

## CHAPTER II

### LITERATURE SURVEY



#### 2.1 Polyaniline

The emeraldine salt form of polyaniline was synthesized electrochemically as a film exhibiting a well defined fibrillar morphology closely resembling that of polyacetylene by Huang *et al.* (1986). It was proposed that the emeraldine form of polyaniline had the symmetrical conjugation structure having extensive charge delocalization resulting from a new type of doping of an organic polymer-salt formation rather than oxidation which occurred in the *p*-doping of all other conducting polymer systems.

Cao *et al.* (1989) studied the relationships between the chemical polymerization conditions and the physicochemical properties of polyaniline. The results showed that the reaction yield was not strongly sensitive to most synthesis variables, while the viscosity, or molecular weight, and the electrical conductivity of the as-polymerized and/or post-treated polyaniline salt were found to be markedly affected.

Stejskal and Kratochvil (1996) studied the oxidative polymerization of aniline. The results indicated that the variety forms of polyaniline have different conductivity and colour.

The chemical polymerization of aniline was carried out in media containing different linear dicarboxylic acids with the use of oxidants such as  $K_2Cr_2O_7$ ,  $KMnO_4$ ,  $K_2S_2O_8$ ,  $KIO_3$  and  $FeCl_3$  (Erdem *et al.* 2004). The results showed that among the oxidants employed the best result was obtained with  $K_2Cr_2O_7$ . Furthermore, it was not observed a remarkable change in the conductivities of polyaniline samples in air within the period of 50 days. Doped polyaniline were partly soluble in organic solvents such as DMF, DMSO and NMP. The intrinsic viscosity and density values of polyaniline samples were observed to decrease as the dopant anion becomes larger.

## 2.2 Polyaniline Base Polymer Blend

Tchmutin *et al.* (2003) investigated electrophysical and electrochemical properties of the composite materials based on undoped conjugated polymers, i.e. polyaniline (PANI) and polyacetylene (PA), and conductive filler, i.e. graphite and single-wall nanotubes. Typical polymer dielectric, polypropylene (PP) were used as matrices. The investigation of the dependencies of conductivity on filler concentration show that in contrast to PP and PANI, PA becomes conductive due to injected charge carriers from filler particles. It was further found that for the PA-based composites the percolation threshold is essentially lower than for the PANI- or PP-based composite.

Yang *et al.* (2003) blended oligomeric polyaniline (o-PANI) in emeraldine base (EB) form with epoxy resin to form interpenetrating network using an acetic acid solution of p-toluene sulphonic acid as a dopant. Oligomeric polyaniline exhibited much better compatibility with the epoxy resin compared to the high molecular weight counterpart. Moreover, the PANI/epoxy resin composites showed a very low threshold concentration of o-PANI (lower than 1 part o-PANI per 100 parts resin) for electrical conduction.

Cho *et al.* (2004) prepared nano-sized polyaniline (PANI) particles dispersed in aqueous solution using both poly(vinyl alcohol) (PVA) and poly(styrene sulfonic acid) (PSSA) as polymeric stabilizers. Size of the spherical PANI particle synthesized using PVA with a HCl dopant (PANI-HCl/PVA) was about 150 nm in diameter, while with PSSA (PANI-PSSA) was about 50 nm, with a uniform size distribution. In addition, A percolation threshold of PANI concentration for conductivity of composite was found only around 10 wt. % of PANI for the PANI-PSSA/PVA, and furthermore, the PANI-PSSA/PVA became more conductive above the threshold point than PANI-HCl/PVA.

Mirmohseni *et al.* (2003) synthesized the polyaniline-poly(vinyl alcohol) composite films by chemical polymerization of aniline in media containing poly(vinyl alcohol) (10 %w/w). The mechanically robust composite films were obtained by solution casting technique. These composite materials were electroactive

material. Moreover, it was also found that the electrical conductivity of the films increased with increasing the amount of polyaniline.

Yin *et al* (1998) synthesized a conductive composite film based on polypyrrole and crosslinked poly(styrene/butylacrylate/acrylic acid) (PSBA) via vapor phase polymerization of pyrrole within the silicon crosslinked PSBA using anhydrous ferric chloride as oxidant. These films had high conductivity, good mechanical properties, and the lowest surface resistance. However, the over oxidative reaction of polypyrrole strongly affected the surface resistance and the conductivity of polypyrrole whereas the mechanical properties were largely unaffected.

### 2.3 Chitosan

Kurita (2001) discussed on the controlled modification reactions to prepare chitin derivatives with well-define structures and thereby to construct sophisticated molecular architecture having various advanced functions. The reaction discussed include hydrolysis of main chain, deacetylation, acylation, N-phthaloylation of chitosan, tosylation, alkylation, Schiff base formation, reductive alkylation, O-carboxymethylation, N-carboxyalkylation, silylation, and graft copolymerization.

Four different grades of chitosan varying in molecular weight and degree of deacetylation were used to prepare chitosan films (Puttipatkhachorn *et al.* 2001). Salicylic acid and theophylline were incorporated into cast chitosan films as model acidic and basic drug, respectively. The results of Fourier transform infrared and solid-state  $^{13}\text{C}$  NMR spectroscopy demonstrated the drug-polymer interaction between salicylic acid and chitosan, resulting in salicylic formation, whereas no drug-polymer interaction was observed in theophylline-loaded chitosan films. Most chitosan films loded with either salicylic acid or theophylline exhibited a fast release pattern, whereas the high viscosity chitosan films incorporate with salicylic acid show sustained release pattern in distilled water.

Berger *et al.* (2004) provided a detailed overview of physical chitosan hydrogels and related networks formed by aggregation or complexation, which are intended for biomedical applications. The physical chitosan hydrogels was prepared

by direct interactions between polymeric chains, i.e. by complexation or by aggregation to avoid the potential negative influence on biocompatibility of covalent crosslinkers. The results showed that the dissolution can occur due to the non-permanent network. However, these chitosan can enhance certain intrinsic properties of chitosan such as bacteriostatic and wound-healing activity.

#### 2.4 Chitosan Base Polymer Blend

Qurashi *et al.* (1992) studied on modification of chitosan by blending with poly(vinyl pyrrolidone) (PVP). It was found that the modified films had water absorption capacities superior to those of pure chitosan films. But the other properties of chitosan such as elongation at break, relative crystallinities, and tensile strength were found to be decreased, when PVP in the blend was increased.

Hasegawa *et al.* (1993) prepared cellulose-chitosan blend films with varied mixing ratios (0-100 %) by dissolving the polymers in chloral/dimethylformamide followed by casting onto glass plates. The results showed that the mechanical properties of the blend films were improved when blending various ratios of cellulose and chitosan. The highest value of mechanical properties appeared at 10-20 % chitosan contents. Furthermore, the stability of chitosan to extraction with acetate buffer (pH 4.5) and solute permeability in the blend films were improved.

Khor *et al.* (1995) prepared chitosan-polypyrrole hybrid biomaterials by the chemical polymerization of pyrrole in the presence of chitosan. The black colour indicated of the presence of polypyrrole. the presence of chitosan in the hybrids was verified by FTir, thermogravimetry and scanning electron microscopy. However. FTir, solubility in water and electrical conductivity of the hybrids appear to be contrary to this trend. Hybrids at the opposite ends of the concentration gave similar solubility and electrical behaviour while a maxima effect was found for the mid-concentration.

Gubta *et al.* (2000) prepared the spherical, semi-interpenetrating polymer network beads of chitosan and glycine, crosslinked with different concentration of glutaraldehyde for controlled release of drug. The release experiments were performed in solution of pH 2.0 and pH 7.4 using chlorpheniramine maleate as a

model drug. The result indicated that, chitosan might be useful as a vehicle for controlled release of drug.

Xiao *et al.* (2000) prepared the blend films from chitosan/konjac glucomannan (KGM). The blend films gave high miscibility and thermal stability at the weight ratio of chitosan to KGM was 7:3. This is due to the intermolecular hydrogen bonding formation between hydroxyl groups, amino groups, acetyl groups. The crystallinity of the blend films was inversely proportional to the amount of KGM. The water solubility of the blend film was improved by blending with KGM.

Kweon *et al.* (2000) prepared the silk fibroin /chitosan blend films and investigated the effect of blend composition that impact on the physical properties and mechanical properties of the blend films. It was found that the mechanical properties were markedly improved by the blending of silk fibroin with 10-40 % chitosan content. In addition, the blend film containing 40-50 % chitosan content showed very high oxygen permeability.

Sung *et al.* (2002) studied electrorheological (ER) properties of the suspensions containing chitosan particles in corn oil under various applied electric field strengths, finding that natural organic polymers such as chitosan possessing amino polar groups can effectively induce ER behavior. Chitosan-based ER fluids exhibited ER characteristics by showing an increased yield stress ( $\tau_y$ ) when electric field strength (E) and concentration of chitosan particle increase. Furthermore, it was also found that the measured yield stress was proportional to  $E^{1.5}$ , which verifies the nonlinear conduction model.

## 2.5 Electrically Stimulated Controlled Release

The preparation and characterization of a range of conducting polymer-hydrogel composites were done by Small *et al.* (1995). These composites were electroactive and had high rehydration levels (80%-95%). The high water content and the ability to induce efficient electrochemical release, even of larger molecules, suggested that the resultant materials had a open porous structure.

Stassen *et al.* (1995) developed a composite membrane comprising a conductive polymer as an active separation layer with dopamine, a neurotransmitter, used as drug. The results indicated that the controlled permeability through the membrane is achieved, by applying various potentials to the membrane system. Furthermore, the different rates of permeation for water soluble substances depended on the redox state of the conducting polymer.

The possibility of using the conductive polymer polypyrrole as an ion gate membrane for the controlled release of anionic drugs was studied using three model substances with therapeutic activity: salicylate, naproxen, and nicoside. In addition, the release of tosylate, used for the electrosynthesis of the membrane, was investigated (Kontturi *et al.* 1998). The release of drugs from these membrane as a result of negative potential steps was followed using HPLC. It was found that the stability of the membrane doped with the appropriate drugs towards chloride exchange in a 0.1 M NaCl solution was very good. Less than 5% of the theoretical amount of anion in the membranes spontaneously release. The results further showed that controlled release of drugs from polypyrrole membranes can be achieved using simple electrochemical step experiment or staircase signals.

Massoumi and Entezami (2001) prepared conducting polymer bilayer containing polypyrrole/sulfosalicylic acid (SSA) as inner film and poly(N-methyl pyrrole)/polystyrene sulfonic acid (PSS) or PANI/PSS (PANI: polyaniline) as outer film were prepared by electrochemical methods. The release of SSA from inner film was controlled by applying different potential e.g. by applying cathodic potential, the SSA was released out, and in contrast, by applying anodic potential, SSA was reincorporated to inner film.

A relatively new approach in the field of controlled drug delivery-responsive polymeric drug delivery systems was discussed by Kost and Langer (2001). These systems were capable of adjusting drug release rates in response to a physiological need. Furthermore, the fundamental principles of externally and self-regulated delivery systems were examined.