CHAPTER II
LITERATURE SURVEY

2.1 Theoretical Background

2.1.1 Electroactive Polymers (EAP)

Electroactive Polymers (EAP) is the polymers that can converse electrical energy into mechanical energy (Bar Cohen *et al.*, 2004). They offer promising and novel characters: lightweight, high energy density, and high flexibility; they are material candidates for muscle-like actuators.

The EAP can divided into 8 types (Bar Cohen *et al.*, 2004):

2.1.1.1 Piezoelectric Polymers

Piezoelectric polymers are the polymers that can generate electrical energy under an applied mechanical force. They can also produce strain or stress under applied electrical energy. Most of piezoelectric polymers are crystalline polymers: an example is PVDF (Polyvinylidene Fluoride) (Peng *et al.*, 2009 and Ray *et al.*, 2009)

Wang *et al.* (2009) fabricated a nanocomposite between PVDF and poly(*p*-chloromethyl styrene) (PCMS) grafted with high dielectric constant copper phthalocyanine oligomer (CuPc) (PCMS-*g*-CuPc). The dielectric constant of nanocomposites is 7 times larger than that of normal PVDF/CuPc composites. Taylor *et al.* (2001) fabricated a piezoelectric polymer (PVDF) device capable of converting the mechanical energy available in oceans and rivers into electrical power. Lang *et al.* (2006) prepared the polypropylene filled with inorganic particles for use as a piezoelectric transducer

2.1.1.2 Dielectric Elastomers

Dielectric Elastomers are the elastomers that can convert electrical energy to stress and/or strain responses (Raju *et al.*, 2003). Actuating dielectric elastomers should have high dielectric values. Dielectric elastomers have many advantages: light weight, a high degree of mechanical response, and a fast response (Kornbluh *et al.*, 2000).

Ma *et al.* (2004) studied the strain responses under electric field of an acrylic elastomer (VHB 4910) sandwiched between silver electrodes. The strain responses came from two effects: the electrostriction and the Maxwell stress effect. Kyokane *et al., 2001* fabricated a polyurethane film and measured the bending distance under applied electric field due to the electrostriction effect.

2.1.1.3 Electroactive Cellulose

Electroactive cellulose is a biopolymer. It is found in plants as microfibrils forming the major constituent of cottons and woods (Kim *et al.*, 2008). Electroactive cellulose is a currently pursued material towards actuator applications due to several distinct advantages: light weight, low cost, and low actuation voltage.

Kim *et al.* (2008) investigated the piezoelectric effects of an electroactive cellulose by measuring the piezoelectric charge constant to be in the range of 8–28.2 pC/N. Kim *et al.* (2008) studied the electromechanical responses of a cellophane paper by measuring the bending distance: a bending of 3 mm under applied electric field at 2 MV/m. Yun *et al.* (2007) studied the mechanical power and the electromechanical coupling efficiency of an electroactive cellulose; both depended on the thickness of the specimens.

2.1.1.4 Liquid Crystal Elastomers

Liquid Crystal Elastomers can be used as electroactive polymer actuators in which their piezoelectric characteristics are electrically activated by induced heating (Bar-cohen *et al.*, 2004). The actuation mechanism of these materials involves the phase transition between the nemetic and the isotropic phases (Bar-cohen *et al.*, 2004).

Corbett *et al.* (2009) developed liquid crystal actuators from nemetic elastomers. Under applied electric field, the nemetic elastomers shrank along the perpendicular directions and lengthened along the field direction, along with the change of the shape. Lehmann *et al.* (1999) studied the piezoelectric effect of a ferroelectric liquid crystal elastomers (FLCE). The piezoelectricity was caused by electrically or mechanically induced motions of smectic layers (Lehmann *et al.*, 1999). Spillmann *et al.* (2007) fabricated a stacked nemetic elastomer for use as a thermal responsive actuator. The stacking nemetic elastomer can produce 18% strain

between the contracted and the relaxed states, and the blocked stress of the thermally actuated stacked films was 130 kPa (Spillmann *et al.*, 2007).

2.1.1.5 Ionic Polymer Gels

An Ionic Polymer Gel is composed of a cross-linked polymer network, having an ionizable group in which swelling or shrinkage can occur in an electrolyte solution under applied electric field (Shiga *et al.*, 1994). The Ionic Polymer Gel can easily be actuated under low applied electric field strength. The actuation occurs from the diffusion of ions through the polymer gel (Hirai *et al.*, 1994).

Shiga *et al.* (1994) studied the deformation of polyvinyl alcohol-polyacrylamide hydrogel (PVA-PAA gel) in a sodium carbonate solution under applied AC electric field. The PVA-PAA gel bended when subjected to electric field at 1 Hz. In addition, the gel vibrated under AC electric field. Doi *et al.* (1992) studied the swelling mechanism of an ionic polymer gel in a buffer solution under electric field. The swelling behavior was due the movements of the ions and that the swelling speed was proportional to the square of the electric current. Yao *et al.* (2003) fabricated two cross-linked strong acid hydrogels. The first type was 50% sulfonated poly(styrene-b-ethylene-co-butylene-b-styrene) (S-SEBS) and second type was 69% sulfonated polystyrene (S-PS). The polymer gels were immersed into 0.005–0.1 M solutions of Na_2SO_4, Cs_2SO_4, $(CH_3)_4NHSO_4$, and $(C_4H_9)_4NHSO_4$ (TBA). Under applied DC electric field of 1.6 V/cm, the gels bended towards the cathode side [B27].

2.1.1.6 Ionomeric Polymer-Metal Composites (IPMC)

Ionomeric Polymer-Metal Composites (IPMC) are EAPs that bend in response to an electric field as a result of the movement of cations present in the polymer network (Bar-cohen *et al.*, 2004). The polyelectrolyte matrix is neutralized with a certain amount of counter-ions. As an electric field is applied, the mobile counter-ions start their motion and diffuse towards one of the electrodes. That leads to the change in the network shape (Bar-cohen *et al.*, 2004).

Shahinpoor *et al.* (2002) developed the IPMC from Nafion-117 loaded with spherical silver nanoparticles. They measured the displacement of specimens along the y-axis. The spherical silver nanoparticles enhanced the

displacement distance of Nafrion-117. Chung *et al.* (2005) prepared an IPMC based on Nafion with silver nanoparticles and measured the deflection distance along the x-axis. When the DC electric field was applied, the IPMC Nafion deflected. The deflection distance increased linearly with increasing electric field strength from 1 to 5 V.

2.1.1.7 Conductive Polymers

Conductive Polymers are organic materials that generally are comprised of C, H, and simple heteroatoms such as N and S. and consisting of unique π-conjugation electrons (Chandrasekhar *et al.*, 1999). The materials differ from typical organic polymers due to their unique π-conjugation electrons properties which impart higher electrical conductivity at room temperature on oxidation or reduction than ordinary polymers that are insulating materials when compared to metals (Chandrasekhar *et al.*, 1999).

Hiamtup *et al.* (2007) studied the dielectrophoresis force on polymer blends of polyaniline and polydimethylsiloxane between fixed copper electrodes. The dielectrophoresis force increased with increasing electric field strength but decreased with increasing polyaniline concentration. Niamlang *et al.* (2007) investigated the dielectrophoresis force of a pure polydimethylsiloxane and polymer blends of polydimethylsiloxane and poly(p-phenylenevinylene). The conductive polymer particles enhanced the dielectrophoresis force. Shiga *et al.* (1997) reported the similar effect for the poly(p-phenylene) and silicone elastomer blend. They found that the electroviscoelastic effect increased with increasing particle content. The enhancement of shear modulus was negligible below 8.4% vol.

2.1.1.8 Carbon Nanotubes

Carbon Nanotubes (CNT) are the carbon-carbon compound with a cylindrical nanostructure (Bar-cohen *et al.*, 2004). Nanotubes are categorized either as single-walled nanotubes (SWNTs) or multi-walled nanotubes (MWNTs). CNTs have high conductivities due to the network of conjugated bonds which connect all carbons and provide a path for the flow of electrons along the structure (Bar-cohen *et al.*, 2004). Because of the electrical properties of CNTs, they are suitable for use as actuators.

Baughman *et al.* (1999) reported the electromechanical actuation of carbon nanotubes by using a single-walled NT. They used single wall nanotube bucky-papers as the electrodes of an electrochemical cell. Under applied voltage and charge injection, the formation of a double layer at the electrolyte–ion interface occurred. Both electrodes were bent laterally and the strain was generated (Baughman *et al.*, 1999). Roth *et al.* (2002) studied the actuation of an individual carbon nanotube. CNTs were etched into the silicon chip and the device was placed into an electrolyte. As an electric field was applied, the shape of CNTs changed. Mazzoldi *et al.* (2008) fabricated composite films between carbon nanotubes and partially cross-linked polyvinylalcohol–polyallylamine. As an electric field was applied, the composite films started bending.

However all types of EAP have their own disadvantages. Many researchers have attempted to prepare the polymer blends between 2 or 3 types of EAP for solving the mechanical properties and processing problems.

Actuators are the mechanical devices that can be convert electrical energy into motion. The actuators are required in many applications such as controlling pump, motor, robotic parts and etc (Bar Cohen *et al.*, 2004).
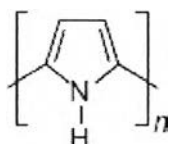
2.1.2 Conductive Polymers

Conductive Polymers, CPs, (Chandrasekhar *et al.*, 1999) are intrinsically conducting polymers without the presence of any conductive filler. The unique intrinsic conductivity of these organic materials, which generally are comprised simply of C, H, and simple heteroatoms such as N and S, and the myriad of properties emanating from it arise uniquely from the n-conjugation. Fairly extended and delocalized conjugations originate from the overlap of n-electrons.

This conductivity of CPs arises because the electrons can be delocalized in the conjugation structure. Most of CPs have the structure with the alternation between the single and the double bonds. The conductivity of CPs can be achieved through a chemical or electrochemical oxidation or reduction, by a number of anionic or cationic species, call "dopants". The sample of conductive polymer is shown below:
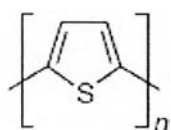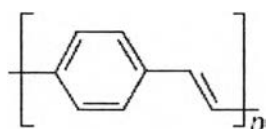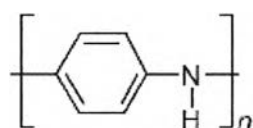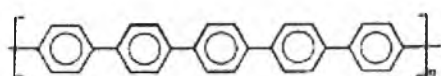
(a) Polyacetylene

(b) Polypyrrole

(c) Polythiophene

(d) Polyphenylene vinylene

(e) Polyaniline

(f) Poly(p-phenylene)

Figure 2.1 Conductive Polymers.

2.1.3 Dielectric Elastomers

Dielectric Elastomer is the elastomer that can convert electrical energy to stress and/or strain responses (Pelrine *et al.*, 2001). Most of dielectric elastomers should have high dielectric value (Kornbluh *et al.*, 2000). Dielectric

elastomers have many advantages; they are light weight, have a high degree of mechanical response, and have a fast responding time [14].

The deformation of dielectric elastomers under applied electric field strength comes from 2 effects. The first is the Maxwell stress and the second is the electrostriction. The Maxwell stress is the force that is generated by the attractive force between unlike charges on the top and bottom electrode surfaces under applied electric field (Diaconu *et al.*, 2006). On the other hand, the electrostriction is the direct coupling between an electric polarization and the mechanical response of the materials (Diaconu *et al.*, 2006). The ratio between Maxwell stress and electrostriction on the electromechanical response depends on the chemical composition, processing conditions of the sample, and thermal and mechanical treatment of the materials (Diaconu *et al.*, 2006).

The strain response from the electrostriction can be expressed as:

$$e = -Q\varepsilon_0^2 (\varepsilon - 1)^2 E^2 ,$$
(2.1)

where e is the strain, Q is the electrostriction coefficient, ε is the dielectric permittivity of the material, ε_0 is the dielectric constant of free space (8.85 pF/m), and E is the electric field strength (V/m) (Diaconu *et al.*, 2006)]. Using Hooke's law:

$$\delta = -Q\varepsilon_0^2 (\varepsilon - 1)^2 E^2 Y ,$$
(2.2)

where δ is the stress. From equations 1, it is expected that the stress should vary nonlinearly with the dielectric constant and the square of the electric field strength.

Acrylic elastomers, polyurethane and silicone elastomers are the most representative materials of this EAP class. Such kinds of polymers are very compliant and have shown the highest actuating deformations among all EAP materials.

2.1.4 Electroviscoelastic Effect in ER Elastomer

While most of research have been focused on ER fluids, which are normally suspension of 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 an electrical field can control the viscoelasticity of the elastomers. Polarizable particles can be dispersed in elastomeric materials to create ER elastomers which 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. The advantages of ER elastomers over ER fluids include no leakage, no attrition or sedimentation of particles, and possibly higher dielectric strength. In addition, there is 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.
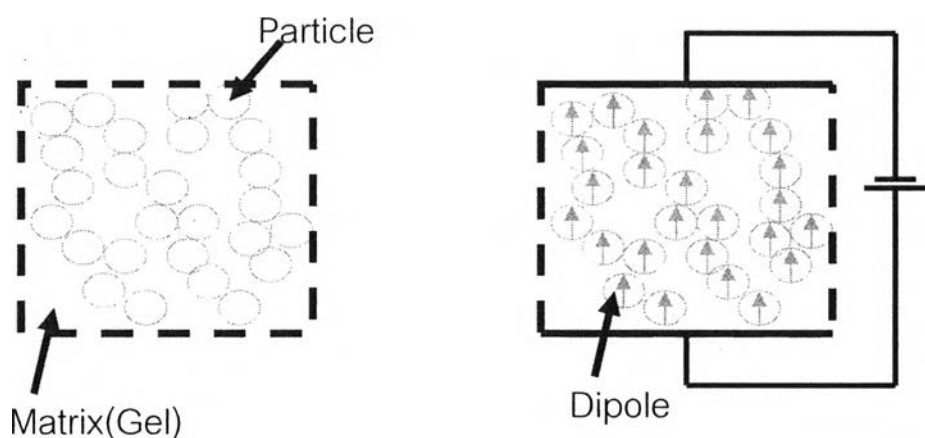

Figure 2.2 Schematic illustration of the electroviscoelastic effect.

2.2 Literature Survey

2.2.1 Poly(p-phenylene) or PPP

The phenylene bonding pattern consists of two benzene rings or benzene with substituent groups that are joined by a divalent (2-bonding) atom, such as oxygen or surphur, or joined by carbon-carbon bond. PPP is the derivative of

PTV. The example of PTV derivative is polyphenylenesulfide and polyphenyleneoxide. This class of CP comprises of "older" CP whose bulk syntheses were established some years before the recent surge in interest in CP. They are singular and attractive in that many of them, e.g. PPP, can undergo both the p-type and n-type dopings, and nearly all have very high thermal stability in their undoped states.

Kovacic *et al.* *(1961)* polymerized benzene to p-polypheny by aluminium chloride-cupric chloride. Benzene was polymerized under remarkably mild conditions on a treatment with aluminum chloride-cupric chloride water to a solid possessing the properties of p-polyphenyl (Kovacic *et al.,* 1961).

2.2.2 Acrylic Elastomers

Acrylic polymers (or acrylates) are the most representative materials of this EAP class which can exhibit high-level actuating capabilities: thickness strains up to 60-70 % at 400 V/μm, area strains up to 200 % at 200 V/μm, and corresponding stresses of some MPa.

Polyacrylate rubbers (ACM) is one type of acrylic elastomer. ACM are saturated copolymers of monomeric acrylic esters and reactive cure site monomers. The first commercial products were based predominantly upon ethyl acrylate or butyl acrylate and in some grades, together with acrylic monomers of the alkoxyalkyl type such as methoxyethyl acrylate and ethoxyethyl acrylate (Yang et al, 1994) (shown in Figure 2.3).
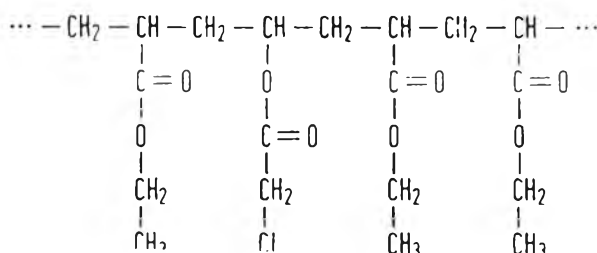

Figure 2.3 Chemical structures of acrylate elastomers.

Ma *et al.* (2004) studied the strain responses under electric field of an acrylic elastomer (VHB 4910) sandwiched between silver electrodes. They reported

that the strain responses came from two effects: the electrostriction and the Maxwell stress effects. The acrylic elastomer generated the highest strain responses under electric field relative to those of other electroactive materials (Ma *et al.*, 2004).

Carpi *et al.* (2003) tried to make actuators form acrylic elastomer. They used acrylic elastomer in a film form and coated it with compliant electrodes (graphite spray, carbon grease, graphite powder and electrolyte solution).

2.2.3   Styrene Copolymers

Styrene copolymers are the thermoplastic elastomers which have elastomeric properties of a crosslinked rubber but they can easily be processed by a conventional processing of the thermoplastics polymers. They contain two different polymer segments of hard (polystyrene) and soft (polyisoprene or polybutadiene or polyacrylate) (Wang *et al.*, 2001).

Nagata *et al.* (2005) prepared and characterized a multi-block copolymer of styrene-isoprene copolymers by casting of SI films from dilute polymer solutions of THF. The lamellar morphology was obtained from casting dilute solution.

Hotta *et al.* (2002) studied polystyrene-polyisoprene-polystyrene (SIS), where the microphase-separated PS blocks acted as physical cross-links for the PI elastic network in the stress relaxation in transient networks. At higher temperatures, this energy barrier became weak and insufficient to resist the elastic force. This was one of the obvious reasons for the transitions on raising the temperature.

2.2.4   Electroactive Polymer from the Polymer Blends Between Conductive Polymers And Dielectric Elastomers

For improving the mechanical, electrical, and thermal properties of the novel actuators, the most famous answer is polymer blends (Bar Cohen *et al.*, 2004).

Recently, incorporation of a conductive polymer into a dielectric elastomer forming a polymer blend has been of keen interest. Conductive polymers

can offer a variety of benefits to the host elastomer: variable conductivity, improved thermal stability, and mechanical properties (Kunanuruksapong *et al.*, 2007).

Wichiansee *et al.* (2009) investigated the electrorheological properties of poly(dimethylsiloxane) and poly(3,4-ethylenedioxy thiophene)/poly(stylene sulfonic acid)/ethylene glycol blends. They found that the storage modulus sensitivities and responses increased with increasing volume fraction of poly(3,4-ethylenedioxy thiophene)/poly(stylene sulfonic acid)/ethylene glycol and electric field strength.

Puvanatvattana *et al.* (2008) studied the electrorheological properties of polythiophene/polyisoprene suspensions. They reported that the storage modulus (G') increased dramatically by 3 and 4 orders of magnitude, with the variations of particle conductivity and particle concentration as the electric field strength was increased from 0 to 2 kV/mm

Thipdech *et al.* (2008) fabricated polymer blends between poly(3-thiopheneacetic acid and acrylonitrile-butadiene rubbers. They measured the dielectrophoresis force of pure acrylonitrile-butadiene rubbers and polymer blends. They found that for the blend system, the bending angle and the dielectrophoresis force varied nonlinearly with electric field strength.

2.3 Objective and Scope of Research Work

2.3.1 Poly(p-phenylene) and Acrylic Elastomer Blends for Electroactive Application

Studying the effects of poly(p-phenylene) concentration, temperature and electric field strength on the electromechanical properties of acrylic elastomers and polymer blend; the storage modulus response, the storage modulus sensitivities, the number of strand, and the temporal response.

2.3.2 Electrical Properties and Electromechanical Responses of Acrylic Elastomers and Styrene Copolymers: Effect of Temperature

Studying the effects of elastomers types, electric field strength, dielectric constants, and temperature on the electromechanical properties of acrylic

elastomers (AR70, AR71, and AR72) and styrene copolymers (SAR, SIS, and SBR) blend; the storage modulus response, the storage modulus sensitivities, the temporal response, and the number of strand.

2.3.3 Effect of Dielectric Constant and Electric Field Strength on Dielectrophoresis Force of Acrylic Elastomers and Styrene Copolymers

Studying the effects of the elastomers type, electric field strength, and the dielectric constant on the electromechanical properties of acrylic elastomers (AR70, AR71, and AR72) and styrene copolymers (SAR, SIS, and SBR) blend; the bending distance, the bending angle, and the dielectrophoresis force.

2.3.4 Effect of Frequencies and Amplitude of AC Field on Bending Behavior and Dielectrophoresis Force of Acrylic Elastomers and Styrene Copolymers

Studying the effects of frequency and amplitude of AC electric field on the electromechanical properties of acrylic elastomers (AR71), styrene copolymers (SAR, and SBR) and polymer blend between doped poly(p-pheylene) and acrylic elastomer AR71; the bending distance, the bending angle, cut-off frequency and the dielectrophoresis force.