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Study on electrorheological properties of novel polymer-Ce^{4+} complex

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A new polymer containing bithiazole ring and *p*-aminobenzoic acid was first synthesized using 2,2′-diamino-4,4′- bithiazole with paraformaldehyde and *p*-aminobenzoic acid. The polymer –Ce^{4+} complex was prepared from the polymer and $CeCl_4$ in DMSO. The electrorheological suspensions were prepared by the polymer-Ce^{4+} powder and bromodiphenylmethane. Under external electric field, the yield stress and dielectric constant of ER fluid were measured. The results showed that the polymer-Ce^{4+} complex ER fluid has higher dielectric properties, exhibits much stronger ER effect than pure the polymer under our experimental conditions.

1. Introduction

In general, electrorheological fluids (ERF) are 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 drastic increase in apparent viscosity [1, 2] which is also reversible when subjected to the application and removal of an electric field [3, 4]. Various kinds of ER materials including hydrous materials such as corn starch, cellulose and mesoporous particles with small amounts of absorbed water [5, 6] have been investigated. Semiconducting polymers, biopolymer, and polymer/clay nanocomposite systems [7–9], anhydrous ER material have drawn much attention because of their important thermal stability in engineering applications such as dampers and brake systems etc [10].

In this paper, we present a novel anhydrous ER system consisting of the polymer-Ce^{4+} complex material suspended in bromodiphenylmethane. Several other key physical properties of the polymer-Ce^{4+} complex were also measured by FTIR spectroscopy and thermogravimetric analysis (TGA). ER properties of the polymer-Ce^{4+} complex suspensions were investigated as a function of applied electric field and the polymer-Ce^{4+} complex particles concentration. The dielectric properties and conductivity of the ER fluid were discussed.

2. Experimental

The polymer was synthesized from 2,2′-diamino-4,4′-bithiazole [11] condensed with paraformaldehyde and *p*-aminobenzoic acid. A mixture of *p*-aminobenzoic acid and 2,2′-diamino-4,4′-bithiazole with paraformaldehyde in the ratio 1:1:1 was incubated in the presence of 2 mol L^{-1} HC1 as catalyst at 100°C for 8 h. A brown precipitate was formed and filtered, washed successively with water, ethanol and ether, and dried under vacuum at 60°C for 48 h.

The polymer-Ce^{4+} complex was prepared from the polymer and $CeCl_4$ in DMSO at room temperature under purified nitrogen atmosphere for 7 days. The polymer-Ce^{4+} complex was filtered off, washed successively with ethanol and ether, and then the precipitated complex was soaked in ethanol for 24 h. The complex was isolated by filtration and dried under vacuum for 48 h.

The polymer: yield 91%; IR (KBr, cm^{-1}): 3680–3200 (broad, s), 3190–2500 (broad, s), 1623 (s), 1523 (s), 1438 (s), 1374 (s), 1298 (s), 1218 (m), 1090 (m), 875 (m), 667 (m).

The polymer- Ce^{4+}: yield 38%; IR (KBr, cm^{-1}): 3680–3212 cm^{-1} (broad, s), 3190–2506 cm^{-1} (broad, m), 1635 cm^{-1} (s), 1531 cm^{-1} (s), 1442 cm^{-1} (s), 1379 cm^{-1} (s), 1308 cm^{-1} (s), 1223 cm^{-1} (m), 1085 cm^{-1} (m), 874 cm^{-1} (m), 669 cm^{-1} (m).

The thermogravimetric analysis was performed with a WRT-3 thermal analyzer at a heating rate of 10°C-min^{-1}

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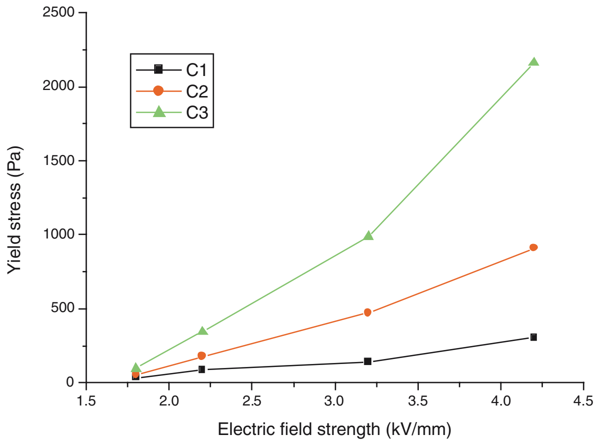

Figure 1 Variation of yield stress with electric field strengths for pure polymer ER fluid (Cl = 10, C2 = 15, C3 = 20 wt%).

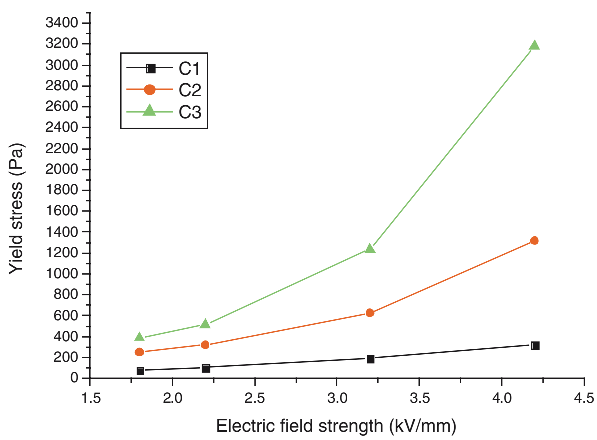

Figure 2 Variation of yield stress with electric field strengths for polymer-Ce^{4+} complex ER fluid (Cl = 10, C2 = 15, C3 = 20 wt%).

in nitrogen gas. Results indicated that decompositions of the pure polymer and the polymer-Ce^{4+} complex occurred at about 300°C.

Using bromodiphenylmethane (density: 1.45×10^3 kg m^{-3}, viscosity: 1.5×10^{-2} Pa s, 20°C) as disperse medium, ER fluids with different composition (10, 15, 20 wt% of the polymer or the polymer-Ce^{4+} complex in the disperse medium) were prepared by suspending the polymer particles in disperse medium using a mechanical stirrer (1200–1500 rpm). The theological properties were measured with a Couette-type rheometer manufactured by Haake (Germany). This rheometer has been modified so that a DC electric fields E of 0–5 kV mm^{-1} can be applied across the gap during shearing measurements. The results were shown in Fig. 1–4.

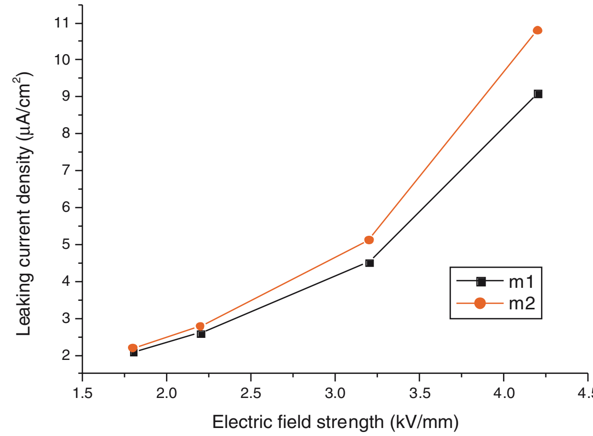

Figure 3 Variation of the leakage current density with electric field strengths for 20 wt% ER fluids (m1: pure polymer, m2: polymer-Ce^{4+} complex) (20°C).

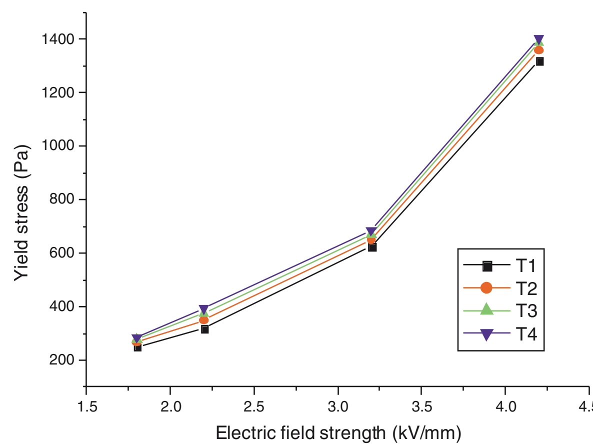

Figure 4 Variation of yield stress with electric field strengths for 15 wt%polymer-Ce^{4+} complex ER fluid at different temperature (T1 = 20°C, T2 = 40°C, T3 = 60°C, T4 = 80°C).

Because of the difficulty of directly measuring the dielectric properties of the polymer particles, we used the polymer suspensions for the measurements. Having considered the influence of the particle arrangement induced by an external electric field on the dielectric property [12, 13], we kept the ER fluids in a randomly dispersed system whose structure would not be disturbed by the bias field of 4.2 kV/mm to make a reasonable comparison for two materials. The dielectric properties of suspensions were measured by an automatic LCR meter (WK-4225, Germany) at the frequency of 10^2, 10^3, and 10^4 Hz, respectively. The results were shown in Table I.

TABLE I Dielectric properties of polymer ER fluids (C = 20 wt%)

	Dielectric constant		Dielectric loss tangent		Conductivity($\times 10^{-10}$ S/m)	
Frequency (Hz)	polymer	polymer-Ce^{4+}	polymer	polymer-Ce^{4+}	polymer	polymer-Ce^{4+}
10^2	4.86	6.97	0.122	0.196	10.5	21.8
10^3	4.07	5.35	0.079	0.147	32.2	75.5
10^4	3.78	4.65	0.038	0.081	186.3	432.1

3. Results and discussions

Fig. 1–2 shows the Theological characterization of the ER fluid prepared from 10 wt%, 15 wt% and 20 wt% suspension of the pure polymer and the polymer-Ce^{4+} complex in the bromodiphenylmethane at different electric field strengths, respectively. Results showed that yield stress increased with the increase in the polymer particles concentration and electric field strengths. The yield stress of 20 wt% the polymer-Ce^{4+} complex ER fluid was 9 times higher than that of 10 wt% at $E = 3.2$ kV m^{-1}. The yield stress of 20 wt% pure polymer ER fluid was 5 times higher than that of 10 wt% at $E = 3.2$ kV mm^{-1}. It is clear that there was a considerably higher ER effect of the polymer-Ce^{4+} complex suspension than pure polymer suspension at same polymer particles concentration.

Table I lists the variations of the dielectric constant and dielectric loss tangent as a function of the applied electrical frequency for ER fluids. Results shows that the dielectric constant of the polymer-Ce^{4+} complex ER fluid is about 1.4 times higher than that of pure polymer (100 Hz, 20□), the dielectric loss tangent of the polymer-Ce^{4+} complex ER fluid is about 1.6 times higher than that of pure polymer (100 Hz, 20□), the conductivity is about 2 times higher than that of pure polymer (100 Hz, 20□).

Fig. 3 shows the change of leakage current density of ER fluids prepared from pure polymer or polymer-Ce^{4+} complex in the disperse medium with the increase of electric field strength at 20 □, respectively. For polymer-Ce^{4+} complex ER fluid the leaking current degree was less than 12 μA cm^{-2} at 4.2 kV mm^{-1}.

Fig. 4 shows the temperature dependence of yield stress for 15 wt% polymer-Ce^{4+} complex ER fluid. The yield stress of polymer-Ce^{4+} complex ER fluid increases with temperature under our experimental conditions.

4. Conclusions

A new polymeric complex containing bithiazole ring and rare earth was synthesized. The electrorheological suspensions were prepared by the polymer-Ce^{4+} powder and bromodiphenylmethane. The results showed that the polymer-Ce^{4+} complex ER fluid has higher dielectric properties, exhibits a much stronger ER effect than pure the polymer ER fluid under our experimental conditions.

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