

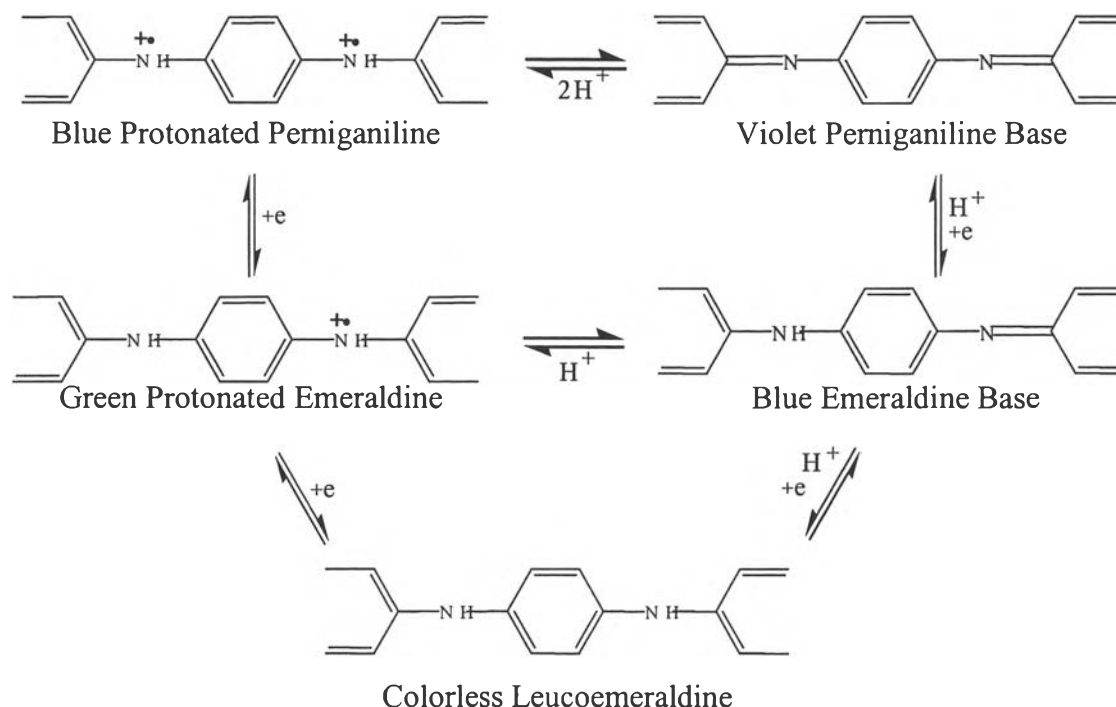


CHAPTER II LITERATURE SURVEY

2.1 Polyaniline

Polyaniline has been synthesized in various forms both chemically and electrochemically in aqueous media. In 1985a, MacDiarmid *et al.* chemically synthesized polyaniline to obtain a quinoid-benzenoid-diimine, an insulator form. Then doped the insulator by dilute aqueous protonic acids to reach a metallic regime ($\sigma = 5 \text{ S/cm}$; compress pellet), which gave an iminium salt in a conductive form. Both insulator and conductive forms were stable in the presence of air and/or water. Moreover, the reversed process could be obtained by treatment with aqueous alkali. Later work that confirmed the electrochemical redox structure of polyaniline was the study by Genis *et al.* (1985). They used cyclic voltammetry (CV) to follow a solvation-desolvation phenomenon in hydrogen fluoride. This was used to confirm the non-protonated and protonated forms, or an insulator and conductive forms, respectively. In the paper by MacDiarmid *et al.* (1985b), they reported that polyaniline had an excellent cathode characteristic including recyclability between quinoid-benzenoid-diimine form and an iminium salt form. A Zinc anode and PbO_2 cathode could be used to employ in a rechargeable battery cell.

The formation of polyaniline and nature of its structures have been studied by many researchers. In 1996, Stejskal *et al.* used spectroscopic method to correlate the color with the conductivity as shown in Scheme 2.1.



Scheme 2.1 Polyaniline forms and their interconversions (Stejskal *et al.*, 1996).

Adams *et al.* (1996) modified the molecular structure of polyaniline. They synthesized a high molecular weight polyaniline at very low temperatures. Synthesizing at sub-zero temperatures yielded a polyaniline with a molecular weight five to ten times higher than that prepared at room temperature.

Doping process is an important process that induces a transition from an insulation state to a conductive state. It can be achieved by introducing the dopant molecules into polyaniline chain. In recent years, polyaniline and its derivative have become a prototype system for the study of electrical properties due to its intrinsic redox properties. Kang *et al.* (1995) studied the protonation and deprotonation of polyaniline films and powders. In their work, the change in intrinsic oxidation state of emeraldine base as a function of treatment time in aqueous acid was measured through the technique of XPS. It was concluded that the treatment time increased as the intrinsic redox state ($[=N-]/[-NH-]$) decreased for all types of acid. There are many researches that studied the effects of dopant type, amount and doping method on PANI. One study used macromolecular acids such as sulfonated PS, PPO and PEEK to dope PANI (Geng *et al.*, 1997). They found that the conductivity of the

doped PANI depended on the solution concentration, preparation method and structure of macromolecular acid. The PANI doped with a macromolecular acid also showed a higher environmental stability than that doped with a small molecular acid. Another work was studied by Yin *et al.* (2000), they polymerized a PANI in the presence of dodecylbenzene sulfonic acid co-doped with HCl. Aniline dodecylbenzenesulfonic acid stimulated the solubility while aniline hydrochloride enhanced the conductive structure of the synthesized polymer. A co-doped PANI with high conductivity was obtained without any additional doping. At an ANIHCl/ANIDBSA molar ratio of the feed of 3:7, the polymer showed σ equal to 7.9 S/cm and a maximum yield of 30.8 %.

The electrical conductivity and other properties of PANI and its derivatives are highly dependent on its oxidation states. Many researchers have studied various methods that are used to define its oxidation state. In 2000, Albuquerque *et al.* used UV/VIS spectroscopy to estimate the interconversion between pernigraniline (PB), emeraldine (EB) and leucoemeraldine (LEB). By correlating the absorbance peaks at 634 nm and 320 nm of EB, the quinoid and benzenoid parts, the redox state of PB and LEB could be obtained.

2.2 Polymer Blend as Conductive Polymer

A potential advantage of polymer blends is that they possess a favorable combination of properties from two homopolymers. The development of conducting polymer blends consisting of PANI with other processable polymers has been studied for some time. Cao *et al.* (1992) demonstrated a variety of polyblends made from PANI. The resulting conducting polymer materials can be melt-processed or solution-processed. For a PANI/PMMA blend, an electrical conductivity could reach to 1 S/cm when PANI content was only 2 %. For drawn PANI/PE blend, it could be seen from WAXD that PANI was oriented along fiber axis more than an undrawn fiber. Also, they found no loss of mechanical properties at the modest levels of the conductive PANI complex relative to PE. A PANI/SBS composite was studied by Xie *et al.* (1998). In their work, PANI was polymerized in the presence of SBS. The conductivity could reach a magnitude of 1 S/cm, also a percolation threshold was found. At PANI content lower than 12 wt%, the composite behaved like a

thermoplastic elastomer with a high elongation (~600%) and a low permanent set (<50%).

Other PANI/thermoplastic blends were studied by Zilberman *et al.* (1998). PS, LLDPE, CoPA, LDPE and PCL were melt blended with PANI. The lowest percolation threshold was found to be 5 wt% where the conductivity of the blends could reach order of 10^{-1} S/cm. The SEM observation of the blends found that PANI particles were dispersed in the matrix polymer. It can be concluded from their work that the level of interaction between the components determined the PANI particles' level of fracturing and mode of dispersion within the matrix polymer. Wilson *et al.* (1999) studied the thermal behavior of a conductive elastomeric blend based on PANI. They found that the thermal stability increased as the PANI content in the blend decreased. The electrical conductivity of elastomer was increased by three orders of magnitude when PANI was added up to 10 wt%.

In 1998, Han *et al.* proposed a processable conductive blend of polyaniline/polyimide by using camphorsulfuric acid (CSA) to protonate polyaniline. The polyaniline-CSA complex was processed in a solution phase and was introduced into poly(amic acid) matrix by using N-methyl-2-pyrrolidinone as a co-solvent. Then poly(amic acid) was converted to polyimide by thermal imidisation at 150 °C for 30 minutes. As the thermal imidisation proceeded, the molecular order of polymer chain structure was improved due to the annealing effect on polyaniline chains. Polyaniline-CSA/polyimide showed a higher conductivity and a better thermal stability than a pure polyaniline-CSA. In their next report in 1999, they prepared a conducting film of dodecylbenzene sulfonic acid (DBSA) doped polyaniline/polyimide blends by solvent casting. The result showed the same findings as in their previous work. Polyaniline-DBSA/polyimide was found to have somewhat higher conductivity than that of polyaniline-CSA/polyimide. In their latest work in 2000, they used XPS to study the changes in protonation level ($[N^+]/[N]$), doping state and condition for polyaniline-complex/polyimide and thermally cured polyimide with CSA and DBSA doped. They found that the doping level and the doping state were functions of the dopant type in the blends and the thermal curing up to 180 °C resulted in the increase of the conjugation level.

2.3 Polyimide as Conductive Blends

Recently, electrically conducting polymer composite films have been reported where they combined the electrical conductivity with the good mechanical properties and improved thermal stability. Among insulating matrix polymers, polyimide has been popular because of its well-known thermal and mechanical stability. Tieke *et al.* (1990) reported a novel polypyrrole-polyimide composite films, which was prepared either by electrochemical polymerization of polypyrrole on polyimide coated electrode (type I) or exposing polyimide films containing ferric chloride as an oxidizing agent to pyrrole vapor (type II). The conductivity of film type I was 10 S/cm, whereas the threshold value of film was equal to 10%. As for the film type II, the maximum value of conductivity was 5×10^{-4} S/cm at the FeCl_3 concentration in polyimide equal to 10.7 wt% and polymerized for 16 hours. The composite films from both preparing method were thermally stable up to 350 °C.

Polyimide was modified to be an environmentally stable electrically conductive material with copper molecule inside (Venkatachalam *et al.*, 1993). Thermal treatment could be used to control the electrical conductivity and thermal stability as well. It was found that after a thermal treatment, the conductivity could increase from 2.11×10^{-9} S/cm to 2.2 S/cm.

Jinwei *et al.* (1999) proposed a new method of making polymer films with conductive surfaces by permeation of polythiophene, conducting guest species, into the PI surface. This composite was made for iodine detection. Polythiophene in the composite structure had a higher decomposition temperature compared to a pure conducting polymer.

The chemical durability of PI blend films was studied by Niyogi *et al.* (2000). PI was blended with Nylon-6 then the durability, chemical stability in 2N H_2SO_4 and 40% NaOH and resistance in organic solvent were performed. When comparing between BTDA type and PMDA type of PI, BTDA type has a better chemical durability.

The effect of film thickness on the electrical properties of polyimide thin films (80-2000 nm) was studied by Liang *et al.* (2001). With decreasing film thickness, the dielectric constant decreased but the conduction current increased.

From IR reflection absorption spectroscopy, they found that PI chains were oriented parallel to the electrodes.