnO_2$–methylcellulose nanocomposite particles were synthesized with the $SnO_2$/pyrrole weight ratio of 7.0 and 0.3 g methylcellulose. A power-law dependence on the volume fraction $\tau_o = K\phi^m$ fits adequately the dependence of the yield stress on the particle volume fraction. $\phi$ is the particle volume fraction. The values of $m$ are 1.78, 1.38, 1.01, and 1.0 for $E$ = 500, 1,000, 1,500, and 2,000 V/mm, respectively, decreasing with the electric field strength. The value of $m$ is larger than 1. According to the polarization model and the conduction model, the yield stress is proportional to the volume fraction [22–24]. Block et al. [15] showed that the value of $m$ is larger than 1. Variation of the value of $m$ is probably related to the structure change with the electric field strength. As the particle volume fraction increases, structure formed between the electrodes is more complex than an ideal chain structure (particles would form cluster).

The dynamic yield stress as a function of $SnO_2$/pyrrole weight ratio is presented in Fig. 3 for 4.5 vol% PPy–$SnO_2$–methylcellulose nanocomposite suspensions. The amount of methylcellulose used in the synthesis was 0.3 g. The yield stress increases with the increase in the electric field strength. The yield stress is proportional to $E^n$ a where $n < 2$ and the values of $n$ is around 1.3, indicating that the nonlinear ER behavior is related with the increased particle conductivity. However, this phenomenon is different from the nonlinear conduction [25, 26] in that the increased conduction arises from the high particle conductivity, not from the field dissociation of the continuous phase. The yield stress also increases with the increase in the $SnO_2$/pyrrole ratio. The ER response increase with the $SnO_2$/pyrrole ratio may arise from the different degrees of polarization of PPy–$SnO_2$–methylcellulose nanocomposite particles of different $SnO_2$/pyrrole ratios.

It was reported that the increased particle conductivity enhanced the particle polarization and hence increased ER responses [27, 28]. The dc conductivity of the PPy–$SnO_2$–methylcellulose nanocomposite particles were

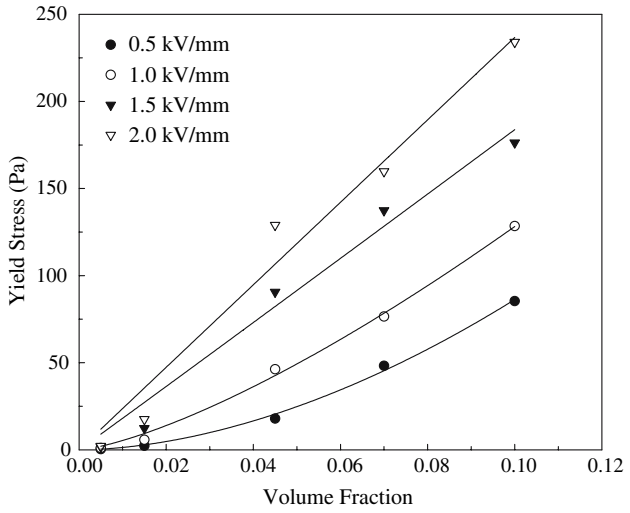


**Fig. 2** Yield stress as a function of volume fraction for PPy–$SnO_2$–methylcellulose nanocomposite suspensions under various electric field strengths ($SnO_2$/pyrrole weight ratio during the polymerization = 7.0)

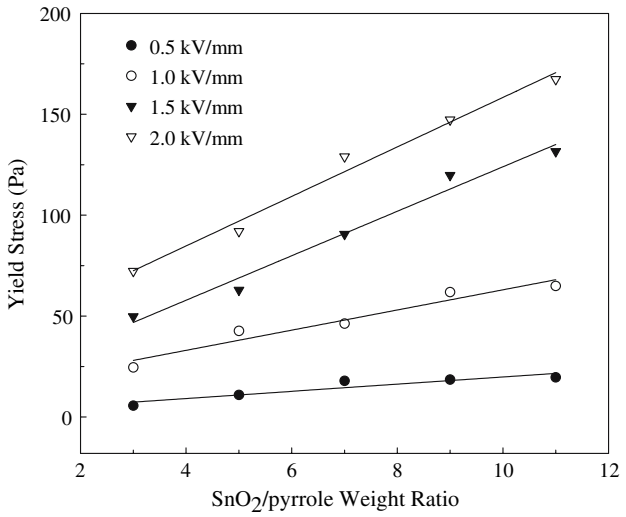


**Fig. 3** Yield stress as a function of $SnO_2$/pyrrole weight ratio under various electric field strengths for 4.5 vol% PPy–$SnO_2$–methylcellulose nanocomposite suspensions

measured as $5.51 \times 10^{-7}$, $6.73 \times 10^{-7}$, $8.24 \times 10^{-7}$, $1.89 \times 10^{-6}$, and $2.37 \times 10^{-6}$ S/cm for 3.0, 5.0, 7.0, 9.0, and 11.0 $SnO_2$/pyrrole weight ratio, respectively, increasing with the increase in the $SnO_2$/pyrrole ratio. It is an interesting result considering that PPy has higher conductivity than $SnO_2$ 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 [29] and polyaniline–iron oxide nanocomposite [30]), consistent with our result. Furthermore, the conductivity of the PPy–silica nanocomposite increased with the increase in the silica/pyrrole ratio in a certain range [21]. The dc conductivity data indicate that the increasing dc conductivity of PPy–$SnO_2$–methylcellulose nanocomposite particles with the increase in the $SnO_2$/pyrrole ratio would enhance the particle polarization. As a result, the enhanced particle polarization seems to contribute the increasing ER behavior with the increase in the $SnO_2$/pyrrole ratio.

Most ER fluids are characterized by a rapid and reversible change in suspension structures under an applied electric field [31, 32]. The dependence of the complex dielectric constant ($\varepsilon^*$) on frequency ($\omega$) can distinguish between polarization mechanisms. The complex dielectric constant is given by

$$\varepsilon* = \varepsilon' - j\sigma/\omega\varepsilon_0 = \varepsilon' - j\varepsilon'' \quad (1)$$

where $\varepsilon'$ is the dielectric constant, $j$ is $\sqrt{-1}$, $\sigma$ is the conductivity, $\varepsilon_0$ is the permittivity of free space, and $\varepsilon''$ is the dielectric loss. The dissipation factor or loss tangent is expressed as

$$D \equiv \tan\delta = \frac{\varepsilon''}{\varepsilon'} \quad (2)$$

The particle polarization controlling the ER behavior depends on the dielectric properties of the suspensions. The suspension dielectric property as a function of electric field frequency is presented in Fig. 4 for the suspensions in Fig. 3. As expected, the dielectric constants of the ER suspensions (Fig. 4a) show the similar behavior to the ER response—increasing with the $SnO_2$/pyrrole weight ratio. But, the dissipation factors do not show any notable differences. The dielectric constants keep increasing due to the increasing particle conductivity with the $SnO_2$/pyrrole weight ratio. The suspension polarizability, proportional to the dielectric constant, increases with the increase in the $SnO_2$/pyrrole weight ratio, indicating that particle polarization enhances with the increase in the $SnO_2$/pyrrole ratio. Therefore, the increasing ER response with the increase in the $SnO_2$/pyrrole ratio arises from the enhanced particle polarization, which originates from the increasing particle conductivity.

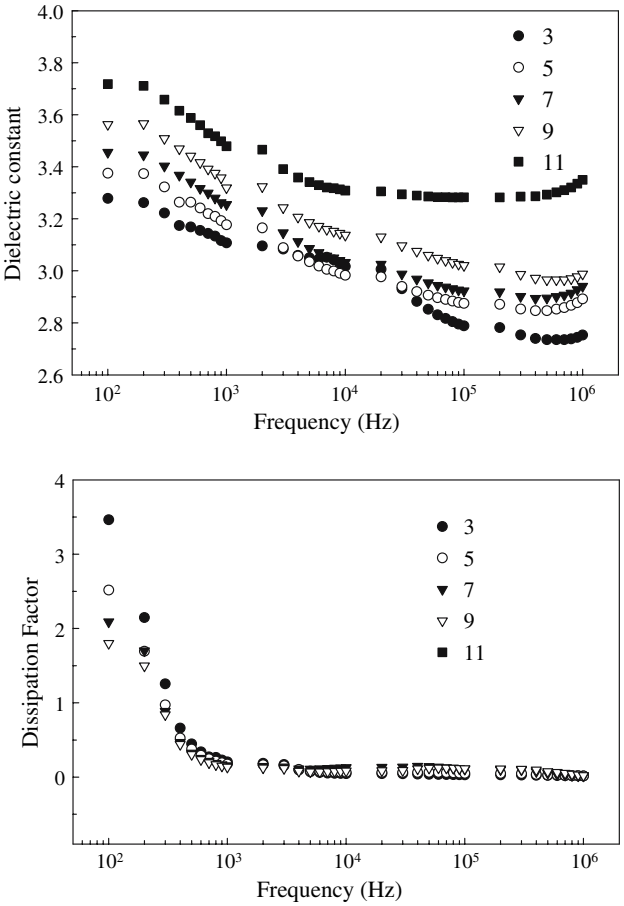


**Fig. 4** Dielectric properties as a function of electric field frequency for 4.5 vol% PPy–$SnO_2$–methylcellulose nanocomposite suspensions of various $SnO_2$/pyrrole ratios

The yield stress as a function of methylcellulose amount is presented in Fig. 5 for 4.5 vol% PPy–$SnO_2$–methylcellulose nanocomposite suspensions. The $SnO_2$/pyrrole weight ratio during the synthesis was 7. The yield stress initially increases with the methylcellulose amount, passes through a maximum, and then decreases with the methylcellulose amount. The maximum yield stress is at the methylcellulose amount of 0.4 g.

## Conclusion

The ER behaviors of the PPy–$SnO_2$–methylcellulose nanocomposite suspensions in silicone oil were investigated. PPy–$SnO_2$–methylcellulose nanocomposite particles were prepared to enhance the ER response by improving particle properties by forming conducting polymer–inorganic nanocomposites and stabilizing the particles. Various PPy–$SnO_2$–methylcellulose nanocomposite particles were

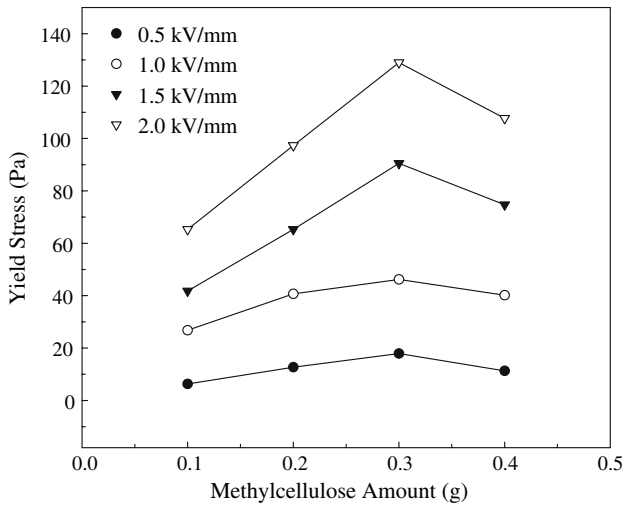


**Fig. 5** Yield stress as a function of methylcellulose amount under various electric field strengths for 4.5 vol% PPy–$SnO_2$–methylcellulose nanocomposite suspensions

synthesized by suspension polymerization controlling the amount of pyrrole, $SnO_2$, and methylcellulose during the polymerization. The ER response increases with the increase in the $SnO_2$/pyrrole ratio and the dc conductivities of the PPy–$SnO_2$–methylcellulose nanocomposite particles are consistent with the ER behavior. The ER behavior also depends on the amount of methylcellulose amount during the polymerization. The yield stress initially increases with the methylcellulose amount, passes through a maximum, and then decreases with the methylcellulose amount. The dielectric properties of PPy–$SnO_2$–methylcellulose nanocomposite suspensions show that the increased ER response arises from the enhanced particle polarization, which depend on the $SnO_2$/pyrrole ratio and the methylcellulose amount during the polymerization.

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