Electrorheological Properties of Suspensions Prepared from Polystyrene-*Block*- Polyisoprene Copolymer

Mustafa YAVUZ
Süleyman Demirel University, Science and Arts Faculty,
Chemistry Department, 32200 Isparta-TURKEY
Halil İbrahim ÜNAL, Yılmaz YILDIRIR
Gazi University, Science and Arts Faculty,
Chemistry Department, 06500 Teknikokullar, Ankara-TURKEY

Considerable scientific and industrial interest is currently being focused on a class of materials known as electrorheological (ER) fluids, which display remarkable rheological behaviour, being able to convert rapidly and repeatedly from a liquid to solid when an electric field (E) is applied or removed. In this article, the synthesis, characterization, partial hydrolysis and ER properties of polystyrene-*block*-polyisoprene copolymer (COP) were investigated. The block copolymer was characterized by GPC, viscosity measurements, ^{1}H-NMR and FTIR spectroscopies, particle size measurements, and elemental analysis. The polystyrene block of the copolymer was partially hydrolyzed by a series of chemical reactions and then converted to a lithium salt by washing with a lithium hydroxide solution. Colloidal suspensions of this polymeric salt were prepared in silicone oil, at a series of concentrations (5-33% m/m). Colloidal stabilities of these suspensions were determined at 20°C and 80°C. Flow times of suspensions were measured under no electric field ($E = 0$), and under an applied electric field ($E \neq 0$), and ER activity was observed. Further, the effects of solid particle concentration, shear rate ($\dot{\gamma}$), electric field strength, addition of a polar promoter and high temperature on ER activities of colloidal suspensions were investigated, and excess shear stresses were determined.

Key Words: Electrorheological fluids, polystyrene-*block*-polyisoprene copolymer, colloidal dispersions

Introduction

The term rheology refers to the deformation and flow of matter[1]. The phenomenon of electrorheology was first reported by Winslow[2] in 1947. It is concerned with the influence of electric field on the rheology of fluid dispersions, and manifests itself in an increase of resistance to flow and, in some cases, the conversion of fluid to a solid. Important factors influencing the phenomenon are field strength, field frequency, shear rate, temperature and fluid composition.

The number of investigations on ER fluids increased dramatically in the 1980s[3,4] and these have recently been reviewed in numerous publications[4,5]. Surprisingly few investigations, however, have attempted to probe the colloid chemistry of the ER fluids.

ER fluids can contain suspensions of polar particles in insulating liquids at solid volume fractions ranging from 5 to 50%[6,7]. In order to achieve a large ER response relative to that of zero-field suspensions, one desires a stable suspension at a moderate concentration. Maintaining colloidal stability over long periods of time through a variety of environmental conditions is one of the challenges in ER fluid design. Many researchers in the field of ER have proposed scenarios for the development of ER effect[8]. It is generally agreed that the initial step in the development of ER involves polarization under an applied electric field. This then introduces some form of interaction between particles, or between particles and the impressed electric or shear field, which results in the rheological manifestations of the effect[8]. ER fluids have considerable potential use in hydraulic control fluids, vibration damping systems, robotics, couplings and automotive applications (i.e., electronically controlled shock absorbers, engine mounts, clutches, brakes, alternators, power steering pumps, control valves and artificial joints)[9,10]. The attractive features of the fluids for pratical applications are the speed and reversibility of the liquid-to-solid and solid-to-liquid transitions[9]. Despite potential application fields, there are currently no commercially available ER devices, due largely to a lack of suitable fluids. A major limiting factor is still the need for fluids with better overall performance. In some applications there is a particular requirement for fluids with low zero-field viscosity ($\eta_{E=0}$), stability against sedimentation and sludge deposit formation, and long service stability, particularly at high temperatures. There is also a need for fluids which are non-corrosive, non-abrasive and non-toxic[11]. Previously we have studied the ER properties of the poly(t-butylacrylate-*stat*-lithiumacrylate)-*block*-polyisoprene copolymer system in pentaerythritol heptanoate insulating oil, which formed a micellar colloidal system and showed stronger ER activity, and greater colloidal stability than the conventional ER fluids, and its activity was found to be insensitive to the presence of trace moisture[12,13].

In the present study, promoter-free ER suspensions were prepared from lithium salt of a polystyrene-*block*-polyisoprene copolymer (COPLi) system in insulating silicone oil. The polymer was chosen for the study because it could be expected to associate in solution to form micellar particles having a core of poly(p-caboxylithiumstyrene) block and an outer flexible fringe of polyisoprene block. The present investigation was undertaken to provide additional information on the ER properties of block copolymers, which are not sufficiently studied in the literature. Attention is given to: (a) partial hydrolysis and salt formation of polystyrene block; (b) colloidal stability of suspensions; (c) electrical properties of suspensions; (d) the effects of amounts of polymeric particles and moisture and high temperature conditions.

Experimental

Materials

Isoprene (BDH) was stirred in the dark with crushed CaH_2 under nitrogen atmosphere for 96 h, and then vacuum distilled into a breakseal ampoule from its living polymer solution initiated with n-butyllithium[14].

Styrene (BDH) was also stirred in the dark with crushed CaH_2 under nitrogen atmosphere for 96 h, and then vacuum distilled into a breakseal ampoule from its living polymer solution initiated via a sodium mirror[15].

n-Butyllithium (Aldrich) was obtained in hexane solution ($c = 1.4$ mol/dm^3); the precise concentration was determined before polymerisation by the method of Gilman and Haubein[16].

Tetrahydrofurane (THF, Merck) purification was performed in the polymerization vessel by distill-

ing the solvent from a solution of living polymer.

All other chemicals (Aldrich analar grade) were used as received.

Polymerization

Block copolymer was prepared by sequential anionic polymerization with THF as solvent and n-butyl lithium as initiator, utilizing vacuum-line techniques, which have been fully described elsewhere[17−19], and the resulting polymer was precipitated in excess methanol and recovered with 100% yield.

Fractionation

GPC analysis showed the main peaks which could be attributed to the polystyrene-*block*-polyisoprene block copolymer and the minor peaks to homopolystyrene. Homopolystyrene was removed from the copolymer by liquid/liquid fractionation using toluene/methanol as the solvent/non-solvent system at 20°C.

Characterization of the block copolymer

Gel permeation chromatography (GPC) was carried out at 25°C with THF as solvent at a flow rate of 1 cm^3/min using four μ-styragel columns (nominal pore size 10^6, 10^4 10^3 and 500 A°) and a Waters 401 differential refractometer detector.

The FTIR spectrum of the block copolymer was recorded using a Mattson Model 1000 FTIR spectrometer. Samples were analyzed as films cast from dichloromethane onto a sodium chloride plate.

Intrinsic viscosity measurements were made in toluene using a Ubbelohde capillary flow viscometer mounted in a water bath maintained at 25.00°C ± 0.01°C.

Elemental analysis was performed by the Scientific and Technical Research Council of Turkey (TUBITAK) Microanalytical Laboratory, and the results were used as a check for purity by comparison with the calculated composition.

^{1}H-NMR spectrum was obtained in $CDCl_3$ at a concentration of 0.2 g/cm^3 at room temperature using a 400 MHz Bruker 400 DPX Avonce Nuclear Magnetic Resonance Spectrometer at the TUBITAK research laboratory.

Hydrolysis of the block copolymer

To form ER active material from the copolymer of styrene and isoprene, the styrene block needs to be partially hydrolyzed to carboxylic acid units and converted to the lithium salt. The reaction mechanism for the partial hydrolysis of the copolymer and the formation of lithium salt are described in scheme 1.

Characterization of the polymeric salt

Elemental analysis of the polymeric salt was also performed by the TUBITAK Microanalytical Laboratory, and the results were used as a check for the degree of hydrolysis and percentage conversion to the lithium salt.

The particle size of the samples was 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 Fraunhafer diffraction theory[20]. The average diameter of particles was determined to be 56 μm.
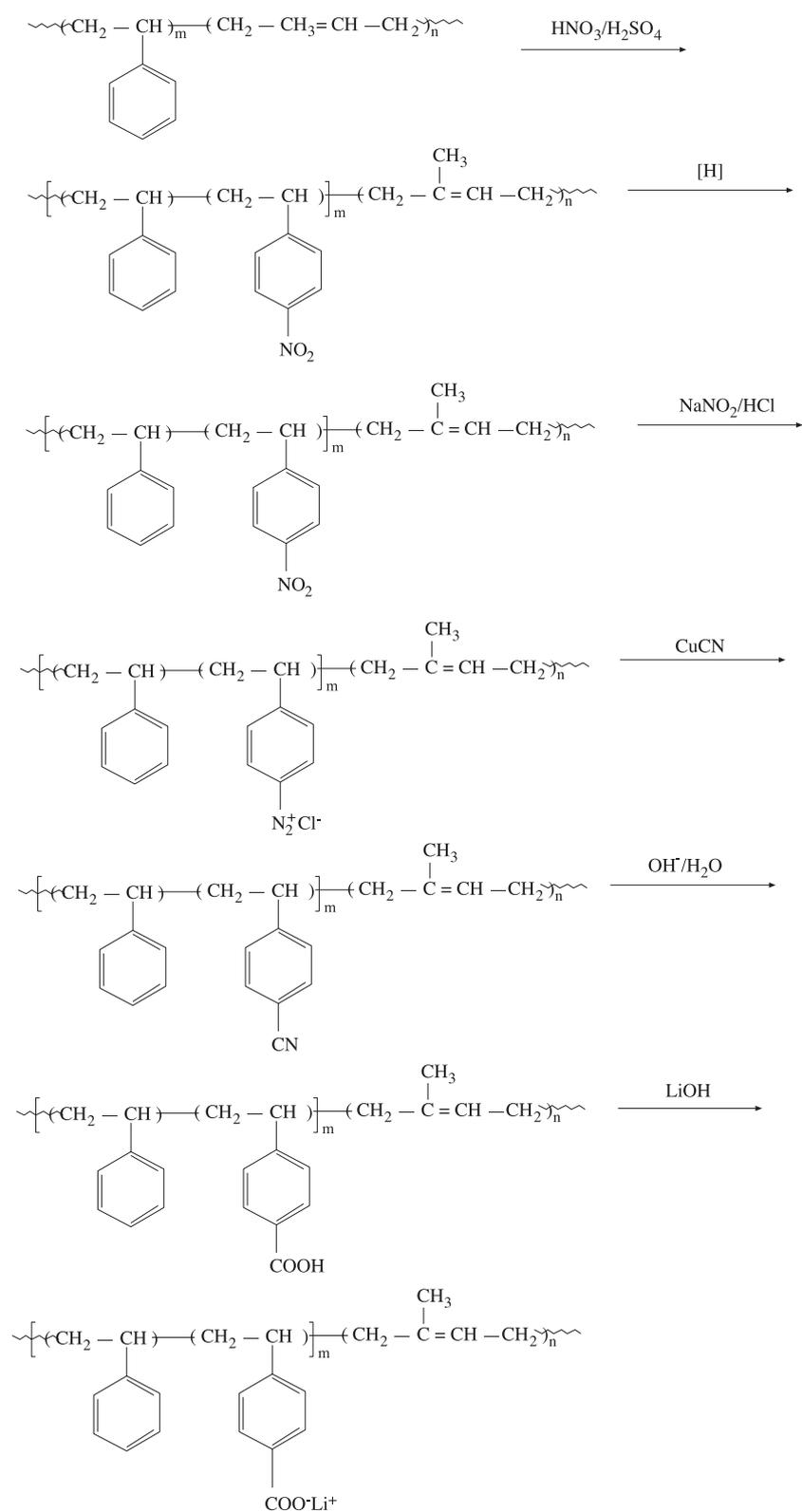
Scheme 1. Partial hydrolysis and salt formation reaction mechanism.

Preparation of suspensions

Colloidal suspensions of the polymeric salt (COPLi) were prepared in silicone oil, at a series of concentrations (5-33 m/m%), by dispersing a definite amount of polymeric salt in a calculated amount of silicone oil, according to the formula

$$(m/m\%) = [m_{\text{polymer}}/(m_{\text{polymer}} + m_{\text{oil}})] \times 100$$

Determination of colloidal stability of COPLi

The colloidal stability of suspensions prepared in silicone oil at 5-33 (m/m%) concentrations was determined at constant temperatures of 20°C and 80°C. Glass tubes containing the suspensions were immersed in a constant temperature water bath and the formation of first precipitates was taken to be the indication of colloidal instability.

Rheometry

Rheological experiments were carried out for the suspensions prepared in silicone oil, for the experimental determination of flow behaviour and viscoelastic material properties which influence processing technology and the polymer's stability and consistency. Flow rate measurements were carried out between two brass electrodes, as illustrated in Figure 1. The gap between the electrodes was 0.5 cm, the width of the electrodes was 1 cm and the height of liquid on the electrodes was 5 cm. During the measurements these electrodes were connected to a high voltage dc electric source and a voltmeter.
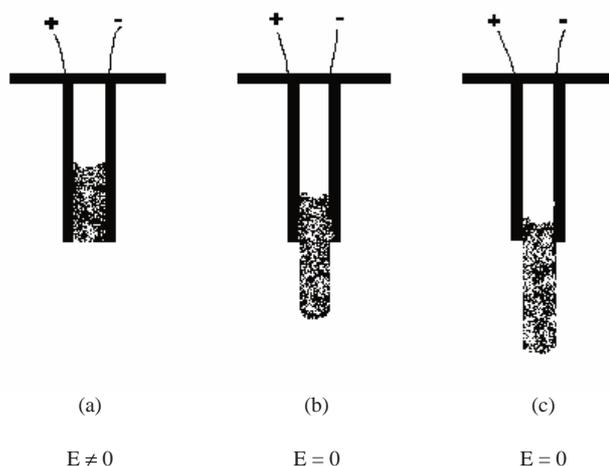

Figure 1. Apparatus used to study the effect of d.c. electric field on flow behaviour. (a) fluid retained when electric field is applied; (b) and (c) show flow occurring after field was switched off.

At the beginning of the experiment, the electrodes were dipped into a vessel containing the ER fluid and after a few seconds the vessel was removed and the flow time for complete drainage measured using a digital stopwatch. At the second stage, the electrodes were again dipped into the same vessel containing the ER fluid and the high voltage applied above the yield point. After several seconds the vessel was removed

and the flow time for complete drainage measured under the applied electric field ($E \neq 0$). This procedure was repeated for each ER fluid concentration under various field strengths. Flow rate measurements were undertaken at 20°C and 80°C for the COPLi/silicone oil system. For flow between parallel plate electrodes, the flow time, t, for volume V of fluid is related to the viscosity, η, of the fluid by the relation

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

where ρ is the density of the fluid, g is the gravitational constant, d is the separation distance of the plates and b is the width of the plates. 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 calculated from the relation

$$\dot{\gamma} = 3V/bd^2 t \tag{2}$$

Rotational viscometry was carried out at two different temperatures, 20°C and 80°C. The shear rates used were relatively low (0.1-20 s^{-1}), due to instrumental limitations. To measure the viscosity of a liquid, a spindle was simply immersed in the liquid container, the motor was switched on and the viscosity was read on the calibrated dial of the instrument. For measuring the viscosity of suspensions under an applied electric field, those parallel plate electrodes were immersed into the fluid container, keeping the 5 mm gap between the brass electrodes constant, an electric field was created in the fluid and the spindle was forced to rotate. The voltage used was supplied by a 0-10 kV (with 0.5 kV increments) dc electric field generator, which enabled resistivity to be created during the experiments.

Results and Discussion

Characterization

The block copolymer (COP) was partially hydrolyzed (COPH) and converted to the lithium salt (COPLi). Characterization of the COP and COPLi is discussed below.

From GPC chromatograms, polystyrene equivalent number average molar masses of polystyrene precursor and the COP were determined to be 45,000 g/mol and 60,000 g/mol respectively.

Intrinsic viscosities of COP and COPLi were determined by extrapolating to infinite dilution from plots of $\ln\eta_r/c$ and η_{sp}/c against concentration and were found to be 0.52 dm^3/g and 0.25 dm^3/g respectively. It was observed that the polymeric salt reached a lower zero-field viscosity after partial hydrolysis and salt formation.

The data obtained from the ^{1}H-NMR spectrum of COP contained peaks that can be assigned to polystyrene and polyisoprene blocks. Chemical shifts of particular groups in COP are given in Table 1, in view of the structure given in scheme 2, although ^{1}H-NMR data contained peaks corresponding to both 1,4 and 3,4 additions.

Table 1. Chemical shifts obtained for COP by ^{1}H-NMR spectroscopy in CDCl₃.

Assignment	Chemical shifts (δ, ppm)
-C$\underline{H}_3$ (isoprene)	1.6, s
-C$\underline{H}_2$ (isoprene)	2.1, m
-C$\underline{H}$ (isoprene)	5.2, t
-C$\underline{H}_2$ (isoprene-3,4 add.)	4.7-4.8, dd
Ar-$\underline{H}$	6.8-7.1, b
C$\underline{H}_2$ (styrene)	2.1, m
C$\underline{H}$ (styrene)	2.3, m

s: singlet, m: multiplet, t: triplet, b: broad, d: doublet
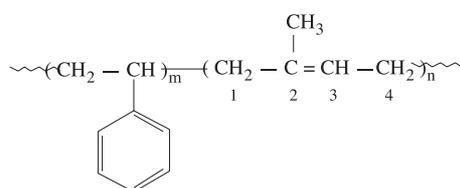
Scheme 2. Structure of unhydrolyzed copolymer (COP)

where, $m = 432$ and $n = 220$

As seen in scheme 2, 1,4 addition product of vinyl hydrogenes at C_3 was spin-spin coupled with methylene at C_4 and gave a triplet peak at 5.2 ppm and methylene hydrogenes at C_4 (sp^3) gave a multiplet peak at 2.1 ppm. Beside these data, peaks corresponding to 3,4 addition was also observed for isoprene at 4.7-4.8 belon ppm ging to methylene hydrogenes.

The FTIR spectrum of COP showed the expected distinctive absorptions. The absorptions at 1600 cm^{-1}, 2900 cm^{-1}, 3100 cm^{-1} and 1400 cm^{-1} are typical of vinyl C=C, aliphatic C−H, aromatic C−H stretchings and C−H bending due to CH₃ absorptions respectively. COPLi also gave a FTIR spectrum similar to that of COP.

The experimental and calculated composition obtained from elemental analysis for the COP and COPLi are shown in Table 2. As shown in the table, the measured composition agrees very well with the calculated values. The partially hydrolyzed block copolymer (COPH) and its Li-salt (COPLi) are assumed to have the chemical structures given in schemes 3 and 4 respectively.

Table 2. Elemental analysis results of COP and COPLi.

		C (%)	H (%)	O (%)	Li (%)
COP	Calculated	89.2	10.8	-	-
	Found	87.6	12.3	-	-
COPLi	Calculated	86.0	9.6	3.6	0.8
	Found	88.7	8.3	2.2	0.5
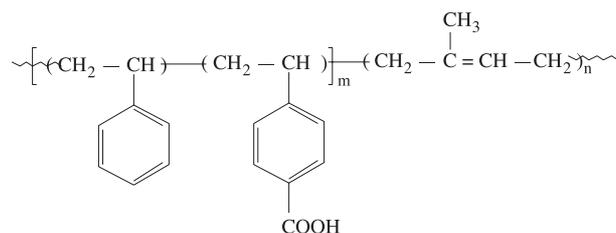
Scheme 3. Structure of partially hydrolyzed copolymer (COP)
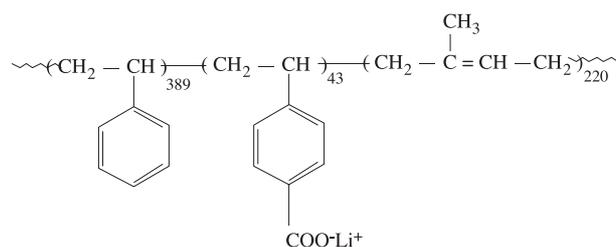
Scheme 4. Structure of Li-salt of copolymer (COPLi)

It was shown by the elemental analysis results that the amount of Li in COPLi was approximately 0.5% within the experimental error.

Colloidal stability of COPLi

The colloidal stability of COPLi was determined in insulating silicone oil at 20°C and 80°C, before ER measurements were carried out, and the results are shown in Table 3. The colloidal stability of suspensions decreased with increasing particle concentration, and remained almost constant with increasing temperature. Maximum colloidal stability was found to be 52 days at 5% suspension concentration.

Table 3. Colloidal stability of COPLi, in silicone oil. Concentration (m/m%)

Concentration (m/m)	5	5	10	10	15	15	20	20	25	25	33	33
Temperature (°C)	20	80	20	80	20	80	20	80	20	80	20	80
Colloidal stability (days)	42	52	34	36	22	24	18	20	16	19	15	17

Electrorheology

Results obtained from parallel plate electrodes: Flow times of COPLi suspensions, prepared in silicone oil at the range of 5 to 33% concentrations, measured between the parallel plate electrodes at the zero applied field ($E = 0$) and under various applied electric field strengths ($E = 0 - 2$ kV/mm), are shown in Figure 2.
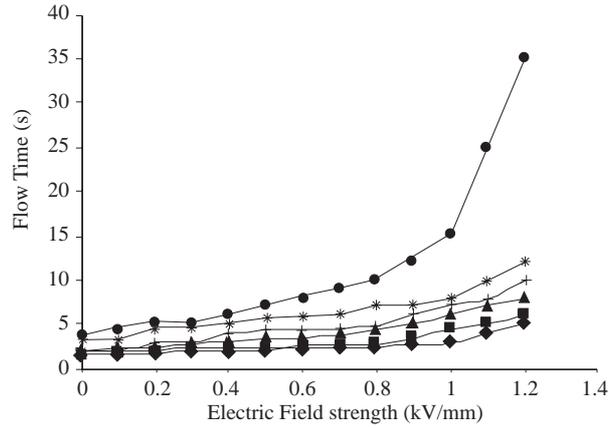
Figure 2. The change of flow time with electric field strength. c (m/m%): (♦) 5, (■) 10, (▲) 15, (+) 20, (∗) 25, (●) 33

The flow times of suspensions increased with increasing electric field strength and suspension concentration. The highest flow time (37 seconds) was obtained from a 33% suspension concentration at $E = 1.2$ kV/mm. The flow times illustrated in Figure 2 are the maximum flow times which could be measured under 1.2 kV/mm applied electric field strength. When the applied electric field strength was further increased, the flow of the liquid between the electrodes was completely stopped and the measurement could not be taken even after waiting 24 h.

Results obtained from rotational viscometry

Effect of particle concentration: Figure 3 shows the change in electric field viscosity $(\eta_{E\neq0})$/zero field viscosity $(\eta_{E=0})$ with suspension concentratio of COPLi particles dispersed in silicone oil at various shear rates $(\dot{\gamma} = 0.01 - 20)$ s^{-1}. Up to a 20% particle concentration, the viscosity ratio increases with increasing particle concentration. This trend is due to the polarization forces acting between the ionic particles. The magnitude of this polarization force (F) in the direction of applied electric field (E) is[21]

$$F = 6\epsilon_2.r^6.E^2/\rho^4 \quad (3)$$

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 shown by this from equation, an increased suspension concentration will decrease the distance between the particles, which will result in an increased polarization force. When the particle concentration further increases above 20%, $\eta_{E\neq0}/\eta_{E=0}$ decreases with increasing particle concentration. This may be attributed the to following reasons:

(i) At higher suspension concentrations, particles are close to each other and the electric double layers around particles overlap.

(ii) The mutual action between particles increases, and the electric double layers may drop out of particles.

(iii) As a result, suspension's electric field viscosity, in other words ER effect, decreases. The ER effect was also observed to increase with decreasing shear rate.
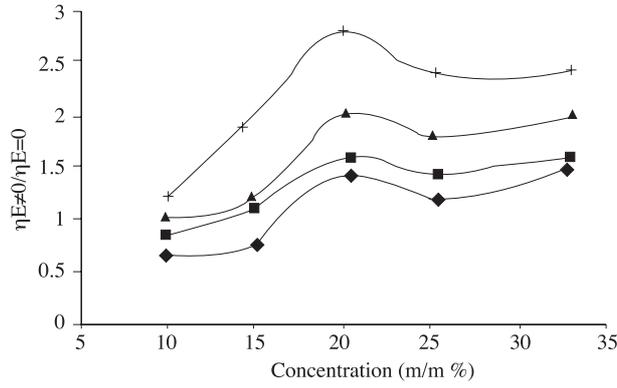
Figure 3. The change in viscosity with concentration, $T = 20°C$ and $E = 0\text{-}500$ V/mm. $\dot{\gamma}$ (s^{-1}): (+) 2, (▲) 4, (■) 10, (♦) 20

Effects of electric field strength and shear rate: Electric field strength against viscosity obtained at 20% optimum particle concentration is shown in Figure 4. The following conclusions may be drawn:

(1) ER activity of suspensions increases with increasing field strength.

(2) Effect of field strength is larger at low shear rates and smaller at high shear rates.

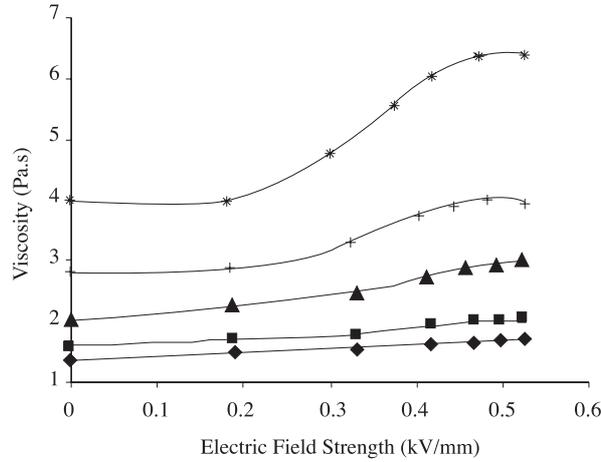(3) ER activity of suspensions increases with decreasing shear rates.

Figure 4. The change of viscosity with electric field strength. $T = 20°C$ and $c = 20\%$. (s^{-1}): (*) 1, (+) 2, (▲) 4, (■) 10, (♦) 20

When electric field was applied to the suspensions, the polarization forces caused the aggregation of particles, and fibril (or chain) formation between the electrodes occurred. This structural skeleton is across the direction of the shear field and leads to increased viscosity. Under an applied shearing force, particles are also acted on by the effects of viscous forces, which is due to the hydrodynamic interactions of particles in the suspension. The magnitude of these viscous forces is[22]

$$F = 6\pi.\eta.\dot{\gamma}^6. \tag{4}$$

Where η_s is the viscosity of suspension, r is the radius of particle, and $\dot{\gamma}$ is the average shear rate.

At higher shear rates, the suspension viscosity almost becomes independent of the applied electric field strength. It may be concluded that, at higher shear rates, the viscous forces are dominant, and the fibrillar structure of the suspension does not vary appreciably with field strength.

Change in shear stress with electric field strength: Figure 5 represents the change in excess shear stress with electric field strength which was obtained at constant suspension concentration ($c = 20\%$), shear rate ($\dot{\gamma} = 20 \text{ s}^{-1}$) and temperature ($T = 20°\text{C}$). As reflected from the graph, excess shear stress sharply increases with increasing field strength, which indicates that the ER suspension becomes more stable under a strong electric field strength. Similar results were observed in ER studies of water doped microcrystalline cellulose dispersed in mineral oil, by Foulc and Atten[23].
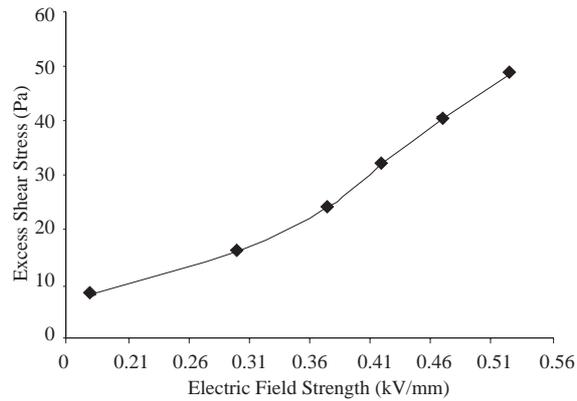

Figure 5. The change in excess shear stress with electric field strength. $\dot{\gamma} = 20 \text{ s}^{-1}$, $T = 20°\text{C}$ and $c = 20\%$.

Change in shear stress with concentration: The effect of suspension concentration on the excess shear stress was studied at constant shear rate. ($\dot{\gamma} = 20 \text{ s}^{-1}$), temperature ($T = 20°\text{C}$) and electric field ($E = 0\text{-}1 \text{ kV/mm}$) conditions. It is seen in Figure 6 that excess shear stress increases with increasing particle concentration. This due is to the increased polarization forces as the particle concentration was increased, which results in increased ER activity. A similar trend was observed by Wu and Shen in ER studies of chitin and chitosan suspensions prepared in silicone oil[21].
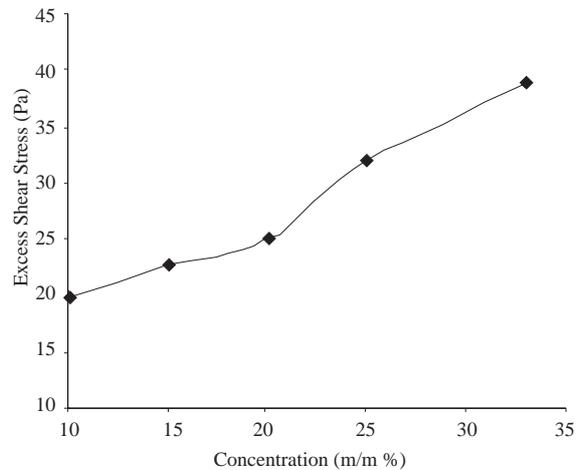

Figure 6. The change in excess shear stress with concentration. $\dot{\gamma} = 20 \text{ s}^{-1}$, $T = 20°\text{C}$ and $E = 0\text{-}1 \text{ kV/mm}$.

Change in viscosity with shear rate: Change in the viscosity of the suspension with shear rate at optimum suspension concentration (20%) is shown in Figure 7. As is evident, with and without applied electric field, the viscosity of suspensions decreases sharply with increasing shear rate, giving a typical curve of shear thinning non-Newtonian[24] viscoelastic behaviour. Similar results were reported for studies of polyaniline and magnesium hydroxide solutions prepared in silicone oil[25,26].
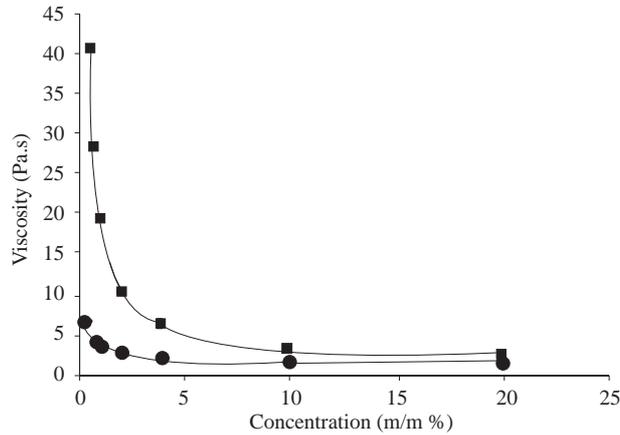

Figure 7. The change in viscosity with shear rate. $T = 20°C$ and $c = 20\%$. E (kV/mm): (●) 0, (■) 1.

Effect of temperature and promoter on ER activity: ER activity of suspensions prepared at optimum concentration was measured at two different temperatures (20°C and 80°C) and the results are shown in Table 4. The viscosity of suspensions was found to slightly decrease at high shear rates as the temperature was increased from 20°C to 80°C ($\dot{\gamma} = 20$, 10, 4, 1, and 0.2 s^{-1}) and high temperature had no effect at low shear rates within the experimental error.

Table 4. Effect of temperature on ER activity of COPLi COPLi

COPLi $c = 20$ (m/m%)		
$\dot{\gamma}$ ((s^{-1})	η (Pa.s) 20°C	η (Pa.s) 80°C
20	0.68	0.40
10	0.72	0.48
4	0.80	0.60
1	0.80	0.80
0,8	1.00	1.00
0,4	2.00	2.00
0,2	4.00	4.00

The influence of moisture on the ER activity was also investigated by adding polar solvents (i.e., water, ethanol, ethanolamine, glycerol and sodiumlaurilsulphate) at 5 ppm concentrations into COPLi suspensions at optimum concentration (20%). It was observed that the copolymer system studied in the present work was not sensitive to the amount of moisture present over the range studied. The most likely explanation is that the inherent polarizability of the ionic cores was sufficient to outweigh the effect of any adsorbed moisture. The ability of micelles to strongly couple mechanically via interpenetrating miceller fringes could also be a significant factor.

The variability of ER activity with temperature and moisture content is known to be a major problem with most conventional ER fluids[25] and can limit their high temperature use. The observation that the copolymer system investigated in the present work is not affected by the addition of promoter and high temperature could prove particularly important from an application standpoint.

Conclusions

1. We have shown that the polystyrene block of COP can be partially hydrolyzed and converted to the Li salt by approximately 0.5%.

2. Colloidal stability of polymeric salt in silicone oil was found to be 52 days at 5% suspensions concentration.

3. Flow time of suspensions was observed to increase with increasing electric field strength and suspension concentration. The highest flow time (37 seconds) was obtained from 33% suspension concentration at $E = 1.2$ kV/mm.

4. The viscosity ratio $\eta_{E \neq 0}/\eta_{E=0}$ was found to increase up to 20% suspension concentration and then decrease.

5. ER activity of suspensions was observed to increase with increasing field strength and decreasing shear rate.

6. Excess shear stress was found to sharply increase with increasing field strength and suspension concentration.

7. It was observed that the viscosity of suspensions decreased sharply with increasing shear rate, causing typical shear-thinning non-Newtonian viscoelastic behaviour.

8. It was found that the copolymeric salt system studied in the present work was insensitive to high temperature and moisture within the limits studied.

Acknowledgement

References

1. H.A. Barnes, J.F. Button and K. Walters, **An Introduction to Rheology,** Elsevier, New York, 1989.

2. M.W. Winslow, **J. Appl. Phys. 20,** 1137 (1949).

3. H. Block, in **Polymers in Solution,** Ed. W.C. Forsman, Plenum Press, New York, 1986.

4. H. Block and J.P. Kelly, **J. Phys. D: Appl. Phys., 21,** 1661 (1988).

5. A.P. Gast and C.F. Zukoski, **Ad. Coll. Int. Sci., 30,** 153 (1989).

6. T.C. Hasley and W. Torr, **Physical Review Letters, 65,** 2820 (1990).

7. V.B. Russel, D.A. Saville and W.R. Schowalter, **Colloidal Dispersions,** Cambridge University Press, Cambridge, 1989.

8. K.M. Blackwood, H. Block, P. Rattray, G. Tsangaris and D.N. Vorobiev., **"The polarization, Structuring and Rheology of ER Fluids" in Electrorheological Fluids: Mechanisms, Properties, Technology and Applications,** Eds. R. Tao and G.D. Roy, World Scientific Publishing Co, London, 1994.

9. Hartsock, D.L., Novak, R.F., and Chaundy, G.J., **J. Rheol. 35,** 1305 (1991).

10. **Electrorheological Fluids: Mechanisms, Properties, Technology and Applications,** Eds. R. Tao and G.D. Roy, World Scientific Publishing Co, London, 1994. Chapter 4.

11. P.J. Rankin and D.J. Klingenberg, **J. of Rheol. 42(3),** 639 (1998).

12. H.I. Unal, **Ph.D. Thesis**, Manchester University (1993).

13. H.I. Unal, **J. Fac. Of Eng. and Arch., Gazi Univ. 9(2),** 69 (1994).

14. H. Kimura, K. Aikawa, Y. Masubuchi, J. Takimoto, K. Kayama, T. Uemura, **J. Non-Newtonian Fluids Mechanics, 76,** 199 (1998).

15. S. Wu, S. Lu and J. Shen, **Polymer International, 41,** 363 (1996).

16. H. Gilman and A. H. Haubein, **J. Am. Chem. Soc. 66,** 1515 (1944).

17. M. Swarc, **Nature, 178,** 1168 (1956).

18. M. Swarc, **Carbanions, Living Polymers and Electron Transfer Process,** Wiley, London, 1968.

19. N. P. Briggs, **Ph.D. Thesis,** Manchester University (1988).

20. J.F. Watts and T.J. Carney, **Powder Metallurgy-An Overview, The Institute of Materials,** London, U.K., 1991, pp. 28-81.

21. V.I. Bezruk, A.N. Lazarev, V.A. Malov and O.G. Usyarov, **Coll. J., 34,** 142 (1972).

22. S.Wu and J. Shen, **J. Appl. Polym. Sci. 60,** 2159 (1996).

23. J.N. Foulc, and P. Atten, **"Experimental Study of Yield Stress in Electrorheological Fluids", in Electrorheological Fluids: Mechanisms, Properties, Technology and Applications,** Eds. R. Tao and G.D. Roy, World Scientific Publishing Co, London, 1994, pp. 358-371.

24. K.D. Weiss and T.G. Duclos, **"Controllable Fluids: The temperature dependence of post-yield properties" in Electrorheological Fluids: Mechanisms, Properties, Technology and Applications,** Eds. R. Tao and G.D. Roy, World Scientific Publishing Co, London, 1994, pp. 43-59.

25. K. Tanaka and Y. Orwa, **Polymer Journal, 30 (3),** 171 (1998).

26. H.P. Garvin, **J. Non-Newtonian Fluid Mechanics, 71,** 165 (1997).