

CHAPTER II

LITERATURE SURVEY

The ER effect generally depends on many parameters: electric field strength, frequency, shear rate, composition, concentration, temperature, and so on. Understanding all of these parameters is important to develop and improve the ER fluids.

2.1 The Particle Dispersion ER fluids

The first report on the particle dispersion ER fluids appeared in 1949. Winslow (1949) demonstrated that certain dispersions composed of finely divided solids such as starch, carbon, limestone, gypsum, flour, etc., dispersed in a non-conducting liquid such as a lightweight transformer oil, olive oil or mineral oil, etc. exhibited electrorheological behavior. These materials showed a dramatic increase in flow resistance when exposed to an electric field of the order of 4 kV/mm. He termed the dispersions with an enhanced viscosity the 'electroviscous fluids'. The potential value of such fluids was immediately recognized and several firms attempted to utilize them in vibrators and dampers, employing the silica gel the most active material as described by Winslow.

After Winslow discovered the electroviscous effect or the Winslow effect, there were several investigators who continued to develop new electroviscous fluids. Silica and calcium titanate dispersions are typical of most electroviscous systems. Klass *et al.* (1967) studied the electroviscous properties of silica and calcium titanate dispersions in terms of composition.

shear rate, field strength, frequency, and temperature. Electroviscous effects increased with increasing volume fraction of the disperse phases, field strength, and temperature, but decreased with increasing shear rate and frequency.

A number of theories to explain the ER effect have been proposed. One theory was proposed by Stangroom (1983); he reported that the additive such as water played an important role for ER effect. Under the influence of an applied electric field, the ionic migration of water causes the water molecules to move to the surface of the particle at a particular pole. A thin water film or bridge between adjacent particles is then created, leading to extensive water binding between particles.

Block *et al.* (1990) suggested a new type of ER fluid: anhydrous or water-free ER fluid. Conductive materials can be used as substrates because when they are bounded by insulating surfaces they can spontaneously undergo interfacial polarization. The naphthalene (PNQR) and anthracene (PanQR) homologous proved to be particularly effective and can compare very favorably with more traditional water-activated ER fluids.

The structures of nonaqueous suspensions subjected to electrical fields and continuous shear were described by Klingenberg and Zukoski (1990). They suggested that a finite shear force was necessary to destroy the columnar or chain-like structures.

Gow and Zukoski (1990) reported electrorheological characteristics of suspensions of polyaniline dispersed in silicone oil. Polyaniline is a stable conducting polymer in air and a promising material for ER fluid applications.

There have been other attempts to find alternative materials to be used as ER fluids. Cipriano *et al.* (1991) used a polymeric or monomeric crown ethers and quaternary amines in mineral and silicone oils. ER effect increased with increasing volume fraction of the disperse phases, field strength but decreased with increasing shear rate. These ER fluids had good thermal

stability and low abrasiveness. Ahmed *et al.* (1991) prepared PMMA particles dispersed in mineral oil by dispersion polymerization in order to improve stability against sedimentation, to reduce current density, and to achieve good electrorheological responses. Halsey and Martin (1992) studied the rheology of ER fluid by using monodispersed silica sphere coated with an organophilic silane-coupling agent dispersed in 4-methylcyclohexanol. They observed power law shear thinning with an exponent equal to $2/3$, but yield stress was not observed in this material.

Yoshino *et al.* (1993) employed poly (3-alkylthiophene) suspended in anisole to investigate ER effect. The ER fluid exhibited anomalous voltage dependent viscosity. For temperatures between 10-40°C, the viscosity increased with increasing applied voltage, but at the temperature of about 60°C the viscosity decreased with increasing applied voltage, with a tendency towards saturation. Kuramoto *et al.* (1994) compared the ER effect between polyaniline-coated silica particles (prepared by oxidative polymerization of aniline with ammonium persulfate) and bare silica particles dispersed in silicone oil at various electric field strengths at 150°C. The polyaniline-coated silica particles showed a better ER effect; the bare silica particles showed a lesser ER effect because of the desorption of physically absorbed water molecules from the silica particle surfaces.

Powell *et al.* (1995) explored new materials to use as ER fluids, fullerene and fullerene-like particles in mineral oil and silicone oil. The fullerene and fullerene-like particles are highly polarizable; the electrons are quite mobile on the surface of the particles, producing a charge separation (dipoles) on the surface of particles in the presence of an externally applied electric field. Wu and Shen (1996) studied suspensions of chitin and its derivatives particles in silicone oil with glycerin as the activators. Since the polar liquid-glycerin has a much higher boiling point than that of water, so the glycerine-based ER fluid has a better thermal stability. Its ER effect was found

to depend on particle concentration and the balance between the viscous and polarization forces.

Kuramoto *et al.* (1996) prepared poly (*o*-anisidine) and poly (*o*-anisidine)-coated silica particles dispersed in silicone oil. These ER fluids showed greater ER effects in nonaqueous solutions than those of silica particle suspensions at high temperatures, because for the latter ER fluid the desorption of physically absorbed water molecules occurred. Ptocharski *et al.* (1997) used a doped conjugated polymer [poly(*p*-phenylene) (PPP) treated with ferrous chloride] particles dispersed in silicone oil. The moderately doped PPP had high dielectric constant and low conductivity so the magnitude of the observed ER effect was dramatic. Wu *et al.* (1996) studied ER effect of suspensions containing dihydroxypropyl chitosan particles in silicone oil with glycerin as activator as functions of activator content, field strength, concentration, and shear rate. The ER effect increased with increasing activator content, field strength, and particle concentration but decreased with increasing shear rate.

Cho *et al.* (1998) studied effect of ionic pendent groups on a polyaniline-based electrorheological fluid. Particles of semiconducting polyaniline and a copolyaniline bearing ionic substituents were synthesized. ER fluids consisting of these particles were tested and compared with each other in terms of rheological and dielectric properties. The shear stress of these ER fluids at different applied electric field strengths could be scaled into a universal curve by the dynamic yield stress, which increased linearly with the square of the electric field strength. The results of this experiment suggested that ER performance can be improved by increasing the conductivity of the polyaniline particles.

2.2 The Homogeneous ER Fluids

The earliest reported observations of the ER effect for homogeneous fluids were glycerin and paraffin oils in the 1890s. In the 1930s, the ER effect was also observed in polar liquids such as nitrobenzene and anirin and in suspensions of superfine metal powders. The ER effects of low molecular weight LC materials have been observed since the 1960s. In the 1970s, polar liquids and nonpolar liquids containing ionic compounds were also shown to exhibit such an ER effect. In all cases, the viscosity in the electric field was only two or three times above the zero-field viscosity (Inoue *et al.*, 1998 and Inoue and Maniwa, 1996).

In the early 1990s, the discovery of an extremely large ER effect in certain liquid crystalline (LC) polymer fluids were observed, many times greater than those previously found in the low molecular weight LC materials (Inoue *et al.*, 1998). A dramatic ER effect could be obtained from a solution of poly(γ -benzyl-*L*-glutamate) (PBLG), which is a lyotropic liquid crystalline polymer in a low-boiling point solvent, such as dioxane, tetrahydrofuran, or *m*-cresol or in a low-boiling chlorine-containing solvent, such as methylene chloride or chloroform.

Yang and Shine (1992) studied liquid crystalline polymer solutions, specifically the nematic solutions of poly(*n*-hexyl isocyanate) (PIHC) in *p*-xylene; they showed increases in viscosity upon applying an electric field. The increases varied from a factor of 2 to 35.

Sasaki *et al.* (1996) studied solutions of poly(*n*-hexyl isocyanate) and poly(γ -benzyl-*L*-glutamate) in a solvent, at low concentrations such that they were in non-crystalline states. These ER fluids could provide a large difference in torque before and after the application of an electric field; therefore, they demonstrated a potential for the ER fluids to be used in automotive clutches or in trust bearing.

Inoue and Maniwa (1996) compared the ER effect between a thermotropic LC polymer and a lyotropic LC polymer namely side-chain LC silicones and poly(γ -benzyl-*L*-glutamate) solution respectively, subjected to a DC voltage. Both fluids showed a dramatic ER effect. The thermotropic LC polymers exhibited Newtonian and viscoelastic behaviors similar to that of low molecular LC materials, while the lyotropic LC polymer solutions exhibited viscoelastic behaviors with a yield stress similar to particle dispersion ER fluids. They suggested different ER mechanisms responsible: for the thermotropic LC polymer, the ER effect was dominated by the interaction between LC domains; for the lyotropic LC polymer, the ER effect was due to the orientation of the dipoles.

Tanaka *et al.* (1996) studied the ER effect of the suspension of poly(*n*-hexyl isocyanate) or (PHIC) in *p*-xylene by applying DC voltages. The maximum shear stress could be enhanced by the electric field up to a factor of 20. The ER effect was attributed to the orientation of the PHIC molecules. The stress overshoots were observed at 1.0-1.5 kV/mm. They further studied the solutions of poly(γ -benzyl-*L*-glutamate) in 1,4-dioxane subjecting to a stepwise electric field plus a DC voltage. In this case, the maximum shear stress was enhanced by a factor of 10. The ER effect was suggested to be caused by the orientation of the rod-like molecules of PBLG (Tanaka *et al.*, 1997).

Yang and Huang (1997) studied the solutions of poly(*n*-hexyl isocyanate) in *o*-xylene by applying DC voltages. For the three morphologies studied (isotropic, biphasic, and full LC), the solution viscosities could be increased by amounts depending on the electric field strength.

Inoue *et al.* (1998) investigated the ER effect of several lyotropic and thermotropic LC polymer fluids and compared them with low molecular weight LC materials and particle dispersion ER fluids. For the lyotropic LC polymer solutions, the choice of solvent was important for ER effect and in

particular the electric resistance. Solvents for these polymers should have high dielectric constants and high dipole moments. For the two thermotropic LC polymers types synthesized, they differed mainly in the degree of polymerization (total number of siloxane groups) and in the mesogenic group content (ratio of side-chain bearing siloxane groups to the total siloxane groups in the polymer). In type A, the mesogenic group content was close 0.3. Its ER mechanism was similar to that of low molecular weight LC: the LC domain orientation mechanism. In type B, the mesogenic group content was between 0.2 to 0.4 and the degree of polymerization varied between 30 to 50. Its mechanism was similar to that of the particle dispersion: the morphological change or chain formation mechanism.

ER fluids using the poly(γ -benzyl-*L*-glutamate) are still difficult to put into practical use due to problems arising from the solvent used: an electrical current readily runs through; the electrodes are susceptible to corrosion; the solvent readily evaporates; and the solvent has high toxicity. *Haji et al.* (1999) investigated the ER effect of poly(γ -benzyl-*L*-glutamate-co- γ -dodecyl-*L*-glutamate) in cyclic ketone solvent or in mixed solvents between the cyclic ketone solvent and electrically insulating solvents. The use of cyclic ketone solvent provides an ER fluid having a reduced inertial torque under zero electrical field, and produces a greater difference in torque under electrical field relative to ER fluids using hydrocarbon solvents.