

# Electrorheological properties and creep behavior of polyindole/poly(vinyl acetate) composite suspensions

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**Abstract** In this study, electrorheological (ER) properties of polyindole (PIN) and polyindole/poly (vinyl acetate), (PIN/PVAc) conducting composites having different compositions were investigated. Conductivities and dielectric properties of these composites were determined. The particle sizes of the composites were determined by dynamic light scattering method. Suspensions of PIN and PIN/PVAc composites were prepared in silicone oil, at several concentrations ( $c = 5\text{--}25\%$ , m/m) and their sedimentation stabilities were determined. Then the effects of dispersed particle concentration, shear rate, electric field strength, frequency, and temperature onto ER activities of suspensions were investigated. The flow times of these suspensions at various dc electric field strengths were measured. Further, creep tests were applied to the composite suspensions and a reversible viscoelastic deformation was observed.

## Introduction

Electrorheological (ER) fluids consist of dispersions of solid particulates within an insulating liquid. Application of

an external electric field cause changes in their flow behavior and can completely suppress the flow until a critical shear stress is reached [1]. Important factors influencing the ER effect are electric field strength, electric field frequency, shear rate, fluid composition, temperature, and addition of a polar promoter [2]. There are very wide range of potential applications for ER fluids in such areas as damping, robotics, hydraulics, couplings, and automotive [3]. Recently, ER fluids have found some newly developed application areas such as human muscle stimulators, spacecraft deployment dampers, seismic controlling frame structures, ER tactile displays, and photonic crystals [4]. A major limiting factor is still the need for fluids with better overall performance. Most applications require fluids that possess a large field-induced yield stress, stable to settling and irreversible aggregation, environmentally friendly [5, 6].

To overcome some of the limitations (i.e., thermal stability, aggregation, and corrosion) of water-based (wet) systems, dry-based systems have been investigated with anhydrous particles. Some examples of anhydrous ER suspensions using polymer particles are: poly(acene quinone) radicals [7], polyaniline [8], polypyrrole [9], copolyaniline [10], poly(methyl methacrylate)-*block*-polystyrene [11], polystyrene-*block*-polyisoprene [12], and polymeric composite particles [13].

Most of the studies on the literature are on the ER activity of acrylate salts and zeolitic materials [14], and none of these researchers have investigated the influence of colloidal stability of suspensions on the ER activity. Another target is, for ER fluids, with long service stabilities, particularly at high temperatures and rigid environmental conditions [15].

Among various ER materials, polymeric particles have attracted great interest because of their thermal stability at

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high temperature, lower density, and ease of preparation [16]. Often conducting polymer composites are prepared to improve the physical and chemical properties of conducting polymers [17].

Creep behavior is a time–temperature-dependent phenomenon and various theoretical and mechanical models have been used to describe this viscoelastic behavior of materials. Polymer composites exhibit a time-dependent degradation in modulus and strength, as a consequence of the viscoelasticity of the polymer matrix [18].

In present study, polyindole and polyindole/poly(vinyl acetate) composites (having various compositions) were used. Colloidal stabilities and electrorheological properties of the suspensions prepared in SO were determined and their viscoelastic properties were also investigated by creep tests.

## Experimental

### Materials

Silicone oil (SO, Aldrich) was used after drying at 130 °C for 3 h in a vacuum oven, to remove any moisture present ( $\rho = 0.97 \text{ kg m}^{-3}$ ,  $\eta = 200 \text{ mPas}$ ,  $\varepsilon = 2.61$ ).

PIN and PIN/PVAc composites were chemically synthesized using  $\text{FeCl}_3$  as an oxidizing agent.

### Synthesis of polyindole (PIN)

Polyindole was chemically synthesized using  $\text{FeCl}_3$  as oxidizing agent. The molar ratio of oxidant to monomer was taken as 2:1.  $\text{CHCl}_3$  was used as solvent. The polymerization was carried out in  $\text{N}_2$  (g) atmosphere at 15 °C for 5 h.

### Synthesis of polyindole/poly(vinyl acetate) composites

Varying amounts of PVAc were dissolved in  $\text{CHCl}_3$ . On to this solution, a definite amount of indole monomer and  $\text{FeCl}_3$  were added, respectively, and the composite formation reaction was carried out for 5 h at 15 °C. The full details of synthesis and characterization were given in our previous publication [19].

### Characterization

For ER purposes, the following further characterization studies were also carried out:

Dielectric constant and conductivity measurements were carried out with HP 4192 A 6F Impedance Analyzer (UK).

The current–potential measurements were performed on samples as discs (20 mm long, 5 mm wide, and 1 mm thick) with a Keithley 220 programmable current source and a Keithley 199 digital multimeter (Ohio, U.S.A) at ambient temperature. The capacitance,  $C$ , of ER particles was measured with an HP 4192 A LF Impedance Analyzer at frequency of 1.0 MHz at constant temperature ( $20.0 \pm 0.1 \text{ }^\circ\text{C}$ ).

Densities of the PIN and PIN/PVAc composites were measured using the same discs prepared for dielectric measurements, i.e., after preparing the discs, height and masses of the discs were measured and the corresponding volumes and densities were calculated.

Particle sizes of the samples were determined using a Malvern Mastersizer E, version 1.2b particle size analyzer (UK). During the particle size measurements, some samples were dispersed in ethanol and stirred at a constant temperature of 20 °C. The data collected were evaluated according to Fraunhofer diffraction theory by the Malvern Software computer [20].

### Preparation of suspensions

Suspensions of PIN and PIN/PVAc conducting composites were prepared in SO at a series of particle concentrations (5–25 m/m, %), by dispersing definite amount of dispersed phase (composites) in calculated amount of continuing phase (SO) in glass tubes according to formula:

$$(\text{m/m } \%) = \left[ \frac{m_{\text{dispersed phase}}}{m_{\text{dispersed phase}} + m_{\text{oil}}} \right] \quad (1)$$

### Determination of sedimentation stability

Glass tubes containing the suspensions prepared above were immersed into a constant temperature water bath (25 °C) and formation of first precipitates was recorded to be the indication of colloidal instability.

### Electrorheological tests

#### *Flow measurements*

Suspensions were mechanically stirred before each measurement against sedimentation. Flow rate measurements were carried out between two brass electrodes, which were connected to a high voltage dc power supply (0–12.5 kV, with 0.5 kV increments, FUG Electronics, Germany). The gap between the electrodes was 0.5 cm, the width of the electrodes was 1.0 cm, and the height of the liquid on the electrodes was 5.0 cm. During the measurements the electrodes was immersed into a vessel containing

suspensions, with a specific concentration, and after a few seconds the vessel was removed and flow time for complete drainage measured, using a digital stop-watch under  $E = 0$  kV/mm and  $E \neq 0$  kV/mm conditions. This procedure was repeated for various electric field strengths and concentrations.

*Electrorheometer measurements*

To measure the ER strength of PIN and PIN/PVAc suspensions, Thermo-Haake RS600 Rheometer (Germany) was used with a plate-to-plate system. Applied shear rate was altered between 0.1 and 1,000  $s^{-1}$ . The gap between the plates was 1.0 mm. To measure the electric field viscosity, an electric field was created in the fluid perpendicular to the plates, and the rotor was forced to rotate. The voltage used in ER experiments was supplied by a 0–12.5 kV (with 0.5 kV increments) FUG (Germany) dc external electric field generator, which enabled resistivity to be created during the experiments. All the measurements were carried out between 20 and 70 °C.

**Results and discussions**

Table 1 shows conductivity, dielectric constant, density and average particle sizes ( $d_{50}$ ) data of PIN, and PIN/PVAc composites. Average particle size of PIN was measured to be 41.3  $\mu m$  and PIN/PVAc composites were  $12.00 \geq d_{50} \geq 9.36 \mu m$ . It was observed that densities of the composites were decreased with increasing PIN content. Although Chwang et al. reported conductivity increases with increasing content of polyaniline in polyaniline/polyurethane blends [21], in this study, it was observed that, conductivities and dielectric constant values of PIN and

PIN/PVAc composites were closer to each other ( $9.64 \times 10^{-5} > \sigma > 1.98 \times 10^{-7} Sm^{-1}$ ). Even though, these conductivity and dielectric constant values of PIN and PIN/PVAc composites were well in the range of ER active materials reported in the literature [3], a breakdown problem was observed during the ER measurements of PIN/SO suspension system.

Sedimentation stability of suspensions

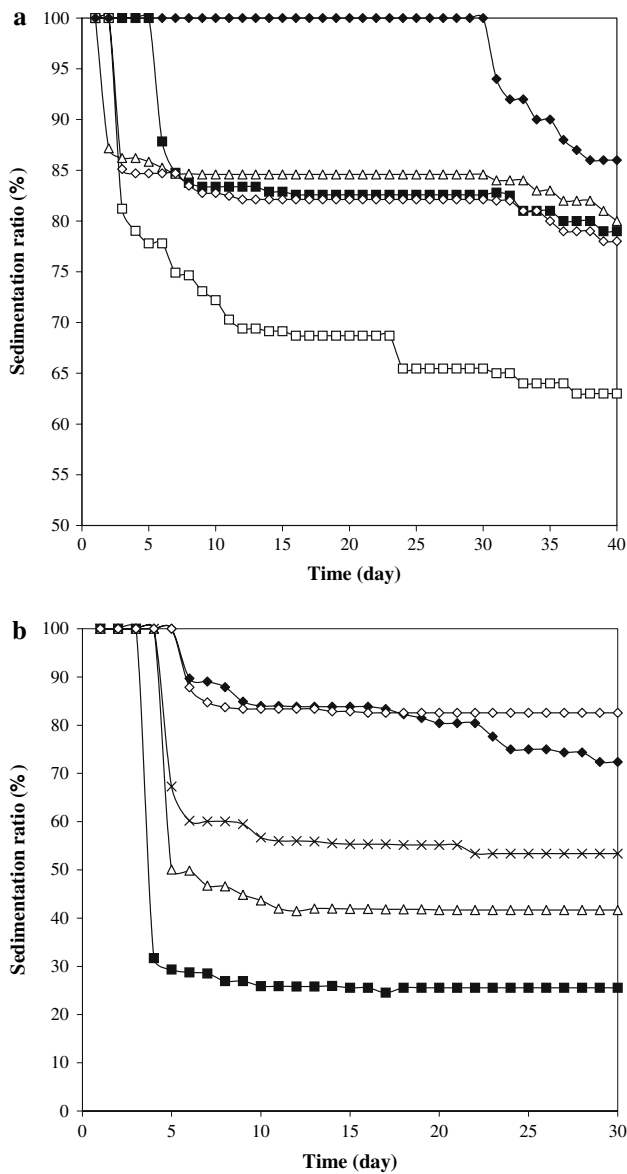
Despite the recent activities surrounding ER fluids and ER effect, little efforts was focused on the colloidal stability of these suspensions. Few investigations probe the colloidal chemistry of ER fluids [16]. When the density of particles is not the same as that of the medium, the particles with micron size settle down according to Stoke’s law [22]. In order to solve the traditional problem of particle sedimentation, several workers have developed different solutions [23]. Figure 1(a, b) shows the change of sedimentation ratio with time for PIN and PIN/PVAc composites in SO. It was observed that, PIN/SO suspensions have shown the highest stability against sedimentation. In the period of first 30 days, PIN/SO suspension ( $c = 5\%$ ) system showed no sedimentation, between 30 and 40 days, first settlings were observed and at the end of 40 days of observation 15% sedimentation was recorded. This high colloidal stability may be attributed to the density mismatch of PIN and SO ( $\rho_{PIN} < \rho_{SO}$ , see Table 1). As reflected from the graph, sedimentation stability of composites were changed as following:  $K4(87\%) = K3(87\%) > K2(85\%) > K1(81\%)$ . As expected, sedimentation stability of all the suspensions was observed to increase with decreasing density, particle size, and increasing PIN content of the composites. Besides, sedimentation stability of K1/SO system was observed to decrease with increasing dispersed particle concentration and this increase was sharp for high concentrations (Fig. 1(b)). Changing sedimentation stabilities were reported for (poly(lithium-2-acrylamido-2-methyl propane sulfonic acid)/SO system as 60 days [24], for organic/inorganic colloidal hybrid fluid catalytic cracking slurry as 49 days [25], and for BaTiO<sub>3</sub>/SO system as 70 days [26].

**Table 1** Conductivity, density, dielectric constant and average particle size values of PIN and PIN/PVAc composites

Sample	Conductivity ( $Sm^{-1}$ ) $\times 10^7$	Dielectric constant	Density ( $kg m^{-3}$ ) $\times 10^{-3}$	Average particle size ( $d_{50}$ ) ( $\mu m$ )
K1 (14% PIN/86% PVAc)	1.98	6.49	1.11	12.00
K2 (18% PIN/82% PVAc)	2.45	7.15	1.08	9.94
K3 (28% PIN/72% PVAc)	3.98	7.88	1.04	9.62
K4 (35% PIN/65% PVAc)	4.83	5.63	1.03	9.36
PIN	964	6.90	0.80	41.03

Flow rates

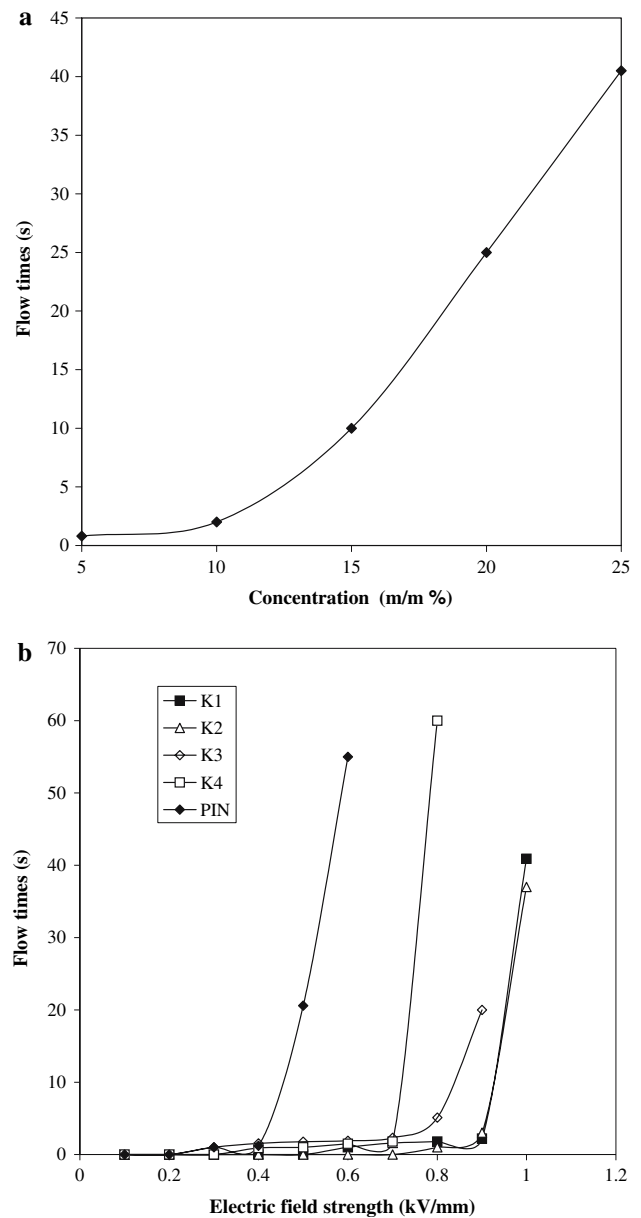
To observe the effect of dc electric field on the ER activity, flow rate measurements were carried out on PIN and PIN/PVAc/SO suspensions. For this purpose, PIN and PVAc composites were prepared at a series of particle concentrations (5–25%) in SO and flow times measured under  $E = 0$  kV/mm and  $E \neq 0$  kV/mm conditions.



**Fig. 1** (a) Effect of composite content on sedimentation ratio. (◆) PIN, (□) K1, (◇) K2, (Δ) K3, (■) K4,  $c = 5\%$ ,  $T = 25\text{ }^{\circ}\text{C}$ . (b) Effect of concentration on sedimentation ratio. Sample: K1, (◇) 5%, (◆) 10%, (×) 15%, (Δ) 20%, (■) 25%,  $T = 25\text{ }^{\circ}\text{C}$

Change of flow times with concentration (sample K4) was represented in Fig. 2(a). It was observed that, flow times of PIN/PVAc composite suspensions increased with increasing dispersed particle concentration. Flow times given for the suspensions are the maximum flow times, which could be measured under the applied external electric field ( $E = 1.0\text{ kV/mm}$ ). When the electric field was further increased, a highly stronger bridge formation occurred for all the suspensions and no flow was observed.

To observe the effect  $E$  and composite composition, a series of experiments were carried out at a constant dispersed particle concentration ( $c = 25\%$ ) and the results



**Fig. 2** (a) The changes in flow times with concentration. Sample K1,  $T = 25\text{ }^{\circ}\text{C}$ ,  $E = 1.0\text{ kV/mm}$ . (b) The changes in flow times with electric field strength. (◆) PIN, (■) K1, (Δ) K2, (◇) K3, (□) K4,  $c = 25\text{ wt.}\%$ ,  $T = 25\text{ }^{\circ}\text{C}$

obtained are depicted in Fig. 2(b). Flow times of suspensions increased with increasing external electric field strength and PIN content of composites. Threshold energy ( $E_t$ ) of samples were changed in the following order: PIN ( $E_t = 400\text{ V}$ ) > K4 ( $E_t = 700\text{ V}$ ) > K3 ( $E_t = 800\text{ V}$ ) > K2 = K1 ( $E_t = 900\text{ V}$ ). An increasing  $E_t$  values were determined with decreasing PIN content of the composites, which are consistent with the conductivity data of composites.

Similar behaviors were observed in our previous studies for poly(Li-2-hydroxy ethyl methacrylate)/SO [27],

calcium carbonate/SO [28], polystyrene-*block*-poly(methyl methacrylate)/SO suspensions [11].

Electro-rheometry

Since the ER phenomena are widely attributed to the chaining of micron-sized polarizable particles, when subjected to an external electric field, flow and electro-rheometer studies are conducted to observe the viscosity change and ER response of PIN/PVAc suspensions.

Effect of concentration

The change in ER efficiency  $[(\eta_{E \neq 0} - \eta_{E=0})/\eta_{E=0}]$  with suspension concentration for K1 (contains 14% PIN) at a constant shear rate ( $\dot{\gamma} = 0.2 \text{ s}^{-1}$ ), electric field strength ( $E = 0$  and  $3.65 \text{ kV mm}^{-1}$ ), and temperature ( $T = 25 \text{ }^\circ\text{C}$ ) is shown in Fig. 3. For other samples, the ER efficiency and corresponding leakage current density data is given in Table 2. The leakage current density data was varied between  $5.0 \times 10^{-3}$  and  $0.99 \text{ } \mu\text{A/mm}^2$ , depending on the nature of the sample. The ER efficiency increases with rising particle concentration. Suspension concentration exerts principle effect on the ER activity. The increase in ER efficiency may be attributed to the polarization forces acting between suspended particles. This polarization force ( $F$ ) in the direction of the applied electric field ( $E$ ) increases according to the formula [29]

$$F = 6\epsilon_2 r^6 E^2 / \rho^4 \tag{2}$$

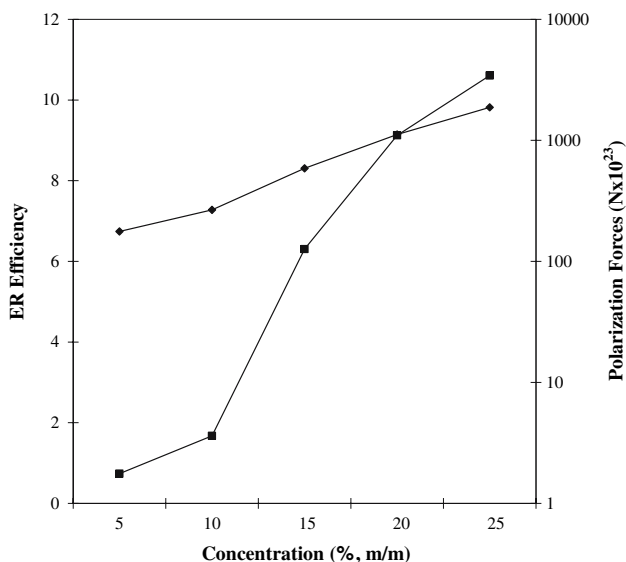


Fig. 3 Effect of concentration on ER efficiency and polarization forces, sample: K1, (◇) ER efficiency, (◆) polarization forces,  $E = 0 \text{ kV/mm}$  and  $E = 3.65 \text{ kV/mm}$ ,  $T = 25 \text{ }^\circ\text{C}$ ,  $\dot{\gamma} = 0.2 \text{ s}^{-1}$

Table 2 Leakage current density data of samples

Sample	ER efficiency	Electric field strength (kV/mm)	Leakage current density ( $\mu\text{A/mm}^2$ )
K1	3.07	3.13	$5 \times 10^{-3}$
K2	6.70	3.13	$5 \times 10^{-3}$
K3	11.90	2.60	0.1264
K4	17.90	3.65	$6 \times 10^{-2}$
PIN	2.60	1.25	0.999

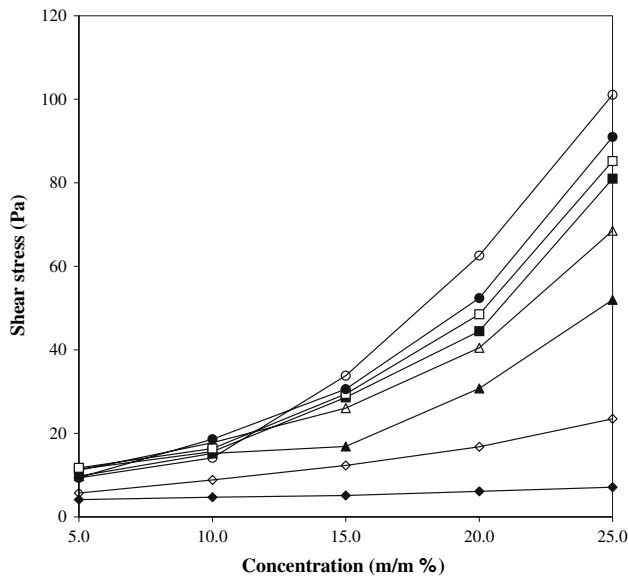
where  $\epsilon_2$  is the dielectric constant of the particle,  $\rho$  is the distance between particles, and  $r$  is the radius of the particle. An increased suspension concentration will decrease the distance between the particles, which will result in an increased polarization force.

When electric field was applied to PIN/PVAc composite/SO suspensions, polarization forces caused the aggregation of particles and a chain formation between the upper and lower plates occurred during the measurements in the electro-rheometer (Fig. 3). It is known that, in two component ER systems (containing dispersed and continuous phases), the interfacial polarization is reported to be responsible for ER effect [3]. Electric field-induced polarization forces were observed to increase with rising concentration. This trend is due to the increased magnitude of polarization forces acting between the electric field-induced charged particles of PIN. Similar behaviors were observed in our previous studies on  $\text{CaCO}_3/\text{SO}$  [27] and polyaniline derivatives/SO systems [30].

Dependence of shear stress on particle concentration is given in Fig. 4. It is clear that, the shear stress increase is directly related to the suspension concentrations. The shear stress of K1/SO suspension was observed to increase from  $\tau = 9.37 \text{ Pa}$  ( $c = 5\%$ ) to  $\tau = 101.04 \text{ Pa}$  ( $c = 25\%$ ) under  $E = 3.65 \text{ kV/mm}$  external electric field. Increase in the shear stress with increasing concentration may be attributed to the increased interparticle interactions with raising particle concentration in the suspension, which results with an enhanced ER activity. Similar results reported by Yoon and Kim in polypyrrole-silica-methylcellulose/SO suspensions [17] and Tian et al. [31] zeolite/SO suspension and Unal et al. [32] for sepiolite/silicone oil suspensions

Effect of electric field strength on viscosity and shear stress

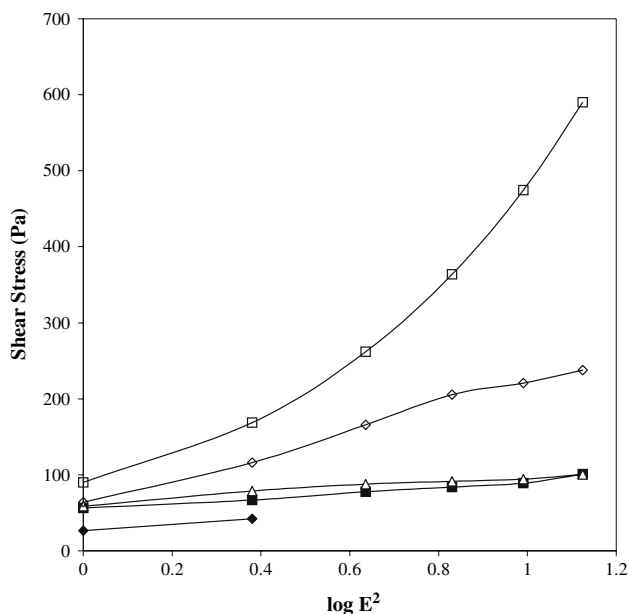
Shear stress is one of the critical design parameter in ER phenomenon and has attracted considerable attention both theoretically and experimentally [33]. Figure 5 shows the dependence of shear stress on the square of the electric



**Fig. 4** Change of shear stress with concentration. Sample: K1,  $T = 25\text{ }^{\circ}\text{C}$ ,  $\dot{\gamma} = 0.2\text{ s}^{-1}$ , ( $\blacklozenge$ )  $E = 0\text{ kV/mm}$ , ( $\diamond$ )  $E = 0.5\text{ kV/mm}$ , ( $\blacktriangle$ )  $E = 1.0\text{ kV/mm}$ , ( $\Delta$ )  $E = 1.5\text{ kV/mm}$ , ( $\blacksquare$ )  $E = 2.0\text{ kV/mm}$ , ( $\square$ )  $E = 2.5\text{ kV/mm}$ , ( $\bullet$ )  $E = 3.0\text{ kV/mm}$ , ( $\circ$ )  $E = 3.5\text{ kV/mm}$

field strength for the five samples studied. Shear stress increases proportionally to the square of electric field strength as expected (Eq. 3).

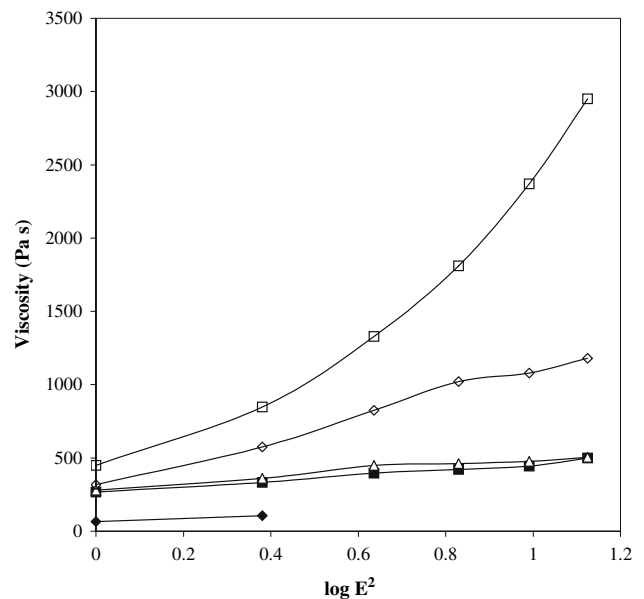
$$\tau_E \propto \phi K_f E^2 \beta^2 \tag{3}$$



**Fig. 5** Effect of electric field strength on shear stress. ( $\blacklozenge$ ) PIN, ( $\blacksquare$ ) K1, ( $\Delta$ ) K2, ( $\diamond$ ) K3, ( $\square$ ) K4,  $c = 25\%$ ,  $T = 25\text{ }^{\circ}\text{C}$ ,  $\dot{\gamma} = 0.2\text{ s}^{-1}$

where,  $\phi$  is the volume fraction of particles,  $K_f$  is the dielectric permittivity of the base fluid,  $E$  is the electric field strength, and  $\beta$  is the relative polarizability at dc or low-frequency ac fields given by Conrad and Chen [34] and Davis [35]. Electric field-induced shear stress values were observed to increase with increasing PIN content of the composites and changed in the order: K4 ( $\tau = 590.3\text{ Pa}$ ) > K3 ( $\tau = 237.7\text{ Pa}$ ) > K2 = K1 ( $\tau = 100.4\text{ Pa}$ ) > PIN ( $\tau = 42\text{ Pa}$ ). When PIN/SO suspension was subjected to  $E > 1.5\text{ kV/mm}$ , an electrical breakdown occurred and no further data was collected. Similar trend was reported by Lu and Zhao [36] for polyaniline/montmorillonite composites.

Figure 6 shows the change in the electric field viscosity with electric field strength at constant conditions ( $\dot{\gamma} = 0.2\text{ s}^{-1}$ ,  $c = 25\%$ ,  $T = 25\text{ }^{\circ}\text{C}$ ). Electric field viscosity ( $\eta_{E \neq 0}$ ) increases with increasing electric field strength for all the suspensions studied. Under applied electric field strength, magnitude of the polarization forces between particles increases, and in turn, the particles rapidly aggregate into the chain formation perpendicular to the lower and upper plates, hence resulting in the improvement of the electric field viscosity. On the other hand, it was observed that, as the PIN content increases in the PIN/PVAc composites, electric field viscosity also increases. The maximum electric field viscosity was observed as 3.0 kPas for K4, which contains the highest amount of PIN.



**Fig. 6** Change of viscosity with square of electric field strength.  $c = 25\%$ ,  $T = 25\text{ }^{\circ}\text{C}$ ,  $\dot{\gamma} = 0.2\text{ s}^{-1}$  ( $\blacklozenge$ ) PIN, ( $\blacksquare$ ) K1, ( $\Delta$ ) K2, ( $\diamond$ ) K3, ( $\square$ ) K4



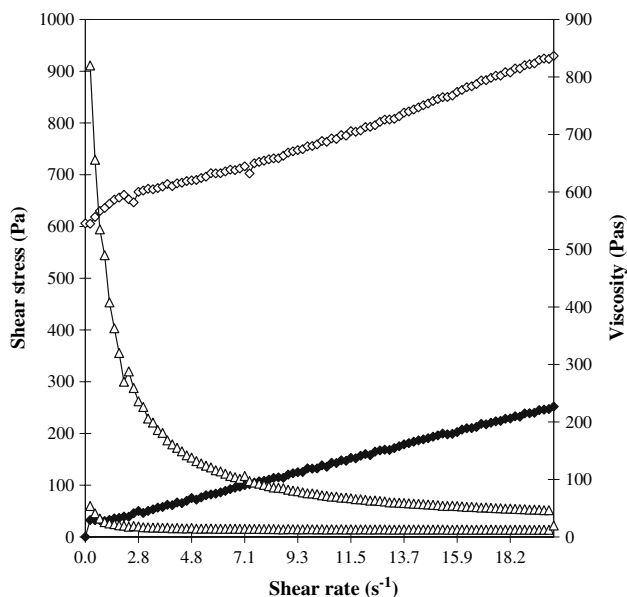
Effect of shear rate on shear stress and viscosity

Change of shear stress and viscosity of suspensions with shear rate at  $E = 0.0$  kV/mm and  $E = 3.65$  kV/mm electric field strengths is shown in Fig. 7. It was observed that, shear stress of K4 (containing 35% PIN) suspension increases with increasing shear rate and shows a Newtonian flow behavior in the absence of electric field ( $E = 0$  kV/mm), but when the electric field is applied ( $E = 3.65$  kV/mm), the suspension again shows a shear stress increase with a Bingham behavior; which is caused by the role of electric field-induced polarization forces [37].  $\tau_y = 605$  Pa yield stress was recorded for K4 and this yield stress values were observed to decrease with decreasing content of PIN in the other composites.

Besides, viscosity of K4/SO suspensions decreased sharply from 820 to 270 Pas with increasing shear rate from  $\dot{\gamma} = 0$  s<sup>-1</sup> to  $\dot{\gamma} = 2.0$  s<sup>-1</sup> and shows a typical curve of shear thinning non-Newtonian viscoelastic behavior. After  $\dot{\gamma} = 2.0$  s<sup>-1</sup>, the electric field-induced structure of suspension is broken and the viscosity becomes almost independent of shear rate. Similar trends were observed for the PIN and PIN/PVAc/SO suspension. Inside the suspensions, the particles are affected by the hydrodynamic interactions and the viscous forces ( $F$ ), which have the following magnitude [33]:

$$F = 6\pi\eta_s r^2 \dot{\gamma} \tag{4}$$

where,  $\eta_s$  is the viscosity of the suspension and  $\dot{\gamma}$  is the average shear rate. Similar results were reported by

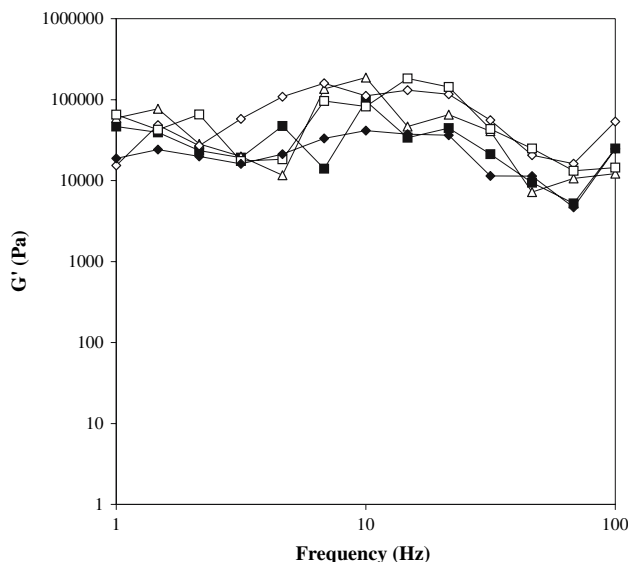


**Fig. 7** Change of shear stress and viscosity with shear rate. Sample: K4,  $c = 25\%$ ,  $T = 25$  °C, (◆)  $\tau(E = 0$  kV/mm), (◇)  $\tau(E = 3.65$  kV/mm), (▲)  $\eta(E = 0$  kV/mm), (Δ)  $\eta(E = 3.65$  kV/mm)

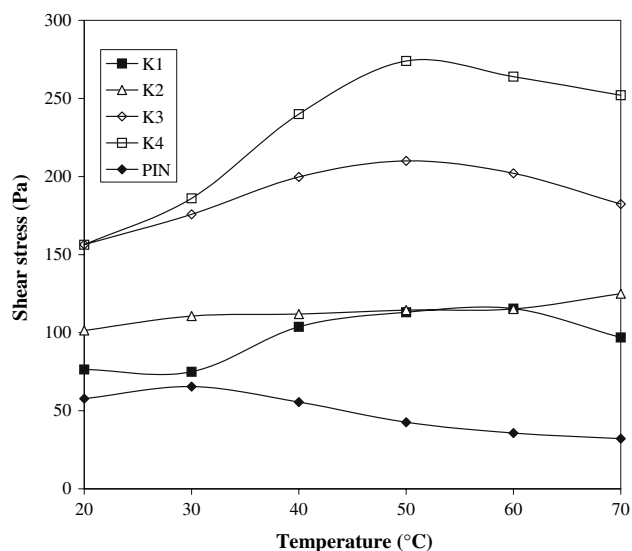
Lengalova et al. [8] in polyaniline/SO suspensions, Woo et al. [38] in polyaniline derivatives/SO suspensions and Yavuz and Unal [39] in polyisoprene-*b*-poly (tert-butyl-methacrylate)/SO suspensions.

Effect of frequency

The external stress frequency ( $f$ ) is an essential factor for characterizing the dynamic viscoelastic properties of ER fluids [40]. Figure 8 demonstrates the change of electric field-induced complex shear modulus ( $G'$ ) with  $f$  at constant conditions ( $c = 25\%$ ,  $E = 3.0$  kV/mm and  $T = 25$  °C). The setting shear stress for this experiment was  $\tau = 10$  Pa, which ensures that the measurements are conducted in the small strain region. The shear modulus of PIN and PIN/PVAc composites/SO system was observed to slightly increase at low frequency region (up to 20 Hz), shows a vibration dumping viscoelastic property, and then gradually decreased with further increase in frequency. The situation can be compared with the dipole relaxation, in an electromagnetic field: when the field frequency is too high, the dipoles are no longer able to follow the direction of the electric field. The fluctuations observed in the graph was due to the increased leakage current density occurred during the measurements. The same features were also reported by other investigators in the studies of polyaniline/SO suspensions by Hiamtump et al. [41] and polyaniline-Na<sup>+</sup>-montmorillonite/SO suspensions by Kim et al. [42].



**Fig. 8** Change of complex shear modulus with frequency, (◆) PIN, (■) K1, (▲) K2, (◇) K3, (□) K4  $c = 25\%$ ,  $T = 25$  °C,  $E = 3.0$  kV/mm,  $\tau = 10$  Pa



**Fig. 9** Change of shear stress with temperature  $E = 2.0$  kV/mm, (◆) PIN, (■) K1, (Δ) K2, (◇) K3, (□) K4,  $c = 25\%$ ,  $T = 25$  °C,  $\dot{\gamma} = 1.0$  s<sup>-1</sup>

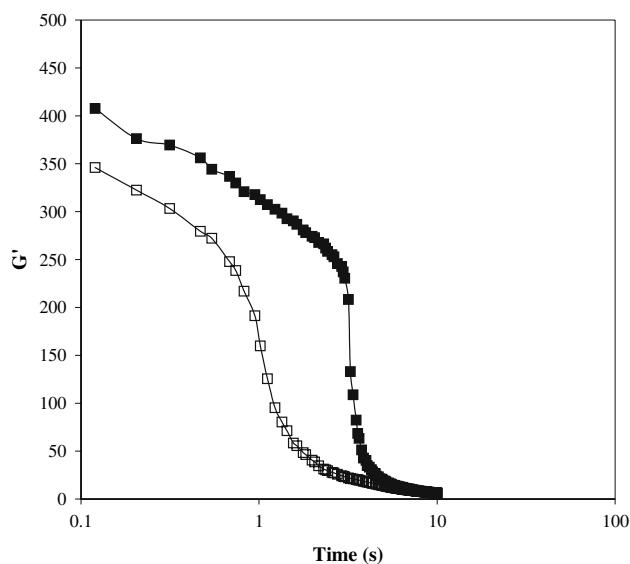
#### Effect of temperature and shear stress

Figure 9 shows the changes in the shear stress of PIN and PIN/PVAc composites suspensions under various temperatures at constant conditions ( $E = 2$  kV/mm,  $\dot{\gamma} = 1.0$  s<sup>-1</sup>,  $c = 25\%$ ). The shear stresses of the suspensions were observed to increase up to 50 °C, and then slightly decreased with increasing temperature. This may be attributed to the increased magnitude of intermolecular forces at low temperatures, and enhanced viscoelastic properties of the composites at elevated temperatures, which impact the polarizability of the suspended particles leading to increased fluidity of the suspensions. On the other hand, it was observed that, when homopolyindole was subjected to thermal tests, its shear stress loss started at 30 °C, whereas, PIN/PVAc composites started shear stress losses at 50 °C, which indicates the thermally more stable structure formation. This is also proven with DSC thermograms of the PIN and PIN/PVAc composites [19].

Similar shear stress losses were also reported by Block in silica/SO suspensions and by Yanyu in inorganic/polymer blend/SO suspensions [14, 43].

#### Creep behavior of PIN and PIN/PVAc composite suspensions

Conducting a creep test is a critical method to obtain information on the material deformation and recovery properties. In a creep experiment, a constant stress ( $\tau = 10$  Pa) was applied instantaneously to PIN and PIN/PVAc composite suspensions at constant conditions



**Fig. 10** Creep behavior of (■) PIN and (□) K1,  $T = 25$  °C,  $c = 25\%$ ,  $E = 0$  kV/mm

( $T = 25$  °C,  $c = 25\%$ ,  $E = 0$  kV/mm) and change in the elasticity modulus ( $G'$ ) was measured over a period of time (Fig. 10). In PIN/SO and K1/SO suspensions, viscoelastic, elastic recovery, and viscoelastic recovery creep behaviors were observed. When all the composites were considered (K1, K2, K3, K4), elastic and viscoelastic recoveries and unrecovered viscous flow decreased with increasing PIN content of the composites.

In the literature, viscoelastic creep deformation was reported for polypyrrole and poly(ethylene-co-methyl methacrylate) blends by Genovese and Shanks [44], besides, reduced viscoelastic creep deformation was reported for polypyrrole/jute composite with increasing jute content by Acha et al. [45]

#### Conclusions

In PIN and PIN/PVAc composites conductivities changed between  $9.64 \times 10^{-5} \geq \sigma \geq 1.98 \times 10^{-7}$  Sm<sup>-1</sup> and increased with increasing content of PIN. Sedimentation stabilities of suspensions increased with increasing PIN content and decreasing dispersed particle concentration, density, and particle sizes of composites. ER activity of all the suspensions was observed to increase with increasing electric field strength, dispersed particle concentration, and decreasing shear rate. All the suspensions were observed to show Newtonian flow behavior in the absence of electric field, and Bingham plastic flow behavior in the presence of externally applied electric field. Viscosities of all suspensions sharply decreased with increasing shear rate, thus showing a shear thinning non-Newtonian flow. Shear



modulus of samples slightly increased with external frequency and shows a potential of vibration damping. ER strength of suspensions was observed to be slightly sensitive in high temperature and insensitive to promoter, and they were classified as dry-base ER fluids. From the creep measurements it was concluded that, composites show a reversible viscoelastic deformation.

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