CHAPTER II
LITERATURE SURVEY

2.1 The ER Phenomenon

Under the application of electric field, ER fluids are generally recognized as behaving according to the Bingham plastic model for fluid flows, meaning that they will behave as a solid up to a certain yield stress. At stresses higher than this yield stress, the fluid will flow, and the shear stress will continue to increase with the shear rate, so that:

$$\begin{aligned} &\tau(\dot{\gamma}, E_o) = \tau_y(E_o) + \eta\dot{\gamma} \qquad \tau \geq \tau_y, \\ &\dot{\gamma} = 0 \qquad \tau < \tau_y, \end{aligned} \qquad (2.1)$$

where τ is the shear stress, τ_y is the yield stress, E_o is the applied field strength, η is the shear viscosity, and $\dot{\gamma}$ is the shear rate.

Both the yield stress and the viscosity are two major important parameters that affect the design of ER fluid-based devices. The field induced yield stress τ_y depends on the electric field strength. For this dependence, some theoretical models have been derived but neither one is able to reflect the relation properly. There are two important values for the yield stress: the static yield stress and the dynamic yield stress. The static yield stress is defined as the value of stress needed to initiate flow, i.e., the stress needed to change from solid to liquid. The dynamic yield stress is the value of stress needed in zero-strain rate conditions to go from liquid to solid (Mavroidis C. *et al.*).

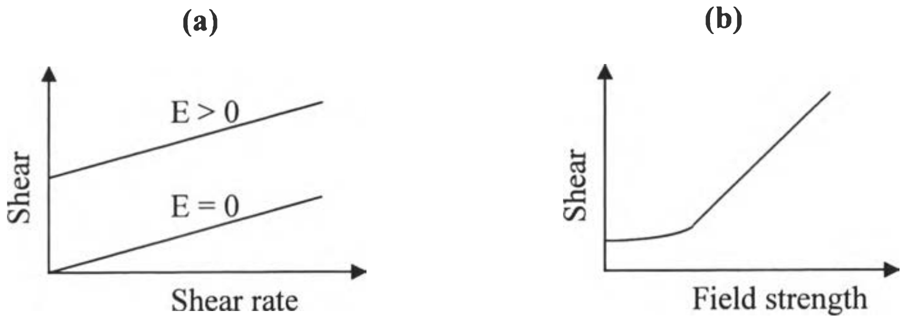

Figure 2.1 Schematic draw of rheological behavior of the electrorheological fluids.

As shown in Figure 2.1(a), the ER fluids behave in the same way as a Newtonian liquid in the absence of electric field. The dramatic field-induced rheological changes are accompanied by equally dramatic changes in the suspension structure. Following the application of electric field, the particles rapidly aggregate into fibrous columns or particle chains perpendicular to the electrodes as shown in Figure 2.2. The columns become thicker with increasing particle concentration and electric field strength (Choi *et al.*, 2001). These structures cause the fluids behave like a solid until the shear stress reaches a critical level and assumes a liquid character once this threshold value has been exceeded. The critical shear stress can be adjusted according to the electric field. A qualitative depiction of this relationship is given in Figure 2.1(b). When the field strength exceeds E_o, there is a virtually linear increase in shear stress and field strength.

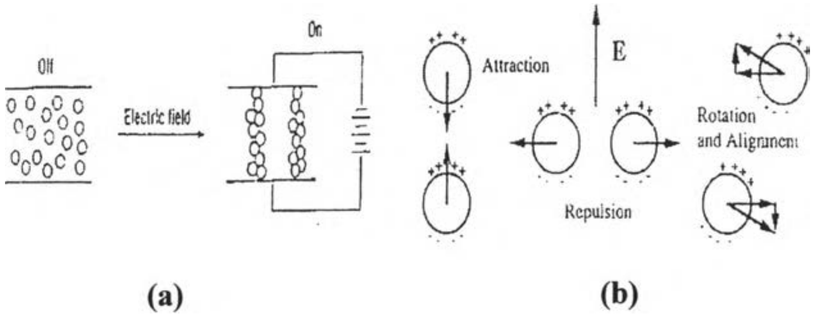

Figure 2.2 (a) In the presence of an electric field, the particles in an ER fluid form chains or fibrillated structures; **(b)** Mechanism of chains formation and alignment of dipole particles. The interactions of these dipoles cause attraction, repulsion, rotation, and alignment of particles, creating chains that align with the applied electric field.

2.2 Proposed Mechanisms

Several different phenomena have been proposed as the origin of the ER response. Although, the electrostatic polarization mechanism appears to explain most experimental observations, other phenomena are likely influence behavior in some systems or under some conditions.

2.2.1 The Electrostatic Polarization Mechanism

The electrostatic polarization mechanism, proposed originally by Winslow (Winslow, 1949), attributes the origin of the ER effect to the field-induced polarization of the dispersed phase particles relative to the continuous phase. In this model, polarization can arise from a number of charge transport mechanism, including electronic, atomic, dipolar, nomadic, or migration polarization. Particles in an electric field will be polarized and appear approximately as electric dipoles. Neighboring dipolar particles are attracted to each other when pairs are aligned with the external field, and repel when perpendicular to the field, thus producing the fibrous structures observed experimentally. In order for the suspension to flow, the fibrous columns must be deform or broken; the large increase in shear stress, and thus the apparent viscosity, arise from the work required to overcome the attractive dipolar particle interactions.

The Maxwell-Wagner model (Choi *et al.*, 2001) is the simplest description of particle polarization accounting for both the particle and fluid bulk conductivities, as well as permittivities. From this theory, for DC and low-frequency AC electric fields, particle polarization and particle interactions will be controlled not by the particle and fluid permittivities, but rather by the particle and fluid conductivities. Conductivity in the bulk of both phases will result of free charge accumulation at the particle/fluid interface. In a DC field, mobile charges accumulating at the interface screen the field within the particle, and particle polarization is completely determined by conductivities. In a high-frequency AC field, mobile charges have insufficient time to respond, leading to polarization dominated solely by permittivities, unaffected by conductivities. At intermediate frequency, both permittivities and conductivities play a role.

2.2.2 The Overlap of Electric Double Layers Mechanism

In this mechanism, each particle is surrounded by a diffuse counter ion cloud that balances its charge (an electric double layer). Under the applied field, this cloud will distort and overlap with the counter ion clouds of its neighbors. This enhances the electrostatic repulsion between particles which must be overcome in order for particles to flow past one another. This mechanism has been criticized because double layers in ER fluids will be very large even prior to any distortion. No quantitative theory has been developed based on this mechanism, but as the deformation of the electric double layer is a polarization phenomenon, this mechanism is simply a special case of the electrostatic polarization mechanism, as noted by Block and Kelly (Kim and Park, 2002).

2.2.3 The Water Bridging Mechanism

This model attributed the large increase in suspension viscosity to the formation of water bridges between particles, which must be broken (i.e., interfacial tension must be overcome) in order for the suspension to flow. The electric field strength dependence was associated with the migration of ions through the particle pores. When the field is applied, ions move out of the pores, carrying water to the particle surface and thus permitting the formation of bridges between particles. When the field is removed, surface tension pulls the water back into the particle pores.

The water bridging mechanism has received some merit because many systems show a decreased ER response with decreasing water content. However, some systems exhibit a significant ER response while being essentially anhydrous, providing evidence against this mechanism. The proposed explanations also do not include a long-range attractive force capable of rapidly producing aggregates in quiescent suspensions.

2.3 Literature Review

The first report on the electrorheological fluids appeared in 1949; Winslow (1949) demonstrated that certain dispersions composed of finely divided solids dispersed in a non-conducting liquid showed the electrorheological behavior. These materials showed a very marked increase in flow resistance when exposed to electric field of 4 kV/mm. He supposed that the field increased the viscosity of the dispersion in term of 'electroviscose 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, there were many scientists who continued to work on electroviscous fluids. 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, electric 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.

In general, there are two types of ER fluids which are wet-base and dry-base type (Choi et al., 1999). In the wet-base system having hydrophilic particles, the particle chain structure is caused by the migration of ions in the absorbed water, such as corn starch, silica gel, and cellulose. However, they have some limitations on the applications such as thermal stability because of the evaporation of water and the corrosion of the device. Therefore, development of the dry-base ER system has received great attention due to the dry-base ER fluids render better rheological properties for application in a wide temperature range (Xu and Liang, 1991).

Recently, there has been interest in using conductive polymers as suspended particles for dry-base ER fluids. Conductive polymers can offer a variety of advantages for ER systems: better thermal stability, insolubility, and more controllable viscosity. Suspensions of conductive polymers exhibit intrinsic ER properties without the necessity to introduce other additives. The polarization is induced by the motion of electrons within the suspended particles under application of electric field. Among them, polyaniline and is derivatives are widely investigated.

Choi *et al.* (1998) investigated suspension of polyaniline in silicone oil as a potential candidate for dry-base ER systems. The steady shear experiments were conducted to investigate the effect of imposed electric fields and particle conductivity. ER performance of this fluid found to be improved by increasing both electric field strength and the conductivity of the polyaniline particles. Moreover, the shear stress of this fluid at different applied electric fields could be scaled into the universal curve by the dynamic yield stress which increased linearly with the square of the electric field strength.

Various types of dopants were used to adjust the particle conductivity of conductive polymers. Kim *et al.* (2000) investigated the effects of electric field strength and particle concentration on the ER properties of dodecylbenzene sulfonic acid (DBSA) doped polyaniline suspensions in silicone oil. Similar to many other ER fluids, this suspension also possessed the properties that yield stress increased as particle concentration increase. The camphorsulfonic acid (CSA) doped polyaniline base ER fluids were investigated by Jang *et al.* (2001). The ER response of this system increased with electric field strength and showed the best electrical stability in the region of pH 10. They proposed that the electron movement within the PANI-CSA particles and electron hopping between the PANI-CSA particles play the important role in the surface polarization, the yield stress increases.

Cho *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 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 performance. ER fluids with polyaniline particles synthesized at -10°C showed the best ER characteristic 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 acid 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.

Plocharshi *et al.* (1997) studied the ER response of the suspension of poly(p-phenylene), PPP, in silicone oil. PPP was chemically synthesized and doped with ferrous chloride and the ER performance was measured using rotational rheometer with a two-concentric-cylinder geometry. It was found that the magnitude of the ER effect increased with dielectric constant and the moderately doped PPP had high dielectric constant, low conductivity and sufficient stability.

Kim et al. (2002) investigated the ER response of polypyrrole-coated polyethylene suspensions in mineral oil. PPy was coated on PE particles to enhance the particle polarization by increasing the particle surface conductivity. It was found that the ER response of the PPY-coated PE suspension was greatly enhanced compared to that of the PE suspension. The ER response initially increased with the amount of pyrrole, due to the enhanced particle polarization, past through a maximum, and then decreased with the amount of pyrrole. They suggested that the decrease in the ER response at large amount of pyrrole developed from the increase conduction between the Ppy-coated PE particles.

Despite their wide spread use in controlling the properties of colloidal and particulate suspensions, very few studies have reported the effect if 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.

2.4 Objective and Scope of Work

Our objective for this dissertation is to develop conductive polythiophene as a potential candidate for anhydrous particles in high-performance electrorheology applications.

In this research work, the perchloric acid-doped poly(3-thiopheneacetic acid), PTAA/silicone oil suspension is used as electrorheological fluid. We have studied the rheological properties of this suspension under the application of DC electric field. Since electrorheological fluid is operated in both dynamic and steady conditions in the actual applications, the ER materials should be able to maintain the ER characteristic under either condition. Therefore, the investigation of ER properties is done in both dynamic, i.e., oscillatory and steady shear conditions.

In chapter IV of this dissertation, the electrorheological properties of the PTAA/silicone oil suspension is investigated under oscillatory shear flow. The dynamic moduli, storage (G') and loss (G"), are measured. The effects of electric field strength, particle concentration, and particle conductivity are reported in this chapter. An additional, the equilibrium rheological properties of PTAA/silicone oil suspension which satisfy the sol-gel transition criteria can be observed. We have analyzed the equilibrium ER properties according to Winter and Chambon gelation criterion as illustrated in chapter VI. Further study on the ER properties of this suspension under steady shear flow is done and reported in chapter V. In this chapter, static yield stress values of PTAA/silicone oil suspension are examined to study the effects of electric field strength, particle concentration, particle conductivity, operating temperature, and nonionic surfactant addition. Finally, the creep and recovery behaviors of this polythiophene suspension are investigated to study the effects of the magnitude of applied stress, electric field strength, particle concentration, and particle conductivity. The investigated results are reported in chapter VII.