

## CHAPTER III EXPERIMENTAL

### 3.1 Materials and Instruments

#### 3.1.1 Materials

Pyrrole monomer (Sigma) was stored at 8–10 °C and dried with calcium hydride (CaH<sub>2</sub>, Fluka) for 24 h prior to use. Ammonium persulfate (APS, BDH Laboratory Supplies) was used as the oxidant without further purification. Dodecylbenzene sulfonic acid (DBSA, Sigma) was used as received as the dopant. M-Cresol (Merck) was used as the solvent in dissolving synthesized polypyrrole. Polydimethyl siloxane (PDMS, Aldrich), poly(styrene isoprene styrene), (SIS, Shell), poly(styrene butadiene), (SBR, Dow Chemicals), poly acrylate copolymer, (AR71 and AR72, Zeon), and poly acrylate copolymer, (AR70, and SAR, Dow Chemicals) were used as the polymer matrices.

#### 3.1.2 Instruments

A Fourier Transform Infrared Spectrometer (Thermo Nicolet, Nexus 670) with number of scans of 32, a UV-Visible absorption spectrometer (Perkin Elmer, Lambda 10), a Thermal gravimetric analyzer (DT-TGA 1790) with the temperature scan from 60 to 1000°C with a heating rate of 10°C/min under N<sub>2</sub> atmosphere were used to characterize the synthesized poly(pyrrole). A Scanning electron microscope (JOEL, model JSM-5410OW) was used to determine the morphological structure of the synthesized polymers and polymer blends with the magnifications of 350 and 1500 times at 20 kV. A custom-built two-point probe electrometer (Keithley, Model 6517A) was used to determine electrical conductivity of the conductive polymer and polymer blend. A melt rheometer (Rheometric Scientific, ARES) was used to measure electrorheological properties. A DC power supply (Instek, GFG 8216A) was used to supply electric field strength up to 2 kV/mm.

## 3.2 Experimental Methods

### 3.2.1 Preparation of Poly(pyrrole) (Ppy)

Poly(pyrrole) were chemically synthesized following by the method of Lee *et al.* (1995). Pyrrole monomer was dried by mixing with  $\text{CaH}_2$  at the ratio of 100 g of  $\text{CaH}_2$  per liter of pyrrole and the reaction was allowed to proceed for 24 h before use. 0.3 mole of dried pyrrole monomer and 0.15 mole of DBSA were dissolved in 500 ml of distilled water.

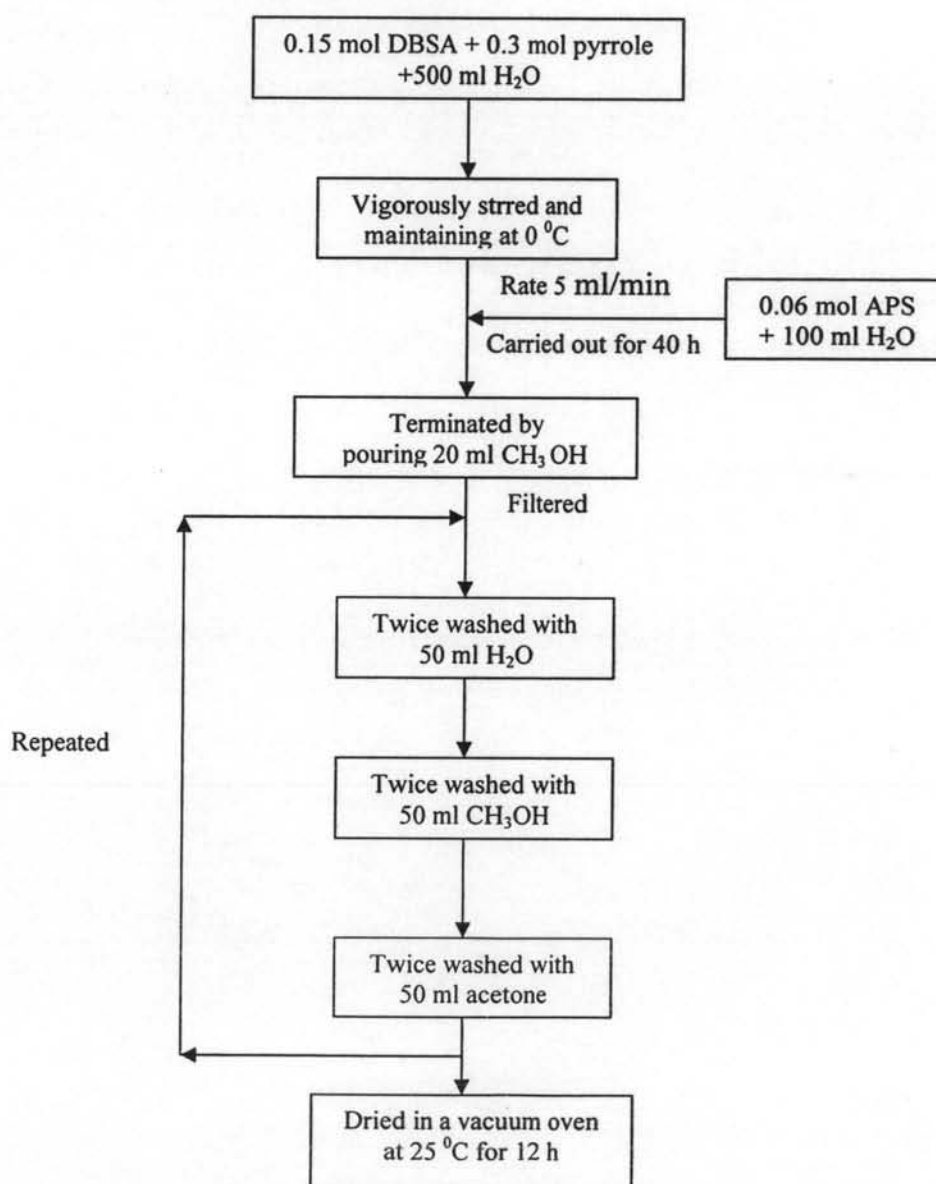


Figure 3.1 Flow chart of polypyrrole chemical polymerization.

The mixture was stirred vigorously for 15 min at 0 °C. The 0.06 mol of APS in 100 ml of distilled water was slowly added to the mixture solution at a rate of 5 ml/min. Reaction was allowed to occur for 40 h and then terminated by pouring 20 ml of methanol. The resultant polypyrrole powder was filtered and washed sequentially twice with 50 ml of distilled water, 50 ml of methanol and 50 ml of acetone. The washing procedure described was repeated again followed by filtering and drying in a vacuum oven at 25 °C for 12 h. Synthesized poly(pyrrole) was stored in a desiccator. For synthesizing the undoped polypyrrole, the procedure was the same as that of the doped polypyrroles except that DBSA was not added into the mixture.

### 3.2.2 Preparation of Elastomer and Ppy/Elastomers Blends

All of elastomer specimen were formed by solution casting except PDMS which was in the liquid form. AR70, SBR, SAR were formed by water evaporation but SIS, AR71, and AR72 were formed by toluene evaporation. Their solutions were cast on the mold (diameter 25 mm) and bubbles were removed under a vacuum atmosphere at 25°C for 12 hours. Concentrations used must be specified here in water and in toluene

The poly(pyrrole) powder was sieved with a mesh particle size of 50 µm and dried at room temperature for 12 hours prior to using. The blends were prepared by mechanical blending of undoped synthesized poly(pyrrole) at various particle concentrations (1, 2, 3, 4 and 5%vol.). A specific amount of particle was then added and the mixture was mechanically stirred for 3 hours to disperse the particles. The mixture was cast on the mold (diameter 25 mm) and specimens were dried in oven at 40°C for 12 hours.

### 3.2.3 Characterization Method

Fourier Transform Infrared Spectra (Bruker, Equinox 55/FRA 1065) was operated in the absorption mode with 32 scans and a resolution of  $\pm 4 \text{ cm}^{-1}$ , covering a wavenumber range of 4000-400  $\text{cm}^{-1}$  using a deuterated triglycine sulfate detector. Optical grade KBr (Carlo Erba Reagent) was used as the background material.

UV-Visible spectra (Perkin-Elmer, Lambda 10) the undoped and doped polypyrrole were measured in the absorbance mode in the wavelength range of 800-200 nm, scan speed of 240 mm/min, a slit width of 2.0 nm, and using a deuterium lamp as the light source. Ppy solution was prepared by grinding synthesized Ppy into a fine powder and 0.05 g of Ppy was dissolved in 100 ml. of m-cresol.

Particle sizes of poly(pyrrole) were determined by using a particle size analyzer (Malvern Instruments Ltd. Masterizer X Version 2.15). The lenses used in this experiment were 45 mm. The sample was placed in a sample cell across a laser beam. This instrument measured the average particle size and the standard size distribution. Consequently, the specific surface area was calculated from the particle diameter with the assumption of being a spherical particle.

A scanning electron microscope (JOEL, model JSM-5200-2AE) was used to examine the morphological structure and PPy dispersion. The samples in pellet form was cut into small pieces and adhered on a brass-stub by using an adhesive tape. Then, they were coated with thin layer of gold by using JFC-1100E ion-sputtering device with a magnification of 7,500, 1,500 and 350 times.

A thermal gravimetric analyzer (DT-TGA 1790) was measured with the temperature scan from 60 to 1000 °C, and a heating rate of 10°C/min. The samples were weighed in the range of 1-5 mg, loaded into a platinum pan, and heated under N<sub>2</sub> flow. The degradation temperatures for undoped and doped poly(pyrrole) were observed.

X-ray Diffraction Microscopy (Rigaku, DMAX 2200) was used to determine the amount of crystallinity and the crystal size of polymer. The conductivity strongly depends on the degree of the order region, the synthetic route, the processing procedure, and the dopant used. This experiment was carried out by monitoring the intensity versus the diffraction angle.

Conductivity Measurement: (Two-Point Probe Meter, and Keithley Model 8009) Electrical conductivity is the inversion of specific resistivity ( $\rho$ ) which indicates the ability of material to transport electrical charge. The meter consists of two probes for polypyrrole particles and a Keithley electrometer (Model 8009) for elastomers and elastomers blends, making contact on a surface of film sample.

These probes were connected to a source meter (Keithley, Model 6517A) for a constant voltage source and for reading current. The applied voltage was plotted versus the current change to determine the linear Ohmic regime of each sample. The applied voltage and the current change in the linear Ohmic regime were converted to the electrical conductivity of polypyrrole using equation (3.1) but the elastomers and elastomer blends using equation (2) as follow:

$$\sigma = \frac{1}{\rho} = \frac{1}{R_s \times t} = \frac{I}{K \times V \times t} \quad (3.1)$$

where  $\sigma$  is specific conductivity (S/cm),  $\rho$  is specific resistivity ( $\Omega \cdot \text{cm}$ ),  $R_s$  is sheet resistivity ( $\Omega$ ),  $I$  is measure current (A),  $K$  is geometric correction factor,  $V$  is applied voltage (voltage drop, V), and  $t$  is pellet thickness (cm).

$$\sigma = \frac{1}{\rho} = \frac{t \times I}{22.9 \times V} \quad (3.2)$$

where  $\sigma$  is the specific conductivity (S/cm),  $\rho$  is the specific resistivity ( $\Omega \cdot \text{cm}$ ),  $I$  is the measured current (A),  $V$  is the applied voltage (voltage drop) (V),  $t$  is the sheet thickness (cm).

The geometrical correction factor was taken into account of geometric effects, depending on the configuration and probe tip spacing and was determined by using standard materials where specific resistivity values were known; we used silicon wafer chips ( $\text{SiO}_2$ ). In our case, the sheet resistivity was measured by using the two-point probe and then the geometric correction factor was calculated by equation (3.2) as follow:

$$K = \frac{\rho}{R \times t} = \frac{I \times \rho}{V \times t} \quad (3.3)$$

where  $K$  is the geometric correction factor,  $\rho$  is the known resistivity of standard silicon wafer ( $\Omega \cdot \text{cm}$ ),  $t$  is the film thickness (cm),  $R$  is the film resistance ( $\Omega$ ), and  $I$  is the measured current (A).

A melt rheometer (Rheometric Scientific, ARES) was used to measure rheological properties. It was fitted with a custom-built copper parallel plates fixture (diameter of 25 mm). A DC voltage was applied with a DC power supply (Instek,

GFG 8216A), which can deliver electric field strength to 2 kV/mm. A digital multimeter was used to monitor voltage input. In these experiments, the oscillatory shear strain was applied and the dynamic moduli ( $G'$  and  $G''$ ) were measured as functions of frequency and electric field strength. Strain sweep tests were first carried out to determine the suitable strain to measure  $G'$  and  $G''$  in the linear viscoelastic regime. The appropriate strain was determined to be 170% for pure PDMS fluid, and 1% for other elastomers. Then frequency sweep tests were carried out to measure  $G'$  and  $G''$  of each sample as functions of frequency. The deformation frequency was varied from 0.1 to 100 rad/s. Prior to each measurement the samples were presheared at a low frequency (0.039811 rad/s), and then the electric field was applied for 10 minutes to ensure the formation of equilibrium polarization before each measurement was taken. Each measurement was carried out at the temperature of 27°C and repeated at least two or three times.