

## CHAPTER II

### LITERATURE SURVEY

Most works on preparation of PPy deal with processing problems which can be overcome by making composites or blends. To obtain more homogeneous uniform distribution, core-shell technique was usually employed to coat PPy on latex particles. The technique is different from admicellar polymerization in that the latter uses a quite small amount of surfactant (below CMC) in aqueous medium. Most of the study involved the film formation, colloidal stability/flocculation, film transparency and phase separation so low PPy content was typically used.

Attempts have been put on methods to synthesize PPy in aqueous solution. Yin and Ruckenstein, 2001 reported copolymerization of polysulfonic acid with pyrrole in water. The optimum conductivity of PPy was at 1 wt% equal to 3.4 S/cm. The reaction is highly exothermic so it had to carry out in ice bath. Ramelow *et al.*, 2001 suggested a convenient PPy polymerization in aqueous or ethanol solution with ferric chloride aqueous solution that yielded PPy without water entrapped and thus high conductivity was achieved. They reported that in aqueous medium higher conductivity products (27.5-56.9  $1/\Omega\text{cm}$  increasing with  $\text{FeCl}_3$ , about ten times) were obtained than those prepared in acetonitrile (1.43-3.20  $1/\Omega\text{cm}$ ). They used this method for coating PPy on cloth and measured the conductivity from cloth not on the PPy film. Conductivity was enhanced to about 145  $1/\Omega\text{cm}$  and 398  $1/\Omega\text{cm}$  by increasing temperature (25-45<sup>0</sup>C) and adding small amount of dopant, iodine. Iodine was a good dopant (185  $1/\Omega\text{cm}$ ) better than perchlorate (110  $1/\Omega\text{cm}$ ) and *para*-toluene sulfonic acid sodium salt (90  $1/\Omega\text{cm}$ ).

For the past decade, there have been many researchers studying about polypyrrole coated onto polystyrene latex (soft substrate). Their results are as followed:

The chemical polymerization of pyrrole onto latex particles in aqueous solution was investigated by Yassar, A., Roncali, J., and Garnier, F. (1987). In this polymerization, the oxidants used were  $\text{FeCl}_3$  and  $\text{H}_2\text{SO}_4$ . Conductivity measurement was carried out on pressed pellets of latex particles after washing with

water and evaporating the solution. The morphology of latex particles was then observed by SEM. Lastly, the conclusion was that latex particles in aqueous solution could be coated with a conducting PPy film. The controlled factor was the film thickness and hence the conductivity of the particles could be obtained at a high value of about 0.25 S/cm.

Lascelles and Armes (1997a) reported the method using excess amount of poly(*N*-vinylpyrrolidone) or PVP as steric stabilizer to make PPy coated polystyrene film. The long chain stabilizer (MW 44,000 and 360,000) provide enough surface area for pyrrole to reside at the surface of substrate and polymerize. However, it is believed that stabilizers yielded patchy pattern rather than continuous coverage. Consequently, conductivity increases with smaller surface area of latex particles and of course, with PPy loading (from  $<10^{-6}$  S/cm at 0.9 wt% PPy to 6 S/cm at 18.4 wt% PPy). Flocculation of coated particles could be formed when low MW stabilizer was used. Moreover, using ammonium persulfate as oxidant gave higher conductivity than using peroxide-HBr-Fe<sup>3+</sup>. The colloidal stability was found in the systems using cationic surfactant as well as non-ionic surfactant (PVP) and it was not necessary that the stabilizer had to be chemically connected to the particle; physical absorption of stabilizer was sufficient for PPy coating. The non-ionic stabilizer was believed to solvate nicely and thus the chains stretched out to the solvent rather than laid flat like train on the surface. Later Li and Ouyang, 2000 conducted the same approach using non-ionic surfactant for pyrrole polymerization in aqueous; however, size of nonionic surfactant was studied. Winnik *et al.*, 2000 reported that nonionic surfactant deposited on poly(butyl methacrylate) or PBMA latex by endothermic reaction of hydrophobic part, regardless of concentration of the nonionic surfactants and particle size of latex. Length of non-ionic surfactant showed significant effect on surface area coverage. Longer hydrophobic part in the surfactant gave more surface area coverage and higher binding energy. The adsorption was driven by entropy.

In contrast to earlier studies, synthesis and characterization of submicrometer-sized, PPy/PS composite particles (Cairns, D.B., Armes, S. P., and Bremer. L.G.B. (1999)), the expected “core-shell” morphology was not observed and pressed pellet conductivity measurements indicated relatively low conductivities

about  $10^{-2}$  S/cm for the composites at PPy loadings less than 20 weight%. TEM studies showed that at a pyrrole concentration of  $5.0 \times 10^{-3}$  M the PPy had deposited onto the latex as discrete PPy nanoparticles of 20-30 nm diameter. The relative colloid stability of the PPy/PS composites were assessed by disk centrifuge photosedimentometry (DCP) studies.

The other substrate that is of interest is PMMA latex coated by conducting polymers, may be PPy or the others. The results are described below.

The preparation of conducting films by casting aqueous dispersion of mixed polymer latexes on supporting glass microscope slides show that one of the latexes was conducting (PPy and polyaniline) and the other was film-forming (a copolymer of PMMA and polybutylacrylate). Cooper *et al.* (1989) observed that PPy formed roughly spherical in shape showed a highly increase in percolation threshold at a weight fraction of 20%. Whilst the lower percolation threshold at about 5% was formed in needle-shaped polyaniline particles. Composite beads (50-100  $\mu\text{m}$ ) having a non-conducting core (PMMA) and a conducting shell (PPy) were also prepared.

Omastova, M. and co-workers (1998) prepared the conductive polymer composites of poly(methyl methacrylate) and polypyrrole (PMMA/PPy composites) by a chemically oxidative modification method. These composites occurred as a network-like structure of PPy embedded in an insulating polymer matrix. They obtained the electrical conductivity of these composites from a mixture of coated and non-coated PMMA particles. These composites were characterized by X-ray photoelectron spectroscopy (XPS). The results that were obtained from this analyzer indicated that pyrrole was polymerized inside the PMMA particles.

Powder form of PMMA/PPy composites was prepared by a chemical oxidation of pyrrole in a PMMA latex medium resulting in a network-like structure of PPy embedded in the insulating polymer matrix. Surface of this composite was characterized by XPS and SEM. (Omastova, M. and Simon, F., 2000). The antistatic properties of compression moulding form of composites were also tested. The content of PPy was determined by elemental analysis. The electrical conductivity of prepared composites depends on the concentration of PPy and reached the values in the range of  $1 \times 10^{-9}$  to 0.1 S/cm.

Transparent conducting latex films were prepared from core-shell latices. The latex particles have a poly(butyl methacrylate) (PBMA) core of about 700 nm and a very thin PPy shell. Huijs *et al.* (2001) studied the process of film formation by transparency measurements, atomic force microscopy, surface flattening, and transmission electron microscopy on ultrathin sections of films after various annealing times at 120°C. The result shows that highly transparent (>90%) and antistatic films can be produced using these latices. The determining factor for the speed of film formation is found to be the shell thickness.

Another substrate for making conductive polymers is latex or rubber that is coated with conductive polymer by various methods described below.

The preparation of the conducting thermoplastic elastomer blends by deposition of PPy in SBS block copolymers was studied by Radharishnan and Saini (1994) with varying ferric chloride (FeCl<sub>3</sub>). The structure of these polymers was observed by Optical Microscopy, X-ray diffraction, and infrared spectroscopy. Phase segregated SBS/PPy blends occurred by preferential deposition of PPy domains separated in matrix was found. Deformation in an extension mode and compression mode affected the resistivity of these blends. The electrical resistivity for these blends showed a transition of 273 K and was sensitive to small mechanical deformation of those two modes.

New nanocomposite materials made of an insulating matrix and conducting fillers were prepared and characterized by Fandin, L. *et al.* (2000). A homogeneous composite material composed of electrically conductive fillers with either a spherical shape or a high aspect ratio dispersed in a thermoplastic insulating matrix. The relationship of filler content in the composite to electrical and mechanical properties was investigated. In order to characterize the connectivity of the fillers in the matrix, electrical measurements were performed and these results have been compared with the predictions of the statistical percolation theory. It has been shown in recent development that these materials used as coating on various substrates could be good sensors, allowing determining of some specific features of the substrate deformation.

A new conductive composite film based on PPy and poly(styrene/butyl acrylate/acrylic acid) (PSBA) had been synthesized by vapour diffusion method. Yin, W. *et al.*, 1998 reported that the film had high conductivity (2.2 S/cm) and good

mechanical properties (e.g. elongation yield: 94.7%, tensile strength: 6.2 MPa). The over-oxidative reaction of PPy was found by increasing the amount of oxidant.

Rigid substrates were also studied such as alumina, silica, mica, and glass fiber, etc. The results reported by some researchers are as followed.

Funkhouser and co-workers (1995) studied the solubilization and adsolubilization of pyrrole on alumina by sodium dodecyl sulfate. They measured the solubilization of pyrrole by the semiequilibrium dialysis. The result was that the highest solubilization constant (K) was  $2.85 \text{ M}^{-1}$  in the absence of NaCl and the minimum K was  $1.95 \text{ M}^{-1}$  at 0.1 M salt. The concentrations of pyrrole in the range of 0-0.016 M cause a decrease in surfactant adsorption. Addition of salt 0-1.5 M improves pyrrole adsolubilization.

Genetti *et al.* (1998) prepared nickel-filled LDPE composites involving coating the nickel with PPy by admicellar polymerization. The reduction in particle-particle contact and the tunnelling resistance of this material was due to the PPy “molecular wires” forming chain entanglements at high filler loading. The coated product (the nickel particles with PPy) was obtained with increasing in conductivity. The values that did not change are the thermal and the mechanical properties.

The effects of varying the oxidant, monomer, silica sol concentrations, silica sol diameter, polymerization temperature, stirring rate, and oxidant type on the particle size of PPy/silica nanocomposite particles were studied. The results show that these particles were intensive to almost all of these functions (Lascelles *et al.*, 1998). The colloid stability of these particles depended on the silica content. A silica-rich nanocomposite was synthesized by using  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  in the presence of electrolyte. Whilst the preparation of PPy-rich nanocomposite by using ferric chloride ( $\text{FeCl}_3$ ) exhibited lower colloidal stability than that of a silica-rich nanocomposite.

Cho *et al.* (2000) reported the formation of PPy thin film on alumina particles using adsorbed hexanoic acid. This surfactant worked well at low pH for pyrrole polymerization and provide high pyrrole adsolubilization to limit of pyrrole solubility in water. Conductivity of the PPy coated alumina ( $-5.04$  to  $-1.8 \log (\sigma \cdot \text{cm/S})$ ) increased with PPy/hexanoic acid content (5-13 wt%). The AFM results confirmed to have complete coating of PPy on alumina although adsolubilized PPy

was not enough to cover all area. The PPy from bulk solution could possible deposit additionally to cover up all area.

Cho *et al.* (2001) further developed this technique to zeolite substrate (100 nm) using cetylpyridinium chloride as a template to make conductive nanocomposites of 5 S/cm at 8 wt% PPy greater than the binary mixtures of both powder (0.03 S/cm). Poorer adsorption of PPy in the template than in the zeolite was shown.

Self-assembled monolayers and adsorbed amphiphilic molecular layers on the surface have been used as the template for PPy growth. Such templates can afford ordered molecular arrays on the surfaces and be used as 2-D reaction media to produce ultrathin polymer films. Adsorbed surfactants bilayers have comparable properties and are also used as templates for practical and convenient purposes. However, there is a side effect to be concerned as following.

Lai *et al.*, 1995 applied this technique for polymerization of tetrafluoroethylene (TFE) gas on alumina substrate with anionic surfactant, sodium perfluoroheptanoate. They mentioned that TFE could dissolve in water with alumina (no surfactant) at 145 psi.  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  was used as an initiator; the more initiator, the higher conversion. However, use of high initiator concentration could cause bulk polymerization in solution although surfactant used was below CMC. The high friction but high contact angle deduced that polytetrafluoroethylene might not have uniform distribution over the alumina surface or the thin film was soft and scratched off upon friction testing. Therefore, strong bonding between coated film and substrate should be improved by cross-linking or UV-radiation.