

One-Step Preparation of Electrorheological Suspension Containing Poly(lithium acrylate) via Inverse Emulsion Polymerization and Study of Its Electrorheological Effect

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Received 30 July 1997; accepted 21 November 1997

ABSTRACT: Electrorheological (ER) fluid or suspension containing lithium salt of poly(acrylic acid) were synthesized directly by inverse emulsion polymerization. Effects of the amounts of crosslinking agent and the stabilizer and neutralization degree used in the polymerization, as well as water content of the polymer particles on the ER activity were investigated. The ER suspension exhibited maximum yield stress at optimum amounts of stabilizer and crosslinking agent used in the inverse emulsion polymerization, as well as at optimum water content of the polymer particles. Glycerol was tried to be used as an activator instead of water and was shown to have a favorable effect on the thermal stability of the ER suspension. Core-shell-type polymer particles were synthesized through inverse emulsion polymerization with supplemental addition of a second monomer. The ER suspension containing particles with poly(lithium acrylate) as core and polyacrylamide as shell showed better ER behavior than those without the polyacrylamide shell. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 68: 2169–2174, 1998

Key words: electrorheological fluid; poly(acrylic acid); inverse emulsion polymerization

INTRODUCTION

Early in 1949, Winslow discovered that some suspensions can undergo evident changes in rheological properties, such as development of a yield stress and increased viscosity upon application of the kV/mm order of electric field, and called them electrorheological (ER) fluids or suspensions. This kind of smart material may possibly be revolutionary in some areas of industry and technology due to attractive features of rapid and reversible response to electric fields. From the early 1980s, ER fluid has attracted the interest of many scientists and been developed as one of the hot spots in the research areas of material science.

The ER fluid can be applied in clutches, brakes, viscous dampers, pumps, and robotic actuators.

Using polymers for dispersed particles in high-performance ER fluids is now becoming common because of their low density, high plasticity, and easy processibility into fine particles.^{2–5} Stangroom and Harness^{6–7} obtained highly electrorheological 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 benzene or methylene bisacrylamide (MBAM) in a 10% aqueous solution, followed by complicated posttreatment. However, these ER fluids have the crippling problem of poor stability.

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

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Journal of Applied Polymer Science, Vol. 68, 2169–2174 (1998)
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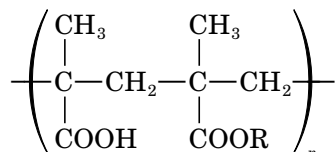
emulsion polymerization, and its suspension is stable and can be dried by azeotropic distillation. Recently, we have reported the direct synthesis of ER suspensions containing salts of poly(methacrylic acid) by inverse emulsion polymerization in liquids with low dielectric constant, followed by azeotropic distillation, and indicated that the product obtained showed high ER activity.⁸

This article deals with the direct synthesis of ER suspensions polymerization in chlorinated paraffin oil and the core-shell polymerization with supplemental addition of a second monomer in order to enhance the yield stress (τ_s) and decrease the current density (J) for the ER fluid, as well as study of using glycerol instead of water as an activator so as to improve the thermal stability of the ER suspension.

EXPERIMENTAL

Materials

Acrylic acid (AA), C. P. was purified by distillation under reduced pressure. Lithium salt of AA was obtained by reaction of AA with LiOH. Azobisisobutyronitrile (AIBN) was recrystallized with 95% ethanol. Polymeric stabilizer (PSR) was self-made, with the following structure:



where $R = C_mH_{2m+1}$. Chlorinated paraffin oil (containing 52% Cl), supplied by Gedian Chemical Factory, was used as a dispersing medium. Acrylamide (AM) was purified by recrystallization from water. Methyl methacrylate (MMA) was purified by distillation under reduced pressure. Other reagents used were standard chemical reagents without treatment.

Synthesis of ER Fluids Based on Poly(lithium acrylate)

To an oil phase involving Span 80, PSR, and AIBN, aqueous solution of lithium salt of AA and MBAM was added. After emulsifying for 40 min, polymerization was initiated by heating in N_2 atmosphere with stirring. Polymerization lasted for 4 h 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. Conversion of AA in most cases reached above 98%.

Synthesis of ER Fluids Containing Core-Shell-Type Particles

Inverse emulsion polymerization of lithium salt of AA was carried out for 4 h as above. After completion of the polymerization, a second monomer (MMA or AM) with a certain amount of MBAM and AIBN in the absence of emulsifier was added under nitrogen atmosphere. The inverse emulsion polymerization was continued at 70°C for 4 h. Then water and xylene were removed by azeotropic distillation until water content of the polymer particles reached a certain value, and, thus, the ER fluid was obtained.

Characterization of the ER Fluids

Content of Dried Polymer Particles

About 10 g ER fluid (W_1) was weighed accurately, diluted with 10 mL of diethyl ether, and then added to 200 mL of 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 6 h and weighed (W_2).

The weight percents of dried particles (S)

$$= (W_2/W_1) \times 100\%.$$

The weight percents of dried polymer particles were fixed at 33.2 wt % in ER fluids in this article.

Water Content of Particles

A certain amount of ER fluid (W_3) was weighed and put into a vacuum oven at 100°C for 6 h, then the dried residue was taken out and weighed (W_4). The water content of particles (Q) = $(W_3 - W_4)/(W_3 \times S + W_3 - W_4) \times 100$.

The size of polymer particles was observed by transmission electron microscopy (TEM) using a Hitachi JSM-200 CX II microscope after the suspension was diluted with kerosene and stained with OsO_4 vapor for 24 h.

Measurements of Static Yield Stress and Current Density of ER Fluids

Static yield stress was measured by the static yield stress apparatus made by ourselves ac-

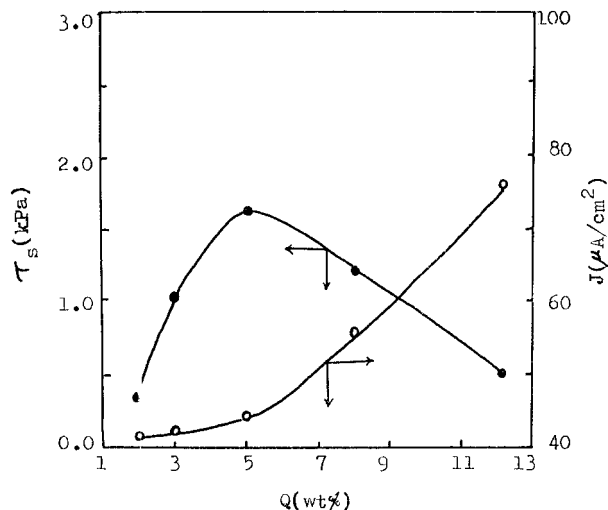


Figure 1 Effect of water content (Q) of the polymer particles on yield stress (τ_s) and current density (J) for the ER suspension of PAALi in chlorinated paraffin oil at an electric field of 2.1 kV/mm (PSR = 6 wt %; MBAM = 0.2 wt %, based on AA).

According to the literature² and calculated as $\tau_s = (mg - m_0g)/A$, where mg is the load needed to cause the suspension to flow under electric field, m_0g is the load needed to cause the suspension to flow under zero electric field strength, and A is the electrode area ($1.5 \times 10^{-3} m^2$). 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

Effect of Water Content of the Polymer Particles on ER Behavior of the Polymerization Product

It is well known that the ER effect for hydrous ER fluid depends strongly on the water content of the particles. For example, both Uejima⁹ and Stangroom¹⁰ found that the ER effect increased with increasing water content until a maximum was reached. Figure 1 indicates that when the suspension obtained from the inverse emulsion polymerization, followed by azeotropic distillation, are put under an electric field of 2.1 kV/mm, τ_s initially increases then decreases with increasing water content (Q) of the PAALi particles; τ_s shows a maximum value at Q about 5 wt %. The initial increase of τ_s may be explained as follows. Li^+ ions become mobile only when they adsorb

enough water. Then the hydrated ions move to one pole of particles under an electric field. The induced dipoles can align up and exhibit the ER effect. However, when the adsorption of water for ions is saturated, excess water desorbs from Li^+ ions and moves to the surface of the particles. It is reasonable to suppose that the particles with the induced dipoles can form a fibrous structure spanning the electrode gap under an electric field. When water moves to the surface of particles, a passageway for ions to migrate along the fibrous structure is built.¹¹ Figure 1 also shows the influence of the water content of PAALi particles on current density of the ER fluids. With increasing Q , the current density increases slowly first, then rapidly when Q is more than 5 wt %. τ_s also declines when $Q > 5$ wt %. As water moves to the surface of the particles, Li^+ not only moves to the surface of the particles but also migrates to neighboring particles, thus increasing current density rapidly and decreasing yield stress.

Effect of Amount of Stabilizer Used in the Polymerization on ER Behavior of the Suspension

In order to carry out the inverse emulsion polymerization successfully, it is necessary to add PSR in addition to the emulsifier Span 80 to the system. Figure 2 shows that with the increase of PSR amount the yield stress of the polymerization product raises at first and then decreases. A maximum τ_s occurs at 6 wt % of PSR. 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 brid-

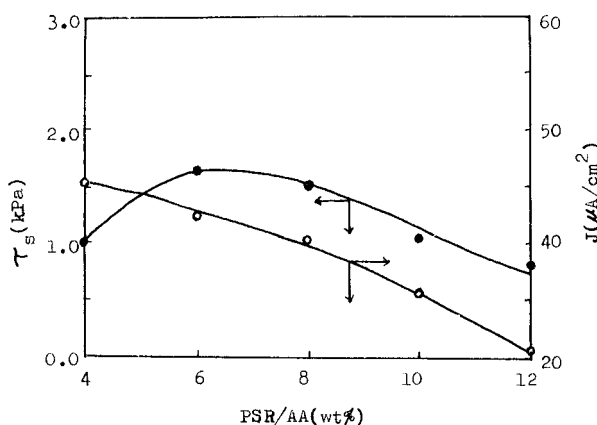


Figure 2 Effect of the amount of PSR used in polymerization on τ_s and J for the ER suspensions (MBAM = 0.2 wt %, based on AA; $Q = 5$ wt %, based on PAALi particles).

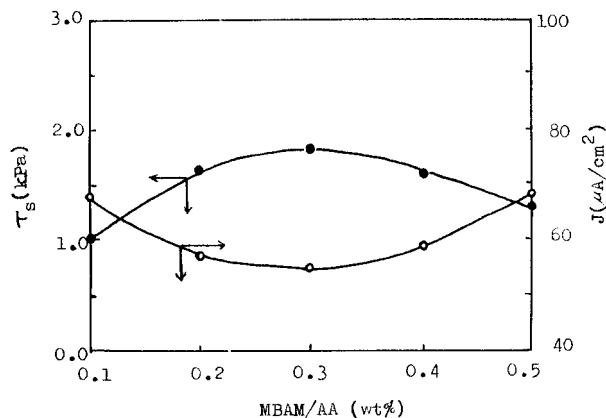


Figure 3 Effect of the amount of the crosslinking monomer used in polymerization on τ_s and J of the ER suspensions ($Q = 5$ wt %; PSR = 6 wt %, based on AA).

ges between particles, thus improving the interaction forces of particles and the ER effect. On the other hand, PAALi particles covered by excess PSR may produce considerable steric repulsive forces to prevent 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. The current density of the ER fluids diminishes as the amount of PSR used is increased, as shown in the Figure 2. This phenomenon may be due to the reason that the polymer stabilizer, which contains long alkyl groups, can prevent the Li^+ ions from migrating between particles.

Effect of Amount of Crosslinking Agent on the ER Behavior of the Suspensions

The crosslinking agent used in the inverse emulsion polymerization was MBAM, a monomer with two double bonds. Figure 3 shows the influence of the amount of MBAM on yield stress and current density for suspensions of crosslinked PAALi particles in chlorinated paraffin oil at an electric field of 2.1 kV/mm. It can be seen that τ_s exhibits 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 PAALi particles with different crosslinking degrees have different porosities and abilities to absorb water, which affect their polarizations. Stangroom¹⁰ and Tamura et al.¹² indicated that the ability to absorb water and the porosity of particles strongly influence the ER effect.

The same figure illustrates that current density of the ER fluids exhibits a minimum value at the same MBAM amount used in the polymerization as that showing the maximum τ_s . The phenomena may be interpreted as follows. A certain amount of crosslinks favors the water absorption within particles, thus increasing the hydrated Li^+ ions and promoting migration of the ions within particles under an electric field, resulting in enhancement of dipolar moment, the interparticle force, and, hence, the ER effects. But excess crosslinking can lower the water absorption capacity within the particles and favor migration of hydrated Li^+ ions not only to the surface of the particles but also to neighboring particles, thus increasing the current density and decreasing τ_s .

Effect of Neutralization Degree of Acrylic Acid on ER Behavior of the Suspension

τ_s of the ER suspension increases monotonically with neutralization degree of AA or the mol % of $\text{COOLi}/(\text{COOH} + \text{COOLi})$, as shown in Figure 4. It is known that hydrated Li^+ ion has a great 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 to generate induced dipoles. The existence of more ions in particles will help to improve the ER effect. Current density of the ER suspension also increases with the neutralization degree of AA, probably due to tendency of hydrated Li^+ ions to migrate not only within particles but also between particles. When AA was neutralized in slight excess, the ER fluid was broken down by high voltage.

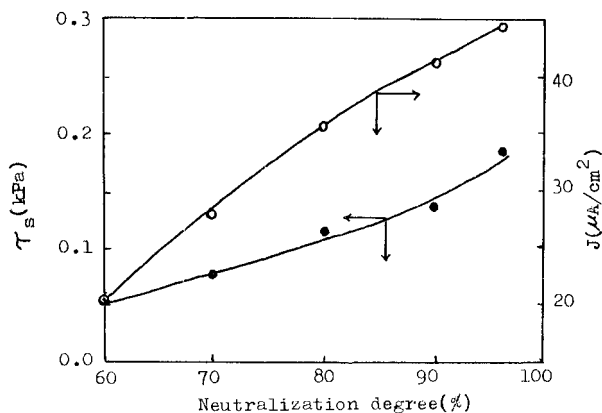


Figure 4 Effect of the neutralization degree of AA used in polymerization on τ_s and J for the ER suspensions (PSR = 6 wt %; MBAM = 0.3 wt %; $Q = 5$ wt %).

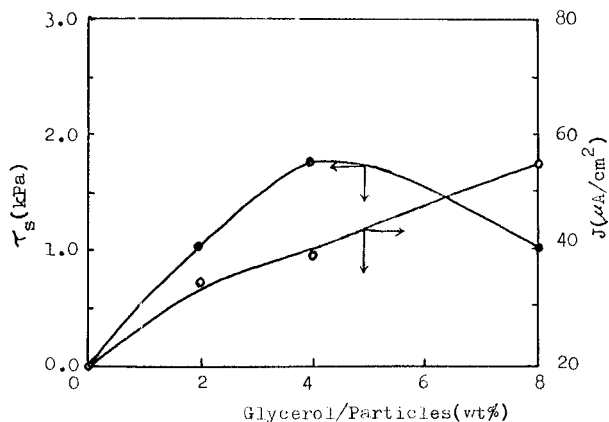


Figure 5 Effect of the amount of glycerol added to the dried ER suspensions on τ_s and J of the ER suspensions (PSR = 6 wt %; MBAM = 0.3 wt %).

Effect of Glycerol on the ER Behavior of PAALi Suspension

Glycerol was tried to be used as activator instead of water in order to improve thermostability of the hydrous ER fluid. The ER fluid obtained by the inverse emulsion polymerization, following by azeotropic distillation, was vacuum-dried thoroughly at 100°C for 6 h. Then different amounts of glycerol was mixed with the ER fluids. The ER behavior versus glycerol amount added is shown in Figure 5. It can be seen that a maximum value of τ_s occurs at about 4 wt % of glycerol based on PAALi particles, whereas J increases with the amount of glycerol added. The OH groups containing glycerol plays the same role as water in the hydrous ER fluids. This kind of ER fluid still showed the same ER activity, even after it was heated at 90°C under vacuum for 48 h, whereas the ER fluid without glycerol lost its ER activity completely at the same drying conditions. Hence, the ER fluid containing glycerol as activator exhibited higher thermostability than the original hydrous ER fluid containing PAALi particles.

Effect of Core-Shell Structure of the PAALi Particles on the ER Activity

PAALi particles with core-shell structure were obtained by inverse emulsion polymerization of lithium salt of AA first, followed by an additional polymerization of a second monomer containing MBAM and AIBN without emulsifier. The second monomer used was AM or MMA. Conversion of the second monomer was determined by weight difference to be about 99%. The ER suspensions

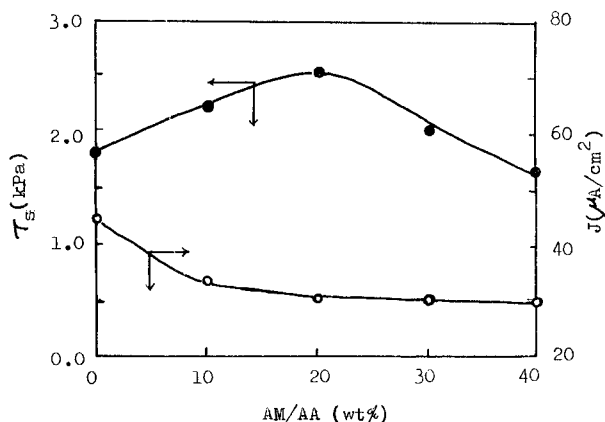


Figure 6 Effect of the amount of AM added in the second step of core-shell polymerization on τ_s and J for the ER suspensions (MBAM = 0.3 wt %).

containing such a kind of particles exhibit different ER behavior, as shown in Figures 6 and 7. In the case of AM used as the second monomer, a maximum τ_s exists for the ER fluid containing PAALi particles with about 20 wt % of PAM based on AA as shell, whereas J decreased at first and then kept constant with increasing AM amount added in additional polymerization. This phenomenon can be interpreted as follows: AM polymerized on the outside of PAALi particles since no additional emulsifier was added during addition of the second monomer; thus, no new emulsion particles were formed. The ion-dipolar interaction between PAALi and PAM offers a strong adhesion between core and shell of the particle. The shell can inhibit the ion migration between particles, resulting in decreasing current density and increasing polarization of the particles and,

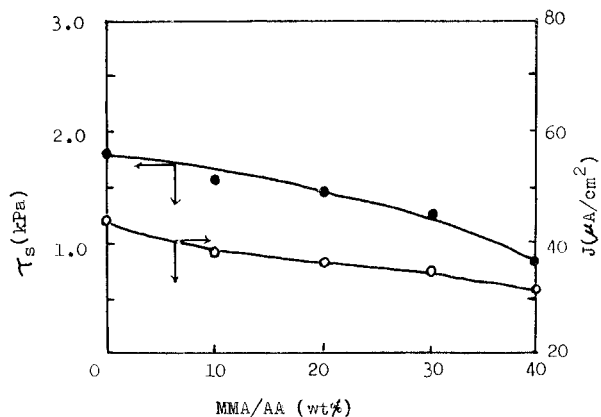


Figure 7 Effect of the amount of MMA added in the second step of core-shell polymerization on τ_s and J for the ER suspensions (MBAM = 0.3 wt %).

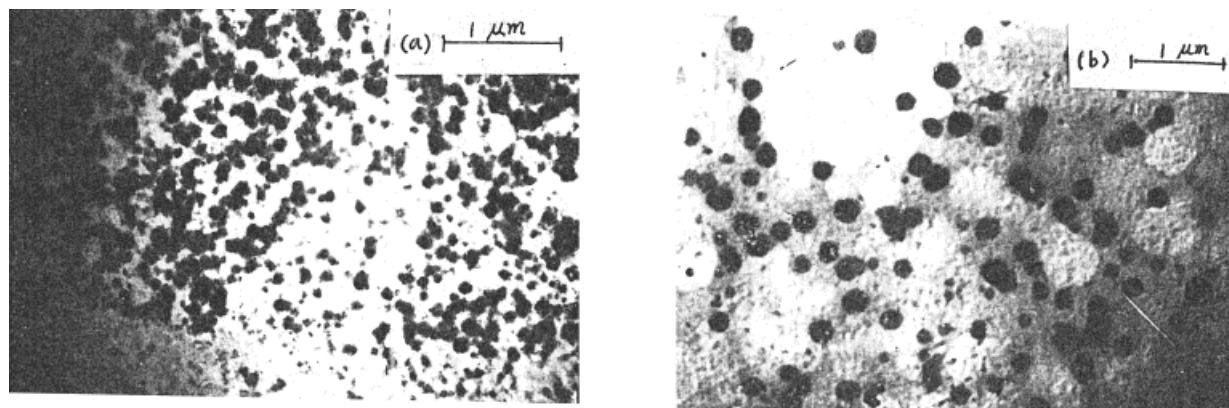


Figure 8 Microphotographs of (a) suspension containing PAALi particles and (b) suspension containing particles with PAALi as the core and PAM as the shell.

hence, raising τ_s . However, when MMA was used as the second monomer added after the polymerization of Li salt of AA, the suspension obtained showed a bad effect on the ER behavior, as illustrated in Figure 7. Both τ_s and J decreased with the increase of the amount of MMA used in the polymerization for shell. The decrease of J is attributed to the inhibition of ion migration between particles by the PMMA shell, whereas the decrease of τ_s may be due to the poor adhesion between PAALi and PMMA, which lowers the dipolar-dipolar interaction between particles. Besides, since the water solubility of MMA is much poorer than AM, some homopolymer of MMA may be formed in the oil phase, and the resulting PMMA particles hinder the ER behavior.

The core-shell-type PAALi-PAM particles were compared with the PAALi particles under a transmission electron microscope. The microphotographs (Fig. 8) indicate that the size of the core-shell-type particles is larger than that of the PAALi particles, which demonstrates that without addition of new emulsifier, the second monomer, AM, was polymerized on the PAALi particles.

CONCLUSION

ER suspension composed of PAALi as dispersed particles and chlorinated paraffin oil as a dispersing medium can be synthesized directly via inverse emulsion polymerization. The ER suspension showed maximum yield stress at 5 wt % wa-

ter content, 0.3 wt % MBAM, and 6 wt % polymer stabilizer. Glycerol can be used as an activator when water is absent in the ER suspension. The ER suspension containing glycerol as activator exhibited higher thermostability than the hydrous ER suspension. The ER suspension obtained by core-shell-type inverse emulsion polymerization and containing PAALi particles with PAM as shell showed better ER behavior than that containing PAALi particles without PAM shell.

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