CHAPTER II
THEORETICAL BACKGROUND AND LITERATURE REVIEW

2.1 Electroactive Polymer (EAPs)

Electroactive Polymer or EAPs are polymers which can respond to electric field by changing shape or stress. They can be used as an actuator or a sensor. As an actuator, used in robotic, they must be able to undergo a large amount of deformation. These polymers must show several required properties, such as light weight, high processability, and low cost. As an artificial muscle, they are polymer gels which are intermediate between a liquid and a solid consisting of a polymer network and an interstitial fluid. EAP materials can be classified into two major categories (Fukushima T. et al, 2005).

2.1.1 Dielectric EAPs

Dielectric EAPs are the polymers that can convert electrical energy into mechanical response. The actuation of dielectric elastomers comes from the electrostatic force between two electrodes which squeeze the polymer, and the interaction within the matrix. This kind of EAP is characterized by a large actuation voltage, but very low electric power consumption. Dielectric EAPs require no power to keep the actuator at a given position. Examples are dielectric elastomers and piezoelectric polymers (Fukushima T. et al, 2005).

2.1.2 Ionic EAPs

Ionic EAPs in which actuation is by the displacement of ions inside the polymer. Only a few voltages (order of 1 V) are needed, but the ionic flow implies a higher electric power needed for actuation, and energy is needed to keep the actuator at a given position. Examples are conductive polymers, carbon nanotubes, and polyelectrolyte gels (Fukushima T. et al, 2005)

2.2 Conductive Polymers (CPs)

Generally, carbon based polymers are regarded as insulators meaning that there are of high resistance or low conductivity. Absolutely, polymers have been

extensively used by the electronic industry. So, the idea of these polymers could be made to conduct electricity. Conductive Polymers or CPs are polymers that can conduct electricity: a semiconductor. CPs are known as intrinsically conductive polymers or electroactive polymers. There are 2 types of CP (Pratt C., 1996):

2.2.1 Filled Polymers or Conductive Polymers; Composite

Filled polymers or Conductive Polymers are composites of insulating polymer matrix and electrically conductive material fillers usually carbon, aluminum, or steel. Adding of a conductive material filler we have to consider its concentration will be higher than critical concentration at the percolation threshold because the filler may form a continuous phase and electrical conductivity increases drastically.

2.2.2 Inherent Conductive Polymers

Inherent Conductive Polymers are polymers which have the conjugated π-electron system, which is the alternating between single and double bond along the polymer chain (Aldissi M., 2006).
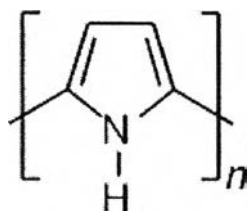
Electrically conductive polymer has to imitate a metal, that is, its electrons need to be free to move and not bound to the atoms. However, it is not enough to have conjugated double bonds but it has to be disturbed either by removing electrons (oxidation) from the material, or inserting electrons (reduction) into the material. The process is known as doping. 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".
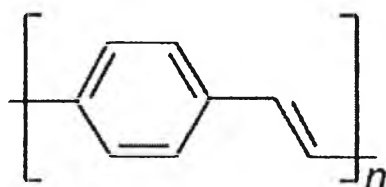
The sample of CPs is shown below:
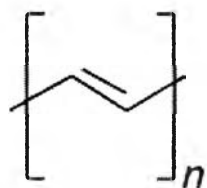
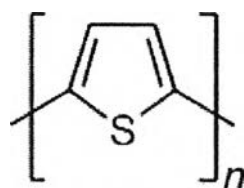|		
1977		**Polyacetylene, PA**
1979		**Polypyrrole, PPy**
1976		**Poly(p-phenylenevinylene), PPV**
1982		**Polythiophene, PT**
1985		**Polyanilline, PANI**
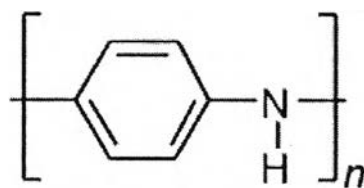
Natta *et.al.* (1958) was the first to synthesize polyacetylene as a black powder. This was found to be a semi-conductor with conductivity between 7×10^{-11} to 7×10^{-3} S/cm.

Hatano *et.al.* (1961) discovered that a polyacetylene sample had conductivity in the order of 10^{-5} S/cm.

Discovery of the conductive properties of polyacetylene occurred in the early 1970s by Shirakawa *et.al.* This revealed the polyacetylene to be a silver, non-conductive film. Shirakawa later collaborated with a physicist Heeger and MacDiarmid and discovered in 1976 that oxidation of this material with iodine resulted in 10^8 fold increase in conductivity. The conductivity of this doped material approached the conductivity of the best available conductor, silver. This was one of the first known example of a conductive organic polymer.

Shirakawa, co-discoverer of the field of conducting polymers, more commonly known as "synthetic metal", was the chemist responsible in 1977 for the chemical and electrochemical doping of polyacetylene, the prototype conducting polymer. Shirakawa shared a Nobel Prize 2000 in Chemistry with Heegee and MacDiarmid. The Royal Swedish Academy of Science awarded the prize to the three for the discovery and development of CPs.

2.3 Conductivity

The property of conductive polymer to conduct electricity can be explained by the band theory. The band theory explains electrical conductivity in terms of the energy gap existing between valence and conduct band which are formed in the solid state by the overlapping of orbital between identical atom neighbors (Casiday R., and Frey R., 2006):
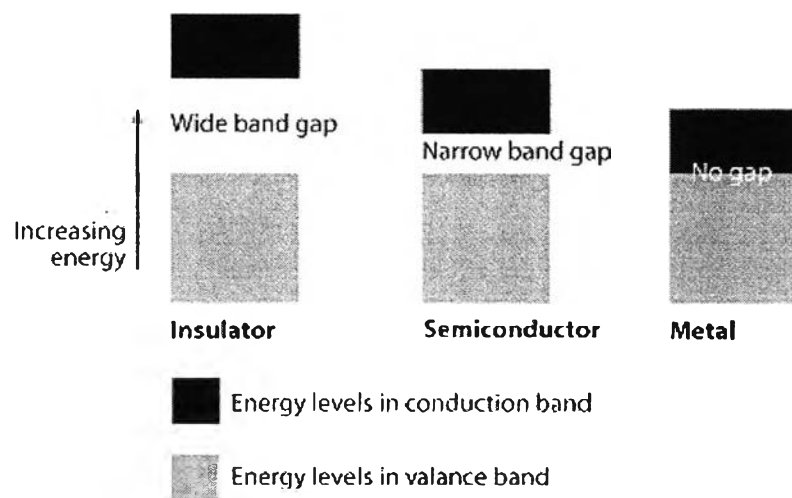
2.3.1 Insulator

When the gap between these bands is board, thermal excitation at room temperature is insufficient to shift the electrons from one band to the other. (Figure2.1)

2.3.2 Semi-conductor

If the band gap is narrow, thermal excitation at room temperature is insufficient to shift the electrons from valence band to conduction band. (Figure2.1)

2.3.3 Conductor

In metal, the high conductivity results from the absence of band gap which allow electrons to flow continuously on the dual band. (Figure2.1)

Figure 2.1 Simple band picture explaining the difference between an insulator, a semiconductor and a metal.

2.4 Ethylene Propylene Diene Rubber (EPDM)

EPDM Materials generally have a high resistance to hot water, steam, ageing and chemicals, and are suitable for a wide range of temperature applications. EPDM rubber , a type of synthetic rubber, is an elastomer which is characterized by wide range of applications. The E refers to Ethylene, P to Propylene, D to diene and M refers to its classification in ASTM standard D-1418. The "M" class includes rubbers having a saturated chain of the polymethylene type. The diene(s) currently used in the manufacture of EPDM rubbers are DCPD (dicyclopentadiene), ENB (ethylidene norbornene) and VNB (vinyl norbornene)

(http://en.wikipedia.org/wiki/EPDM_rubber). The ethylene content is around 45% to 75%. The higher the ethylene content the higher the loading possibilities of the polymer, better mixing and extrusion. During peroxide curing these polymers give a higher crosslink density compared with their amorphous counterpart. The amorphous polymer is also excellent in processing. This is very much influenced by their molecular structure. The dienes, typically comprising between 2.5 wt% up to 12 wt% of the composition serve as crosslinks, which provide resistance to unwanted tackiness, creep or flow during end use. Limitations of EPDM are poor resistance to oil; gasoline and hydrocarbon solvents; adhesion to fabrics and metal is poor (http://www.grandriverrubber.com).

The saturated backbone and non-polar structure of EPDM chains give this material excellent electrical resistivity (Zonghuan Li et al., 2009). Reinforcing fillers for elastomers include carbon black, silica, clay, plastics and glass fiber. Carbon black, the commonly used reinforcing filler, modifies the mechanical, electrical and aging properties of EPDM. The conductivity is enhanced with a carbon black added into EPDM (Zonghuan Li et al., 2009).

2.5 Doping

The semiconductor band structure of CPs permits the electronic excitation or the electron removal/addition leading. This process is called doping.

The polymer is transformed into a conductor by doping it with either an electron donator or an electron acceptor. This is reminiscent of doping of silicon based semiconductor where silicon is doped with arsenic (n-type semiconductor) that creates electrons retaining inside silicon produces a donor energy level close to the conduction band or boron (p-type semiconductor) that creates hole inside silicon and make the next electron try to move and fill this hole produces an acceptor level close to the valence band.

Two kinds of doping may affect electronsto move freely from the valence band to the conduction band. So, the main cause that makes polymer to conduct

electrically is the jump of the electrons from the valence band to the conduction band (Pratt C., 1996).

2.6 Polyazine and its Derivative

Polyazine $H_2N-(N=C(R)-C(R)=N)_x NH_2$ is the polymer that contain extensive conjugation along the polymer backbone like other polymers. Because of nitrogen heteroatoms, they are not reactive in air. In the presence of the nitrogen atoms, they are much more environmentally stable. Polyazine can be oxidized into a conducting state. With R=H, the polyazine is not a simple linear, it is the complexity of the structure of this material, along with the nature of the chain conjugation and the presence of hydrocarbon structure, ring, and etc. (Euler W. B., 1989).

Most desirable at the present time is to investigate the simplest linear polymeric material, a polyazine derivative, when $R=CH_3$ called the permethyl polyazine, $H_2N-(N=C(CH_3)-C(CH_3)=N)_x-NH_2$ a well defined linear polymer free of defects; it can be doped with iodine to give powder conductivities as high as 0.1 $S.cm^{-1}$. Unfortunately, this derivative is rather intractable, decomposing rather than melting at raised temperature, and it is insoluble in any solvent (Euler W. B., 1989).

2.7 Synthesis of Polyazine

Most highly conjugated materials, semiconductor polymers usually show poor solubility in organic solvents for processability. In study of the properties of polyazine, we face some difficulties, due to the extremely limited solubility of the polyazine. One method of improving the processability of conducting polymers is to add long-chain alkyl side groups to the polymer backbone to improve the solubility of the polymer in organic solvents (Euler W. B., 1989).

Polymers containing polyazine structure have been successfully synthesized by various procedures and various precursors (T. A. Sidorov, 1967).

B. É. Davydov *et.al.* (1963) prepared a linear polyazine with alternating atoms of carbon and nitrogen obtained by direct polymerization. The polyazine was obtained by the polycondensation of glyoxal, which is an organic compound, it is the

smallest dialdehyde (Ronzio, 1955) and hydrazine in dimethylformamide. For the electrical property, they observed that the electrical conductivity and the increase in the energy of activation on heating must probably be connected with the elimination of solvent. Some chemical processes as polymerization may take place on thermal treatment, should lead to the reverse effect to an increase in conductivity.

William B. Euler, (1989) reaction of of 2, 3-hexanedione with 2, 3-hexanedione dihydrazone led to a polyazine that is soluble in organic solvents. This synthetic method gave a polymer with statistically alternating methyl and propyl substitute on the carbon atoms along the chain known as the propylmethylpolyazine (PMPAZ). The addition of propyl groups at alternate carbon atoms along the chain had the desired effect of inducing solubility in organic solvent. Further, the conjugation along the polymer backbone appeared to be relatively unaffected by the presence of the propyl group, in the undoped state. The propyl group altered the reactivity with iodine significantly, and it made the polyazine chain much more chemically robust so that more powerful oxidizing agents must be used to form charge carrier.
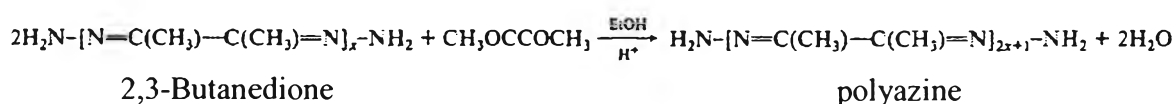
T. A. Sidorov *et.al.* (1967) reported the synthesis and certain properties of polyazines; they obtained in the polycondensation of a number of dicarbonyl compounds and hydrazine hydrate, by using various dicarbonyl compounds. The types of dicarbonyl compound affect the electric conductivity. The IR spectra of polyazines from glyoxal and 1, 1'-diacetylferrocene gave a narrow electron paramagnetic resonance (EPR) signal (Figure 2.2) and possesed an increase in electric conductivity in comparison with other polyazines.
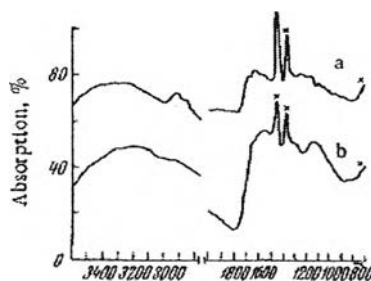
Figure 2.2 IR spectra of polyazines: a) from 1,1'-diacetylferrocene; b) from glyoxa.

Charles. R. Hauer *et.al.* (1987) reported that polyazine of various chain lengths have been prepared from 2,3-Butanedione dihydrazone (x=1), and butanedione dihydrazone azine (x=2). The chemical mechanism was described by Stratton and Busch (eq. 1). This method could produce the oligomer up to x=5. The higher molecular weight of oligomers could be synthesized by refluxing a 2:1 mole ratio of the appropriate hydrazone azine with 2,3-butanedione in ethanol, with acetic acid as a catalyst, and characterized by IR spectroscopy. The higher molecular weight polymers are yellow to brown powder, high melting point, and surprisingly resistant to hydrolysis. Correlation of the IR spectra of the monomer and sequentially increasing chain length polymers showed that the highest molecular weight polymers is at least 45 monomer units length.

$$2H_2N-[N=C(CH_3)-C(CH_3)=N]_x-NH_2 + CH_3OCCOCH_3 \xrightarrow[H^+]{EtOH} H_2N-[N=C(CH_3)-C(CH_3)=N]_{2x+1}-NH_2 + 2H_2O$$

2,3-Butanedione   polyazine

Orazio A. Attanasi *et.al.* (2008) reported that polyazine can obtained from 2,3-butanedione dihydrazone by thermal polymerization, or by condensate of α,β-dihydrazones with α,β-diones under acidic conditions. Unfortunately, there are few studies on this process because of the experimental difficulties due to instability of the polymers and/or its intermediates. The synthetic usefulness of 1,2-diaza-1,3-butadienes in the 1,4-conjugated addition, we decided to investigate the polymerization reactions of these conjugated heterodienic compounds, the first preparation of polyazine from substituted 1-aminocarbonyl- or 1-alkoxycarbonyl-

1,2-diaza-1,3-butadienes by using both photochemical or anionic polymerization. Then we will obtain a polyazine which could be useful for specific applications.

2.8 Ethylene Propylene Diene Rubber (EPDM)

Zonghuan Li *et.al.* (2009) reported the effect of carbon blacks on the electrical properties of filled EPDM by comparing five types of carbon blacks. The result of this research showed that conductive carbon black (CCB) introduceed the highest conductivity and lowest dielectric strength to EPDM/carbon black composites (Figure 2.3) and the dissipation factor of EPDM/carbon black composites declined slightly with increasing frequency, except for the case of EPDM filled with CCB (Figure 2.4).

This indicated that a carbon black with large surface area induced high conductivity into filled EPDM. EPDM/CCB composites also have a lower dielectric constant and higher dissipation factor compared to the other filled EPDM samples.
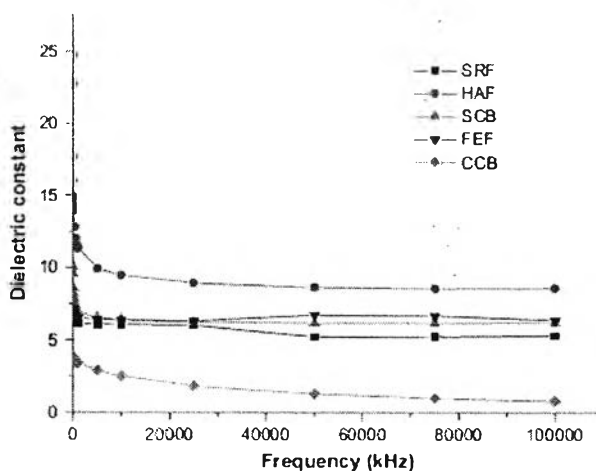
Figure 2.3 Dielectric constant of EPDM/carbon black composites.
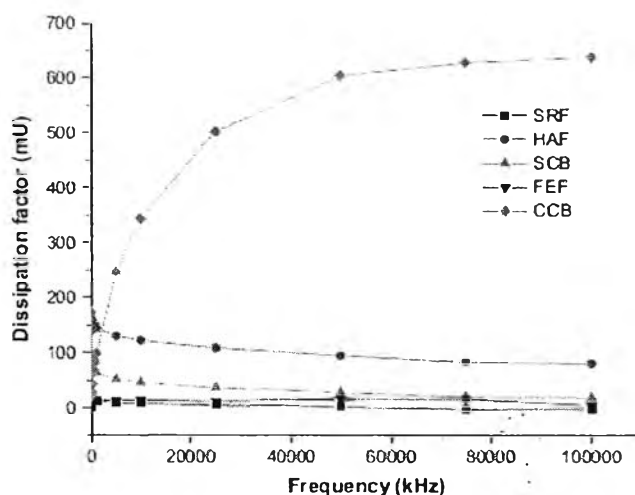
Figure 2.4 The dissipation factor of EPDM/carbon black composites.

Hence, CCB with large surface area is useful for conductive applications; whereas other carbon blacks, such as SRF, SCB, HAF and FEF are useful for insulation products (Zonghuan Li et al., 2009).

Ginic-Markovic M. *et.al.* (2000) reported that the viscoelastic behavior of filled and unfilled EPDM elastomer and the effect of filler loading compared to the gum systems were when compared to the gum system. The filled system has higher E' and E'' values over the whole range of temperatures throughout all the three regions and filled system had a lower glass-transition temperature (α) compared to that of the gum system (E'max at -48°C compared to -44°C for the gum system)(Figure 2.5).

Filler aggregates adsorbed a part of the molecular chain between, and within, the filler aggregate agglomerated and reduced the mobility of a part of the chain segment (Ginic-Markovic M. *et.al.*,2000).
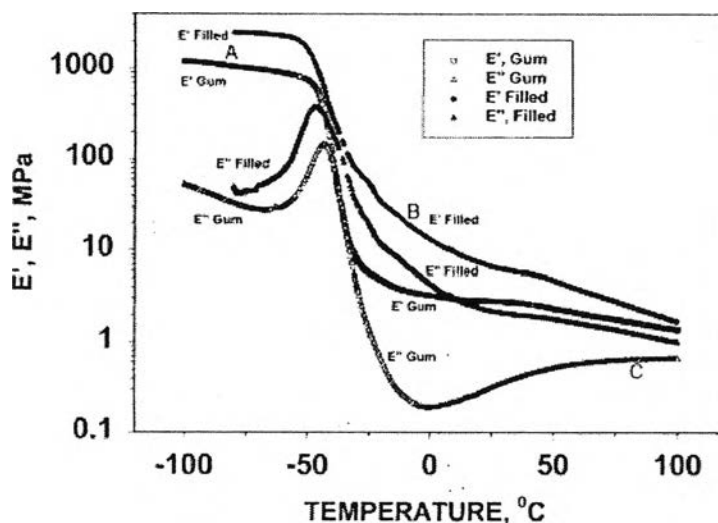
Figure 2.5 Effect of temperature on elastic and loss moduli for uncuredgum and filled systems.

Faez *et.al.* (2002) studied effect of crosslinking of a conductive elastomer based on EPDM and polyaniline, they found that the tension at break for all blend increased with PAni–DBSA loading until 30% (w/w). This was assigned to the reinforcement effect of the conductive polymer. Above this concentration (30% w/w), the molecular mobility decreased owing to the formation of physical bonds between filler particles and polymer chains which was the basis for the mechanism of reinforcement. Consequently, the tension droped with an increase in PAni-DBSA loading.
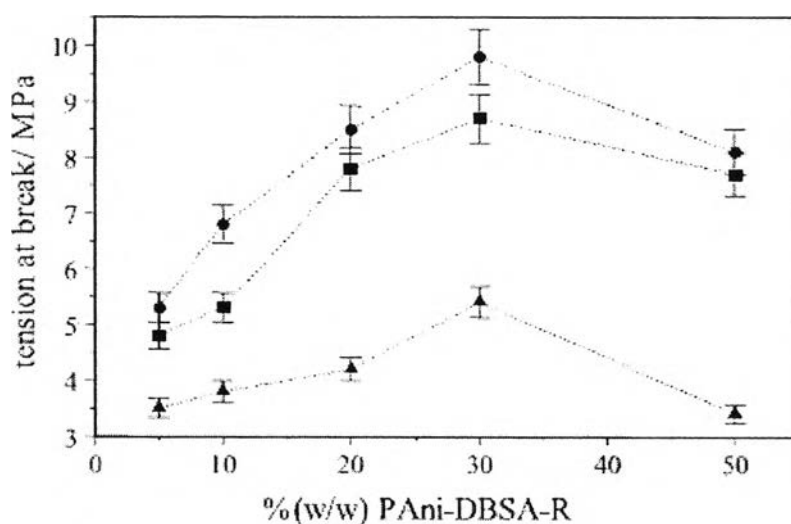
Figure 2.6 Tension at break for EPDM/PAni-DBSA-R crosslinked.

2.9 Doping Polyazine

The conductivity of polyazine can be improved by the doping process.

Typically "doping" the conductive polymers involves actually oxidizing/reducing of the compound (Noel S. Hush *et al.*, 2003).

Charles R. Haure *et.al.* [1987] investigated a polyazine that can be reacted with iodine to give electrically conducting materials. The electrical conductivities of iodine-doped polyazine reached as high as 1.3 $\Omega^{-1}cm^{-1}$ at room temperature. The IR spectra of doped polymers showed that the structural integrity of the chain was retained upon exposure to iodine, I_2.

In 1989, Euler et al. doped the polymer with iodine. Since the polymer was readily soluble in chloroform, any level of "doping" could be achieved by simply weighing the amount of the two reactants which were 2,3-hexanedione and 2,3-hexanedione dihydrazone, mixing in chloroform, and eliminated the solvent by evaporation. At low iodine levels, the doped product had a burnt orange color, while at high doping levels, the product was black.

At the high iodine levels, the product could be recovered off of the evaporating flask walls as a shiny, brittle, thick film. Although no iodine odor was

present, the doped polymers did lose (Euler et al., 1989) iodine upon standing. This was in contrast to the iodine-doped MMPAZ polymers, permethylpolyazine which have been obtained only as dispersed powders and did lose iodine, even under vacuum.

In 1992, Douglas S. Dudis *et.al.* prepared iodined-doped polyazine. The iodine accepted electrons from the polymer chain, and created a positively charged "hole" on carbon or nitrogen atom. However, this hole was unstable, which was "filled" by an adjacent nonbonding pair of electrons to form a new double bond with the adjacent nitrogen. (Figure 2.7)
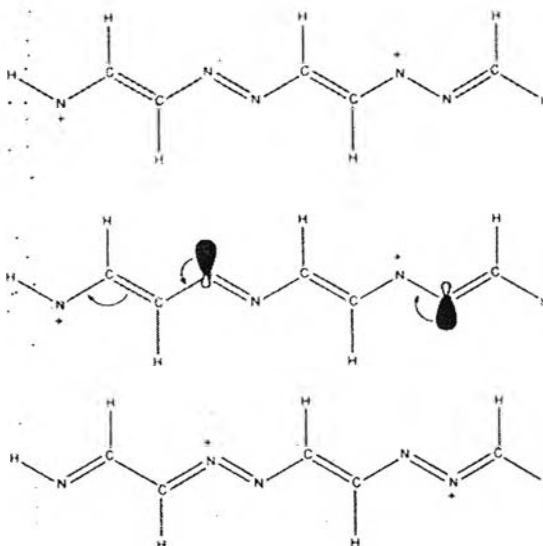
Figure 2.7 Mechanism of iodine-doped polyazine.

In 1997, Jordan Del Nero *et.al.* reported the electronic structure of a polyazine derivative, in the presence of conformational defect, which is the random distribution of defects like bipolaron. The Negative Factor Counting technique and the Inverse Iteraction Method were used to identify the electronic density of states and the wavefunctions, respectively. The results showed a red shift (Figure 2.8) at the Fermi energy for high concentration defect in disordered systems and in ordered system we have localized wavefunctions. Together with the highest occupied

molecular orbital (HOMO) state, this showed that the possibility to have the polymer in the metallic regime.
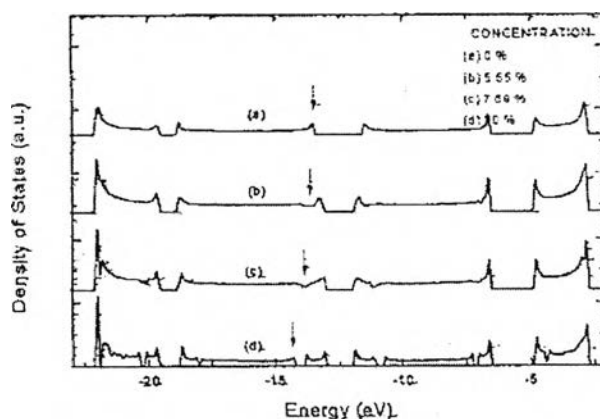

Figure 2.8 DOS of the polyazine derivative with disordered defect (arrows show the position of HOMO).

2.10 Electroactive Polymer (EAPs)

One severe drawback for the newly developed field type EAPs, as has been shown is the high electric field required in order to generate high strain with high elastic energy density. For actuator materials, elastic energy density, U_s is a key parameter measuring the strain and stress generation capability of an electromechanical material. From an energy conservation point of view, the output elastic energy density cannot exceed the input electric energy density, which is equal to $K\varepsilon_0 E^2 /2$. Therefore, a high input electric energy density is required in order to have a high elastic energy density output (Yoseph Bar-Cohen, Electroactive Polymer Actuator as Artificial Muscles, Second Editor, page 133-134). Electroactive polymers (EAPs) are a new class of smart materials, that can response to external stimuli such as pH, temperature and electric field.

Bassil M. *et.al.* (2008) studied of the electromechanical behavior of a PMMA hydrogel actuator can be defined as lightly crosslinked polymers that are insoluble but swell dramatically in the presence of water leading to a rubbery gel. Electroactive hydrogel, like PMMA can sense the physical, chemical and biological

environment and respond to external stimuli in a controllable way. They show an immediate and large volume change in response to various stimuli from the surrounding environment and can be driven by electric field. In this research, a new characterization method of the pH distribution in hydrogel actuators was induced by an electrical field applied. When an electrical field was applied, the gel bended always toward the anode, where the pH was low compared to the cathode(electrical energy to be convert into mechanical work). The bending was explained by the response of the gel to different pH values. The actuator underwent a more important contraction (quicker shrink) in an acidic environment than in a basic environment. (Figure 2.9)
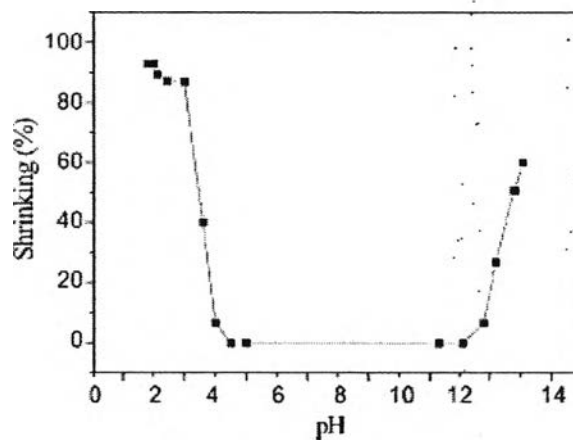

Figure 2.9 Response of the gel to different pHs.

Skov A.L. *et.al.* (2008) reported the basic physical and chemical properties of elastomers essential for their use in dielectric elastomer actuators. The elastic modulus, the dielectric constant, and the dielectrid breakdown strength determine the ultimate static performance of an actuators. The chemical and thermal properties determine the environmental compliance of the actuator including temperature service range and resistance towards various solvent.

In 2009, Shankar R. *et.al.* reported polymeric materials that can convert electrical energy to mechanical work which are broadly classified as electroactive polymers (EAPs) and typically exhibited considerable stress and/or strain upon

electrical stimulation. EAPs offer comparatively low actuation stresses. Due to their light weight, resilience, large actuation strain and toughness. Recently, all the EAPs reported, dielectric electroactive polymers (D-EAPs) posses the most promising and versatile properties such as the highest actuation strain, highest energy density, highest electromechanical coupling efficiency and fastest actuation time.

In 2000, Feher *et.al.* studied the bending of a TiO_2-loaded polydimethylsiloxane (PDMS) gel measured in a uniform (a) and a non-uniform (b) electric field (Figure 2.10). The gel cylinder between parallel copper electrodes gradually bent to the cathode. The bending behavior was found to be reversible, when positive and negative electrodes were alternated. As one of the electrodes was modified to create a non-uniform electric field, a metal ball replaced one of the electrodes, the bendings were the same. Watanabe *et.al.*, 2004 studied the electromechanical responses of pure polyurethane with compliant electrodes. The responses were due to the difference in charge densities between the anode and the cathode.

(a) (b)
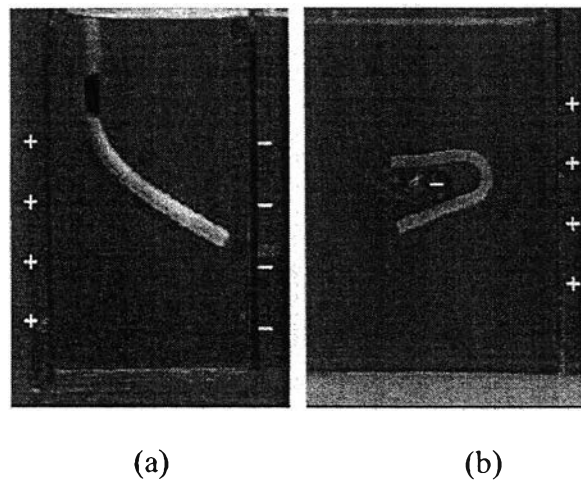
Figure 2.10 Bending of an electric field responsive PDMS gel in a uniform (a) and a non-uniform (b) electric field.

Yun *et al.* (2007) studied the performance of electroactive paper (EAPap) that have three different samples of 20, 30, and 40 μm. EAPap actuators exhibited bending deformation in the presence of electric field which depended on thickness,

the thickness increased the electric field strength and the displacement were decreased due to the bending stiffness was too high.