CHAPTER II
LITERATURE SURVEY

Electrorheological fluids are a class of materials whose rheolgical properties are controllable by the application of an electric field. The discovery of this type of material was made by Winslow (1949), who observed the ER effect with cornstarch suspended in oil. These materials have a variety of potential applications in stress transfer and damping devices.

2.1 Mechanisms

The electrostatic polarization mechanism, originally proposed by Winslow (1949), is now generally accepted as the origin of the ER response. Particles in an electric field will polarize and appear approximately as electric dipoles. These dipoles attract head-to-tail in the direction of the electric field, forming the fibrous structures commonly observed. Apparent rheolgical properties are enhanced because work is required to break these fibers to make the suspension to flow.

Particles can be polarized from a variety of mechanisms. Polarization in ER suspensions is commonly attributed to an interfacial polarization, arising from permittivity and conductivity differences between the particulate and continuous phases as Wen *et al.* (1997) and Rankin *et al.* (1998) described. They employed the linear Maxwell-Waxner model to describe interfacial polarization in ER suspensions. The dielectric properties of each phase k, the relative dielectric constant ε_k, and the conductivity σ_k - are treated as field strength and frequency-independent parameters. For uncharged particles, this leads to anisotropic, frequency-dependent interparticle forces that give rise to particulate chains, and yield stresses that scale with the square of the electric field strength. The frequency-dependence of the yield stress thus depends on the dielectric properties of both phases.

2.2 Structure Formation

Because the suspension microstructure is intimately related to the phenomenon of electrorheology, the structure growth and decay, and the behavior of these structures under applied stresses have long been of considerable interest. The substantial refractive index mismatch between particulate and suspending liquids limits the kinds of optical experiments possible in most ER fluids to optical microscopy on thin fluid layers or turbidity and diffuse transmittance measurements on bulk samples (Rankin *et al.*, 1998). Adolf and Garino (1995) instead used permittivity measurements to probe structure formation in metal-titanate-based ER fluids. These measurements revealed the time-scales for chain formation and coarsening and indicated that this process was strongly affected by quenching caused by interactions between clusters and between aggregates and the sample container walls. Adolf *et al.* (1995) have also used permittivity measurements to probe structural changes in oscillatory shear of ER fluids.

It is also possible to perform classical light scattering in model ER fluids prepared with index-matched particles. These model fluids involve weaker particle interactions and lower volume fractions than in practical ER fluids. Martin *et al.* (1998) found that particle aggregates grew in a power-law fashion at a rate that was consistent with the role of thermal fluctuation-induced interchain attractive forces. In a steady shear flow, the aggregates attained a steady-state size and tilt angle consistent with a droplet model. In oscillatory shear, the aggregate size and tilt angle exhibits a complex dependence on shear rate and field strength. They developed a kinetic chain model to qualitatively describe these observations.

2.3 Materials

Considerable progress has been made in synthesizing ER fluids with large yield stresses (greater than 1kPa at 3 kV/mm), wide operating temperature range, and low current density. A number of industrial organizations have even produced practical ER fluids on a pilot-plant scale for potential device applications. For recent reviews there of see Havelka *et al.* (1996).

The first report on the electrorheological fluids appeared in 1949, *W.M. 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, and etc. showed the electrorheological behavior. These materials showed a very marked increase in flow resistance when exposed to electric field of the order of 4 kV/mm. He supposed that the field increased the viscosity of the dispersion in term of 'electroviscous fluids' to describe his materials. The potential value of such fluids was immediately recognized and several firms attempted to use them in vibrators and dampers working with silica gel, the most active of the materials described by Winslow.

After Winslow discovered the electroviscous effect or the Winslow effect, there were many scientists who continued to work on 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 dispersion as a function of several parameters such as composition, shear rate, field strength, frequency, and temperature. Electroviscous effects increase with increasing volume fraction of disperse phase, field strength, and temperature, but decrease with increasing shear rate and frequency.

Otsubo *et al.* (1991a) studied the effect of surface modification of colloidal silica on the electrorheology of suspensions. Monodisperse silica particles were formed by hydrolyzing tetraethylorthosilicate in an ethanol solution. Silica suspensions dispersed in silicone oil were prepared by converting the medium from an ethanol solution to silicone oil. The effects on the ER behavior of surface modification of particles with silane coupling agents were studied under an oscillatory shear. The magnitude of the complex viscosity increases on the application of the electric fields. When the silica particles were treated with silane coupling agents which produce hydrogen bonding between organic groups, the ER effect was markedly improved and significant flow occurred only after some critical stress was exceeded. The suspensions changed from viscous liquids to solid-like pastes. The development of high yield stress was achieved under partial coverage of silica surfaces. The time-dependent behavior on the application of electric fields was examined for suspensions in which partial coverage take place. The thixotropic behavior was attributed to the structural breakdown induced by hydrodynamic interactions. On the other hand, the complex viscosity gradually increased with time at low stresses. Since the dielectric polarization forces overcame the hydrodynamic forces and induced the acceleration of structural formation, this rheopectic tendency served to produce higher yield stresses. Otsubo *et al.* (1992), studied the effect of adsorbed water on the electrorheology of silica suspensions under an oscillatory shear. The physically adsorbed water was primarily responsible for the ER effect. However, the fluids containing large amounts of adsorbed water did not always show excellent ER performance. The surface silanol groups had an important role in promoting the ER effect. Not only the amount but also the situation of silanol groups determined the ER activity of adsorbed water. Otsubo *et al.* (1992b), invented ER properties of silica suspensions, measured the steady shear viscosity and dynamic viscoelasticity under electric fields up to 3.0 kV/mm. At low shear rates and high field strength, the flow curve showed a plateau indicating the development of a yield stress. The yield stress was proportional to the volume fraction of particles (ϕ) and to the square of the electric field (E) for $\phi < 0.3$. The number of chains linearly increased with volume fraction. At higher volume fractions, it varied as $(\phi E)^{2.4}$. The larger value of the exponent was attributed to the crosslinking of chains.

2.4 Polymer-Based ER fluids

The presence of water in water-containing ER fluids cause the abrasion and no ER effect when water evaporates (Otsubo *et al.*, 1991b). Recently, polymers have been adopted as dry-base, nearly anhydrous ER fluids (Rankin *et al.*, 1998). This is because of the advantages polymers have over conventional materials. Polymers tend to be softer; hence they reduce or eliminate the problem of abrasion, which can lead to metallic contamination and electrical failure of the system. Polymers are less dense than minerals, which slows or reduces the rate of sedimentation of ER fluids. Perhaps the greatest contribution of polymers to the field is that the chemical and physical properties of a polymer can be changed in order to enhance its dielectric and electrical properties to meet specific requirements; for example, to improve the temperature range of application of ER fluids.

Block *et al.* (1990) suggested a new type of ER fluid: anhydrous or water-free ER fluid. Conductive materials as substrates are still preferred because when bounded by an insulating surface they can undergo an interfacial polarization. The naphthalene (PNQR) and anthracene (PanQR) homologous provided to be particularly effective and can be compared 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.

Among these ER fluids, are acene quinone radical polymers (Block *et al.*, 1990 and Choi *et al.*, 1997), salt of poly (methacrylic acid) (Xie *et al.*,1995) and polyphenylene (Ptocharski *et al.*, 1997). Polyaniline has advantages over the others with respected to density, conductivity control, and thermal stability. Polyaniline is also easy to polymerize by oxidation polymerization at relatively low temperature (near 0°C) (Choi *et al.*, 1997).

Gow and Zukoski (1990) reported the electrorheological characteristics of suspensions of polyaniline dispersed in silicone oil. Polyaniline is a stable conducting polymer in air and a promising material for various applications. Choi *et al.* (1997) investigated suspension of polyaniline in silicone oil as a potential candidates for dry-base ER fluid systems and ER experiments were conducted with a Haake rheometer for steady shear experiments to investigate the effects of imposed electric fields, the polymerization temperature (molecular weight), and the dispersing oil on ER performance. ER properties of polyaniline were found to be improved by increasing both the imposed electric field and the polymerization temperature. Suspensions using kerosene also showed greater ER effect than that using silicone oil because of the smaller dielectric constant of kerosene than that of silicone oil. Choi *et al.* (1998) also reported the experimental results of electrorheological and dielectric characteristics of the polyaniline suspension. They found that the shear stress of this ER fluid at different applied electric fields can be scaled into a universal curve by the dynamic yield stress which increases linearly with the square of the electric field strength. The ER performance could be improved by increasing the conductivity of the polyaniline particles and the difference in ER characteristics due to changing conductivity was consistent with the relaxation time obtained from the dielectric spectrum observed for these ER fluids.

Choi *et al.* (1998) also synthesized semiconducting polyaniline and a copolyaniline bearing ionic substituents particles. ER fluids using these particles were compared with each other with respect to their rheological properties and dielectric spectra. In the steady shear rheological experiment conducted at 3 kV/mm (DC) at 25°C, the copolymer system showed a higher stress than the polyaniline system in the whole range of shear rate. These results were interpreted in terms of the conductivities of the particles and their dielectric spectra. Especially, the different behavior in the high shear rate region can be related to the electrical relaxation phenomena observed in the dielectric spectra. They also investigated the effect of polymerization temperature of polyaniline on its ER characteristic. ER fluids with polyaniline particles synthesized at -10°C showed the best ER performance (yield stress) compared with those synthesized at higher temperatures. Semiconducting poly (aniline-*co*-*o*-ethoxyaniline) was synthesized by a chemical oxidation polymerization of aniline and *o*-ethoxyaniline with two different molar ratios in an acidic media as Choi *et al.* (1999) suggested. It was found that the ER fluids using copolyaniline showed lower ER performance due to the existence of the ethoxy side group in the main chain.

Kuramoto *et al.* (1994) coated silica particles with polyaniline by oxidative polymerization of aniline with ammonium persulphate in the presence of the silica particles. The ER property of polyaniline-coated silica suspension was found to exhibit a high performance even at high temperature. Kuramoto *et al.* (1995a) studied the ER properties of poly (*o*-anisidine) and poly (*o*-anisidine)-coated silica suspensions which were prepared by oxidative polymerization of *o*-anisidine using ammonium persulphate in the absence and presence of silica particles, respectively. The entire surface of the silica particles was completely covered with PANs polymerized using low concentration of *o*-anisidine. The effects on the ER behavior of surface modification of the silica particles coated with PANs were studied under an oscillatory shear. ER properties of PANs and PANs-coated silica particle suspensions were found to exhibit higher performance in nonaqueous solutions than those of silica particle suspensions even at high temperatures. Kuramoto *et al.* (1995b) also prepared polyaniline-coated copoly (styrene styrenesulphonate) (PSS) particles by oxidative polymerization of aniline hydrochloride using ammonium persulphate in the presence of anionic PSS particles. Polyaniline-coated PSS particles were found to be of higher dispersibility than polyaniline itself in an organic solvent. A suspension of polyaniline-coated PSS particles in silicone oil was found to exhibit high performance at higher temperature without the necessity for water.

There are three ways to improve ER properties of polyaniline-based suspensions as Xie *et al.* (1997) suggested. In order to further improve the ER properties, i.e., to enhance the static yield stress and to reduce the current density, here are three methods proposed namely; a) coating of the PAN particles with polymer; b) grafting on the particles with acrylamide; and c) nonequilibrium dedoping of the PAN particles with concentrated ammonia water. The results showed that PAN particles coated with poly (vinyl alcohol) or grafted with polyacrylamide can increase the static yield stress and decrease the current density of the ER suspension, whereas coating with poly (methyl methacrylate) or polystyrene reduced both the current density and the static yield stress. Nonequilibrium dedoping of the dried, protonated PAN particles with concentrated ammonia water showed the best effect on the ER properties of the suspension, exhibiting a static yield stress of 16 kPa with a current of 2.7 $\mu A/cm^2$ under a 2.8 kV/mm dc electric field.

Another approach to improve the performance of ER fluids that has enjoyed a wider attention recently is to use composite particles or, more specifically, multilayer or core-shell particles. Qi and Shaw (1997) coated glass microballoons with poly (vinyl alcohol) to solve the sedimentation problem. Sedimentation is often a problem in ER fluids featuring solid particles suspended in low-density hydrocarbon oil. This problem was addressed by synthesizing particles comprising silica microballoons coated with PVAL using a salt-induced coacervation process. The ER performance of the fluids based on these particles was equivalent to prototypical commercial fluids, both with respect to current leakage and shear stress under steady simple shear flow. Otsubo *et al.* (1997) invented an excellent ER suspension with composite particles consisting of polymer core and inorganic shell. When the composite particles were subjected to jetstream agitation, the ER effects were strikingly enhanced. Since the ER effects can be attributed to the shell layers on the polymer particles, the surface of inorganic particles must be barely exposed to the surrounding oil. The importance of surface conditions is demonstrated by a scaling analysis. The creep curves at low stresses for suspensions in electric field were composed of instantaneous elastic and retarded elastic regions. But the suspensions showed no elastic recovery after the removal of stresses. The creep and recovery behaviors were purely plastic. The thick column formed by several chains was responsible for purely plastic response. The particle concentrations in column were increased in nonuniform electric fields. Since the increase in particle concentration of column led to high yield stresses, the ER performance of suspension as an overall response can be improved by the electrode design.

Despite their wide spread use in controlling the properties of colloidal and particulate suspensions, very few studies have reported the effect of additives on ER activity. Kim and Klingenberg (1996) observed that adding a nonionic surfactant to an alumina-particle-containing ER fluid modified the ER response by two mechanisms: surfactant-enhanced interfacial polarization, and surfactant phase separation and interparticle bridging at high surfactant concentrations. These phenomena could also conceivably occur in water-containing ER fluids.