

CHAPTER I INTRODUCTION

Material science has undergone a distinct evolution: from the use of inert structure materials to materials built for a particular function, and finally to smart materials with more acute recognition, discrimination and reaction capabilities (Akhlas, 2000). The sensing and actuating functions of smart materials are explored to develop smart structures. As seen in Fig. 1.1, the smart or active materials can exchange a kind of input stimulus into a kind of output response. Consequently, the materials can be classified as actuator and sensor according to the type of input driving force. Piezoelectric materials, shape-memory alloys, electrostrictive materials, magnetostrictive materials, and electrorheological liquids are some examples of currently available smart materials (www.intellimat.com).

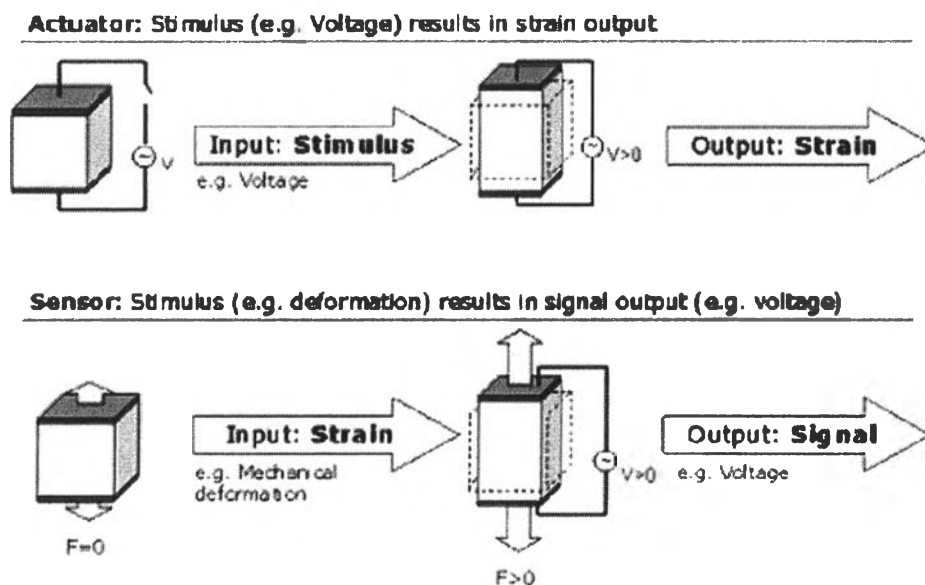


Figure 1.1 Approach for classification of smart or active materials.

Actuator is the device that transforms motion and force from an input source such as an electric field to an output end-effector location. There are three main types of actuators: hydraulic, pneumatic and electric actuators, in which they are used by the majority of robotic and automated mechanical systems. The first two types are considered as fluid machines in that they use fluid to create mechanical motion. The larger concerns with hydraulic and pneumatic systems are the containment of the fluid within the actuation system, the hydraulic fluid is flammable, lags in the control of the system due to the transmission lines, and oil viscosity changes from temperature. The electric actuator converts electrical energy into mechanical energy. It has many advantages such as the energy medium is easily stored and re-supplied by recharging batteries, more adaptable to environments since volumetrically they take up less space, and the flexibility of control of the mechanical system is far greater. They are also easy to install, clean, and relatively quiet. Examples of actuators include shape memory alloy, piezoelectric motors, magneto-active transducers, electroactive polymers, and electrorheological fluids (Mavroidis *et al.*).

Nowadays, actuation devices are used for many applications with an increasing need to reduce their size, mass, and power consumption as well as their cost. Existing transducing actuators, such as piezoceramics, induce limited displacement levels. Potentially, electroactive polymers (EAP), such as conductive polymers, are emerging as new actuation materials. They have the potential for low-mass, low-power, fast response time, induce large displacement, and inexpensive miniature actuators that are superior to the widely used actuators (Cohen *et al.*).

1.1 Electrorheological Fluids

Over the past 50 years, it has been known that there are liquids that respond mechanically to electrically stimulation. These liquids, which have attracted a great deal of interest from engineers and scientists, change their viscosity electroactively. These electrorheological (ER) fluids typically composed of electrically polarizable particles on the order of 0.10 to 100 μm dispersed in low-dielectric oil. The volume fraction of the particles is between 10% - 60%. They represent a unique class of the electroactive materials that experience dramatic changes in rheological properties, such as viscosity, in the presence of an external electric field (Mavroidis *et al.*). The phenomenon of electrorheology is first reported by W M. Winslow in 1940s and occasionally bears his name (Winslow, 1949). It is generally accepted that the ER effect, sometimes called the Winslow effect, is thought to arise from the difference in the dielectric constants of the fluid and particles. In the absence of electric field, ER fluids show the Newtonian behavior while on the application of an electric field, particles become polarized, and form chains structure between two electrodes in the direction of applied electric field. This induced structure changes the ER fluid's viscosity, yield stress, and other properties, allowing the fluids to change consistency from that of liquid to something that is viscoelastic, such as a gel, with response times in electric field on the order of milliseconds.

The ability of these materials to transform electrical energy into mechanical energy and milliseconds response has motivated research and development into practical fast electromechanical actuators, such as the active elements of clutches, breaks, shock absorbers, engine mounts, valves, and flow pumps (Voyles *et al.*, 1996, Kamath and Wereley, 1997, Mavroidis *et al.*, 2000). Moreover, any device that relies on hydraulics can benefit from ER fluid's fast response and reduction in device complexity. Obviously, the solidification of particles will seriously affect the viscoelastic behavior. Viscoelasticity is the ability to response to an applied force by exhibiting both elastic and viscous properties depending upon the time scale of the applied force. Under constant shear, a part of the work done on the viscoelastic material is converted into elastic energy and the rest is dissipated. Thus upon

removal of applied force, the deformed material will attempt to recover to its original shape. Similar to this behavior, it has been known that ER fluids exhibit the typical viscoelastic behavior under high enough electric field.

The dispersed phases of polarizable particle in an insulating oil play a very important role in ER phenomena. Recently, the dry-base ER system has been adopted to solve the problem of wet-base ER fluid which requires active substances, such as water, ethylene glycol, and surfactant, to promote the ER effect. Various conductive polymer particles have been used as dry-base ER materials to avoid the thermal breaking, particle settling, irreversible clumping, and abrasiveness (Sung *et al.*, 2003). Examples of polymeric systems include polyaniline (PANI) and its derivatives (Parthasarathy and Klingenberg, 1999, Chin and Winter, 2002, Ha and Yang, 2000, McLeish *et al.*, 1991, Jordan *et al.*, 1992), PANI copolymers (Jang *et al.*, 2001, Kim *et al.*, 2000, Lee *et al.*, 1999, Krause and Katherine, 2001), polypyrrole (Lee *et al.*, 1998, Lee *et al.*, 2001), poly (acene quinone) radical (Krause and Katherine, 2001), poly (naphthalene quinone) radical (Cho *et al.*, 2000), and poly (p-phenylene) (Krause and Katherine, 2001, Jun *et al.*, 2002).

1.1.1 ER Particle Materials

When formulating an ER fluid for a specific application, the requirements of a good ER fluid are the following (Goodwin *et al.*, 1997):

- i. There should be a large change in rheological properties on the application of electric field.
- ii. The off-field viscosity should be close to that of the oil phase and insensitive to temperature.
- iii. The current requirement should be low to minimize power loss as well as heating effects.
- iv. Low temperature sensitivity and hence water-free systems have an advantage.
- v. There should be tenability of the particle properties to enable the maximum control of ER properties as well as the suspension stability properties to be achieved.

- vi. There should be a strong effect in both DC and AC fields.
- vii. For comparison with theoretical models, monodisperse spherical particles would be the system of choice.

A wide variety of particulate materials of different chemical nature have been employed in ER fluids. For simplicity, research in ER particulates is classified in two general categories of materials: extrinsically polarizable and intrinsically polarizable.

1.1.1.1 Extrinsically Polarizable Materials

Extrinsically polarizable ER fluids are composed of hydrophilic particles that require water or some other polar activator to obtain measurable ER activity. The amount of water required in optimizing the ER effect depends on the physical and chemical properties of the particles as well as the desired ER properties. Although extrinsically polarizable ER fluids are able to demonstrate the ER phenomenon, they have significant limitations in application (e.g. thermal stability). 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. Examples of these materials include zeolite, lead zirconate titanate, cellulose, silica, aluminar, and starch particles.

1.1.1.2 Intrinsically Polarizable Materials

The discovery that a polar activator is not necessary to obtain ER activity catalyzed resurgence of interest in electrorheology (Cho and Choi, 2000). The advantages of intrinsically polarizable materials include a simple system, thermal stability, and conductivity controllable. Example of these materials, include metal particles, conductive or semi-conductive polymers.

1.2 Conductive Polymers

In 1977, the first electrically conducting organic polymer, doped polyacetylene, was reported, spurring interest in conductive polymers. The common electronic feature of pristine (undoped) conductive polymers is the π -conjugated system which is formed by the overlap of carbon p_z orbitals and alternating carbon-carbon bond lengths. Figure 1.2 shows the chemical repeating units of pristine forms of several families of conductive polymers. The conductivities of the pristine polymers are transformed from insulating to metallic through the process of doping, 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 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).

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. The well known examples of conductive polymers include polyacetylene, polyaniline, polypyrrole, and polythiophene.

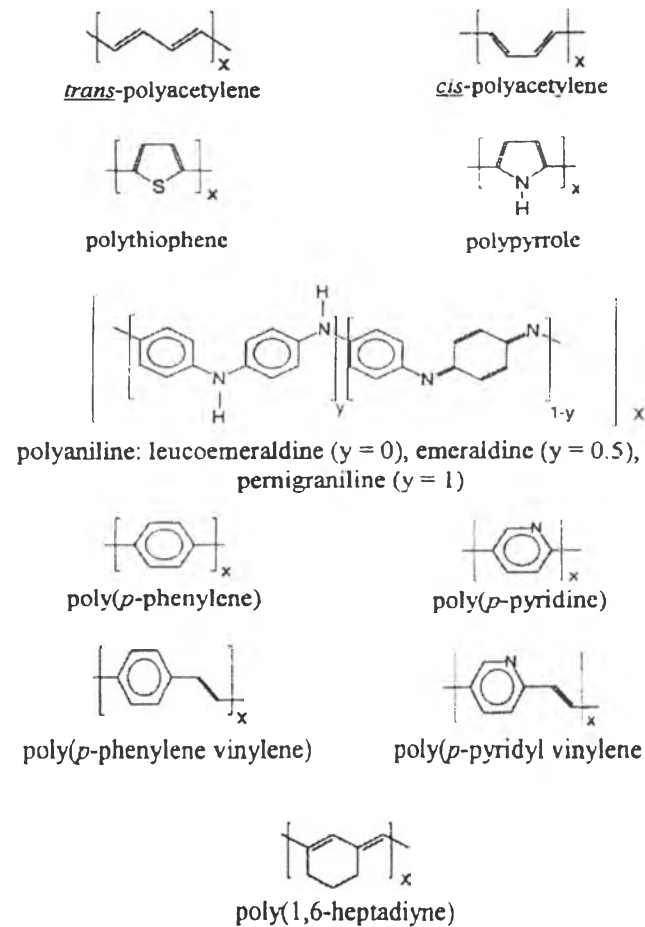


Figure 1.2 Repeating units of several conductive polymers.

1.2.1 Conduction mechanism

Conduction is the transport of charge from one point to the other and is governed by charge carriers that move through a specimen. In general, the conductivity (σ) can be described by the following equation:

$$\sigma = |q| \cdot n \cdot \mu \quad [\text{S/cm}] \quad (1.1)$$

where q is the charge carried by the carrier [A.s], n is the number of charge carriers [cm^{-3}], and μ the mobility of the charge carriers [$\text{cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$].

Conduction in solids can be described with the widely accepted band model. In this model two new molecular orbitals arise when two atoms, both with

half filled orbitals, are brought close enough to each other for the orbitals to overlap (cf. molecular orbital theory). The energy-difference (E_g) between the newly formed orbitals is determined by the degree of overlap between the constituting orbitals. As the degree of overlap is different for every pair of orbitals, a low-energy band, valence band (VB), and a high-energy band, conduction band (CB), are formed (Figure 1.3).

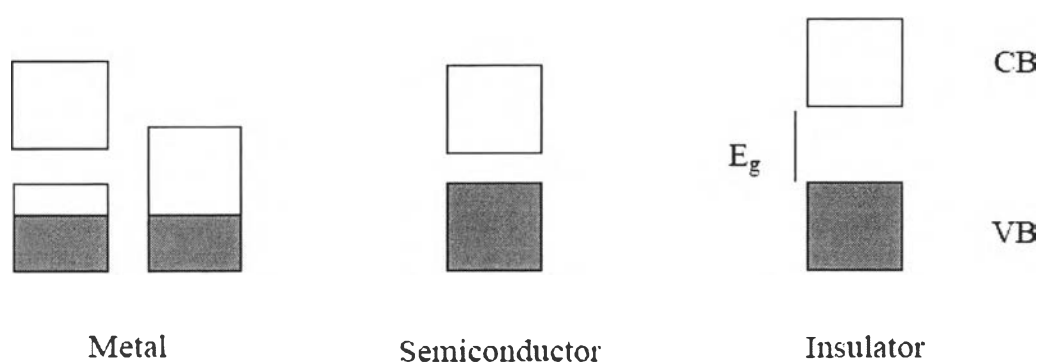


Figure 1.3 Schematic representation of the band structure of a metal, a semiconductor, and an insulator. (E_g is the energy gap between the valence band, VB, and the conduction band, CB).

The extent of occupation of the energy bands and the energy gap between them determine the conductivity of a material. Metals are characterized by either a partially filled VB or an overlap between the VB and the CB. This implies a complete freedom of movement for the charge carriers under the influence of an applied field (Equation 1.1, $\mu \rightarrow \infty$). In semiconductors and insulators the VB is completely filled (Equation 1.1, $\mu = 0$) and the CB is empty (Equation 1.1, $n = 0$). Therefore, conduction can only take place when charge carriers are promoted from the VB to the CB. In insulators the energy gap is too large for charge carriers to be thermally excited, whereas for semiconductors excitation is possible. Because polymer molecules do not extend over the full specimen, charge carriers have to move along the extended π -system of the conjugated backbone (intrachain conductivity) as well as between the individual molecules (interchain conductivity).

The measured macroscopic conductivity is a superposition of these microscopic conduction mechanisms.

The majority of theoretical considerations are based on polyacetylene (Figure 1.4), being the simplest conjugated polymer. In *trans*-polyacetylene two energetically equivalent resonance structures are possible (two-fold degeneration). At the conversion points of these structures unpaired electrons are present, which are called solitons. This conversion point is actually spread out over several bonds.

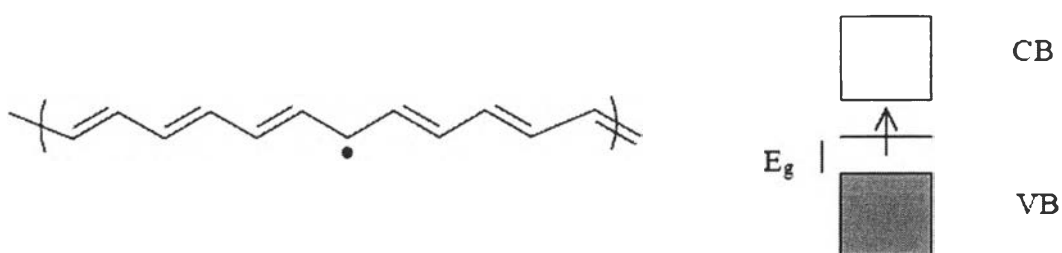


Figure 1.4 Soliton in *trans*-polyacetylene (left) and electronic state induced between the VB and CB by the soliton (right).

Solitons introduce a localised electronic state in the middle of the energy gap between the VB and the CB of polyacetylene. As this reduces the energy gap for charge carriers, conductivity is facilitated. Solitons are chargeless, but spin carrying (i.e., neutral radicals). An interesting feature of solitons in *trans*-polyacetylene is that, because of the degenerate ground state, they can move along the chain without the need to overcome an energy barrier. In fact, this is why they are called solitons: they have the same properties as a solitary wave. For *cis*-polyacetylene the two resonance structures are non-degenerate and therefore the movement of charge carriers along the backbone is energy consuming. This is shown by the lower conductivity of *cis*-polyacetylene compared to *trans*-polyacetylene (10^{-11} and 10^{-6} S/cm, respectively). Other conjugated polymers such as polythiophene (PTh) also do not have a degenerate ground state. Still, different resonance structures can be present (cf. benzoid and quinoid structures of PTh) and unpaired electrons are formed at the conversion points. These electrons polarise the

local environment, which then relaxes into a new equilibrium position. This induces two electronic states in the band gap, again facilitating conductivity. The combination of a charge carrier and its distorted environment is called a polaron. The chemical equivalent is a charged radical.

1.3 Doping

The number of naturally occurring solitons and polarons in conducting polymers is not sufficient to render them highly conducting (e.g., 10^{-6} S/cm for *trans*-polyacetylene). Charge carriers can be generated by oxidation or reduction of the polymer. This process is called doping, after the similar treatment of metals. The mechanism of doping in polymers however is different from that in metals. In doped metals, non-equivalent dopant atoms replace the metal atoms. Depending on the valence of the dopant, either holes (lower valence) or electrons (higher valence) are generated, which can act as charge carrier. Upon doping of polymers, charge is transferred from the dopant to the polymer. Oxidation of the polymer (electrons from polymer to dopant) results in a hole-conducting polymer (p-type), whereas an electron-conducting polymer (n-type) is formed upon reduction. In order to maintain charge neutrality, counter-ions are also incorporated. Confusingly, these counter-ions are sometimes called dopant ions. Counter-ions lower the mobility of the charge carriers by their interaction with the charge carriers on the conjugated polymer (pinning effect). This pinning effect is less when the size and the degree of charge delocalisation on the counter-ion is larger. Furthermore, the stability of the conductivity shows a positive relation with the size of the counter-ion, whereas the diffusion rate of the counter-ion into the doped layer shows a negative relation with size.

Doping of polyacetylene results in the formation of new neutral solitons and the charging of both newly formed and already existing solitons. The chemical equivalents are carbocations or -anions, radical cations or anions (polarons), and carbodianions or -dications (bipolarons). Doping of conductive polymers other than polyacetylene results in the formation of polarons and further oxidation/reduction of newly formed and already existing polarons. The presence of solitons, polarons, and

bipolarons in conjugated polymers has been observed in several studies. The increase in conductivity upon doping can be as high as 14 orders of magnitude for different polymer-dopant combinations. Upon doping with n-type dopants, organic anions are formed that are highly unstable towards air and water. Consequently, the conductivity generated by n-type doping is less stable than by p-type doping. Therefore, p-type dopants are more frequently used. Some examples are I₂, AsF₅, FeCl₃, nitrosonium salts (e.g., NOPF₆) and acids (e.g., H₂SO₄, HClO₄).

1.4 Polythiophene

Polythiophene is one of the most studied conjugated polymers because of its environmental stability in both doped and undoped states (Kim *et al.*, 1999). However, insolubility and non-melting characteristic of this polymer cause it to be not easily processible by conventional techniques. During the past decade, it has been found possible to synthesize novel conductive polythiophene and its derivatives with good solubility, processibility, environmental stability, electroactivity, and other interesting properties by inserting long flexible chain into the 3-position of the thiophene ring (Chen *et al.*, 2000). The synthetic route for the synthesizing of polythiophene may be performed according to two main procedures, chemical and electrochemical synthesis.