

CHAPTER II

LITERATURE REVIEW

Polypyrrole (PPy) is one of the most studied conducting polymers because of its good electrical conductivity, environmental stability and relative ease of synthesis. PPy can be prepared by electrochemical or chemical oxidation of pyrrole in various organic solvents and in aqueous media. In a chemical oxidative polymerization of pyrrole monomer many oxidants have been used: $(\text{NH}_4)_2\text{S}_2\text{O}_8$, H_2O_2 and many kinds of salts containing transition metal ions, for example, Fe^{3+} , Cu^{2+} , Cr^{6+} , Ce^{4+} , Ru^{3+} and Mn^{7+} . Polypyrrole (PPy) presents electrical conductivity (up to 100 S.cm^{-1} , depending on the synthesis method) associated with electrochromic properties, opening perspectives for several potential technological applications. This polymer is synthesized by chemical or electrochemical methods. Depending on the method used, hard and brittle or soft and flexible films are obtained. Lin-Xia Wang *et al.* (2001) reviewed the preparation, properties and applications of polypyrroles. They found that the PPy exhibits a spongy texture, the initial decomposition temperature is at $180\text{-}237^\circ\text{C}$, glass transition temperature is at $160\text{-}170^\circ\text{C}$, and the conductivity is below 3 S.cm^{-1} . When only $(\text{NH}_4)_2\text{S}_2\text{O}_8$ was used as the oxidant, the addition of anionic surfactants caused moderate increases in the yields and great decreases in the conductivities. The combinations of $\text{Fe}_2(\text{SO}_4)_3$ and anionic surfactant enhanced conductivity as well as increased yield of resultant PPy.

In 2003, Omastova' *et al.* synthesized conducting and stable polypyrrole (PPy) by chemical oxidative polymerization of pyrrole in aqueous solution containing an oxidant, ferric sulfate, and a surfactant. In this experiments, two types of the oxidant in PPy synthesis were FeCl_3 and $\text{Fe}_2(\text{SO}_4)_3$. The optimum FeCl_3 /pyrrole molar ratio was 2.3 and the optimum $\text{Fe}_2(\text{SO}_4)_3$ /pyrrole molar ratio was about 1.2. The highest conductivity of about 10 S.cm^{-1} was reached by the sample PPy-DBSA, but the most stable sample at the ambient conditions was PPy-DBSNa. The conductivity of PPy-DBSNa was much more stable than that of PPy- SO_4 . Results of the elemental analysis and FTIR spectroscopy proved that only the anionic surfactants were incorporated into PPy similarly as the doping anion. This led to a better stability towards the deprotonation. Also thermal stability, checked by

TGA in air, was improved. Scanning electron microscopy studies showed that the presence of the anionic surfactant strongly influenced the morphology of the polymer product.

In 2005, Okuzaki studied the zone-drawing method applied to polypyrrole films at different heater temperatures under various applied tensions. The zone-drawing method has some advantages; heat and tension act uniformly on the quite narrow area of the specimen, thermal oxidation or decomposition of the specimen can be minimized even in air because the heating time is very short and various thermal reactions or removal of the solvent can be performed simultaneously with the drawing. It was found that the film could be zone-drawn by a factor of 1.4 at the drawing temperatures of 150-200°C. The electrical conductivity and Young's modulus increased to 327 S cm⁻¹ and 3.6 GPa from 145 S cm⁻¹ and 0.9 GPa of the as-synthesized film, respectively. When dc 3V was applied in the drawing direction, the zone-drawn film exhibited contraction of 0.3% parallel to the electric field, while that perpendicular to the electric field reached 14%.

However, the limitations of polypyrrole are poor processibility and flexibility. The flexible films cannot be processed with the technology currently used in the plastics industry. Therefore, one of the possible ways to adjust the mechanical properties of conductive polymers to the processing technology consists of combining PPy with insulating polymers to obtain block and graft copolymers, blends or composites. Natural rubber is an unsaturated elastomer with some good properties, such as high strength, outstanding resilience, and high elongation at break. By these advantages, it is interesting to be combined with PPy in order to overcome the limitations of PPy.

Natural rubber has been studied for many years to improve performance in commercial applications. Fillers are often added to rubber. There are several fillers used in the rubber industry. Reinforcing silica provides reinforcement with a neutral color. Silica can also provide additional property benefits and compounding flexibility. However, unmodified precipitated silica lacks the ability to make strong silica-rubber bonds. In 2005, Nontasorn *et al.* succeeded to improve the performance of rubber by adding fillers such as silica via a continuous stirred-tank reactor system (CSTR). The use of silica in rubber compounds improves important compound

properties such as tensile strength and cut growth resistance. A difficulty with using silica as a filler is the high energy of mixing due to both poor rubber–filler and strong filler–filler interactions. By surface analyzer, they found that the admicellar polymerization could improve the compatibility between silica and natural rubber resulting in better mixing of silica and better rubber properties. The results also showed that the modified silica reduced T_{90} cure times and improved modulus, abrasion resistance, and compression set. Comparison of the rubber compound properties with the unmodified silica and those modified in batch polymerization systems showed that the continuous system could produce modified silica that were equal or superior in performance in rubber compounds as compared to those produced from batch processes because the CSTR-modified silica had more consistent properties.

Black-filled conductive rubbers have wide applications, such as flooring material to dissipate static electric charge, pressure sensitive sensors which can be used for shock proof switches, sensors for measurement of vehicle weights to collect toll tax on roads, and electromagnetic shielding materials. Whenever such materials are used as sensors for mechanical stress, they are subjected to repeated stress-strain cycles, and it becomes necessary to understand how electrical conductivity changes with repeated mechanical stress-strain cycles. In 1997, Sau *et al.* studied the electrical properties of different pre-strain samples of rubber-carbon black composites, ethylene propylene diene rubber (EPDM) and nitrile-rubber (NBR). The results showed that for all the systems the volume resistivity increased rapidly with the increase in percent elongation up to a certain elongation range then the variation of electrical resistivity against percent elongation became almost marginal. The explanations were that the conductivity of the conductive rubber composite was due to the formation of conductive networks of carbon black aggregates in the insulating rubber matrix. Beyond a certain critical limit these conductive networks became continuous throughout the matrix due to actual physical contacts between black particles or there might be very small gaps between adjacent particles which could be easily hopped or tunneled by electrons. The conductive network formation was very much dependent on the aggregating tendency of carbon black which was known as the structure of carbon black. The higher the structure, the more easily the conductive

networks were formed. During elongation two phenomena occurred in the system: (1) breakdown of existing conductive networks; and (2) reformation of new conductive networks. However, at low elongation the breakdown process was more prominent compared to the formation process. At high strain the formation and breakdown of conductive networks balanced each other, resulting in only marginal change in the conductivity.

In 2003, Job *et al.* prepared the composites of natural rubber and carbon black, aiming the development of composites with good mechanical properties, processability and electrical conductivity for use as pressure sensors. The composites of NR/CB were prepared by casting to obtain films with 0.5 mm thickness. Electrical current was measured as a function of applied pressure. The applied pressure varied from 0 to 2.4 MPa and the voltage bias was 0.1 V. It was found that the electrical conductivity changed from 10^{-11} to 10^{-2} S.cm⁻¹ depending on the percentage of CB in the composite. For CB contents above 20 wt% the conductivity tended to a constant value, literature reported that in order to obtain polymeric composites with conductivity in the order of 10^{-2} S.cm⁻¹, about 25 to 40 wt% of CB was necessary to be added to the polymeric matrix. It was also observed that composites having large percentage of CB were more suitable for sensing applications due to the large variation of the conductivity as a function of the pressure. The linear and reversible dependence of the conductivity on the pressure in the range from 0 to 1.6 MPa was warranty that these composites could be applied for pressure sensors.

Composites of electrically conducting particles in non-conducting polymer matrix are materials increasingly important for variety at practical application. In 2004, Vilcakova studied electrical conductivity in pressure deformation of silicone rubber/composites. The composites were prepared by cast molding of polymer matrix components and chemically synthesized polypyrrole, containing 2.2 to 8.5 vol% of PPy. The study of conductivity of an uncompressed sample demonstrated that PPy percolation threshold concentration was lower than 4 vol%. The results of effect of compression showed that the conductivity increased slowly at first compression then steeply fell down to a value corresponding to the conductivity of the matrix, however, it had a good reproducibility. The change in electrical

conductivity during deformation resulted from particle displacement which affected the conductivity paths in the material.

In 2005, Wu succeeded to prepare conducting polypyrrole-coated textile based on nylon lycra with the ideal function as wearable biochemical sensors that can be used in a range of applications to monitor human motion. The polypyrrole-coated nylon lycra was studied the changes in resistance when stretched to different strain ranges. The resistance of PPy coated textile changes significantly at low strains then reached the minimum when stretched up to 60%. This conducting polymer coated textile fabric had been integrated into truly wearable clothing to create strain sensors with a wide dynamic range.

However, the composites of rubber and other materials are not well miscible, so that thin-film coating is studied. The thin-film coatings have become increasingly important in many areas including MEMS, microelectronics, and composites. Several new methods have been invented and intensively studied for thin-film coating on many kinds of substrates. Some of these methods, for example, chemical vapor deposition, rely on polymerization of monomer directly on the surface. Admicellar polymerization is a fine-coating technique that leads to the formation of ultrathin polymer films on charged surfaces by using surfactant bilayers as a reaction template. Bunsomsit *et al.* (2002) studied the admicellar polymerization of polypyrrole-coated on natural rubber latex using sodium dodecyl sulfate (SDS) as an anionic surfactant to form the surfactant bilayers. This effort has two possible advantages: to facilitate the processing of PPy and to improve the electrical conductivity of the latex. Adsorption of SDS and pyrrole adsolubilization was determined as a function of pyrrole and sodium chloride concentrations. The results from the adsorption isotherm showed that pyrrole caused a decrease in SDS adsorption at equilibrium. Sodium chloride increased the surfactant adsorption and the pyrrole adsolubilization, even a low salt concentration. The conductivity of the polypyrrole coated NR latex film prepared by admicellar polymerization without salt was the lowest; however, with salt addition, the conductivity of the film improved significantly.