

CHAPTER I

INTRODUCTION

1.1 Background

1.1.1 What are Electrorheological Fluids?

During the past decade, the development of materials that respond in a well-defined way to an applied electric field has captured the imagination of scientists and engineers worldwide. Electrorheological (ER) fluids represent a unique class of electroactive materials that exhibit modified flow properties under an electric field. ER fluids demonstrate orders-of-magnitude changes in apparent viscosity in milliseconds with the application of just a few watts of electrical power. This fast, strong, and reversible gelation provides a novel and efficient way to transfer energy and control motion (Havelka and Pialet, 1996).

ER fluids are most broadly classified to be either the particle dispersion or the homogeneous types (Inoue *et al.*, 1998). Particle dispersion ER fluids are typically composed of electrically polarizable particles dispersed in a low-dielectric oil. The first particle dispersion ER fluids were invented by W. M. Winslow in the late 1940s. The 1980s were a period of intensive investigation of various particle dispersion ER fluids by using semiconductor or other anhydrous particles and modified conductor components in a nonconducting liquid (Havelka and Pialet, 1996 and Inoue *et al.*, 1998).

Homogeneous ER fluids which contain no suspended particles have been investigated even longer. The earliest reported observations of the ER effect (an increase in viscosity or shear stress upon exposure to an electric field) were glycerin and paraffin oil in the 1890s. In the early 1990s, there were discoveries of an extremely large ER effect in certain liquid crystalline

(LC) polymer fluids; dramatic changes in rheological properties were many times previously found in low molecular weight LC materials (Inoue *et al.*, 1998).

1.1.2 Desired Properties of ER Fluids

The required properties for goods ER fluids are (Salamone, 1996):

1. High shear stress at low electric field. This property leads to small power requirements.
2. Low zero-field viscosity. This property implies a low viscosity of the nonconducting continuous medium (e.g., oil) and low volume fraction of the dispersed phase. However, an appropriate balance must be sought between low zero-field viscosity and high shear stress at high fields.
3. Low conductivity. This property leads to a lower power requirement. Low power keeps heat dissipation low, minimizes safety hazards, and contributes favorably to the size and economics of the ER fluids-based devices. The desired conductivity range for ER materials is reported as 10^{-8} to 10^{-5} S/cm where S stands for Siemens.
4. Wide temperature range of applications. This would enable ER fluids to operate in cold and hot temperatures (-40 and 250°C).
5. Stable dispersion. Sedimentation of the particulate reduces the effectiveness of ER fluids.
6. Low abrasion. This would reduce wear of device components.
7. Noncorrosive.

8. Good material compatibility. Good compatibility of ER fluids with standard sealing materials is needed so that specialized and relatively expensive materials would not be required in the design of components and the maintenance of reliability of devices.
9. Nontoxic. This is desirable to ensure the safety of users and make the fluids environmentally acceptable.
10. Low cost. The cost of the fluids has to be kept low for ER fluids-based devices to be competitive with conventional devices.

In the formulation of an ER fluid for a specific application, several properties are sought after (Table 1.1). Table 1.1 lists the desirable properties and values and corresponding applications (Havelka and Pialet, 1996).

Table 1.1 Electrorheological properties and corresponding technical applications

ER material property	Value	Comments
Dynamic yield stress at 6.0 kV/mm	> 4.0 kPa	Maintain field-induced stress at high shear rates
Zero-field viscosity	< 100 cP	As low as possible and insensitive to temperature
Current density ^d at 6.0 kV/mm	< 300 mA/m ²	Must be low to maintain particle polarization and to minimize power consumption
Response time	Milliseconds	Rapid turn on and off
Dispersion properties	Stable	Nonsettling, easily redispersing. no electrophoresis

^dDirect current

1.1.3 The ER Phenomena of Particle Dispersion

In the absence of electric field, ER fluids show Newtonian behavior while on the application of an electric field (typically, a few kilovolts per millimeter), particles become polarized, and the local electric field is distorted. The migration of mobile charges within the particle to areas with greatest field concentration increases the polarizability of the particle and results in a larger dipole moment. These field-induced dipoles attract one another and cause the particles to form chains or fibrillated structures in the direction of the field (Figure 1.1). These chains are held together by interparticle forces that have sufficient strength to inhibit fluid flow. Subjecting these fibers to a shearing force pulls particles apart while dipoles on the particles attract replacement particles. An equilibrium is established between chain formulation and breaking. When the electric field is removed, the particles return to a random distribution and fluid flow resumes (Havelka and Pialet, 1996).

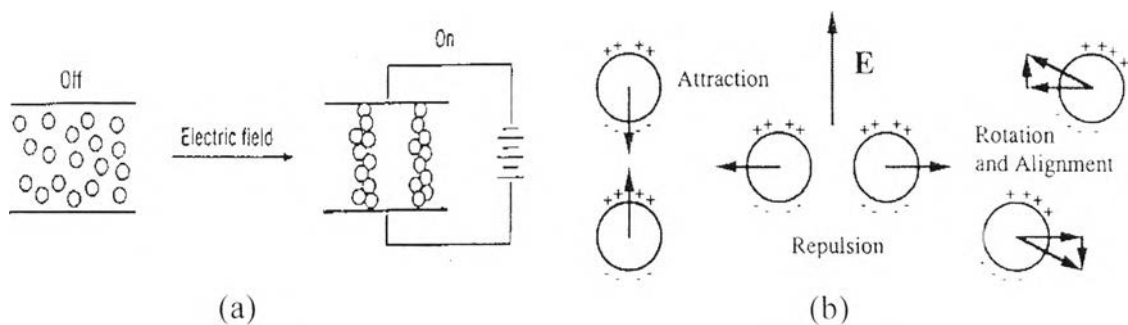


Figure 1.1 (a) In the presence of an electric field, the particles in an electrorheological (ER) fluid form chains or fibrillated structures; (b) Mechanism of fibrillation and alignment of dielectric particles. The interaction of these dipoles cause attraction, repulsion, rotation, and alignment of particles, creating chains that align with the applied electric field (Bonnetcaze and Brady, 1992).

When an electric field is applied, the fluid changes from a liquid to a semisolid and can be described as a Bingham plastic. The shear stress (τ) for the Bingham plastic model is given by

$$\tau = \gamma\eta + \tau_{ER} \quad (1.1)$$

where γ is the shear strain rate, η is the viscosity, and τ_{ER} is the electric field-induced dynamic yield stress (Havelka and Pialet, 1996).

1.1.4 LC Polymers

LC polymers may be divided into two broad categories (Kroschwiz and Mary, 1995), thermotropic and lyotropic, according to the principal means of breaking down the complete order in the solid state.

Thermotropic LC polymers result from the melting of mesogenic (semirigid or rigid unit) solids due to an increase in temperature. These polymers may exhibit LC order in melt. Lyotropic LC polymers may exhibit LC order in solution and possess at least one liquid crystal phase in the certain ranges of concentration and temperature resulting in an anisotropic solution. The mesophasic structure of LC polymers give birefringence in solutions and melts and they have been studied by optical methods (Kroschwiz and Mary, 1995 and Mark *et al.*, 1987).

1.1.4.1 *Anisotropic Solution*

An anisotropic solution consists of domains of ordered molecules, each with high molecular orientation, but are randomly oriented with respect to each other. Schematic representation of domains is shown in Figure 1.2. In an “anisotropic region”, molecules are highly ordered, they align in the same directions. In an “isotropic region”, molecules are highly disordered, they align in random directions (Nakajima, 1994).

The formation of an anisotropic solution can be seen from the graph showing the change in solution viscosity with increase in solution concentration (Nakajima, 1994) (Figure 1.3). At low concentration, the solution viscosity increases with polymer concentration in the normal way like

an isotropic solution. At the critical concentration, when molecules are so crowded they restrict the movement of each other, crystalline domains are formed leading to reduction in the occupied volume and hence, the viscosity starts to decrease. The viscosity then reaches the minimum at which the solution is fully LC formation, when the increase in number of molecules can no longer be compensated by reduction in the occupied volume, and the viscosity starts to increase again.

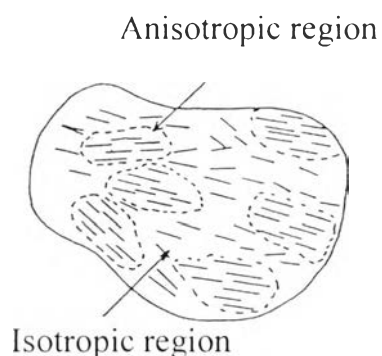


Figure 1.2 Schematic representation of the domain theory.

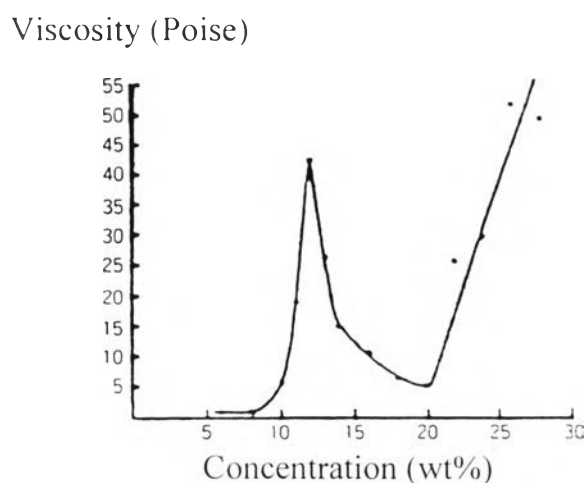


Figure 1.3 The graph showing the viscosity-concentration relationship of a solution of poly(p-phenylene terephthalamide) (PPTA) with a moderate molecular weight in sulfuric acid.

1.1.4.2 Aromatic Polyamides

Typically, lyotropic LC polymers can be classified into twelve polymer families (Mark *et al.*, 1987). Only aromatic polyamides will be discussed.

The para-linked aromatic polyamides are representatives of a class of polymers with a rodlike structure. These polymers yield LC solutions because of an inherently extended rigid chain. The formation of LC solutions of polyamides can be affected by the polymer structure (extended chain and trans configuration of the amide group), the molecular weight and axial ratio (which must exceed a minimum value), solvent-polymer interaction, and the solubility must be sufficiently high to exceed the critical concentration. The temperature affects solubility and liquid crystalline concentration range. With an increase in solution temperature, the critical concentration will be shifted to higher concentration values. Some, but not all, polymers show appreciable inverse dependence of the critical concentration on molecular weight. The range of concentrations at which anisotropy begins is generally 3-10 wt% (Mark *et al.*, 1987).

The LC solutions of aromatic polyamides are normally nematic. Nematic phase, in which the direction along the director is the only kind of long-range order present. The long axes of the molecules remain substantially parallel, but the positions of the centers of mass are randomly distributed. There is orientational order, but there is no positional order. Because physical properties of the material are not the same in all directions, the nematic phase is anisotropic. Orientation of nematic liquid crystals may be achieved easily in electric or magnetic fields (Kroschwiz and Mary, 1995 and Mark *et al.*, 1987).

Poly(p-benzamide) (PBA)

PBA is one in the family of aromatic polyamides. Its repeating unit is shown in Figure 1.4. It contains aromatic rings in its

backbone which provide high rigidity to the main chains. With such a high rigidity, the chains tend to take up the extended chain conformation. The molecules are para-substituted giving a structure of high regularity and planarity. This enables the molecules to get close together for maximum intermolecular interactions and maximum packing. There are extensive H-bonding between adjacent molecules. The molecules behave like rigid-rod (rodlike). PBA forms LC regions in solution at a certain temperature and concentration resulting in an anisotropic solution (Rivas *et al.*, 1996 and Kroschwiz and Mary, 1995).



Figure 1.4 Repeating unit of poly(*p*-benzamide).

1.1.5 The ER Phenomena of LC Polymers

Inoue and Maniwa (1996) pointed out that different mechanisms were involved in the ER effect of thermotropic, and lyotropic LC polymers. Physical structure of LC polymers and the interactions between LC domains were investigated in order to explain the increase in viscosity change in such materials due to an applied electric field.

In the case of thermotropic LC polymers, the mechanism involves a physical reinforcement of the electrical interaction between adjacent LC domains. They attributed the weakness of the ER effect in the LC materials to the weakness of this interaction; the domains themselves are all aligned in an electric field, but they are vulnerable to mutual movements under shear. This led them to consider the introduction of a more flexible molecular chain, which could effectively form a link between adjacent domains, in the belief that the natural extension and tautening of such chains when the domains were aligned by an electric field would create a resistance to mutual

slippage between the domains and thus increase the viscosity of the fluid; the idea is illustrated as shown in Figure 1.5 (Inoue and Maniwa, 1996).

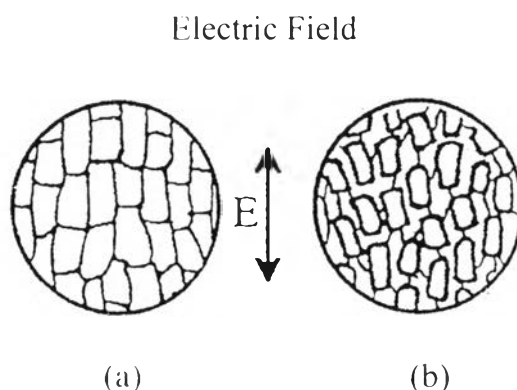


Figure 1.5 Presumed orientation of conventional liquid crystals and LC polymers under applied electric field: (a) low molecular weight liquid crystal; (b) liquid crystalline polymer.

For lyotropic LC polymers, the approach involves a search for liquid crystals exhibiting a high viscous anisotropy. LC domains generally are rod-shaped and possess dipole moments. They exhibit viscosity anisotropy, which is generally referred to as Miesowicz viscosities (Figure 1.6) when these molecules are oriented in an electric field. η_a , η_b and η_c depend on the relative direction of their directors to the flow. When a prevalent external field freezes molecules in the direction transverse to the flow, liquid crystals exhibit the highest viscosity, η_c . In contrast, the lowest viscosity, η_b , represents the flow resistance when molecules are oriented parallel to the flow. Under no applied electric field, liquid crystals normally flow with a viscosity close to η_b . Hence, the maximum viscosity enhancement or the ER effect is closely related to the ratio of these two viscosities: η_c/η_b . The ratios of low molecular weight LC are relatively small and are of no practical interest. However, for lyotropic LC polymers, significant ratios were reported, and certainly, their potential to be an ER fluid may be worthy of investigations. The viscous anisotropy may be

expected to increase with increasing aspect ratio (i.e., the ratio of the molecule's length to its diameter) and dipole moment. The LC polymers composed of rodlike molecules with a large aspect ratio are also expected to show much larger stress enhancement compared with LC of small molecules (Inoue *et al.*, 1998, Inoue and Maniwa, 1996, Tanaka *et al.*, 1997 and Yang and Huang, 1997).

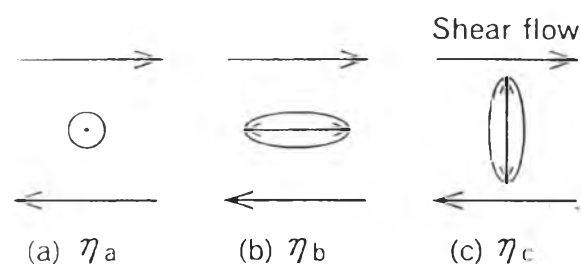


Figure 1.6 Miesowicz viscosities: (a) director perpendicular to flow direction and velocity gradient; (b) director parallel to flow direction; (c) director parallel to velocity gradient ($\eta_a, \eta_b < \eta_c$).

1.2 Applications

Applications on engineering devices or systems are based on the controllable, rapidly variable rheological properties of ER fluids. The proposed applications are, for examples, vibration damping, force transfer/clutches, positioning/chucking, and valves (Havelka and Pialet, 1996).

1. Vibration damping. Vibration damping can be used in vehicles and in industrial equipment. The vehicle applications include primary suspensions, engine mounts, cab mounts, seat dampers, bushings, and torsion bars. The industrial applications of vibration damping include beam stiffening and journal bearings.
2. Force transfer. It is used in primary and auxiliary clutches, servo-clutches, brakes, and tensioning.

3. Positioning applications. These applications are predominantly industrial. One major possible industrial application for available ER fluids is in positioning or chucking. A variation on the chucking application is the use of the ER fluids in a pick-and-place application for robotics.
4. Valve applications. These are also predominantly industrial. They include hydraulic valves, ink-jet printers, hydraulic vibrators, variable displacement pumps, and dynamic balancing.

Other possible uses of ER systems are: peristaltic pumps, actuators, glues, and heat transfer (Havelka and Pialet, 1996).

ER fluids based on LC polymers are superior over particle dispersion ER fluids in certain applications such as torque control and vibration damping. Their Newtonian-like flow characteristics, in contrast to the Bingham flow of particle dispersion fluids, are advantageous for use in linear control systems, since it permits the use of constant voltage under varying shear loads and speeds, and eliminates the problems of stick-slip movement often encountered with the particle dispersion ER fluids. Because they contain no particles, the polymer fluids pose no abrasion problems and permit the use of narrow electrode gap. The electrode gap can be decreased to 50 μm or less, making it possible to use applied electric field of less than 50 V (Inoue *et al.*, 1998).

1.3 Objectives

The objective of this thesis is to synthesize and characterize poly(*p*-benzamide) (PBA) of different molecular weights to be used in formulating electrorheological (ER) fluids.