Electrorheological Fluids of Particle/Emulsion Complexes and Their Properties

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ABSTRACT: Three kinds of emulsifying agents have been used as emulsion droplets to prepare particle/emulsion complex electrorheological fluids (ERFs) to explore the effects of emulsifying agents on rheological properties. The rheological properties and microstructure of such ERFs have been examined, and a model of the complex chain for particle/emulsion complex ERFs has been given. Using emulsifying agents is an efficient way of improving the electrorheological effects in dry-based ERFs. There are three methods for emulsifying agents in ERFs: coating on the particle surface, dissolving in the continuous phase, and distributing in the continuous phase as droplets. This is determined by the interactions between the particles, emulsifying agents, and oil. For higher polarity emulsifying agents, the complex particles aggregate to form a bulk and cannot disperse in oil. For moderate ones, the complex particles disperse in oil and form complex chains or columns; the neighboring complex chain forms a network structure because of the rotation of the complex particles and displays a stronger electrorheological effect. With a lower polarity emulsifying agent dissolved in silicone oil, ERFs show lower electrorheological properties because of the decreasing mismatch of conductivity between the particles and continuous phase. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 101: 638–642, 2006

Key words: conducting polymers; rheology

INTRODUCTION

Electrorheological fluids (ERFs) are a unique class of electroactive materials, which are sometimes called smart materials. Their rheological properties depend strongly and reversibly on an applied electric field. Because of their controllable viscosity, fast response, and simplicity for engineering design, ERFs are ideal interfaces for energy transfer. They have facilitated the development of many devices, such as active engine mounts, shock absorbers, and adaptive structures.

ERFs are suspensions consisting of polarizable particles dispersed in an insulating oil. Various potential electrorheological (ER) particles have been introduced.[1] Among these materials, polyaniline (Pan) is a novel intrinsic ER system because it has the advantages of a wide working-temperature range, reduced device abrasion, low cost, and relatively low density.[2,3] Nevertheless, the performance and stability of Pan are still insufficient for the successful development of specific applicative devices.

Generally, the shear stress of ERFs is equal to the rate change of the electric energy density with respect to the shear deformation. There are three ways of improving the electric energy density at a certain electric field: increasing the volume fraction of the suspended particle, increasing the mismatch between the compounds, and using additives. However, there are many limitations on increasing the electric energy density by the former methods.

However, using an additive is an efficient way of improving the ER effect and the stability of suspensions for ERFs.[4–12] Duan et al.[5] used liquid-crystal 4-heptyl-4′-cyance-biphenyl as an additive in NaY zeolite ERFs and found a great improvement in the yield stress. Chin and Park[6] devised new ER materials composed of both Pan particles and chlorinated paraffin oil (CPO) droplets; these material had higher yield stress than ERFs composed of Pan particles only. Lee et al.[7] explored the surfactant effect on the stability of Pan particle suspensions. Park et al.[10] used a nano-organoclay as an additive to improve the ER yield stress.[10]

An emulsifying agent is one of the most important additives; it plays a key role in promoting the colloidal stability and improving the ER effect if added to a certain threshold concentration. Using a particle/emulsion complex is an alternative method for enhancing the performance of conventional suspension ERFs without the general disadvantages of increasing current leakage and irreversible aggregation of particles, and a complex displays a stronger yield stress

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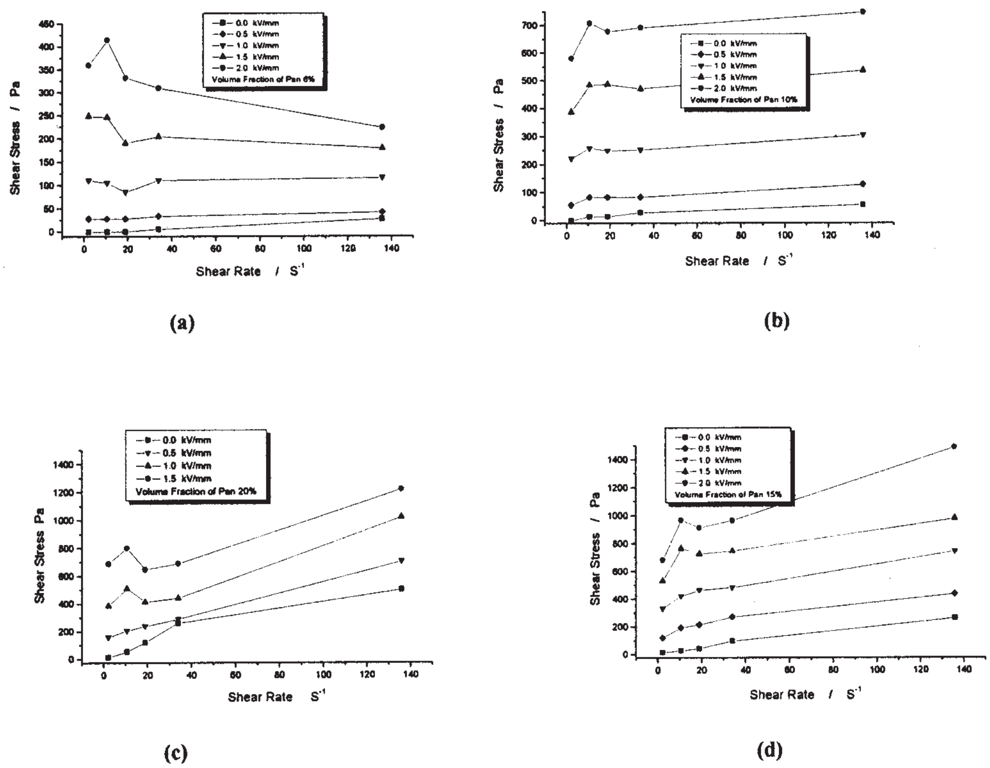

Figure 1 Shear stress of Pan suspensions versus the shear rate at different electric field strengths and different particle concentrations: (a) 6, (b) 10, (c) 15, and (d) 20%.

than homogeneous ERFs. However, there are few works about the effects of the structure, polarization, and viscosity of emulsifiers on ER properties. Moreover, the relative concentrations of the particles and emulsifying agent would be necessary for designing ERFs and solving the underlying mechanism of ER phenomena.

In this study, three kinds of polar liquids were used as emulsion droplets to prepare bidispersed ERFs to explore the effect of emulsifying agents on ER properties. The ER properties and microstructures of such ERFs were examined, and a model of the complex chain for bidispersed ERF was given.

EXPERIMENTAL

Synthesis of ERFs

Pan particles were synthesized by the conventional oxidation polymerization of aniline to produce a fine emeraldine hydrochloride form. A solution of 0.6 mol of aniline monomer in 500 mL of 1*M* HCl was chilled and stirred for 2 h, and the polymerization was initiated at −5°C by the dropping of a prechilled solution of 0.36 mol of ammonium peroxysulfate into 250 mL of 1*M* HCl. The reaction was maintained for another 4 h to complete the reaction to produce the emeraldine hydrochloride form of Pan after washing with distilled water three times, filtering, and drying *in vacuo.* Pan was ground with a ball mill and passed through a 38-μm sieve. To obtain semiconducting Pan, a fine powder was dedoped in aqueous NaOH. The pH of the aqueous Pan suspension remained constant for 3 days. The dedoped particles were filtered and washed with distilled water, ethanol, and cyclohexane to remove the oligomer and excess monomer and make the particle surface hydrophobic. ERFs were prepared by the dispersion of the Pan particles and an emulsifying agent, such as CPO, poly(isobutylene succinimide) (PIBSI), or medial-based synthetic calcium sulfonate (MSCS) in silicone oil, which was ground with a mill before use.

Analytical techniques

The shear stress of the ERFs was measured with a system consisting of a rotary rheometer (NXS-11A, Chengdu Instrument Factory, China; the gap between the outer cup and inner bob was 2 mm) and a high-voltage direct-current power source (GW5-2C, Tiangjing Huida electronic Component factory, China). The formation of particle strands, columns, and networks in an electric field was observed with an optical microscope (XSP-15, Nanjin Optical Instrument Factory, China). Diluted ER suspensions were placed between copper electrodes attached to glass slides. The gap between the two electrodes was set to 1.0 mm.

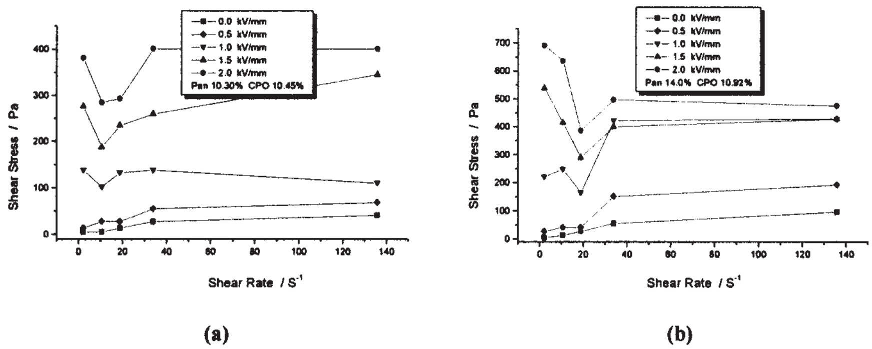

Figure 2 Shear stress of Pan suspensions versus the shear rate at different electric field strengths for Pan/MSCS/silicone oil: (a) 10 vol % Pan and 10 vol % MSCS and (b) 15 vol % Pan and 10 vol % MSCS.

RESULTS AND DISCUSSION

Monodispersed ERF

The typical behavior of an ERF under the influence of an external electric fluid in the postyield state is characterized with the Bingham fluid model. Figure 1 displays the shear stress of Pan suspensions versus the shear rate at different electric field strengths and different particle concentrations. For Pan particles dispersed in pure silicone oil with a volume fraction of 6–20 vol %, Bingham plastic behavior can be clearly observed, with the shear stress and yield stress increasing greatly.

The rheological behavior of ERFs changes with an increasing concentration of Pan particles. A dilute suspension ERFs, whose particle concentration is less than 10 vol %, shows pseudoplastic flow behavior, but over 15 vol %, the ERFs display dilatable flow behavior. In low shear rate the particles in dense suspension ERFs disperse in a continuous phase and range in a particular order; the insulating oil fills in the intervals of the particles. With an increasing shear rate, the insulating oil flows out of the intervals, the particles cannot be wetted enough, and the interaction of the particles increases because of particle contact, so the fluids show a higher viscosity at a higher shear rate.

Bidispersed ERF

CPO, PIBSI, and MSCS are emulsifying agents with different polarizations and viscosities. In general, there are three methods for emulsifying agents in EFRs: coating on the particle surface, dissolving in the continuous phase, and distributing in the continuous phase as droplets. The method is determined by the interactions between the particles, emulsifying agents, and oil. With the addition of PIBSI to ERFs, Pan easily aggregates with it and forms a bulk, which cannot disperse in oil. PIBSI has a high viscosity and imide groups. Because of the hydrogen bond between Pan and PIBSI, Pan is coated with PIBSI to form complex particles. The complex particles aggregate to form networks and solidify.

Figure 2 presents the shear stress of ERFs containing Pan and emulsion drops of MSCS in silicone oil. It shows a lower yield stress than that of an ERF composed of Pan only. The yield stress of ERFs containing 10 vol % Pan and 10 vol % MSCS decreases 33–55%; it changes little for ERFs containing 15 vol % Pan and 10 vol % MSCS. Compared with Pan, MSCS has lower polarization, so the interaction between Pan and MSCS is lower than that of silicone oil and MSCS. MSCS does not coat on the surface of Pan to form

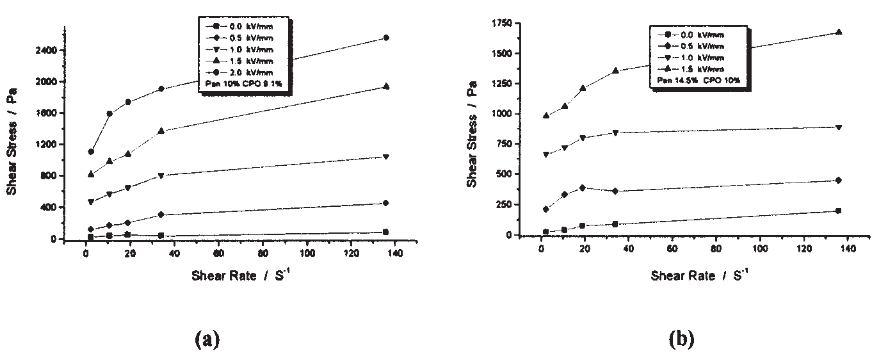

Figure 3 Shear stress of Pan suspensions versus the shear rate at different electric field strengths for Pan/CPO/silicone oil: (a) 10 vol % Pan and 10 vol % 1CPO and (b) 15 vol % Pan and 10 vol % CPO.

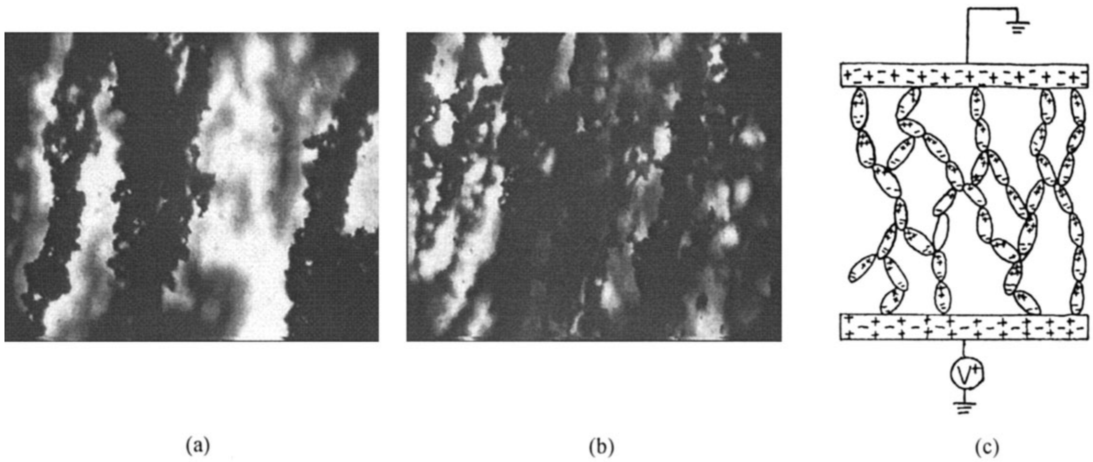

Figure 4 Microstructure of Pan particle suspensions under an electric field: (a) monodispersed ERF, (b) bidispersed ERF, and (c) the mechanism in ER phenomena for bidispersed ERF.

complex particles but dissolves in silicone oil. The continuous phase has higher conductivity because of the addition of MSCS, so the mismatch of the conductivity between the particle and continuous phase decreases; an ERF containing Pan and emulsion drops of MSCS in silicone oil has lower ER properties.

Figure 3 illustrates the same types of flow curves for bidispersed ERF containing 10 vol % Pan particles and 10 vol % CPO droplets in silicone oil; it shows increasing stress over the entire ranges of the shear rate and electric field. With 10 vol % Pan and a 2 kV/mm electric field strength, the yield stress of a monodispersed ERF is only 580 Pa, but it is as high as 1106 Pa in bidispersed ERF. The increasing yield stress is as high as 90–110% at a lower Pan concentration and 80% in at a higher Pan concentration.

The great enhancement of the yield stress can be explained by the two kinds of particulates in silicone oil and their interaction; in this case, they are Pan particles and Pan–CPO complex particles. Because the polarities of Pan and CPO are larger than that of silicone oil, some interaction between Pan and CPO takes place; Pan easily forms complex particles with CPO. The complex particles with CPO on its surface form complex chains between two electrodes under an electric field. Because of the rotation of complex particles, the neighboring complex chain forms a network structure, which can have higher shear stress, so the bidispersed ERF displays higher yield stress. The microscopic observations also support this idea. In monodispersed ERF (Fig. 4(a)], the bridges between two electrodes consist of single chains or columns, but there is a network between two electrodes for bidispersed ERF [Fig. 4(b)]. Based on the ER properties and microscopic observations, a model of the chain for bidispersed ERF is given [Fig. 4(c)].

The yield stress increases with increasing CPO concentration, as shown in Figure 5. For ERFs containing Pan and silicone oil, there is no CPO; Pan particles form single chains or columns under an electric field, so the yield stress is lower. By the addition of CPO, Pan is coated with CPO to form complex particles; the complex particles and Pan particles cooperate to supply yield stress, which is higher than that of an ERF

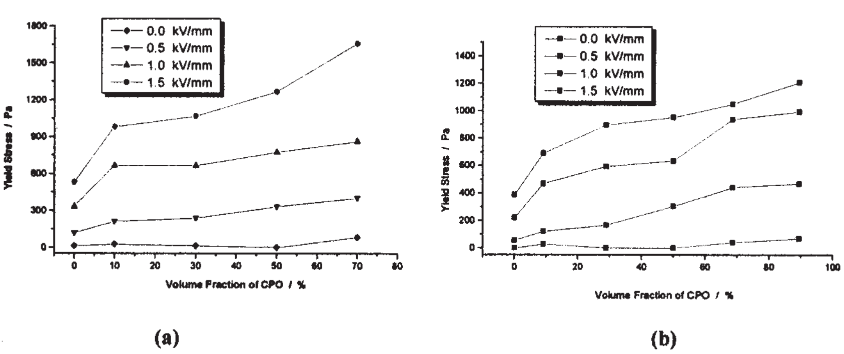

Figure 5 Yield stress of Pan/CPO/silicone oil suspensions versus the CPO concentration at different electric field strengths: (a) 10 vol % Pan particles and (b) 15 vol % Pan.

containing Pan only. When all Pan particles form a complex, residual CPO disperses in silicone oil as droplets, and this is responsible for the electroviscosity of the continuous phase; therefore, the yield stress increases with increasing CPO concentration.

CONCLUSIONS

The rheological behavior of ERFs changes with an increasing concentration of Pan particles. Dilute suspension ERFs show pseudoplastic flow behavior; dense ones display dilatable flow behavior.

Using emulsifying agents is an efficient way of improving the ER effect in dry-based ERFs. There are three methods for emulsifying agents in EFRs: coating on the particle surface, dissolving in the continuous phase, and distributing in the continuous phase as droplets. This is determined by the interactions between the particles, emulsifying agents, and oil. For higher polarity emulsifying agents, the complex particles aggregate to form a bulk and cannot disperse in oil. For moderate ones, the complex particles disperse in oil and form complex chains or columns; the neighboring complex chain forms a network structure because of the rotation of complex particles and displays a stronger ER effect. Lower polarity emulsifying agents dissolve in silicone oil; the ERFs show lower ER properties because of the decreasing mismatch of the conductivity between the particles and continuous phase.

References

1. Whittle, M.; Bullogh, W. A. Nature 1992, 358, 373.
2. Block, H.; Kelly, J. P. J Phys D: Appl Phys 1988, 21, 1661.
3. Gao, Z.-W.; Zhao, X.-P. J Appl Polym Sci 2004, 93, 1681.
4. Zhang, L.-C.; Su, K.; Li, X.-C. J Appl Polym Sci 2003, 87, 733.
5. Duan, X. D.; Chen, H.; He, Y. J. J Phys D: Appl Phys 2000, 33, 696.
6. Chin, B. D.; Park, O. O. J Rheol 2000, 44, 397.
7. Lee, H.-J.; Chin, B. D.; Yang, S.-M.; Park, O. O. J Colloid Interface Sci 1998, 206, 424.
8. Chin, B.-D.; Park, O. O. J Colloid Interface Sci 2001, 234, 344.
9. Durrschmidt, T.; Hoffmann, H. Colloids Surf A 1999, 156, 257.
10. Park, J.-H.; Lim, Y. T.; Park, O. O. Macromol Rapid Commun 2001, 22, 616.
11. Lim, Y. T.; Park, J.-H.; Park, O. O. J Colloid Interface Sci 2002, 245, 198.
12. Lu, J.; Zhao, X.-P. J Mater Res 2002, 17, 1513.