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An Investigation of Some Parameters on Electrorheological Properties of Polypyrrole Suspensions

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In this study, polypyrrole (PPy) was synthesized by cationic addition polymerization. The polymer was characterized by FTIR spectroscopy, scanning electron microscopy (SEM), particle size, magnetic susceptibility, and four-probe conductivity measurements. From the magnetic susceptibility measurements, it was found that the polymer was a bipolaron conducting mechanism. From the particle size measurements, the average particle size of PPy was determined to be 3.2 μm. Suspensions of this polymer were prepared in silicone oil, mineral oil, trioctyltrimellitate (TOTM), dioctylphthalate (DOP) and marlotherm-s in different concentrations (5-20%, m/m). The electrorheological (ER) properties of these suspensions were investigated under various d.c. electric field strengths (E = 0-1kV/mm), and shear rates ($\dot{\gamma}$ = 0.1-20 s^{-1}). The effects of temperature and promoter on ER activity were also studied, and the stabilities of suspensions against sedimentation were determined. The suspensions of PPy, prepared in TOTM insulating medium, showed the highest ER activity (1200 Pa) at 12.5% particle concentration. Excess shear stress ($\Delta\tau$) was found to increase with increasing concentration and reached 231 Pa. Further, sedimentation stabilities of suspensions were also observed to increase with decreasing particle concentration, and maximum colloidal stability was obtained in TOTM as 71 days. From the experiments, it was concluded that PPy suspensions exhibited a shear-thinning visco-elastic behavior and their ER activities were not temperature or promoter dependent and they were classified as dry-ER fluids.

Introduction

Electrorheological fluids consist of dispersions of solid particulates within an insulating liquid. Application of an external electric field causes 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, field frequency, shear rate, fluid composition, temperature and addition of a polar promoter[2].

Since the effect was first reported by Winslow[3] for dispersions of moist silica gel, a variety of particulate types have been investigated including natural and hydrophilic polymers and conducting polymers[4,5]. Whilst

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the systems investigated in early research required the presence of small amounts of moisture, more recently it has been shown that some electronically semi-conducting particulates are ER active in the absence of moisture[5].

It is now clear that polarization is the essence of the effect, although formulation of the various mechanistic possibilities (including concepts such as clustering and fibrillation) in the form of a general quantitative theory has not yet been achieved.

There is a very wide range of potential applications for ER fluids in such areas as damping, robotics, hydraulics, couplings and automotive. The patent literature on the subject suggests a growing interest in such devices after a period of research and assessment[6]. A major limiting factor is still the need for fluids with better overall performance. In some applications, there is a particular requirement for high yield stress without incurring great power loss or high zero field viscosity ($\eta_{E=0}$).

There is also a need for fluids with enhanced colloidal stability against sedimentation and sludge deposit formation[7]. Most of the studies in the literature are on the ER activity of acrylate salts and zeolitic materials[8−13], and none of these researchers have investigated the influence of colloidal stability of suspensions on the ER activity. Another target for ER fluids is to have long service stabilities during operations, and particularly at rigid environmental conditions (i.e., low and high temperature range and humidity)[14].

In the present study, PP_y was chemically synthesized, after characterization and conductivity measurements, dopant free suspensions were prepared in five insulating fluids, and the ER properties of PPy were investigated. The purpose of preparing a promoter free ER fluid is to control the polarization ability by using semi-conducting polymers as particulates which could provide large interfacial polarization when surrounded by an insulating liquid in moisture free suspensions.

Experimental

Materials

Pyrrole monomer (Merck) was purified by vacuum distillation at 30°C and 5 mm Hg.

Insulating oils: Silicone oil, DOP, TOTM, mineral oil and marlotherm-s (Aldrich) were used as received. Physical properties of the insulating oils are given in Table 1[15].

Table 1. Physical Properties of the Oils[15].

Oil	IUPAC Name	Boiling Point (°C)	Density (g/mL)	Colour	Viscosity (Pa.s)
DOP	Bis(2-ethylhexyl ftalate)	384	0.981	Light yellow	0.04
TOTM	Tris(2-ethylhexyl trimellitate)	163-165	0.821	Light yellow	0.08
Silicone oil	Poly(dimethyl-siloxane)	>140	0.963	White	0.08
Mineral	-	>110	0.862	White	0.04

Polymerization of pyrrole

Polypyrrole was chemically synthesized according to the procedure described by Kaneko and coworkers[16]. The polymer was dried in a vacuum oven at 50°C for 2 days prior to characterization and ER studies.

Characterization

Solubility tests

It was not possible to dissolve PP_y in any solvent (i.e., methanol, ethanol, chloroform, acetone, sulfuric acid, perchloric acid, dimethylsulfoxide) either at room temperature or at the boiling point of the solvent.

Infrared spectroscopy

FTIR spectrum was recorded using a Mattson Model 1000 FTIR spectrometer with a resolution of 2. Samples were analyzed as KBr discs.

Scanning electron microscopy (SEM)

SEM micrographs were obtained using a World Lender X-Line Analyzer. Samples were coated with gold by a Polaron SC 502 sputter coater for examination.

Gouy balance measurements

Magnetic susceptibility measurements were carried out using a Sherwood Scientific MKI Model Gouy Scale. Finely powdered polymer samples were placed into a glass tube at a height of not less than 2.5 cm. This glass tube was placed into a hole in the magnetic balance, which was on a wooden bench, to obtain a constant value.

Conductivity measurements

Conductivity of PP_y was measured employing the "four-probe" technique.

Particle size measurements

Particle size of the PP_y samples was determined by Fraunhofer Scattering[17] using Malvern Mastersizer E, Version 1.2b Analyzer. The polymer was dispersed in distilled water and stirred at 20°C. The data collected were evaluated by a Malvern computer software according to the Fraunhofer diffraction theory. The average diameter of polymer particles was determined to be 3.2 μm.

Preparation of Suspensions

Suspensions of PPy were prepared in silicone oil, DOP, TOTM, mineral oil and marlotherm-s insulating oils, in a concentration range of 5-20 (%, m/m), by dispersing a definite amount of PPy in calculated amounts of the oils.

Determination of Sedimentation Stability of Suspensions

Stabilities of the suspensions against sedimentation, prepared in those five insulating oils in glass tubes, were determined at ambient temperature. The formation of the first precipitates at the bottom of the tubes were taken to be the beginning of colloidal instability.

ER Measurements

Flow Measurements

Flow rate measurements were carried out for suspensions prepared in the five insulating oils, between two brass electrodes which were connected to a high voltage d.c. electric source (0-10 kV) and a voltmeter. 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.

At the beginning of the experiment, the electrodes were dipped into a vessel containing the ER fluid and after at least 20 s the vessel was removed and the flow time for complete drainage was measured using a digital stopwatch. At the second stage, the same procedure was repeated under an applied electric field (E≠0). This procedure was repeated for each ER fluid suspension system at various concentrations and under various electric field strengths.

For flow between parallel plate electrodes, the flow time of fluid, t, is related to the viscosity, η, by

$$\eta = \rho.\mathrm{g.b.d}^3.\mathrm{t}/12\mathrm{V} \tag{1}$$

where ρ is the density of the ER fluid, g is the gravitational acceleration, b is the width of the plates, d is the separation distance of the plates and V is the total volume of ER fluid. The relation is based on the assumption that the viscous and gravitational forces are just balanced and, therefore, the kinetic corrections are negligible. The average shear rate ($\dot{\gamma}$) at which the measurements were taken was determined using the equation

$$\dot{\gamma} = 3\ \mathrm{V/b.d}^2.\mathrm{t} \tag{2}$$

Electrorheological measurements were also carried out using a rotational spindle viscometer (Brookfield Rheometer DV+ I) to investigate the ER behavior of PPy suspensions. To measure the viscosities of ER fluid systems, the spindle of the rheometer was simply immersed in the liquid container, the motor was switched on and the viscosity of the fluid was read on the calibrated dial of the instrument.

For measuring the viscosity of ER suspensions under an applied electric field, the parallel plate electrodes were immersed in the same fluid container, keeping the 0.5 cm gap between the parallel plate electrodes constant, an electric field was created in the fluid and the rheometer's spindle was forced to rotate between the parallel plate electrodes. The shear rates used during these experiments were relatively low ($\dot{\gamma}$ = 0.1-20 s^{-1}), due to the instrumental limitations. The voltage used in these experiments was supplied by a 0-10 kV (with 0.5 kV increments) d.c. electric field generator at 50 Hz frequency, which enabled resistivity to be created during the ER measurements.

To observe the effect of temperature on the ER activity of suspensions, ER measurements were carried out at two different temperatures (20°C and 80°C).

Results and Discussion

PPy was synthesized by cationic chain polymerization[16] and characterized by a series of methods before the ER measurements were carried out.

FTIR Spectroscopy

The FTIR spectrum of pyrrole showed the expected distinctive absorptions. The absorptions at 3400 cm^{-1}, 3040 cm^{-1}, 1529 $cm^{-1}$and 1420 cm^{-1} are typical of N-H, =C-H, C=C, and =C-N stretching vibrations respectively. It was observed that, after polymerization, N-H stretchings at 3400 cm^{-1} spread and overlapped the =C-H vibrations at 3040 cm^{-1}, which was taken to be proof of polymerization.

Scanning Electron Microscopy

As seen from the SEM micrograph of PP_y (Fig. 1), the surface is rather sponge-like, and has scattered layers with small pores. It is known that the dopants and solvents used during synthesis affect the morphology and the physical, chemical and electrochemical properties of the resultant polymer[18]. It is stated by Price that PPy prepared by using different dopants shows different morphological structures[19].

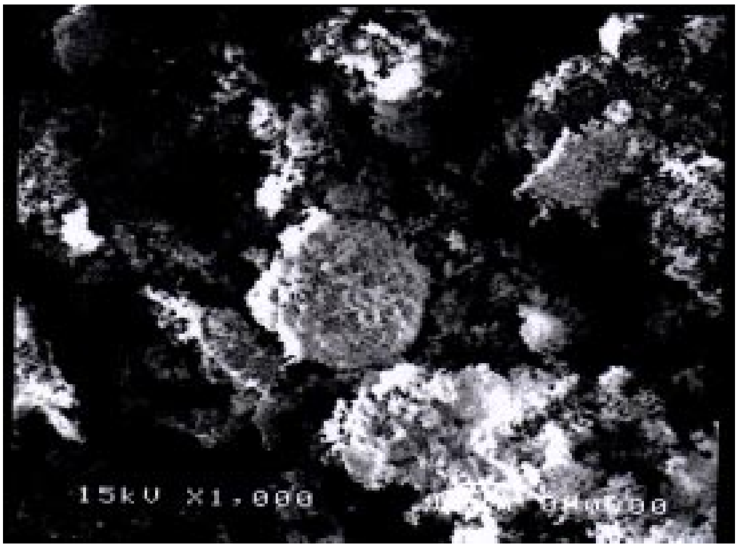

Figure 1. SEM micrograph of PPy

Gouy Balance Measurements

From the Gouy Scale measurements, the magnetic susceptibility balance of the PP_y was determined to be –32 Bohr Magneton (BM). Based on this result, it can be assumed that PP_y is diamagnetic and its conducting mechanism is of a bipolaron nature[20].

Such a structure is known to be more stable in terms of energy. The conductivity mechanism of PP_y was studied in the literature and it was revealed that the influence of bipolarons was stronger than that of polarons on conductivity[21]. Our study also confirmed that the bipolaron structure is responsible for the conductivity.

Conductivity Measurements

The conductivity obtained for PP_y using the four-probe technique was 5.4x 10^{-3} Scm^{-1}. This conductivity value falls into the conductivity range of semi-conductive materials (10^{-7}-10^{2} Scm^{-1})[22].

Particle Size Measurements

Particle size is an important factor for ER measurements. It is known that the origin of ER activity is interparticle interactions[23]. As a result of these interactions, particles form chain-like structures. To form a stable chain structure against gravitational force and have colloidally stable ER suspension, one desires a small ER particle[24]. From the first particle size measurements of crude PP_y, a 125 μm average particle size was obtained. The suspensions prepared from this PP_y were unstable against sedimentation and did not show ER activity. To reduce the particle size, PP_y was ground for a few hours and thus a 3.2 μm average particle size was obtained. The suspensions prepared from this PP_y showed high ER activity.

Sedimentation Stability of Suspensions

Before ER measurements were carried out, the sedimentation stability of PP_y suspensions was determined in the five insulating media at 20°C. The results are shown in Table 2. As seen in table, the stabilities of the suspensions against sedimentation increased with decreasing particle concentration. The maximum sedimentation stability was observed to be 71 days at 5 (%, m/m) particle concentration in TOTM insulating fluid. Stability of an ER active material against sedimentation is a very important factor from industrial and application points of view[25]. It was mentioned by Unal[26] that micelle forming ER suspensions showed greater colloidal stability than the classical ones, and 90 days of colloidal stability was reported for the suspensions prepared from the polyisoprene-*block*-poly(tert-butylacrylate-*stat*-lithiumacrylate) copolymer/pentaerythritolheptanoate insulating oil system. In other studies carried out by Yavuz[27] and Yılmaz[28], 54 and 60 day colloidal stabilities were reported for the suspensions prepared from polyisoprene-*block*-poly(styryllithium) copolymer/silicone oil and 2-acrylamido-2-methylpropanesulfonic acid/silicone oil systems, respectively.

Table 2. Results obtained from sedimentation stability of PP_y suspensions, T = 20°C

	Concentrations (%, m/m)				
Oils	20	15	12.5	10	5
Silicone	20 days	35 days	42 days	58 days	63 days
Mineral	15 days	21 days	25 days	34 days	52 days
TOTM	24 days	38 days	45 days	64 days	71 days
DOP	3 days	5 days	7 days	10 days	12 days
Marlotherm-s	1 day	3 days	5 days	6 days	8 days

Electrorheological Studies

Results obtained from parallel plate electrodes

The flow times of PP_ysuspensions prepared in silicone oil (most resistive to sedimentation), at a range of 5 to 20 (%, m/m) concentrations, measured between the parallel plate electrodes at zero applied electric field strength (E = 0) and under various electric field strengths are shown in Figure 2.

The flow time of PP_ysuspensions prepared in silicone oil was observed to increase with increasing particle concentration. As seen from Figure 2, as the particle concentration was increased from 5% to 20%, the flow time of the suspension increased from 700 s to 2100 s. The same measurements were carried out for the suspensions prepared in the other four insulating oils and similar trends were observed. The shortest flow time (0.2 s) was observed for a 5% particle concentration in marlotherm-s. It was observed from the measurements that the maximum flow time of the suspensions varied in the following order: silicone oil (2100 s)>TOTM (1800 s)>marlotherm-s (1200 s)> mineral oil (900 s)>DOP (800 s). The flow times given are the maximum flow times that could be measured under the applied field strength. When the electric field strength was further increased, the flow of the suspensions between the electrodes was completely stopped and we were unable to take measurements even after several hours of waiting.

Consequently, it was concluded that the occurrence of solidification and the observation of non-Newtonian behavior was shifted to low electric field strengths as the particle concentration was increased for all the suspensions studied. Similar behavior was reported by Block and Kelly for silica/silicone oil and calcium titanate/silicone oil systems[5].

Results Obtained From Rotational Viscometer

Effect of particle concentration on ER activity

The effect of the variation of suspension concentration, prepared in the five insulating oils, on the ER activity was evaluated by chaining the concentrations of suspensions and shear rates in the ranges of 5-20% and 0.1-20 s^{-1} respectively, by keeping the electric field strength (E = 0.1 kV/mm) and temperature (T = 20°C) constant. Since the change in relative viscosity with concentration showed a similar trend in the five insulating oil medium, just the results obtained in TOTM are presented in Fig. 3. As seen in the graph, the highest viscosity was obtained as 50 Pa.s at 0.1 s^{-1} shear rate.

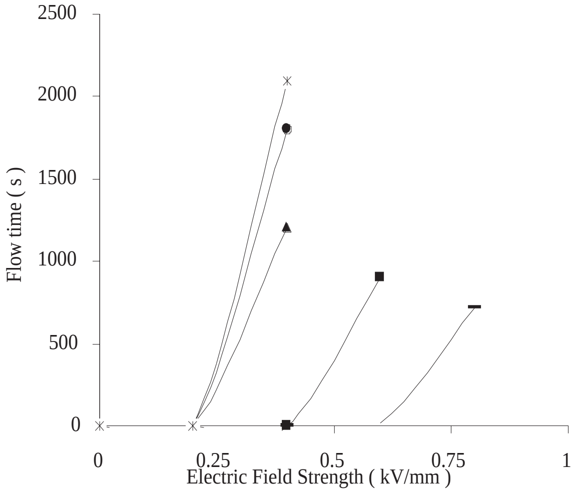

Figure 2. The variation in flow times of PP_y suspensions. c (%, m/m): (–) 5, (■) 10, (▲) 12.5, (♦)15, (•) 20, dispersion medium: Silicone oil.

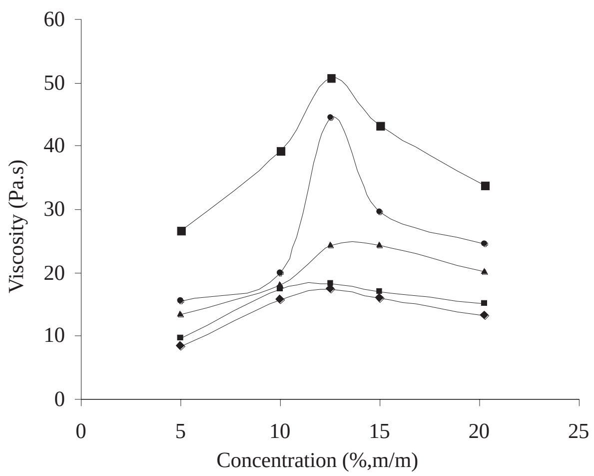

Figure 3. Change in viscosity of PP_y suspensions against the suspension concentration. $\dot{\gamma}$ (s^{-1}): (*) 1, (■) 2, (▲) 4, (♦)10, (–) 20, T = 20°C, dispersion medium: TOTM

It is clear that the increase in relative viscosity ($\eta_{E\neq0}/\eta_{E=0}$), in other words ER activity, is directly related to the suspension concentration up to 12.5%. The increase in the relative viscosity could be attributed to the probable polarization forces acting between the PP_y particles. The magnitude of this polarization force (F) in the direction of the applied electric field (E) is[29]

$$F = 6\varepsilon_2 r^6 E^2/\rho^4 \qquad (3)$$

where ε_2 is the dielectric constant of the particle, ρ is the distance between particles, and r is the radius of the particle. As reflected in equation (3), an increased suspension concentration will decrease the distance between PP_y particles, which will result in increased polarization force. As the suspension concentration increases above 12.5%, a substantial reduction in relative viscosity was observed. That is, 12.5% is the optimal concentration for achieving maximum ER activity in the PPy/TOTM system.

The decrease in relative viscosity at high 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[29]. In this case, interparticle interactions will decrease and result in reduced viscosity and ER activity.

The change in relative viscosity with suspension concentration in the other four insulating oils at optimum particle concentration (12.5%) was shown to follow the same trend, and the relative viscosities obtained were 13 Pa.s, 22 Pa.s, 35 Pa.s and 44 Pa.s in silicone oil, marlotherm-s, mineral oil, and DOP respectively. The relative viscosity was also observed to increase in all the insulating media studied, with increasing shear rate, showing typical shear-thinning non-Newtonian behavior. Similar results were reported in the literature[7,31–37].

Change in viscosity with electric field strength

The effect of electric field strength on viscosity was investigated at an optimum suspension concentration of 12.5% in the five insulating oils within the shear rate range of 1 s^{-1} to 20 s^{-1} at 20°C, and the highest viscosity value obtained in TOTM is shown in Fig. 4. The relative viscosity of the suspension increases with increasing field strength, and decreasing shear rate, and the effect of field strength is larger at low shear rates and smaller at high shear rates.

Under an applied shearing force, ER active particles are affected by polarization forces (which cause the aggregation of particles between the electrodes) as well as viscous forces (due to the hydrodynamic interactions of the particles in the suspensions). The relation of the magnitude of viscous forces (F), with the viscosity of suspension (η_s), the average shear rate ($\dot{\gamma}$), and the radius of particle (r), can be written as[38]

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

As seen in Fig. 4, the highest relative viscosity value (83 Pa.s) was reached under 1 kV/mm applied electric field strength and 1 s^{-1} shear rate and the lowest relative viscosity (5 Pa.s) was obtained under the same field strength and 20 s^{-1} shear rate.

A similar trend was observed for the other suspensions prepared in the other four insulating media, and 12 Pa.s, 18 Pa.s, 23 Pa.s and 55 Pa.s electric field viscosities were obtained for the suspensions prepared in marlotherm-s, DOP, mineral oil and silicone oil respectively.

Similar behavior was reported for the suspensions of carboxymethylchitosan prepared in silicone oil by Wu and Guar[29].

Effect of shear rate on viscosity

The effect of shear rate on the viscosity of the suspensions prepared in the five insulating oils at constant temperature (T = 20°C) and concentration (c = 12.5%) was studied at E = 0 and E $\neq$ 0. The highest electric field viscosities were obtained as 170 Pa.s (E = 0.4 kV/mm), 208 Pa.s (E = 1 kV/mm), 280 Pa.s (E = 0.8 kV/mm), 340 Pa.s (E = 0.5 kV/mm) and 1216 Pa.s (E = 0.9 kV/mm) in marlotherm-s, silicone oil, mineral oil, DOP and TOTM respectively (Fig. 5). Different electric field strengths were taken to be constant due to electrical break-down occurred above those field strengths.

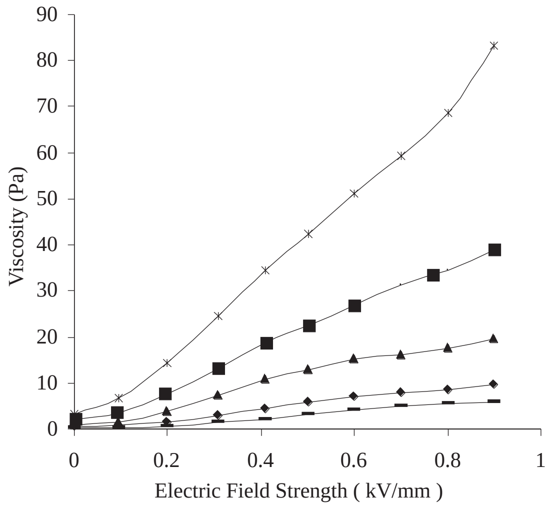

Figure 4. The electric field strength dependence of the viscosity of PP_y suspensions. c = 12.5 %, T = 20°C, $\dot{\gamma}$ (s^{-1}): (*) 0.1, (■) 2, (♦) 4, (♦)10, (–) 20, dispersion medium: TOTM

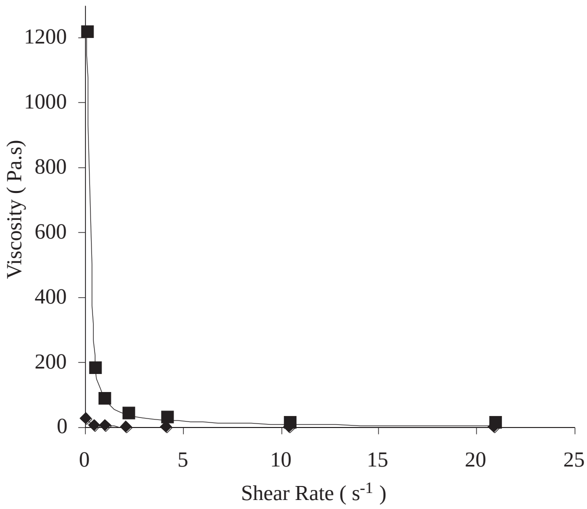

Figure 5. Change of viscosity of PP_y suspensions with shear rate. c =12.5 %, T = 20°C, E (kV/mm): (♦) 0, (■) 0.9, dispersion medium: TOTM

As seen in Fig. 5, under either E = 0 or E $\neq$ 0 conditions, the viscosity of the suspensions sharply decreases with increasing shear rate, giving a typical shear-thinning non-Newtonian visco-elastic curve[39].

These results are consistent with earlier studies of Tanaka and Graven, who carried out ER studies for polyaniline and magnesiumhydroxide suspensions prepared in silicone oil[39−42].

Effect of electric field strength on excess shear stress

Figure 6 represents the effect of electric field strength on excess shear stress ($\Delta\tau = \tau_{E\neq 0} - \tau_{E=0}$) which was obtained at constant suspension concentration (c = 12.5 %), shear rate ($\dot{\gamma}$ = 20 s^{-1}) and temperature (20°C) in the five insulating oils.

As seen in the graph, $\Delta\tau$ increased with the increasing electric field strength. The maximum and minimum $\Delta\tau$ were obtained as 45 Pa and 2 Pa for the PP_y suspensions prepared in silicone oil and marlotherm-s respectively.

Similar trends were reported by Trlica[8] for 1,3 butyleneglycoldimethylacrylate-butyl acrylate copolymer and by other researchers for zeolite and polyaniline particles, all of which were dispersed in silicone oil[9−13].

Effect of concentration on excess shear stress

In Fig. 7, the change in $\Delta\tau$ with suspension concentration is given at constant (E = 1kV/mm, $\dot{\gamma}$ = 0.1 s^{-1}, T = 20°C) conditions. As is evident from the graph, $\Delta\tau$ was observed to increase with increasing suspension concentration for all of the five suspensions prepared. This is due to the increased magnitude of polarization forces as the particle concentration was increased, which caused virtually an increase in the ER activity of suspensions. The highest $\Delta\tau$ (232) Pa was obtained in TOTM. Similar behavior was reported in the literature by a number of researchers for chitin and polyaniline suspensions prepared in silicone oil[12,38,39,42].

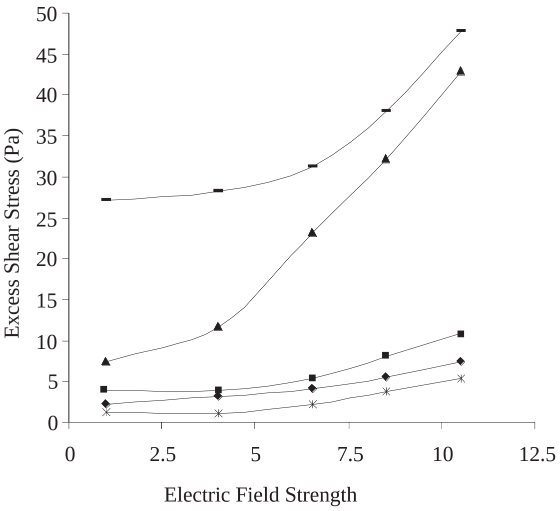

Figure 6. Excess shear stress as a function of field strength. $\dot{\gamma}$ = 20 s^{-1}, T = 20 °C and c=12.5%, Oils: (–) Silicone, (■) Mineral, (▲) TOTM, (♦) DOP, (*) Marlotherm-s

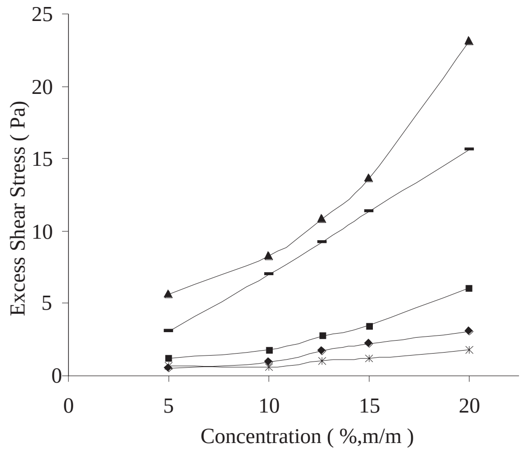

Figure 7. Change in $\Delta\tau$ with suspension concentration at constant E = 1kV/mm, $\dot{\gamma}$ = 0.1 s^{-1}, T = 20°C, Oils: (–) Silicone, (■) Mineral, (♦) TOTM, (♦) DOP, (*) Marlotherm-s.

Effect of temperature and promoter on ER activity

The effect of temperature on the ER activity of PP_y suspensions was studied at 20°C and 80°C at 12.5% optimum PPy concentration prepared in the five insulating oils, and no change was observed in their ER activities as the temperature was increased from 20°C to 80°C.

The variability of ER activity with moisture content is known to be also a major problem with most conventional ER fluids. Moisture content can limit their high temperature use and cause electrical breakdown at low field strengths. To investigate the effect of moisture on ER activity, PP_y suspensions were prepared in the five insulating oils at 12.5% optimum particle concentration. Glycerol, diethanolamine, ethanol, sodium lauril ether sulphate and distilled water were added to these suspensions at levels of a few ppm and no change was observed in their ER activities.

The observations that the polymer/insulating oil systems investigated in the present study are not affected by either high temperature or moisture may prove to be particularly important from an application standpoint[28].

Conclusions

From Gouy balance measurements, PPy was found to have a bipolaron conducting mechanism. It was observed that particle size is an important parameter for suspensions to be ER active. The maximum colloidal stability (71 days) was obtained in TOTM. The ER activity of the PPy suspension was observed to increase with increasing concentration up to 12.5%, and then decrease. The ER activity was also observed to increase with increasing electric field strength and decrease with increasing shear rate. The maximum ER activity (1.2 kPa) was obtained at a 12.5% suspension concentration in TOTM. It was also observed that

PPy suspensions were insensitive to moisture and high temperature within the limits examined, which are very important properties from an industrial point of view.

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