Direct Synthesis of Electrorheological Suspension Containing Salt of Poly(methacrylic acid) and Its Electrorheological Effect

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SYNOPSIS

Colloidal suspensions containing salts of poly(methacrylic acid) which exhibit high electrorheological (ER) activity were synthesized by inverse emulsion polymerization. Factors influencing the ER effect were studied. The results showed that maximum yield stress occurred at optimum amounts of both polymeric stabilizer and crosslinking agent used in the inverse emulsion polymerization as well as a certain water content of the particles, while yield stress increased with electric field strength, average diameter of the particles below 0.9 μm, or the molar ratio of the salt to the acid. The ER activity for the suspensions containing different monovalent counter ions decreased in the following order: $Li^+ > Na^+ > K^+ > NH_4^+$. The phenomena were discussed with the ionic polarization mechanism. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Electrorheological (ER) fluids, or suspensions, first discovered by Winslow,[1] undergo dramatic changes in rheological properties such as development of a yield stress and increased viscosity upon application of kV/mm order of electric field. ER fluids, as a kind of smart material, may possibly be revolutionary in several areas of industry and technology because of their attractive features of rapid and reversible response to electric fields.[2] From the early 1980s ER fluid has attracted the interest of many scientists and been developed as one "hot spot" in the research areas of material science and liquid physics.

Now research on ER fluids mainly focuses on (1) influence of variables on ER effect and ER mechanism; (2) optimization of ER fluids formulas, especially synthesis of particles with high dielectric constants for high performance of ER fluids; and (3) exploitation of engineering application of ER fluids. Using polymers for dispersed particles in high performance ER fluids is becoming common due to

their low density, high plasticity, and easy processibility into fine particles.[3-6] Suspension of the hydrated lithium polymethacrylate dispersed in a chlorinated paraffin oil has a high ER activity.[7] Zukoski and co-workers[8,9] extensively studied the influence of volume fraction and electric field strength on the dynamic ER properties and current density of the above suspension. Stangroom and Harness[10,11] obtained highly electrorheologically active suspensions by mixing chlorinated hydrocarbons, fluorolube FS, dipolar halogenated aromatics, or pentachlorophenyl phenyl ether with lithium polymethacrylate particles with adsorbed water, which were made by copolymerizing lithium methacrylate with divinyl benezene or methylene bisacrylamide (MBAM) in a 10% aqueous solution followed by complicate posttreatment. However, all these ER fluids have the crippling problem of poor stability. And poorly understood are the influences on ER effects of key variables such as particle size, molecular structure of particles, and field strength. These are of primary importance in optimizing ER fluids for applications such as clutches, brakes, viscous dampers, pumps, and robotic actuators.

It is well known that particles of poly(methacrylic acid) and its salts synthesized by inverse

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emulsion polymerization have an adjustable diameter and are easily dried. Furthermore, this method has an advantage of direct synthesis of colloidal suspensions with good stability by removing water using azeotropic distillation. Thus we have obtained a series of nonaqueous colloidal suspensions of poly(methacrylic acid), its salts, or crosslinked copolymer with MBAM by inverse emulsion polymerization. This paper deals with the synthesis and influence of variables such as the structure of particles, amount of polymeric stabilizer covering their surfaces, diameter, and water content of the particles, as well as dispersing media on ER effects and possible ER mechanisms.

EXPERIMENTAL

Materials

Methacrylic acid (MAA), C.P., was purified by distillation under reduced pressure; ammonium, lithium, sodium, and potassium salts of MAA were obtained by reaction of MAA with corresponding alkalis. Azobisisobutyronitrile (AIBN) was recrystallized with 95% ethanol; MBAM was prepared according to Fewer.[12] Polymeric stabilizer (PSR) was self-made, with the following structure:

$$CH_3 \quad\quad CH_3$$
$$| \quad\quad\quad |$$
$$-(C-CH_2-C-CH_2)_n$$
$$| \quad\quad\quad |$$
$$COOH \quad COOR$$
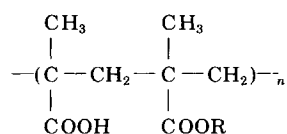
where $R=C_mH_{2m+1}$. Chlorinated paraffin oil, poly(diethyl siloxane), paraffin oil, and transformer oil, all supplied by factories in China, were used as dispersing media. Other reagents used were standard chemical reagents without treatment.

Synthesis of ER Fluids Based on Poly(methacrylic Acid) and Its Salts

To an oil phase involving Span 80, PSR, and AIBN, aqueous MAA or its salt solution (sometimes containing MBAM) was added. After emulsifying for 20 to 60 min, polymerization was initiated by heating in N_2 atmosphere with stirring. Polymerization lasted for several hours at 70°C. Then water and xylene were removed by azeotropic distillation until the suspension of the particles with the expected water content was obtained and thus the ER fluid was obtained.

Characterization of the ER Fluids

Content of particles: About 10 g ER fluid (W_1) was weighed accurately, diluted with 10 mL diethyl ether, and then added to 200 mL acetone during stirring. The solid particles were collected and put under an IR lamp for 4 h, then dried at 100°C in a vacuum oven for 1 day and weighed (W_2).

The weight percents of particles = (W_2/W_1) × 100%. The weight percents of particles were fixed at 38.4 wt % in ER fluids in this paper.

Water content of particles: A certain amount of ER fluid (W_3) was weighed and put into a vacuum oven at 100°C for 1 day, then the dried residue was taken out and weighed (W_4).

The water content of particles (Q) = ($W_3 - W_4$)/ (W_3 × weight percents of particles) × 100%. In most cases, the water content of particles was about 1.4 wt % in the ER fluids unless otherwise noted.

Particle diameter was determined by an SA-CP3 particle size analyzer. The average diameter of particles was about 0.38 μm in the ER fluids unless otherwise noted.

Measurements of Static Yield Stress (τ_s) and Current of ER Fluids

Static yield stress was determined by the static yield stress apparatus made by ourselves according to the literature[3] and calculated as $\tau_s = (mg - m_0g)/S$, where mg is the load needed to cause the suspension to flow under electric field, m_0g the load needed to cause the suspension to flow under zero electric field strength, and S the electrode area (1.5×10^{-3} m²). The distance between the two electrodes is 1.0 mm. High dc voltage was supplied by a high voltage test transformer. Electric current was monitored by a microampere meter.

RESULTS AND DISCUSSION

In order to carry out the inverse emulsion polymerization successfully, it is necessary to add PSR in addition to emulsifier Span 80 to the system. From Figure 1 curve (a) of yield stress versus amounts of PSR used shows a maximum when the ER fluids of lithium polymethacrylate particles (Li-PMAA) dispersed in poly(diethyl siloxane) are put under an electric field (E) of 2.8 kV/mm. PSR is an amphiphilic polymer with the function of preventing particles from coagulating, thus keeping ER fluids stable. Under an electric field, PSR may form bridges between particles, thus improving the interaction
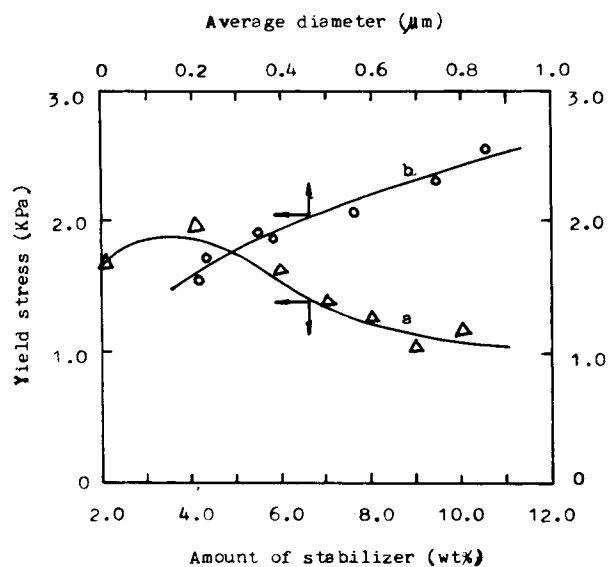
Figure 1 Influence of (a) amount of polymeric stabilizer used in polymerization and (b) average diameter of particles on static yield stress for colloidal suspensions of lithium polymethacrylate in poly(diethyl siloxane) at E of 2.8 kV/mm.

forces of particles and ER effect. On the other hand, Li-PMAA particles covered by excess PSR may produce considerable steric repulsive forces to prevent particles from approaching each other, and weaken the interparticle forces, so the ER effect is reduced. The maximum of τ_s is reasonable to attribute to the balance of these two compensating forces.

By controlling preemulsifying time and stirring speed during polymerization, ER fluids of Li-PMAA particles with different sizes dispersed in poly(diethyl siloxane) were synthesized. Curve (b) in Figure 1 shows that under E of 2.8 kV/mm, τ_s for ER fluid increased with increasing average diameter of particles. A particle in an ER fluid under an electric field may polarize and become a point dipole. The larger the particle diameter, the greater the dipolar moment. Consequently, the interparticle forces are increased and the ER effect is improved. However, as the size of particles increased, the larger particles have a tendency to settle down more easily, and destroy the ER effect and also the ER fluids would respond slowly to the electric field.

Curve (a) in Figure 2 shows the influence of the amount of crosslinking agent on τ_s for suspensions of crosslinked Li-PMAA particles in poly(diethyl siloxane) at E of 2.8 kV/mm. It can be seen that τ_s shows a maximum as the amount of MBAM increased. Since crosslinking of the polymer impedes the different conformational rearrangement of the polymer structure, it is reasonable to expect that Li-

PMAA particles with different crosslinking degrees have different porosities and abilities to adsorb water, which affect their polarizations. Stangroom[13] and Tamura et al.[14,15] indicated that the ability to adsorb water and the porosity of particles strongly influence the ER effect.

From curve (b) in Figure 2, for ER suspensions containing copolymer particles of MAA and its lithium salt under E of 2.8 kV/mm, τ_s increases monotonically with —COOLi groups. It is known that hydrated Li^+ has a greater tendency to move away from the polymer chain than H^+, because the latter is fixed by a strong covalent bond. Thus hydrated Li^+ will more easily move to one pole of the particles by electroosmosis to generate induced dipoles. The existence of more ions in particles will help to improve the ER effect. It is reasonable to suggest that this ER effect is produced by an ionic polarization mechanism.

The ER effect for suspensions based on salts of poly(methacrylic acid) strongly depends on the type of its counterions. From Figure 3, under E of 1.7 kV/mm for different salt suspensions, τ_s exhibits a maximum value with increasing amount of adsorbed water (Q). For suspensions of NH_4-PMAA and K-PMAA particles, a maximum τ_s occurred at a lower water content of particles than for those of Na-PMAA and Li-PMAA and the maximum value decreases in the following order: $Li^+ > Na^+ > K^+ > NH_4^+$. The former phenomenon is in agreement
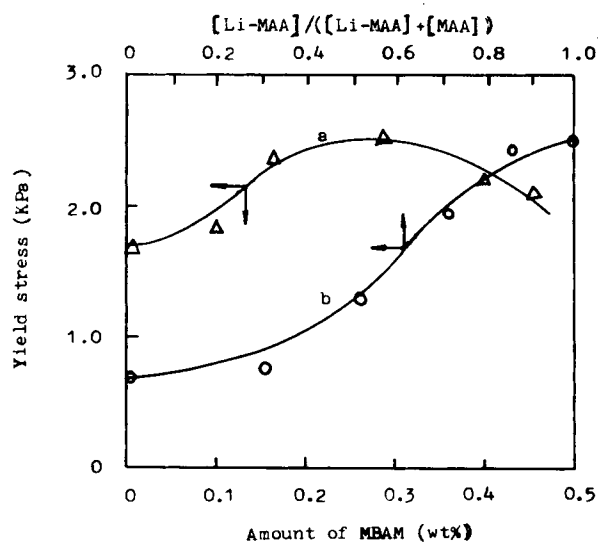

Figure 2 Influence of (a) amount of crosslinking agent and (b) ratio of lithium methacrylate to methacrylic acid plus lithium methacrylate used in polymerization on static yield stress for colloidal suspensions of particles in poly(diethyl siloxane) at E of 2.8 kV/mm.
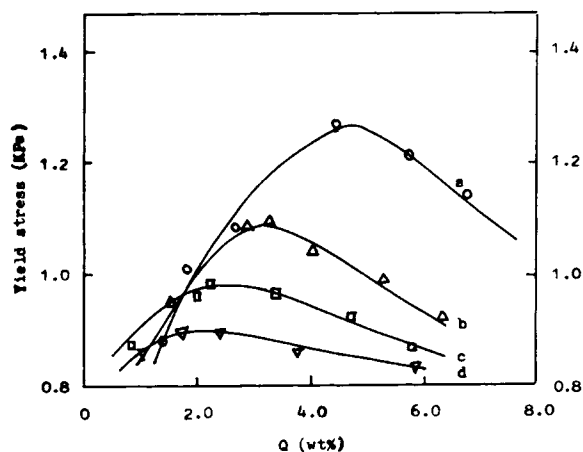
Figure 3 Influence of water content of particles (Q) on static yield stress for colloidal suspensions of (a) Li-PMAA, (b) Na-PMAA, (c) K-PMAA, and (d) NH$_4$-PMAA particles in poly(diethyl siloxane) at E of 1.7 kV/mm.

with the order of crystal radius and charge density of counterions. These are predicted by an ionic polarization mechanism. Because counterions become mobile only when they adsorb enough water, Li$^+$ needs more adsorbed water to become mobile than others. Therefore the τ_s for a suspension of Li-PMAA shows a maximum value at a higher water content. Li-PMAA particles form the most active ER fluid due to the smallest crystal radius and highest charge density of Li$^+$, which make particles polarized through electroosmosis of Li$^+$ to one pole of particles.

It is well known that the ER effect for hydrous ER fluid depends strongly on the water content of the particles. For example, both Uejima[16] and Stangroom[13] found that the ER effect increased with increasing water content until a maximum was reached. The initial increase can be understood in terms of two mechanisms: the enhancement of the induced dipole due to the large dielectric constant of water[17] and the interparticle adhesive force due to the capillary force of water.[18] However, the maximum reported has not been fully explained. In order to optimize ER fluid formulas and clearly understand the role of the absorbed water in ER fluids based on salts of PMAA, the relationship between water content, electric field, τ_s, and current density was studied. Figure 4, curve (a), gives τ_s versus water content of particles (Q) for suspensions of Li-PMAA in poly(diethyl siloxane) at E of 2.1 kV/mm. As can be seen, τ_s initially increases, then decreases with increasing Q. τ_s shows a maximum value at Q of 2.8 wt %. The influence of Q on τ_s under a different electric field is similar, but from curve (b) of Figure
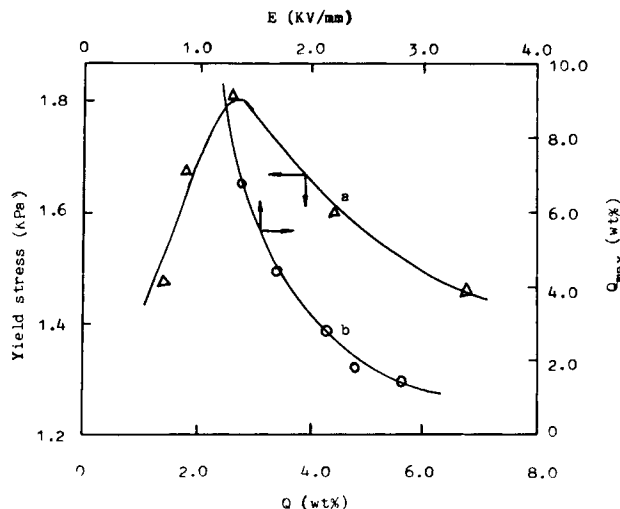

Figure 4 (a) Influence of Q on static yield stress for colloidal suspensions of Li-PMAA in poly(diethyl siloxane) at E of 2.1 kV/mm; (b) water content of particles corresponding to the maximum static yield stress (Q_{max}) versus applied electric field strength for colloidal suspensions of Li-PMAA particles in poly(diethyl siloxane).

4, the water content corresponding to the maximum τ_s decreases with increasing E. This implies that under a stronger electric field, Li$^+$ absorbing less water can move more easily to the surface of the particles. In this case, we may consider that the adsorbed water of particles and the electric field play the same role in the ER effect as the time–temperature superposition principle in polymer science.

Figure 5 shows the influence of the water content of Li-PMAA particles on current density of ER
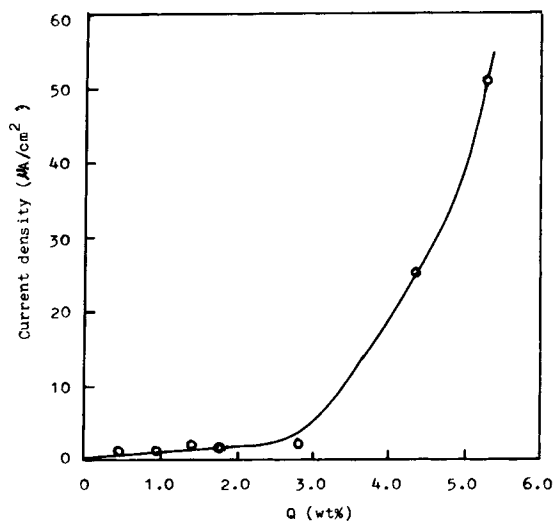

Figure 5 Influence of Q on current density for colloidal suspensions of Li-PMAA particles in poly(diethyl siloxane) at E of 2.1 kV/mm.

fluids at E of 2.1 kV/mm. With increasing Q the current density increases slowly at first, then rapidly when Q is more than 2.8 wt %. An obvious electrophoresis is observed to occur when $Q > 2.8$ wt %; as compared with curve (a) in Figure 4, τ_s also declined when $Q > 2.8$ wt %. It is reasonable to suppose that when particles form a fibrous structure spanning the electrode gap under an electric field, water desorbed from the counterions under a relatively high electric field moves to the surface of the particles, and a passageway for ions to migrate along the fibrous structure is built. Thus Li^+ not only moves to the surface of the particles, but also migrates to neighboring particles. The latter may be responsible for the rapid increase of current density, decrease of ER effect, and occurrence of obvious electrophoresis.

The relation between yield stress and field strength is complicated and is difficult to be express by a simple equation, especially for ER fluids based on colloidal suspensions, where thermal, electric, and viscosity effects are involved. A linear effect of electric field on yield stress[16] or a quadratic effect[1,8] is observed for various ER fluids. Otsubo et al.[17] found the yield stress to be proportional to $E^{2.4}$ at higher volume fractions and attributed it to the crosslinking of particle chains. Evans et al.[18] pointed out that yield stress should be proportional to E based on a "water bridge" mechanism. Zukoski and co-workers[9,19] predicted that yield stress was proportional to the square of E based on a polarization mechanism. Figure 6 shows the logarithmic relationship between τ_s and E. All the data lie very close to a straight line with a slope of 2 under relatively low field strength, while the data are close to a straight line with a slope of 1 under relatively high field strength. The former may be attributed to the polarization forces according to an ionic polarization mechanism. The latter may be due to the saturation of the induced dipoles caused by ionic polarization. It is proposed that under relatively high E, water may have a tendency to desorb from Li^+ and move to the surface of the particles to build a passageway for ions to migrate to the neighboring particles. Thus the saturation of the induced dipoles may occur when the number of Li^+ which disintegrated from the polymer matrix almost equals that of Li^+ migrating to the neighboring particles. In this case, τ_s, proportional to the strength of the mutual attraction of the induced dipoles, increases linearly with increasing E. Comparing curves (a) and (b) of Figure 6, at higher Q, i.e., (b), the induced dipoles become saturated at a lower electric field strength. The Li-PMAA particles with higher water content form more active ER fluid under low E than those with
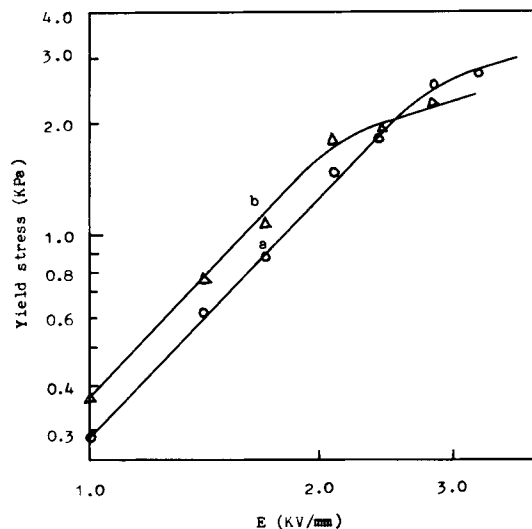

Figure 6   Static yield stress versus E for colloidal suspensions of Li-PMAA particles with Q of (a) 1.4 wt % and (b) 2.8 wt % in poly(diethyl siloxane).

lower water content. On the other hand, the latter forms more active ER fluid than the former under high E. It is reasonable to suggest that under electric field, the surface of the particles with more water content is more easily covered by the water desorbed from Li^+, and the passageway for ions to migrate to the neighboring particles is more easily built. Thus Li^+ moving away from the polymer matrix moves more easily to the neighboring particles rather than to one pole of the particles. As a result, the induced dipoles for particles with higher Q become saturated at lower E. But at E, which is too low to desorb water from Li^+, there exist in particles with higher Q more mobile Li^+ disintegrated from the polymer matrix due to adsorption of enough water, which moves to one pole of the particles and polarizes the particles. Therefore, the particles with higher Q form more active ER fluid at low E. For particles with lower Q, the passageway for ions to migrate to neighboring particles is not easily built even under relatively high E; thus more Li^+ disintegrating from the polymer matrix moves to one pole of the particles rather than to neighboring particles, and contributes to improving the induced dipoles. Consequently, the particles with lower Q form more active ER fluid at high E.

Figure 7 shows the influences of electric field strength on τ_s for different ER fluids of Li-PMAA particles dispersed in chlorinated paraffin oil, poly(diethyl siloxane), paraffin oil, or transformer oil. It can be seen that ER fluid of Li-PMAA particles dispersed in chlorinated paraffin oil is the most
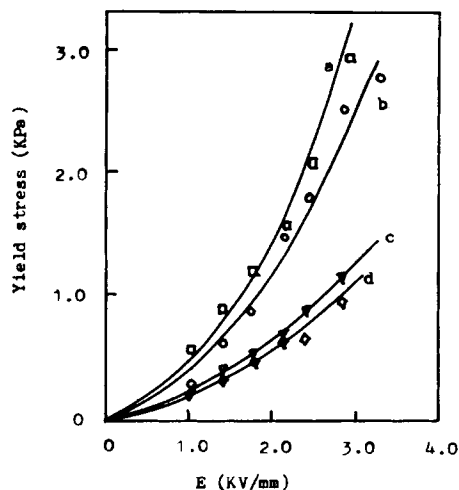
Figure 7 Static yield stress versus E for colloidal suspensions of Li-PMAA particles in (a) chorinated paraffin oil, (b) poly(diethyl siloxane), (c) paraffin oil, and (d) transformer oil.

active. This is attributed to the dielectric constant of the dispersing medium (ε_f). The influence of ε_f on the ER effect may be explained in terms of the polarization mechanism theory, which predicts that $\tau_y \propto \varepsilon_f(\beta CE)^2$, where the dipole coefficient β is ($\varepsilon_p - \varepsilon_f)/(\varepsilon_p + 2\varepsilon_f$), where ε_p is the dielectric constant of dispersed particles and C is the "local field" concentration. When β and C are almost independent on ε_f, i.e., $\varepsilon_p \gg \varepsilon_f$, the yield stress increases with increasing ε_f.

CONCLUSION

The ER suspensions containing salts of PMAA as dispersed particles can be obtained directly by inverse emulsion polymerization followed by azeotropic distillation and can show somewhat high ER activity. The yield stress increased with electric field strength, average diameter of the particles (below 0.9 μm), or the molar ratio of the salt to the acid, while maximum yield stress occurred at optimum amounts of both polymeric stabilizer and crosslinking agent used in the inverse emulsion polymerization and also at a certain water content of the par-

ticles. The ER activity for different suspensions containing different kinds of monovalent counter ions decreased in the following order: $Li^+ > Na^+ > K^+ > NH_4^+$. Chlorinated paraffin oil is the best dispersing medium used in these kinds of ER fluids. All the phenomena can be discussed in terms of the ionic polarization mechanism.

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