CHAPTER I

INTRODUCTION

Development of smart materials is a challenging task due to the increasing demand for materials capable of carrying out various complex tasks. Field-responsive material is one type of the smart materials and can be defined as materials in which a given property can be modified in a measurable way through its interaction with some external stimuli. The detectable characteristics can be either physical, mechanical, optical, electrical or magnetic properties while the external stimuli can be any form of energy or matter (Khan *et al.*, 1999).

Electroactive Polymers (EAP)

Polymers that exhibit shape changes in response to an electrical stimulation can be divided into two distinct groups:

A. Electric EAP Materials – They are mostly in a dry state and are driven by an electric field or the Coulomb force. This category includes ferroelectric polymers, dielectric EAP, electrostictive polymers, electro-viscoelastic elastomers and liquid crystal elastomer (LCE) materials (Cohen, 2001). Ferroelectricity is the phenomenon in which when a nonconducting crystal or a dielectric material exhibits a spontaneous electric polarization. The most exploited ferroelectric polymers are poly (vinylidene fluoride) and its derivative (Cheng *et al.*, 2001, Furukawa, 1997). Polymers with low elastic stiffness and high dielectric constant can be used to induce large actuation strain by subjecting them to an electrostatic field; e.g., polyurethane (Ueda *et al.*, 1997). For an electrostrictive polymer, it exhibits a stress-strain response proportional to the square of an applied electric field. Examples include silicone, polyisoprene, and polybutadiene (Pelrine *et al.*, 1998). The other type is the electro-viscoelastic elastomer which is a composite consisting of dielectric particles embedded in a gel or elastomer. Before crosslinking, it behaves like an electrorheological fluid. An electric field is applied during curing to orient and to fix the position of the particles in the elastomeric matrix. This material changes into a solid state but still has shear moduli that may vary with applied electric field (Martin

and Anderson, 1999). For the last type, the LCE material, it is a composite consisting of a monodomain nematic liquid crystal elastomer and a conductive polymer that is distributed within their network structure (Thomsen et al., 2001, Huang et al., 2003).

B. Ionic EAP Materials – These materials usually contain an electrolyte and they involve transport of ions/molecules in response to an external electric field (Cohen et al., 2001). Examples of such materials include ionic polymer gels (IPG), ionomeric polymer-metal composites (IPMC), conductive polymers (CP), carbon nanotubes (CNT), and electrorheological fluids (ERF). IPG materials are generally activated by a chemical reaction, changing from an acid to an alkaline environment, or an applied electric field which causes the gel to become dense or swollen. IPMC is an EAP that bends in respect to an electrical activation as a result of mobility of cations in the polymer network. They operate best in a humid environment and can be made as self-contained encapsulated actuators to operate in dry environment as well (Shahinpoor et al., 1998). CP typically functions via the reversible counter-ion insertion and expulsion that occurs during redox cycling. Addition of the ions causes swelling of the polymer and conversely their removal results in shrinkage and as a result the sandwich bends (Skaarup et al., 1996, Baughman, 1996). Examples include polyaniline (Kaneto et al., 1995) and polypyrole (Otero et al., 1996). For CNT, the change in carbon-carbon bond length of nanotubes that are suspended in an electrolyte is responsible for the actuation mechanism (Inganas and Lundstrum, 1999). ERF is typically a suspension consisting of micron-sized polarizable particles dispersed in a non-conducting medium. Under the action of an electric field, the induced particle dipoles tend to attract the neighboring particles forming fibrillar three dimensional network structures, which provide additional resistance against fluid motion (Lee et al., 1998).

Non-Electrical Mechanically Activated Polymers (NEMAP)

There are many polymers that exhibit a volume or shape change in response to perturbation of the balance between repulsive intermolecular forces that act to expand the polymer network and attractive forces that act to shrink it. The type of polymers that can be activated by non electrical means include: chemically activated

polymers (Sayil and Okay, 2002), shape memory polymers (Harai *et al.*, 1992, Monkman, 2000), inflatable structures, light activated polymers (Xu *at al.*, 2003), magnetically activated polymers (Zrinyi, 1997), and thermally activated gels (Chen *et al.*, 2002).

1.1 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:

$$\tau = \tau_y + \mu \dot{\gamma}$$

where τ is the yield stress, μ is the dynamic viscosity, γ is the shear strain, and τy is the dynamic yield stress. In general, boss the yield stress and viscosity will be the functions of the electric field strength. 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 Fig. 2.1 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. When the field strength exceeds Eo, there is a virtually linear increase in shear stress and field strength.
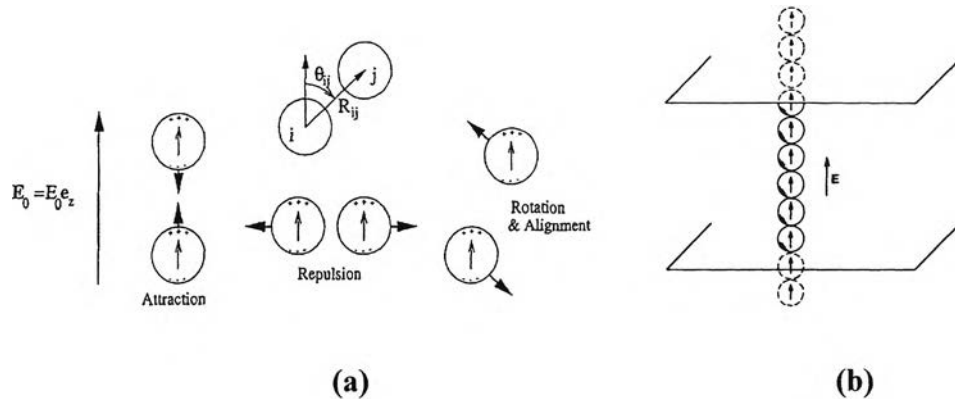
Figure 1.1 (a) Mechanism of chains formation and alignment of dipole particles. The interactions of these dipoles cause attraction, repulsion, rotation, and alignment of particles, creating chains that align with the applied electric field; **(b)** In the presence of an electric field, the particles in an ER fluid form chains or fibrillated structure.

1.1.1 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.

1.1.1.1 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 (Winslow, 1949) 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.

1.1.1.2 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 Co workers (Block *et al.*, 1990).

1.1.1.3 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.

1.1.2 Electroviscoelastic effect in ER elastomer

While most of researches have been focused on ER fluids, which are normally suspensionsof polarizable particles in an insulating oil, however, recent attention are gaining in controllable materials based on elastomers that are loaded with polarizable particles or piezoelectric materials as shown in Fig 2.2. It has also been envisaged for some time that electrical fields can control the viscoelasticity of elastomers. Polarizable particles can be dispersed in elastomeric materials to create ER elastomers, which may be considered as solid analogs of ER fluids. However, ER elastomers have quite different characteristics. The most noteworthy is that the arrangement of particles is locked within the elastomeric matrix. Therefore, these materials are intended to operate in the elastic regime, while ER fluids typically operate in the post-yield and steady-flow regimes. For appropriate applications, the advantages of ER elastomers over ERFs include no leakage, no attrition or sedimentation of particles, and possibly higher dielectric strength. In addition, there is the possibility of producing custom-made ER objects of exactly the right shape and size for the application. An ER elastomer also has advantages for studying the mechanism of the ER effect, as the morphology of the material does not change during measurement and can be determined precisely, at least in principle. Information about the ER mechanism provides a basis for selection of materials and morphologies to achieve the desired responses.
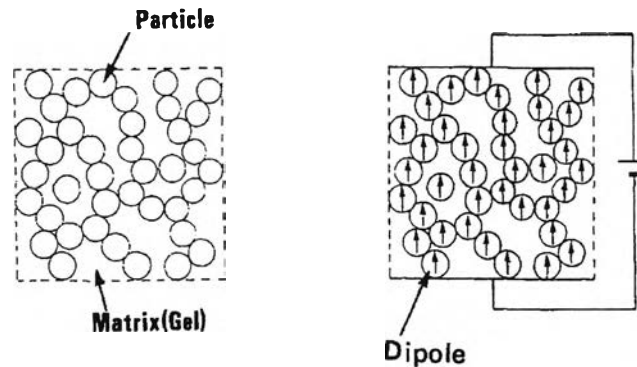
Figure 1.2 Schematic illustration of the electroviscoelastic effect.

1.2 Electrically Conductive Polymers

In 1977, the first electrically conducting organic polymer, doped polyacetylene, was reported, spurring interest in conductive polymers which are polymers that possess electrical conductivity due to the fact that there are Pi-electrons delocalizing along the backbone. They are the conjugated polymers which can be chemically or electrochemically synthesized. The neutral forms of conductive polymers can be insulator or semi-conductor. The examples of conductive polymers are polyacetylene(PAC), polythiophene (PTh), polypyrrole (PPy), and polyaniline (PANI). The chemical structures of their neutral forms are shown in Figure 2.3.
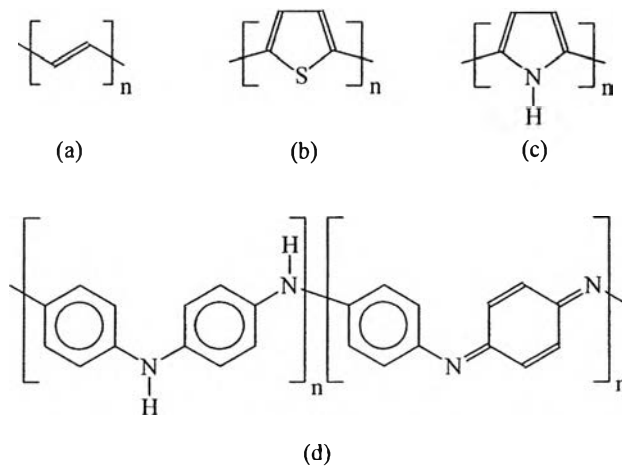

Figure 1.3 The chemical structures of the neutral forms of: a) polyacetylene; b) polythiophene; c) PPy; and d) polyaniline.

Delocalized charge carriers could be introduced by donating electrons to or withdrawing electrons from polymer chain via reduction or oxidation reaction, respectively. This process is known as the 'doping process' with the conductivity increasing as the doping level increases. Both n-type (electron donating) and p-type (electron accepting) dopants have been utilized to induce an insulator-metal transition in electronic polymers. The doping procedures differ from conventional ion implantation used for semiconductors. The doping process for polymers is carried out electrochemically or ny exposing the films to vapors or solutions of the dopants. The dopant atoms are positioned interstitially between chains, and donate charge to or accept charge from the polymer backbone. The polymer backbone and dopant ions form new three-dimensional structures (Sim *et al.*, 2001). The large range of conductivity is obtained by a doping process, which mainly depends on type of dopants (Yamaura *et al.*, 1988, Wang *et al.*, 1990, Cao *et al.*, 1992, Shirakawa *et al.*, 1994) and dopant concentration used (Heeger *et al.*, 1980), where electronic structure of the polymer can be either polaron or bipolaron depending on extent of oxidation.

Conductive Polymers for ER Fluids

Electronically conductive polymers contain conjugated backbone and their properties usually depend on the oxidation or reduction state induced by the introduction of anions or cations as dopants. The well known examples of conductive polymers include polyacetylene, polyaniline, polypyrrole, and polythiophene.

Conductive polymers can offer a variety of advantages for ER systems, such as 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 via electron movement through polymer backbone under an electric field. The conjugated π-electron system in conductive polymers display unusual electronic properties, including high electron affinities, and low ionization potentials. The local electron distribution of particles induces the ER effect under the application of electric field.

In suspensions of many inorganic particles, an activator, such as water or other polar compound adsorbed on the particle surface, is required to improve the ER properties. On the other hand, a semiconducting polymer usually has a high intrinsic polarizability, even in the absence of any activator (Pinto *et al.*, 2000). Examples include polyaniline (PANI) and many PANI derivatives, based upon modification of oxidation state, dopant, and polymerization conditions (Lee *et al.*, 1998, Choi *et al.*, 1998, Jang *et al.*, 2001, Gow and Zukoski, 1990, Gozdalik *et al.*, 2000, Akhavan and Slack, 2001, Kim *et al.*, 2000, Lee *et al.*, 2001, Lengalova *et al.*, 2003, Cho *et al.*, 2004), polythiophene (Chotpattananont et al., 2003,2004), and polyparaphenylene (Sim *et al.*, 2001, Chin *et al.*, 1998). PANI has several advantages over other polymer particles such as low density, ease of conductivity control, and thermal and environmental stability. PANI can be easily polymerized by an oxidative polymerization at relatively low temperatures and can be doped from an insulating state to a conducting state by using simple protonic acids. This allows a controlled variation in the particle dielectric constant and conductivity while keeping all other particle properties and suspension characteristics constant (Jang *et al.*, 2001).

1.3 Polyaniline

Poyaniline (PANI) was first synthesized in 1862 and it has been extensively studied as a conducting polymer since the 1980s. PANI has several advantages : the monomer (aniline) is relatively inexpensive, the polymerization is straightforward and proceeds with high yield. Moreover, the conducting form of PANI has high electrical conductivity and excellent chemical stability (Cao *et al.*, 1992). It can be synthesized by either chemical or electrochemical oxidative polymerization of aniline in aqueous acid media coupled with a variety of oxidizing agent (Chiang and Macdiarmid, 1986). The physical properties and conductivity of the synthesized PANI strongly depend on many parameters, such as nature of the oxidizing agent, the aniline/oxidizing agent ratio, nature of protonic acid medium, pH, temperature, reaction time, deprotonation and reprotonation processes (Cao *et al.*, 1989, Adams *et al.*, 1996, Vilcnik *et al.*, 1998). Depending on oxidation state, PANI can exist in many different forms (Stejskal *et al.*, 1996). The oxidized and reduced states of

PANI are represented by the index of y, reduced unity and 1 − y, oxidized unity as indicated in the chemical structure:
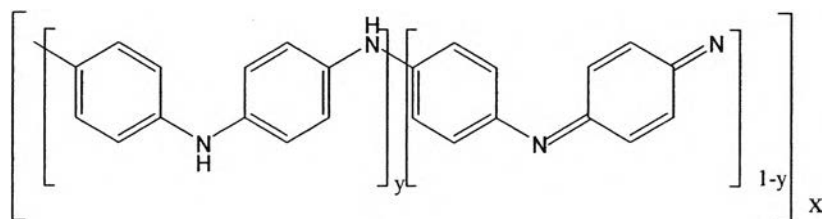
where x is the polymerization degree. The completely reduced form of PANI, the leucoemeraldine (LEB), is obtained when (1 − y) = 0. The oxidized form (1 − y) = 1 is called pernigraniline (PB), while (1 − y) = 0.5 corresponds to the emeraldine base (EB) (Albuquerque et al., 2000). Various oxidation forms of PANI twist among themselves via doping and dedoping processes. Doping process can be done through two routes which are an oxidation process; electrochemically (Mazeikiene and Malinauskas, 2000) or chemically (Hua et al., 2000), or a protonation through acid-base reaction by using a large number of acid such as $HClO_4$ (Li and Wan, 1999), H_2SO_4 (Li and Wan, 1999), HPO_3 (Li and Wan, 1999), p-TSA (Li and Wan, 1999), HCl (Wan et al., 1992), CSA (Huo et al., 1999), DBSA (Davies et al., 1995). Upon doping, there is a change in the electronic structure of polymer done by addition of two protons at the nitrogen sites on either side of the quinoid rings resulting in a spinless bipolaron defect, which then be transformed to an ordered array of polarons. This transition is not energetically favored and two polarons may combine to form a spinless bipolaron (Epstein et al., 1987).This process results in raising electrical conductivity, which strongly depends on temperature and pressure (Lunberg et al., 1987). One of the key problems related to potential applications of PANI is its processibility, which can be solved by two main approaches: using secondary dopants to loosen the intermolecular interactions (Ikkala et al., 1995, Valenciano et al., 2000), or blending (Xie et al., 1998, Koul et al., 2000, Yoon et al., 1993, Mantovani et al., 1997, Haba et al., 2000, Lee et al., 2000).