CHAPTER II
LITERATURE SURVEY

2.1 Synthesis of Polyaniline.

Ram *et al.* (1996) demonstrated that stable Langmuir monolayer of polyaniline can be fabricated by dissolving emeraldine base in a solution comprising of NMP and $CHCl_3$. The monolayers of emeraldine base are thermally stable over a wide range of temperature (19.2- 45°C). It was found also that annealing of the LB films of emeraldine base can modify their optical properties.

Narkis *et al.* (1997) reported that the distributions of carbon black and doped polyaniline in a given polymer matrix, for example, polycarpolactone, polystyrene, and polyethylene, were remarkably different. In the carbon black containing systems, the powders underwent deagglomeration, and finally reagglomeration resulting in either a uniform or more often a non-uniform distribution of the carbon black particles. Because of the structure of carbon black, they distributed uniformly in the amorphous polar polymers, which have high surface tensions. On the other hand, for the doped polyaniline containing systems, the polyaniline powders partially precipitated out to form a fine, short range, and fibrillar structure bridging. It was shown that the dispersability of the doped polyaniline in a given polymer mainly depends on the dopant nature, the specific matrix, and the composition used. Doped PANI/polymer systems were produced by solution blending, generating a single fibrillar-like structure having a sharper insulator-conductor transition. They also suggested that these behaviors were very useful in developing new commercial thermoplastic and thermosetting conductive blends.

Byun *et al.* (1998) discovered that polyaniline-nylon6 composite film (PANI-N) can be prepared by diffusion and chemical oxidative polymerization

It was found that the conductivity of the composite film increases when the polyaniline content increases, and then reached a maximum of 3.5E-2 $S.cm^{-1}$ at 4.4 wt%. Hydrogen bonding between polyaniline and nylon6 results in a weakening in the doping ability of polyaniline. The dynamic mechanical thermal analysis results show that the crystalline region of nylon6 in the composite films are partly destroyed by the formation of polyaniline. It is considered that the thermal crosslinking reaction of polyaniline may be reversibly changed by the chemical doping and de-doping processes.

Jousseaume *et al.* (1998) reported that polyaniline-polystyrene (PANI-PS) blends by using bis(2-ethyl hexyl hydrogen phosphate(DiOHP) as dopant can be synthesized by codissolution method. It was also investigated that XPS analysis can distinguish four different nitrogen species for all samples as well as the proportion of these species in the total amount of nitrogen atoms. It was found that DiOHP can convert the imine nitrogen atoms to positive charged nitrogen. Blending polyaniline with PS did not make any important modification in the polymer electronic structure.

Burthet *et al.* (1998) reported that non-uniform polyaniline coating was obtained by conventional aniline polymerization condition (aniline monomer, ammonium persulfate, 1.2M HCl at 25°C). In contrast, more homogeneous polyaniline coating was obtained when polymerization of aniline hydrochloride was carried out at 0°C in water. The relative proportion of polyaniline at the surface of the PS latex was estimated by comparing the surface nitrogen contents of the coated and uncoated PS latex. The relatively rapid polymerization at room temperature resulted in non-uniform polyaniline coating and reduced polyaniline surface composition.

Davey *et al.* (2000) reported that acid doping of emeraldine base with calix[4]-*p*-tetrasulfonic and calic[6]-*p*-hexasulfonic acid in water or DMSO leaded to facile formation of colloidal dispersions of emeraldine salts. The conductivities of the pressed dried pellets were 3.2E-4 and 2.9E-4 $S.cm^{-1}$,

respectively. In addition, the polyelectrolyte dopants offered enhanced stability on the emeraldine salts due to their counter ions relative to the alkaline (NaOH) doping, where only partial conversion to emeraldine salts occurring even when pH is equal to 14.

Jang *et al.* (2000) reported that organic/inorganic hybrid composite film was made with polyaniline and silica by sol-gel process. The process was controlled by the pH of the organic/inorganic components and was attributed to the solvent pH. Hybrid composite cast film obtained from using N-methyl-2-pyrrolidone (NMP) as the solvent illustrated a uniform crack-free film because NMP played an important role in the formation of stable silica network as well as hydrogen bonding interaction with polyaniline at pH greater than 7. On the other hand, m-cresol did not create the formation of a stable silica network due to the growth and aggregation of silica at pH lower than 7 in the sol-gel process. Nevertheless, the bulk conductivity of the composite cast from m-cresol was higher than that of NMP because of the secondary doping effect of m-cresol. There were conformational changes in polyaniline molecules from 'coil-like' form to 'rod-like' form leading to a greater degree of crystallinity and therefore the bulk conductivity.

2.2 Doping of Polyaniline.

Cao and Smith (1993) discovered that polyaniline (PANI), fully protonated with camphor sulfonic acid (CSA) could display liquid-crystalline behavior above a critical concentration and suggested that protonation induces a chain stiffening and extrusion of the PANI, or the emeraldine base, which result from either electronic delocalization or counter-ion 'crowding'. Such liquid-crystalline solution was effectively useful for preparation of highly oriented fibers.

Avlyanov *et al.* (1995) demonstrated that the viscosity of mixtures between emeraldine base and d,l-camphorsulfonic acid (HCSA) in solutions of m-cresol, chloroform, or in mixtures of m-cresol and chloroform was reduced. It was the first time to propose the importance of polymer chain conformation in solution as a major factor in determining the conductivity of conducting polymer in the solid state. As the chain became more expanded, thus electron delocalization along the chain increased and then resulting to the augmentation of intro-component of the bulk conductivity. It was shown that the higher crystallinity, the higher intermolecular component of the bulk conductivity was.

Hinrichs *et al.* (1996) studied a pressure-temperature-induced conductivity of polyaniline, poly(2-methyloxyaniline), and poly(2-methylaniline). They found that the conductivity was quite stable up to 10 Kbar and then grew continuously up to a factor 50-60 S.cm-1 at 100°C, 25 Kbar. The conductivity increased regularly with temperature and then dropped irreversibly. Furthermore, they found that the charge carriers responsible for the conductivity involved not only electrons but protons as well.

Fu *et al.* (1997) showed that polyaniline base can be protonated with sulfonated polystyrene in polar solvents such as dimethyl sulfoxide (DMSO) and N-methy-pyrrolidone(NMP). Lightly sulfonated polystyrene (LSPS) as the polymer matrix showed a lot of advantages, for example, the randomly placed sulfonic acid groups on the polystyrene chains behaved as a dilute acid, which protonated the imine nitrogen states sites of polyaniline. This resulted in the processability of the blend, an improved conductivity, and improved electrical conductivity stability because of the migration of the small molecules dopants in the polymer matrix. It was shown that the protonation of polyaniline was retarded in NMP compared to DMSO due to prevalent hydrogen bonding, which reduces the available free acid groups between the carbonyl group of NMP and the sulfonic acid.

Nicolau *et al.* (1997) explained that molecular weight, aggregration state of polyaniline, and counter anion nature influenced to the UV-Vis-NIR light absorption spectra of camphorsulfonic acid protonated polyaniline. It was found that high molecular weight polyaniline synthesized at low temperature obtained CSA-PANI film which showed an enhance polaron delocalization. The substitution of the CSA^- counter anions by Cl^- without intermediate deprotonation kept the expanded coil-like formation and the polaron delocalized state.

Singh *et al.* (1997) reported that conductivity and structural properties of polyaniline doped with monovalent (Cl^-) and multivalent $(PO_4)^{3-}$ ions changed significantly in particular pH range, at a pH of 3.0 and 2.5 in the case of HCl and H_3PO_4, respectively. They informed that Mott's 3D variable range hopping (VRH) is the mechanism responsible for charge transport at low temperatures for HCl as well as H_3PO_4 doped polyaniline, whilst a deviation is observed at higher temperatures for all HCl doped and moderately H_3PO_4 doped samples, indicating thereby a temperature and composition depending on charge transport. Due to crosslinking, either inter-, or intrachain sharing of the same species, induced by trivalent nature of phosphate ion, which results form a hindrance in electron transport and a loss conductivity was given in the case of H_3PO_4 doping in comparison to HCl for the same pH value.

Li and Wan (1998) showed that porous polyaniline can be prepared by a new method called 'doping-dedoping-redoping process'. The room temperature conductivity of HCl, $HClO_4$, H_2SO_4, H_3PO_4, and ρ-TSA could touch 200-300 $S.cm^{-1}$. In addition, mechanical properties between porous emeraldine base films prepared by the above method and dense emeraldine base films casted form by NMP solution were not exactly different. However, a change in mechanical properties depended on the using dopants.

Luzny *et al.* (1998) studied structural and electrical transport properties of thermally processable polyaniline protonated with diphenyl

hydrogen phosphate (DPHP) in chlorobenzene. They discovered that polyaniline is orthorhombic unit cell with a, b, and c lattice constants of 4.4, 5.6, and 7.2 A°, respectively. They found also that relative intensity of diffraction peaks of WAXD are strongly dependent on the temperature of the pressing, whereas, weakly dependent on the time of pressing. It can be concluded that the time of pressing has a strong impact on the average size of crystalline regions in polymer, in contrast, they do not change significantly with the temperature of pressing. It can be postulated that the average crystalline size decreased due to the cross-linking process occurring in the polymer upon extended pressing as well.

Faez *et al.* (1999) prepared vulcanised elastomeric conductive blends of poly(ethylene-co-propylene-co-diene monomer) (EPDM) and ρ-toluene sulfonic acid (ρ-TSA) doped polyaniline. It was observed that a higher mixing temperature improved the homogeneity of the mixtures, although the mixtures were immisicible, resulting to a growth of conductivity as well as crosslinking efficiency. They also reported that the formation of bonds between the high molar mass chains of polyaniline and the oligomers influenced the augmentation of conductivity with an increase in polyaniline content. In this case, polyaniline served as a reinforcing agent to the rubber enhancing modulus value.

Pomfret *et al.* (2000) demonstrated that wet spun fiber conductive polyaniline could be processed from a solution of emeraldine base doped with 2-acrylamido-2-methyl-1-propanesulfonic acid in dichloroacetic acid (DCA). It was coagulated in various solvents such as acetone, butyl acetate, and 4-methyl-2-pentanone. As-spun fibers have Young moduli of 40-50 MPa, ultimate tensile strength of 20-60 MPa, and electrical conductivity of 70-150 $S.cm^{-1}$. While drawing fibers at room temperature or above to an extension of 500% yield conductivity of 1950 $S.cm^{-1}$. It was also shown that the fibers may be drawn at elevated temperature, then annealed to give fibers with Young's

moduli up to 2 GPa and ultimate tensile strengths up to 97 MPa whilst retaining conductivities of 600 $S.cm^{-1}$.

2.3 Polyaniline as Gas Sensors.

Jiakun *et al.* (1993) investigated that polyaniline has a high sensitivity to NH_3 gas at normal temperature accompanied with low resistivity, good selectivity, and reliability. The resistance augmented with the number of electron holes because NH_3 molecules acted as donors after being absorbed, and formed an electric barrier near the surface of the sample.

Agbor *et al.* (1997) presented that polyaniline could be deposited onto a substrate as finely thin films which the thickness per layer was 5.5 + 0.6 nm. Exposing a single LB layer of polyaniline to NO_2 and H_2S led to the increasing of reflectivity and resonance angle. The effects were partly reversible, with lower detection limits of about 50 vapor part per million at room temperature.

Dhawan *et al.* (1997) showed that the leaching of the protonic sites in the doped polyaniline grafted surface on exposure to aqueous ammonia led to a change in resistance of the polymer. The surface resistance changed from 102 to 1010 Ohm. This aspect can be utilized in the designation of a chemical sensor for aqueous ammonia.

Grummt *et al.* (1997) reported that thin layers of polyaniline were suitable to measure the pH in the range of 2-12 in the near infrared region. The deposition of such layers was strongly facilitated by the use of solution-processably polyaniline. Testing the sensor layers over a period of 300 hours and up to 500 titration cycles revealed excellent reproducibility and stability.

Kumar *et al.* (1998) exhibited that polyaniline under $^{15}N^{3+}$ ions bombardment could act as an attractive standard for hydrogen estimation on material surfaces by using the nuclear resonance reaction $^{1}H(^{15}N,\alpha\gamma)^{12}C$.

Polyaniline withstands higher doses of radiation compared to other polymeric materials such as polyethylene and polypropylene. It was found that polyaniline offered several advantages, for instance, more stable during ion beam bombardment, no need any special experimental arrangements likes target cooling and rotation, and synthesized easily in laboratory.

Kang *et al.* (1999) investigated that electrical conductivity of polyaniline doped with HCl was reduced upon exposure to oxygen but increased reversibly upon evacuation. The decrease in conductivity in an oxygen environment was interpreted in terms of the reduction in both the concentration and the mobility of polarons. Moreover, the small reduction either in the electrical conductivity or in the transport phenomena of oxygen confirmed that the contribution of charge mobility was much larger than the charge concentration in electrical conductivity.

Chen *et al.* (2000) reported that emeraldine base films are susceptible to surface modification via UV-induced graft copolymerization with methoxy-poly(ethelene glycol) monomethacrylate (PEGMA) macromonomer. It was found that not only UV graft copolymerzation time but also PEGMA macromonomer concentration effected the graft density of the PEGMA polymer on emeraldine base surface. The hydrophilicity of emeraldine base surface was greatly enhanced by the grafting of the PEGMA chains. The high graft concentration of PEGMA polymer on emeraldine base surface readily led to a low extent of protein adsorption and platelet adhesion. The effects were further enhanced through the protonation of the emeraldine base substrate. The biocompatible surface of the PEGMA-graft copolymerized and doped emeraldine base film has greatly extended the potential applications of polyaniline as biomaterials and blood compatible materials.

Li *et al.* (2000) reported that electroactive nanocomposite ultrathin films of polyaniline and isopolymolybdic acid (PMA) were fabricated by a novel molecular self-assembling process in the basis of the alternate

deposition of PANI and PMA from their dilute solutions. The film fabricated by this technique could adhere effectively to the substrate as a result of chemical bonding between the film and the surface of the substrate. The major benefits of layer-by-layer adsorption from solution are that many different materials can be incorporated into individual multilayer films at nanometer scale and film architectures are completely determined by the deposition sequence. It was discovered that the conductivity of the polyaniline films was sensitive to humidity, NO_2, and NH_3. The conductivity grew with the increase of humidity as well as that of NO_2 concentration because it played a role as an oxidative dopant. The conductivity decreased, in the other hand, with the increase of NH_3 concentration. They proposed, furthermore, that this technique may be used to fabricate chemical sensors and other molecular devices. The process is linearly and reversible with the NH_3 concentration below 100 ppm. The NH_3-sensing mechanism based on the dedoping of polyaniline by ammonia, since the conductivity was strongly dependent on the doping level.