

Synthesis, Characterization and Electrorheological Properties of Poly(*o*-toluidine)/Zn Conducting Composites

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ABSTRACT: In this study, the synthesis, characterization, and electrorheological (ER) properties of poly(*o*-toluidine)/Zn, (POT/Zn), composites were investigated. Syntheses of the composites were carried out by a chemical method using ammonium persulfate, (NH₄)₂S₂O₈, (APS), as a free radical initiator. The composites were characterized by Fourier transform infrared (FTIR) spectroscopy, electrical conductivity, magnetic susceptibility, particle size measurements, and scanning electron microscopy (SEM). A series of Zn-containing composites were prepared (0.8–7.6% by mass), and their conductivities were measured to be within the range of 1.7×10^{-3} – 5.0×10^{-2} Scm⁻¹. Magnetic properties of POT/Zn composites were analyzed by Gouy scale measurements; it was found that their conducting mechanisms are bipolaron. A series of particle size (13, 17, 18, 26, 83 μm) were prepared by ground milling the crude POT/Zn composites. Colloidal suspensions of POT/Zn composites were prepared in silicone oil (SO), at a series of concentrations (10–30%, m/m), and sedimentation stabilities were measured at 25°C. ER measurements showed that the

POT/Zn/SO suspension system was ER active. Thus, the effects of solid particle concentration, shear rate, electric field strength, addition of polar promoters, and temperature (25–125°C) onto ER activities of suspensions were investigated. The ER activity of suspensions was increased with increasing particle concentration and electric field strength and decreasing shear rate and showing a non-Newtonian flow behavior. $\tau = 1.1$ kPa shear stress was reached for POT/Zn (4.1 wt %, Zn) composite under $E = 2.0$ kV, $c = 15$ (% m/m), $\dot{\gamma} = 1.0$ s⁻¹, and $T = 25^\circ\text{C}$ conditions. It was found that the ER activity was slightly decreased with increasing temperature. Further, the addition of polar promoters had no promoting effect on the ER activity of the suspensions and POT/Zn/SO system was classified as dry ER materials. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 103: 1058–1065, 2007

Key words: poly(orthotoluidine); composite; electrorheological fluids

INTRODUCTION

Electrorheological (ER) fluids are, in general, heterogeneous colloidal suspensions whose properties strongly depend on the applied electric field, where a characteristic fibrillation with the strings of particles oriented along the direction of electric field is observed. This reversible fibrillation of particles due to the electric field produces a significant increase in apparent viscosity.^{1,2} ER fluids have been the subject of intense theoretical and experimental research due to their emerging technological applications, such as clutches, vibration dumpers, robotics, hydraulics, shock absorbers, ER valves, couplings, and automotive industries.^{3,4} The patent literature on the subject

suggests a growing interest in such devices after a period of research and assessment.^{5,6} Attention has recently been paid to the synthesis and characterization of various anhydrous (dry-base) ER systems, because these systems could overcome several shortcomings of hydrous (wet-base) systems, such as temperature limitation caused by the presence of water, the density mismatch between the particle and the oil, and an insufficient yield stress. Among various polarizable particles for dry-base ER materials, semiconducting polymers, including poly(acene quinone) radicals,⁷ polyaniline,⁸ copolyaniline,⁹ polyphenylenediamine,¹⁰ poly(2-acrylamido-2-methyl-1-propane sulfonic acid),¹¹ polyaniline nanocomposite,¹² and polyacrylonitrile/diatomite composites,¹³ poly(Li-HEMA)-*co*-poly(4-vinyl pyridine) copolymeric salt suspensions in SO,^{14,15} PMMA-*b*-PSt,¹⁶ poly(Li-2-hydroxyethyl methacrylate)/SO system,¹⁷ have been adopted as dry-base ER fluids as a result of handling and superior physical properties.

Among many semiconducting polymers, polyaniline (PANI) is one of the most useful semiconducting

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polymers for various electrochemical applications because of its facile synthetic process, good environmental stability, low cost of material, and high conductivity control.¹⁸ Furthermore, by varying the degree of doping, its conductivity can be continuously tuned. In fact, to obtain semiconducting PANI for ER materials, the PANI particles must be dedoped by alkaline treatment because particle conductivity is identified as a factor limiting the use of highly doped PANI samples. So, additional doping and dedoping steps are needed. Nevertheless, the numbers of papers dealing with the conducting polymer composites including Zn powder are still rather low.^{19,20}

In the work described in this article, synthesis, characterization and ER properties of POT/Zn composites were investigated. The choice of *o*-toluidine as the monomer for this study was based on the following: (1) the *o*-toluidine is a substituted derivative of aniline with a methyl (-CH₃) group substituted at the *ortho*-position and therefore, this study explores the possibility of using the POT as an alternative to polyaniline for ER materials; (2) the *o*-toluidine monomer is commercially available at low cost; and (3) the conversion of monomer to polymer is a straightforward process. Zinc was chosen as a filling material, since it has a high thermal stability (m.p. = 419.5°C) and resistance to atmospheric conditions.

EXPERIMENTAL

Reagents and measurements

The electrical conducting filler used was zinc (Merck) with average particle size of $d = 3.0 \mu\text{m}$, a density of about $\rho = 7.14 \text{ g/cm}^3$, and an electrical conductivity, taken as the tabulated value, of $\sigma = 0.17 \text{ Scm}^{-1}$.

Monomer (*o*-toluidine) was obtained from Aldrich (Steinheim, Germany) and distilled in vacuum ($P = 15 \text{ mm Hg}$) under $\text{N}_2(\text{g})$ prior to use. All the other reagents were Aldrich analytical grade and used as received. Electrical conductivity measurements were performed using pellets and a four-probe technique.

Magnetic susceptibility measurements were carried out using a Sherwood Scientific Model MKI Gouy scale (UK). Finely powdered composite samples were placed into a glass tube with a height of no less than 2.5 cm. The glass tube was placed into a hole in a magnetic balance, and the magnetic susceptibility of samples was recorded at room temperature.

The FTIR spectra were taken in KBr disks and recorded on a Mattson-1000 model spectrophotometer (Unican, USA).

Particle sizes of ground-milled composites were determined using a Malvern Mastersizer E (Malvern, UK), version 1.2b particle size analyzer according to Fraunhofer scattering.

Preparation of POT/Zn composites

A certain amount of *o*-toluidine was dissolved in 100 mL of 1.5 M $\text{HCl}_{(\text{aq})}$. A certain amount of Zn powder was then dispersed into the above solution with stirring at 2–5°C. 1.5 M $\text{HCl}_{(\text{aq})}$, containing the initiator [$(\text{NH}_4)_2\text{S}_2\text{O}_8$], was added dropwise into this dispersed solution. After carrying out the reaction for 24 h, the crude POT/Zn composite formed was recovered and wash with 1.5 M $\text{HCl}_{(\text{aq})}$, distilled water, and diethyl ether, respectively. Finally, the composite was dried in a vacuum oven at 70°C for 24 h. Further, POT/Zn composites containing various percentages of Zn (0.80–7.6 %) were prepared by maintaining constant salt to monomer ratios. The quantity of Zn in the composite was determined gravimetrically.

Determination of particle size

First, the crude POT/Zn composites were ground milled for various hours in a 3D turbula-shaker mixer to obtain a series of particle sizes. Then the particle sizes of the composite samples were determined by Fraunhofer scattering using a Malvern Mastersizer E, version 1.2b particle size analyzer. The samples were dispersed in distilled water and stirred at a constant temperature of 20°C. The data collected were evaluated by the Malvern software computer according to Fraunhofer diffraction theory.²¹ From these measurements, $d_{50} = 13$ -, 17-, 18-, 26-, and 83- μm average particle sizes were observed for the POT/Zn composites.

Scanning electron microscopy

Scanning electron microscopy (SEM) measurements of POT and POT/Zn composite were carried out using a Jeol JSM 6060 LV (Japan) electron microscope.

Preparation of suspensions

Before suspension preparation, POT/Zn composite particles and SO were dried in a vacuum oven for 24 h at 150°C and 4 h at 110°C, respectively to remove any moisture present. POT/Zn composite suspensions were then prepared in SO at a concentration series of $c = 10$ –30 wt %.

Determination of sedimentation stability

Stability of the composite suspensions against sedimentation was determined at constant temperature ($25 \pm 0.1^\circ\text{C}$). Glass tubes containing the suspensions were immersed into a constant temperature water bath and formation of first precipitates at the bottom

of the tubes was taken to be the indication of gravitational instability.

Electrorheological tests

Electrorheological properties of POT/Zn composite suspensions were tested by a Thermo-Haake RS600 rheo-stress electrorheometer (Karlsruhe, Germany). The gap between the parallel plate electrodes was 1.0 mm, and the diameters of the upper and lower plates were 35 mm. All experiments were carried out at various temperatures (25–125°C). The voltage used in these experiments was supplied by a dc electric field generator (0–12.5 kV, with 0.5-kV increments, Fug Electronic, Rosenheim, Germany), which enabled resistivity to be created during the experiments.

RESULTS AND DISCUSSIONS

Evaluation of conductivity, magnetic susceptibility, and particle size of POT/Zn composites

The conductivity of POT was measured to be $9.92 \times 10^{-4} \text{ Scm}^{-1}$. The conductivity, magnetic susceptibility and particle size data of POT/Zn composites are given in Table I. As shown in Table I, the conductivity of POT/Zn composite was slightly increased with increasing content of Zn. The conductivity of the composites was remained constant ($1.7 \times 10^{-2} \text{ Scm}^{-1}$) after 5.3% Zn content.

The POT/Zn composite containing 4.1% of Zn demonstrated the highest particle size value of 83 μm and the highest conductivity value of $5.0 \times 10^{-2} \text{ Scm}^{-1}$. No linear correlation between conductivity of POT/Zn composites and particle sizes were concluded.

Magnetic susceptibility measurements of the composites indicated that they were diamagnetic, i.e., they contained no unpaired electrons.²² This analysis demonstrates that the conducting mechanism of diamagnetic composites is of bipolaron nature in which all the electrons are paired. Such a structure is known to be more stable in terms of energy.²³

TABLE I
Conductivity, Gouy Balance, and Particle Size Measurement Results of POT/Zn Composites

Zn content of POT/Zn (wt %)	Conductivity (Scm^{-1})	Magnetic susceptibility ($^*\mu_e$, BM)	Particle size (μm)
0.8	1.3×10^{-2}	-37	26
2.1	3.3×10^{-2}	-39	18
4.1	5.0×10^{-2}	-41	83
5.3	1.7×10^{-2}	-26	13
7.6	1.7×10^{-2}	-42	17

* μ_e , effective magnetic moment; BM, Bohr magneton.

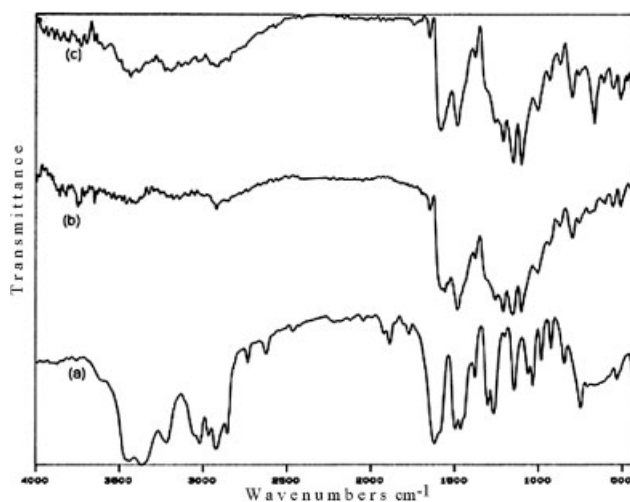


Figure 1 FTIR spectra obtained for (a) *o*-toluidine, (b) POT, (c) POT/Zn composite.

Evaluation of FTIR data

FTIR spectra of *o*-toluidine, POT, and POT/Zn composite are illustrated in Figure 1(a)–(c). As shown in Figure 1(a), the doublet peak belonging to $-\text{NH}_2$ at $\sim 3500\text{--}3300 \text{ cm}^{-1}$ in the spectrum of *o*-toluidine turned into a broad singlet peak at $\sim 3470\text{--}3350 \text{ cm}^{-1}$ in the FTIR spectrum of POT [Fig. 1(b)]. The peak observed at $800\text{--}900 \text{ cm}^{-1}$ is attributed to a *p*-substituted aromatic ring, and it proves that the polymerization proceeded in a head-to-tail fashion. The FTIR spectrum of POT/Zn composite [Fig. 1(c)] was similar to POT. This difference between FTIR spectra of *o*-toluidine and POT/Zn proves that the polymerization occurs through $-\text{NH}_2$ group, and it appears that polymerization has proceeded in a head-to-tail mechanism.^{24–26}

Scanning electron microscopy

The SEMs of POT (Fig. 2) demonstrates a big granular structure whereas, the SEM of POT/Zn (Fig. 3) demonstrates a sponge-like and porous structure. The different surface morphologies of POT and POT/Zn influence their conductivities.

Sedimentation stability

When the density of particles is not the same as that of the medium, the particles with micron order size will settle down according to the Stoke's law.²⁷ To solve the traditional problem of particle sedimentation, several researchers have developed different solutions. Density mismatch between dispersed and continuous phase plays an important role in sedimentation stability of an ER fluid. Sedimentation stability results obtained from POT/Zn/SO system

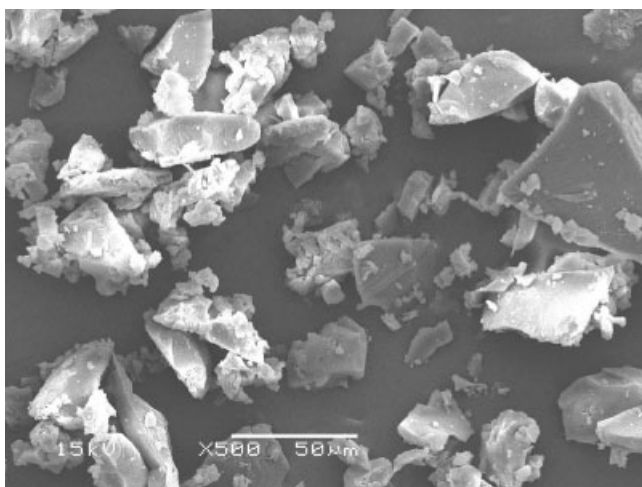


Figure 2 SEM micrograph of POT.

at 25°C are given in Figure 4. As shown in Figure 4, the POT/Zn/SO suspensions possess an excellent anti-sedimentation stability. The sedimentation ratio is about 42–67% within 40 days. Less than 58% oil of total volume fluid could be observed after 40 days, and even for longer periods. It is obvious that the POT/Zn/SO suspensions do not deposit even when they are static for more than 40 days. It was observed that as the particle size and particle concentration of the suspensions decrease, their colloidal stabilities increase. These expected results are in accordance with the earlier studies reported in the literature.^{28,29}

Electrorheometry

Effect of particle concentration on electric field viscosity

Figure 5 shows the change in relative electric field viscosity ($\eta_{E \neq 0}$, viscosity under applied external electric field strength) with suspension concentration at

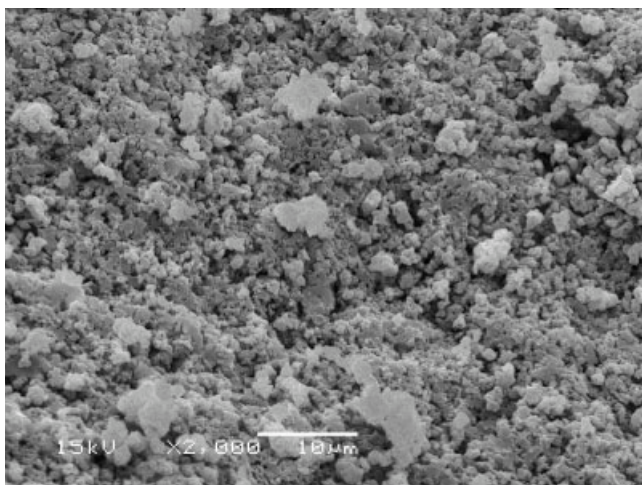


Figure 3 SEM of POT/Zn composite (4.1%).

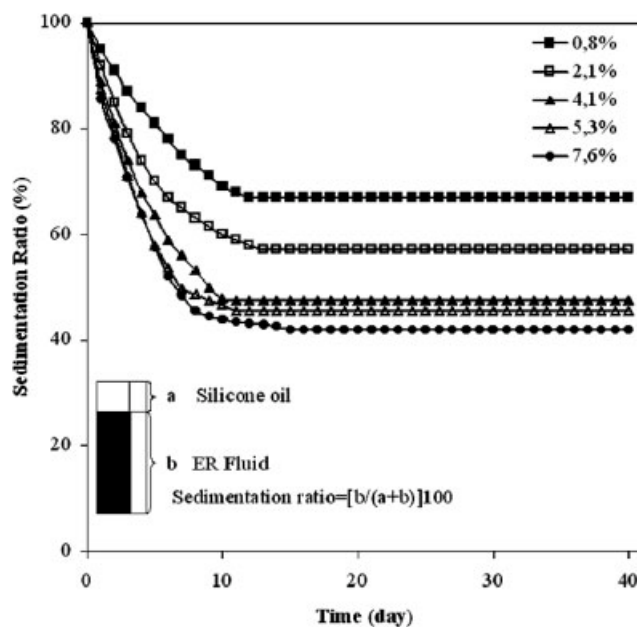


Figure 4 Sedimentation stability results of POT/Zn/SO suspensions. $c = 15\%$, m/m, $T = 25^\circ\text{C}$.

constant shear rate ($\dot{\gamma} = 1.0 \text{ s}^{-1}$). Suspension concentration exerts a principal effect on the ER activity. As reflected in Figure 5, $\eta_{E \neq 0}$ increases with increasing particle concentration. This trend is due to the increased magnitude of polarization forces acting between the charged particles.³⁰

When electric field was applied to the suspension, polarization forces caused aggregation of the particles and a chain formation between the upper and

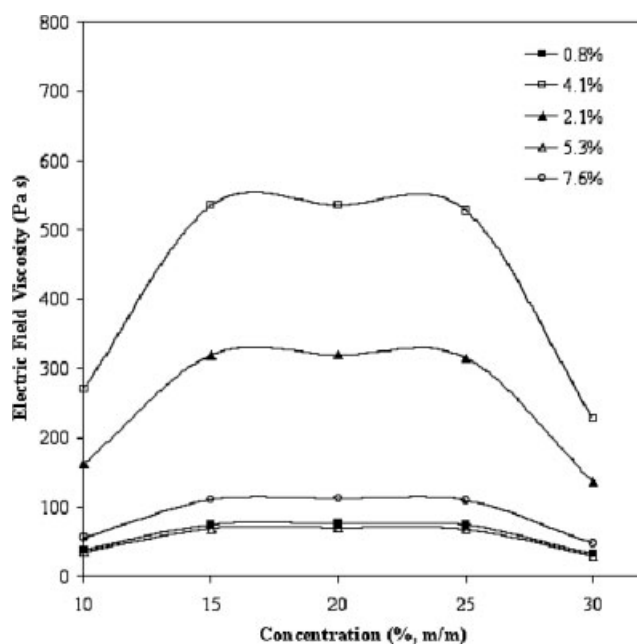


Figure 5 Change of viscosity with concentration. $E = 2.0 \text{ kV/mm}$, $\dot{\gamma} = 1.0 \text{ s}^{-1}$, $T = 25^\circ\text{C}$.

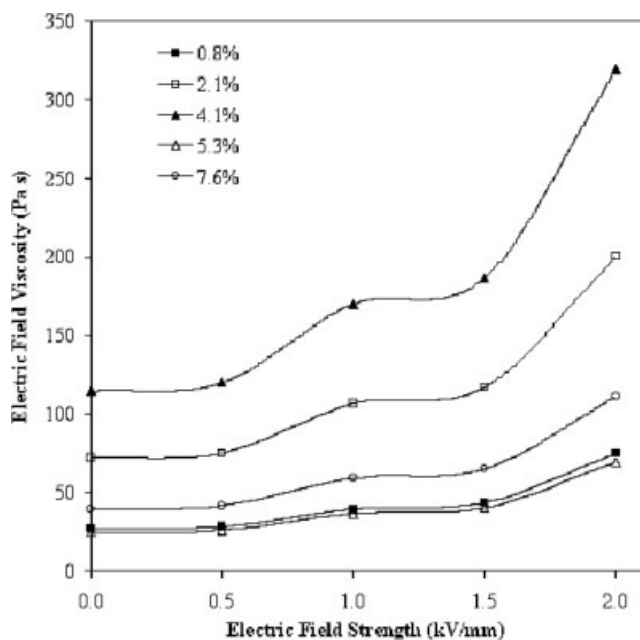


Figure 6 Electric field strength dependence of viscosity. $c = 15$ wt%, $\dot{\gamma} = 1.0$ s⁻¹, $T = 25^\circ\text{C}$.

lower plates occurred. The relation of the magnitude of viscous forces (F), with viscosity of suspension (η_s), the average shear rate ($\dot{\gamma}$) and radius of particle (r) can be written as:³¹

$$F = 6\pi\eta_s r^2 \dot{\gamma} \quad (1)$$

As reflected in eq. (1), increased suspension concentration will decrease the distance between POT/Zn particles, which will result with increased polarization force. As the suspension concentration increases above 25%, a substantial reduction in relative viscosity was observed. That is, 15% is the optimal concentration for achieving maximum ER activity in the POT/Zn/SO system.

The decrease in $\eta_{E \neq 0}$ at higher suspension concentrations could be attributed to the probable formation and overlap of electric double layers around particles, at which the particles are closer to each other.³² In this case, inter-particle interactions will decrease and result with reduced $\eta_{E \neq 0}$ and ER activity. Similar behavior was reported in the studies of calcium carbonate¹⁷ and polyaniline³³ suspensions in SO.

Effect of electric field strength on viscosity

Figure 6 shows the change in viscosity with electric field strength for POT/Zn/SO system at a constant shear rate ($\dot{\gamma} = 1.0$ s⁻¹), suspension concentration ($c = 15$ wt %), and temperature ($T = 25^\circ\text{C}$). As reflected from the graph, electric field viscosity shows a gradual increase up to 1.5 kV/mm and then shows a sharp increase with increasing electric field

strength. The maximum electric field viscosity of composite suspensions were obtained for 4.1% Zn-containing composite as 319 Pa s.

When POT/Zn/SO system subjected to an external applied electric field, due to polarization forces acting between the particles, chain formation took place between the parallel plates, and this structure became stronger at higher electric field strengths. In suspensions, the magnitude of polarization forces in the direction of applied electric field is³⁴

$$F = (6\pi\epsilon_2 r^2 E^2) / \rho^4, \quad (2)$$

where ϵ_2 is the dielectric constant of the particle; r , the radius of particle; E , the electric field strength; and ρ , the distance between particles. Similar behavior was reported for the suspensions of polyaniline³⁵ in silicone oil.

Change in shear stress with electric field strength

Figure 7 shows the change in shear stress (τ) as a function of external electric field strength, keeping the shear rate ($\dot{\gamma} = 1.0$ s⁻¹), suspension concentration ($c = 15$ wt %), and temperature ($T = 25^\circ\text{C}$) constant. It can be seen from the graph that, τ slightly increases with increasing electric field strength up to $E = 1.5$ kV/mm, then shows a sharp increase and reaches to $\tau = 1.12$ kPa for 4.1% Zn-containing composite. Figure 7 shows that the system structure in ER suspension become more stable under a strong electric field. Similar results were reported for the studies of glycerol-activated titania,³⁶ zeolite,³⁷ and β -cyclodextrin polymer,³⁸ all of which were prepared in SO.

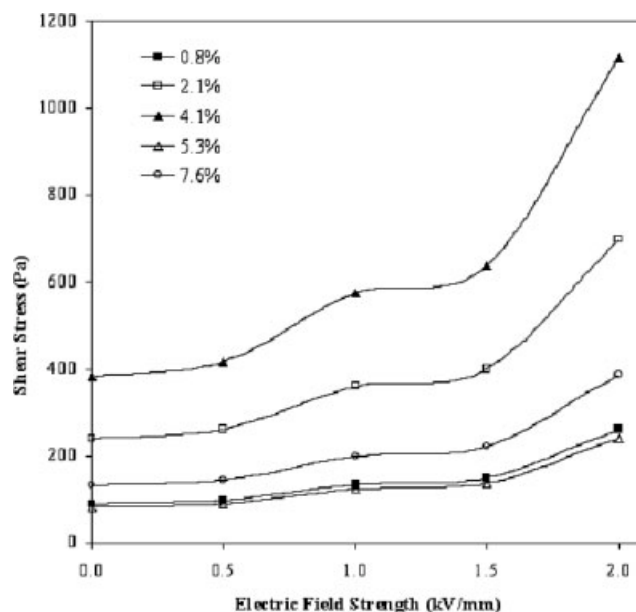


Figure 7 Change in shear stress with electric field strength. $c = 15$ wt %, $\dot{\gamma} = 1.0$ s⁻¹, $T = 25^\circ\text{C}$.

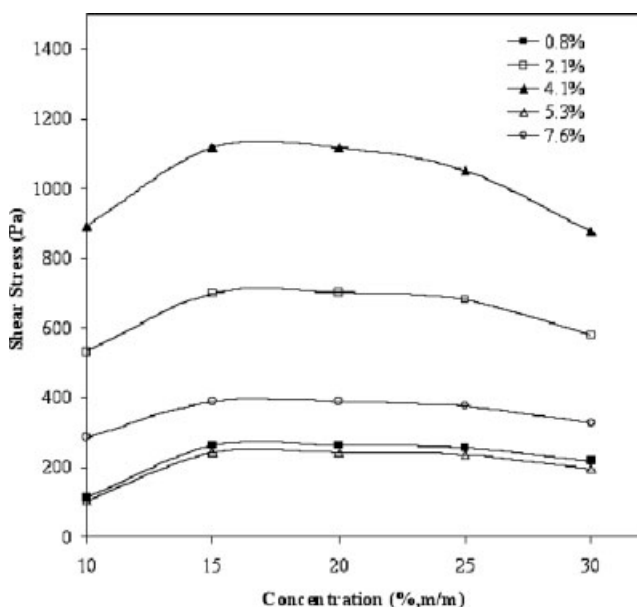


Figure 8 Change in shear stress with concentration. $E = 2.0$ kV/mm, $\dot{\gamma} = 1.0$ s⁻¹, $T = 25^\circ\text{C}$.

Change in shear stress with concentration

In Figure 8 the change in shear stress with concentration is given at constant conditions ($E = 2.0$ kV/mm, $\dot{\gamma} = 1.0$ s⁻¹, and $T = 25^\circ\text{C}$). Shear stress of an ER suspension is largely dependent on particle concentration. As is evident in Figure 8, τ was observed to increase with increasing composite particle concentration, and reached to a maximum of $\tau = 1.12$ kPa. The increase in the τ with increasing concentration is due to the increased magnitude of polarization forces, which results in enhanced ER activity. As the suspension concentration increased above $c = 15$ wt %, a gradual reduction in shear stress was observed. Kim et al.³⁹ reported similar behavior for cellulose suspensions prepared in SO.

Effect of shear rate on electric field viscosity

Figure 9 shows the effect of shear rate on electric field viscosity at constant conditions ($c = 15$ wt %, $T = 25^\circ\text{C}$, $E = 2.0$ kV/mm). The electric field induced viscosity of suspensions was found to sharply decrease with increasing shear rate and giving a typical curve of shear thinning non-Newtonian viscoelastic behavior. As reflected in the graph, viscosity was decreased with increasing shear rate and shown also typically non-Newtonian behavior. These characteristic behaviors of the ER suspension are related to the internal particle structure induced by an applied external electric field. Before shearing the ER fluid, the dispersed particles are aligned through the electric field direction making columnar structures, and these structures become stronger at

higher electric fields. Similar results were reported for the studies of poly(lithium-2-acrylamido-2-methyl propane sulfonic acid),¹¹ sepiolite,⁴⁰ poly(naphthalene quinone) radical,⁴¹ cellulose,⁴² PANI,⁴³ and mesoporous molecular sieve,⁴⁴ in which SO was used as continuous phase for the suspensions.

Effect of temperature and promoter on ER activity

Most ER suspensions contain additives such as surfactants or activators. The former are added to improve colloidal stability of the dispersed particles but also to enhance ER activity, while the presence of the latter is essential for some suspensions to display a significant ER response. The most common ER activator is water although there are also some other polar substances, such as alcohols, ethylene glycol, dimethyl amine, or dimethyl formamide, which can activate ER suspensions.³ The disadvantages of water activated ER suspensions, (i.e. a restricted temperature range of operation and increased conductivity), have been overcome by the introduction of essentially water-free ER fluids (so-called dry ER fluids).⁴⁵

Figure 10 shows the change in the shear stress of POT/Zn/SO suspensions under different temperatures at constant concentration ($c = 15$ wt %). For this type of ER fluid, the ER effect is due to the polarization of mobile solid particles subjected to external electric field. Since the polarizability of the material is temperature dependent, the shear stress of ER fluid is also influenced by the temperature of the environment. As reflected in the graph, we obtained a high shear stress ($\tau = 1.12$ kPa) for a

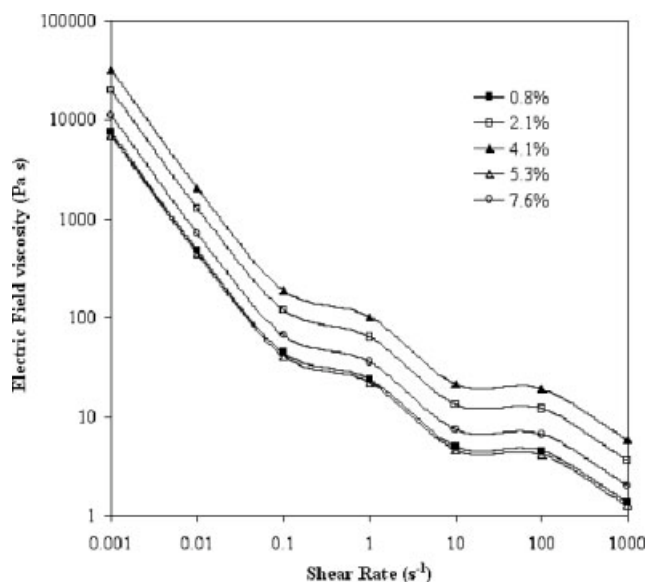


Figure 9 Change in electric field viscosity with shear rate. $c = 15$ wt %, $T = 25^\circ\text{C}$, $E = 2.0$ kV/mm.

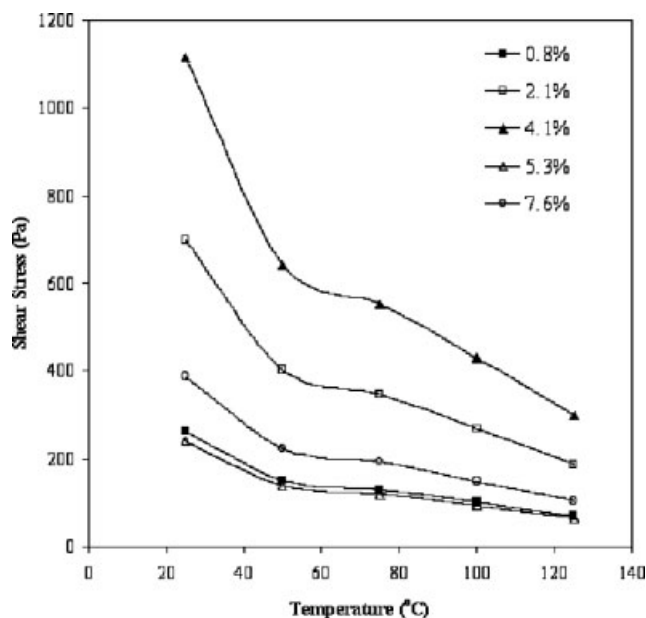


Figure 10 Effect of temperature on ER activity. $c = 15$ wt %, $E = 2.0$ kV/mm, $\dot{\gamma} = 1.0$ s⁻¹.

4.1% Zn-containing POT/Zn/SO system at $T = 25^\circ\text{C}$ and this τ value sharply decreased with increasing temperature and lowered to $\tau = 298$ Pa at $T = 125^\circ\text{C}$. Nevertheless, the loss at the τ of POT/Zn/SO system for $\Delta T = 100^\circ\text{C}$ temperature difference is approximately $\Delta\tau = 0.80$ kPa, which is a high τ loss in terms of potential high-temperature industrial applications.

The temperature effect of ER fluid is one of the important parameters to evaluate ER effect.⁴⁶ Generally, the temperature has two effects on ER fluids: one is the effect on the polarization intensity of particle, and the other is Brownian motion. The increase in the temperature resulted with a decrease in polarization activation energy, but with an increase in the polarization ability of the ER particle. In contrast, Brownian motion does not contribute to chain formation by POT/Zn ER particles. As a consequence, the ER effect decreases while the leaking current density increases (< 60 $\mu\text{A}/\text{cm}^2$). This property may cause the intercalation of Zn microparticles into POT. Yanju et al.⁴⁷ reported similar shear stress loss behavior for the inorganic/polymer blend in SO.

The influence of moisture on ER activity was also investigated by adding various polar promoters, such as water, glycerol, and ethanol up to 1000 ppm concentration, into POT/Zn/SO suspensions at 15 wt % particle concentration. POT/Zn/SO system was dry ER active material and various added polar promoters tried had no promoting effect on the ER activity of the system, and the POT/Zn/SO system classified as dry ER material, which is an important ER property from industrial point of view.

CONCLUSIONS

Synthesis and characterization of the composites containing different percentages of micron-sized Zn powders were carried out. The sedimentation stability ratio of POT/Zn composites in SO was determined to be 40 days. ER activity of all the suspensions was observed to increase with increasing electric field strength, composite concentration, and decreasing shear rate. Shear stress of POT/Zn/SO system was observed to increase linearly with increasing particle volume fraction and the electric field strength. The electric field viscosity of the suspensions was decreased sharply with increasing shear rate and showing a typical shear-thinning non-Newtonian viscoelastic behavior. Finally, POT/Zn/SO system was observed to sensitive to high temperature, but insensitive to polar promoter.

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