



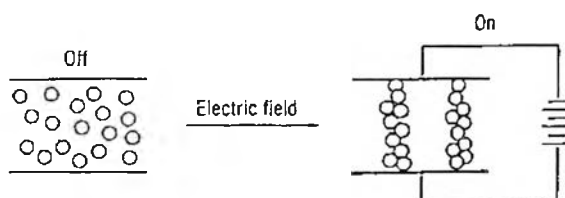
## CHAPTER I

### INTRODUCTION

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, dispersions of polarizable particles in an insulating base fluid, represent a unique class of electroactive materials that exhibit modified flow properties in 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 *et al.*, 1996).

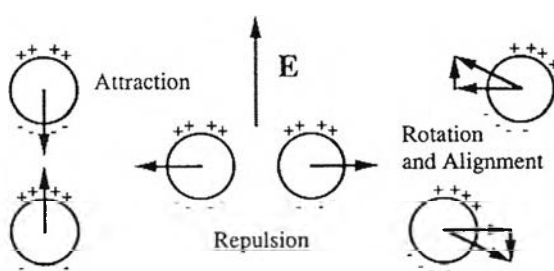
#### 1.1 The ER Phenomenon

ER fluids are typically composed of electrically polarizable particles dispersed in low-dielectric oil. In the absence of electric field, ER fluids show the 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 to areas with greatest field concentration increases the polarizability of the particle and results in a larger dipole moment. These field-induced dipoles attract each another and cause the particles to form chains or fibrillated structures in the direction of the field, (Figure.1) (Havelka *et al.*, 1996).



**Figure 1** In the presence of an electric field, the particles in an electrorheological (ER) fluid form chains or fibrillated structures (Havelka *et al.*, 1996).

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. The increase in apparent viscosity from particle chain interactions under shear corresponds to the yield stress as defined in the Bingham plastic model. When the electric field is removed, the particles return to a random distribution and fluid flow resumes (Bonecaze and Brady , 1992).

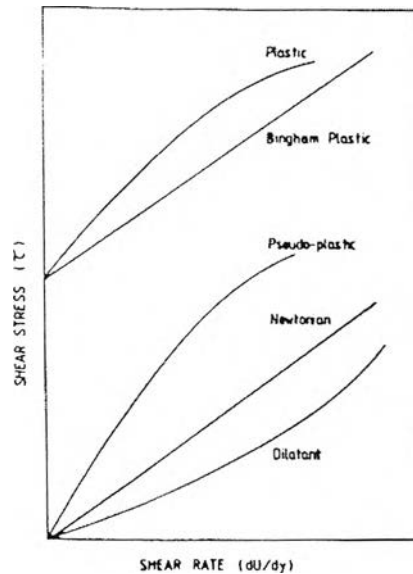


**Figure 2** Mechanism of fibrillation and alignment of dielectric particles. Due to the dielectric mismatch between the particles and the fluid, the particles have an induced dipole as illustrated. The interaction of these dipoles cause attraction, repulsion, rotation, and alignment of particles, creating chains that align with the applied electric field (Bonecaze and Brady , 1991).

A widely recognized fact is that the shear stress versus shear strain rate properties of an ER fluid varies as a function of applied electric field. In the absence of an electric field, an ER fluid obeys the Newtonian behavior. When an electric field is applied, the fluid changes from a liquid to a semisolid and is described as a Bingham plastic. The shear stress ( $\tau$ ) for the Bingham plastic model is given by

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

where  $\gamma$  is the shear rate,  $\eta$  is the viscosity, and  $\tau_{ER}$  is the electric field-induced dynamic yield stress.



**Figure 3** A comparison between different fluid behaviors.

## 1.2 ER Particle Materials

When formulating an ER fluid for a specific application, several properties must be optimized (Table 1). To accurately compare the effectiveness of particular materials used in formulating an ER fluid, these materials must be tested and reported consistently. However, at present there are no established standards for testing ER fluids to indicate their performances – hence there is a difficulty in comparing materials reported in the literature. Nonetheless, many materials interdependent performance properties must be evaluated to determine the commercial viability of an ER fluid. Obtaining all these properties in a single fluid is a considerable materials challenge. Although ER fluid properties will probably be tailored for specific applications, the values in Table 1 are typical performance requirement for various applications (Havelka *et al.* 1995).

Table 1. Electrorheological material requirements for a variety of applications

<u>ER material property</u>	<u>Value</u>	<u>Comments</u>
Dynamic yield stress at 6.0 kV/mm, kPa	> 4.0	Maintain field-induced stress at high shear rates
Zero-field viscosity, cP	< 100	As low as possible and insensitive to temperature
Current density at 6.0 kV/mm, mA/m <sup>2</sup>	< 300	Low to maintain particle polarization and to minimize power consumption
Operating temperature range, °C	- 20 to 140	Maintain ER performance over a broad temperature range
Response time, ms	Milliseconds	Rapid turn on and off
Dispersion properties	Stable	Nonsettling, easily redisperses, no electrophoresis
Tribology properties	Nonabrasive	Lubricious, noncorrosive, compatible with components
Environmental properties	Benign	Nontoxic, nonreactive

Table 2. Desired Base Fluid Properties (Havelka *et al.* 1995)

<b>Boiling point</b>	Higher than the highest expected operating temperature for safety
<b>Compatibility</b>	Required with all metals, plastics, and elastomers in the system
<b>Conductivity</b>	As low as possible to maintain particle polarization, minimize resistance heating, and prevent overloading the power supplies
<b>Cost</b>	Commensurate with the value of the intended application
<b>Dielectric breakdown strength</b>	Higher than the highest electric field that will be applied to prevent arcing and shorting of the system
<b>Flash point</b>	Higher than the highest expected operating temperature for safety
<b>Fluid solvency</b>	Poor for the solid phase and any activator used while solubilizing any other additives
<b>Hydrophobic fluids</b>	Preferred because water absorbed from the environment can result in large performance changes
<b>Lubricity</b>	Adequate to minimize wear of metal-metal and metal-elastomer sliding contacts
<b>Pour point</b>	Below the lowest expected operating temperature
<b>Stability (thermal, oxidative, and electrical)</b>	Sufficient to minimize performance changes with time
<b>Toxicity</b>	Low, to allow for possible leaks and eventual disposal
<b>Viscosity</b>	As low as possible to maintain a high on/off stress ratio
<b>Viscosity index</b>	High, to minimize changes in zero field performance with temperature and to simplify system design

### 1.3 Physical Properties of the Particles

ER properties and dispersion stability are affected by the particles physical properties. The ability to modify the physical properties of organic or hybrid (organic-inorganic) materials in ER fluids offers many advantages over inorganic materials, including lower density, which decreases settling, and softness, which decreases wear. Particle concentration and morphology are also important physical properties to consider (Havelka *et al.*, 1996).

Particle-particle separations are a function of particle concentration. At concentration <10%, a large increase in yield stress is typically not observed, whereas at concentration >40%, the zero field viscosity is usually too high. Most researchers use a volume fraction of 10-40% to provide a practical balance between zero field viscosity and dynamic yield stress (Havelka *et al.*, 1996).

Particle morphology has received a limited attention. ER fluid particulates average in size between 0.5-100 $\mu\text{m}$ . Although neither the upper nor lower particle size limit is clearly defined, the upper limit (which relates to the electrode gap) is recommended to be less than one-tenth of the spacing (Stangroom, 1980). The lower limit relates to the fact that at some level Brownian motion may dominate the interactions that give rise to the ER effect. Very small particles are also limited by the strength of the dipole.

Most ER particles reported in the literature are irregularly shapes. However, it is often assumed that the particles behave in combination with entrapped solvent as if they were roughly spherical (Block *et al.*, 1988). One may expect that an ellipsoidal particle aligned along its major axis will have a greater induced dipole moment than a sphere of the same volume. A systematic investigation conducted under low shear rate indicates that ER response increases as the ratio of the particle increases (Zukoski, 1993). However, because many applications require high shear rates, the study must

be expanded to higher shear rates to determine whether the benefit still appears.

#### **1.4 Chemical Properties of the Particles**

A wide range of materials of different chemical nature demonstrates ER activity. For simplicity, research in ER particulates is classified in two general categories of materials: extrinsically polarizable and intrinsically polarizable. These two material types are then further subdivided (Havelka *et al.*, 1996).

##### **1.4.1 Extrinsically Polarizable Materials**

Water was originally considered necessary for the ER effect. Extrinsically polarizable ER fluids are composed of hydrophilic particles that require water or some other polar activator (e.g. low molecular weight alcohols or amines) to obtain measurable ER activity. The amount of water required in optimizing the ER effect is 1-10% and depends on the physical and chemical properties of the particles as well as the desired ER properties. The ER effect is expected to result predominantly from interfacial polarization.

Although extrinsically polarizable ER fluids are able to demonstrate the ER phenomenon, they are significantly limited by temperature. At extreme temperatures, the polar activator may not be available to activate the ER fluid, for example, because of the activator's freezing and boiling points and because the partitioning of the activator between the various phases tends to change with temperature. An even more serious concern with extrinsically polarizable ER fluids is their very high thermal coefficient of conductance. Fluid conductivity typically doubles every five degree Celsius (Blackwood *et al.*, 1993). Understanding particle-activator interactions is necessary to develop improved fluids. There are two primary classes of extrinsically polarizable particles with an activator.

#### *1.4.1.1 Polar Non-Ionic Materials*

The materials are polar hydrophilic solids that contain only a trace of mobile ions: the most common examples are the polysaccharides (e.g., cellulose or starch) and the inorganic oxides with surface hydroxyl groups (e.g., silica or alumina). Polar nonionic materials generally exhibit little ER effect when an activator is not present. Because there are few mobile ions to form dipoles by charge separation and because the materials generally have low permittivities, one hypothesis is that polarization results from the alignment of the dipoles of the high-permittivity polar activator adsorbed on the surface of the particle. Hydrogen bonding between the solid and the polar activator is believed to be important in these systems

#### *1.4.1.2 Polar Ionic Materials*

In contrast, polar ionic materials contain mobile ions. These materials are generally polymeric salts that allow large dipoles to be formed by charge separation of ions. In most cases, a polar activator is needed to provide ion solvation and mobility. Monovalent ions usually provide the best performance possibly because they are easily solvated and are very mobile (Stangroom, 1980). The most common examples in the literature are the monovalent salts of polymeric carboxylic acids (e.g., the lithium salt of polymethacrylic acid). Some materials, such as zeolites, are able to pass some ions from site to site along the backbone without an activator but are much stronger when used with an activator (Conrad *et al.*, 1991). In other cases, such as the cross-linked polyethers or crown quaternary salts, the polymer is not ionic but acts as a solid conductor for the ions formed from dissolved, low molecular weight salts.



## 1.4.2 Intrinsically Polarizable Materials

The discovery that a polar activator is not necessary to obtain ER activity catalyzed a resurgence of interest in electrorheology (Block *et al.*, 1990). The advantages of intrinsically polarizable over extrinsically polarizable materials include a simpler system (because a polar activator is not required) and a lower thermal coefficient of conductance, which may facilitate expanding the temperature range of ER activity. Intrinsically polarizable materials can function predominantly by bulk polarization (e.g., ferroelectrics and liquid crystals) or by interfacial polarization (e.g., metals, semiconductors, and insulated conductors).

### 1.4.2.1 *Conductive and Semiconductive Particles*

The conducting and semiconducting materials develop large dipoles by allowing electrons or protons to flow along extended delocalized conductance bands. This facilitates large charge separations under an imposed electric field. The materials demonstrate a measurable ER response in which the polarization is probably predominantly interfacial (Havelka *et al.*, 1996). Conducting polymers, such as polyaniline and pyrolyzed hydrocarbons, are the leading materials in this group. The drawbacks cited for conducting polymers in the electronics industry, such as low conductivity and insolubility, are attractive for ER materials. It is desirable to investigate conducting polymers that have different band gaps. The electrical properties of a particular conducting polymer can be modified systematically by both type and concentration of the dopant. The properties can further be modified by the degree of crystallinity and the degree of chain orientation (Bloodworth and Wendt, 1996).

### 1.4.2.2 *Metal*

On the basis of polarization alone, the metals dispersed in an insulating base fluid should provide optimum ER shear stresses. The metals are polarized by electron flow under an imposed electric

field. Their high conductivities should allow for very high dipole strengths. However, the high conductivity makes it difficult to prevent the loss of the dipole by particle to particle charge transfer. In practice, dispersions of metal particles are very conductive and do not provide fluids of significant stress values (Kelly, 1986). The failure of metals to make good ER particles implies that there may be an optimum level of conductivity in the semiconducting region (Blackwood *et al.*, 1993).

#### 1.4.2.3 Coated Particles

Lowering current density while maintaining ER stress continues to be a challenge in extrinsically and intrinsically polarizable ER fluids. In an attempt to reduce the current density of ER fluids, insulating coating and surfactant have been investigated on metals and semiconductive particles. Coatings are usually used with materials that form dipole by interfacial polarization and do not require a polar activator. Most published work involves coating semiconductors such as polyaniline or simple metal powders such as aluminum or iron. The electrostatic polarization model predicts that polarization force falls off as a function of particle-particle separation to the fourth power (Jordan *et al.*, 1989 and Gast *et al.*, 1989). Since application of a coating increases the interparticle distance, most insulating coatings have reduced ER performance under DC fields and have not eliminated conductivity. However, in some systems this compromise is not observed (Pollack, 1995). Some of these systems are reported to perform much better under AC than DC fields (Inoue, 1990). Particle-coating interactions are not well understood, and will likely continue to be an active area of research.