CHAPTER III

EXPERIMENTAL

3.1 Materials

In this study, natural rubber latex used as the substrate for admicellar polymerization was provided by Rubber Research Institute, ~60% DRC. Dodecyl sulfate sodium salt from Aldrich Chemical Company was used as anionic surfactant. Pyrrole from Aldrich was stored in refrigerator at 4 °C before using in polymerization. 99.9% sodium chloride was purchased from Carlo Erba Reagents. Iron (III) sulfate hydrate from Fluka was used as initiator without purification. All the chemicals were used as received.

3.2 Equipment

NR latices were purified by centrifugation at 10000 rpm/20 min with two cycles at 20 °C by centrifugator, Hermle Z383K. Particle Size Analyzer (Mastersizer X) was used to measure the particle size of NR latex particles (45 mm lens, active beam length 2.4 mm). The point of zero charge of latex particles was measured by Zeta-meter 3.0+. Thermogravimetric-Differential Thermal Analyzer (Perkin Elmer, Pyris Diamond) was used to study the thermal stability and the decomposition temperature. The morphology of the admicelled latex films were observed by Scanning Electron Microscopy (JOEL 5200). Tensile testing was carried out using Lloyd LRX Universal Testing Machine under ASTM D882-91. Surface and volume resistivity were measured by using Resistivity Test Fixture (Keithley Model 8009) and Electrometer/High Resistance Meter (Keithley 6517A).

3.3 Methodology

3.3.1 Particle Size Measurement

The particle size of natural rubber was determined by a particle size analyzer, Masterizer X version 2.15 (Malvern Instruments Ltd.). The lens used in this

experiment was 45 mm for particle size 0.1-80 μm and active beam length was set at 24 nm. The sample was placed in a sample cell across a laser beam. This machine analyzed the average particle size and standard size distribution from the laser beam depending on the beam length parameter. Consequently, the specific surface area was calculated from the particle diameter with the assumption of constant volume of spherical particle.

A droplet of surfactant was added in a stirring water chamber in order to help the distribution of natural rubber in water. After that, 0.03 vol% of natural rubber aqueous solution was suspended in a stirring water chamber.

3.3.2   Electrophoretic Mobility Measurement

The change in the surface charge of latex particles with pH is important to determine the surfactant adsorption. Electrophoretic mobility was used to determine the surface charge of the aqueous solution of latex particles at various solution pH (3.0-6.5). The NR colloidal dispersion was diluted in 250 ml distilled water. The pH in the solution was adjusted by 0.1M NaOH or HCl, and was left to equilibrate for 1 day. The electrophoretic mobility of the latex particles was observed at room temperature with a Zeta Meter 3.0.

3.3.3   Polymerization of Pyrrole onto Latex Particles

60% dried rubber content rubber latex of 2 g was mixed with distilled water 50 ml and centrifuged at 20°C, 10000 rpm for 20 minutes 2 times. The latex 25 g was separated and resuspended in water pH 3.0 50 ml which is the pH below the point of zero. Then the rubber latex was mixed with surfactant solution 3.2–16 mM, 400 ml stirred over night to let the surfactant molecules form bilayer at the surface of rubber particles. Pyrrole solution 20–100 mM (0.69–3.36 ml) was added and left for 2 hours. Then the aqueous solution of initiator 25 ml was added to initiate the polymerization and to obtain 500 ml of total volume. In this step, the temperature of the system was reduced to 5°C by adding ice. After the polymerization step for 2 hours, the dark emulsion was filtered through the bushner funnel and washed with water 1000 ml followed by methanol 150 ml. Then it was dried in vacuum oven at 70°C for 12 hours to obtain a black sheet with a constant weight. The synthesis of samples with 0.1-0.3M NaCl addition was repeated all steps and salt was dissolved with surfactant solution. (See T A1 and T A2 for ingredients of each condition)

3.3.4 Morphological Study

The emulsion of the admicelled rubbers was casted in thin films on glass slides and then dried in vacuum oven for 12 hours at70°C. The samples were cut into small pieces and adhered on brass stubs by using adhesive tape. The samples on stubs were painted with thin layer of silver. The morphologies of the admicelled rubbers were observe by a scanning electron microscope (SEM, JOEL model JSM-5200). SEM digitized photographs were obtained with a magnification range between 1,000–5,000 times using an acceleration voltage of 15 kV.

3.3.5 Thermal Properties Measurement

Thermal stability, moisture contents, and degradation process of the admicelled rubbers were studied by a thermalgravimetric analyzer (DuPont, model TGA 2950). The samples were weighed at 5-12 mg and put them in a platinum pan. The instrument was set to operate at temperatures from 30 to 600°C at a heating rate 10°C/min under nitrogen atmosphere 100 ml/min.

3.3.6 FT-IR Observation

The admicelled rubber films with thickness 0.3–0.8 mm obtained by compression at 160°C under pressure 25 tons for 15 min were determined for their absorptions using the horizontal attenuated total reflection accessories for the FTIR (Nexus 670, HATR flat plate system with 45 °C ZnSe crystal) to measure the spectra of materials. The spectra were recorded in the absorbance mode in a wavenumber range of 400-4000 cm^{-1}. The sample spectra were recorded by using air as a background.

The KBr technique was used to prepare the powder sample of pure PPy for recording spectrum. Specimen of pure PPy was prepared by grinding the powdered PPy with the KBr powder. The mixture was molded in special dies under the pressure 10 tons. The sample spectrum was recorded by using KBr as a background.

3.3.7 Mechanical Properties Measurement

The admicelled rubber films from compression with dimension 20x100 mm (thickness 0.3-0.8 mm) were tested following ASTM D882-91 with crosshead speed of 50 mm/min, guage length of 50 mm, and load cell 500 N under room temperature using Lloyd Universal Testing Machine. The test was repeated 3 times.

3.3.8 Conductivity Measurement

The admicelled rubber films from compression (thickness 0.3-0.8 mm) were cut into the round edge shape with six inches in diameter and tested for their surface and volume resistivity by using Keithley 8009 Resistivity Test Fixture and Keithley 6517A Electrometer/High Resistance Meter. The dc voltage from 0.1 to 15 volt was applied to the specimen placed in the Keithley 8009 test fixture. Then, the current was read and the surface and volume resistivity were determined.
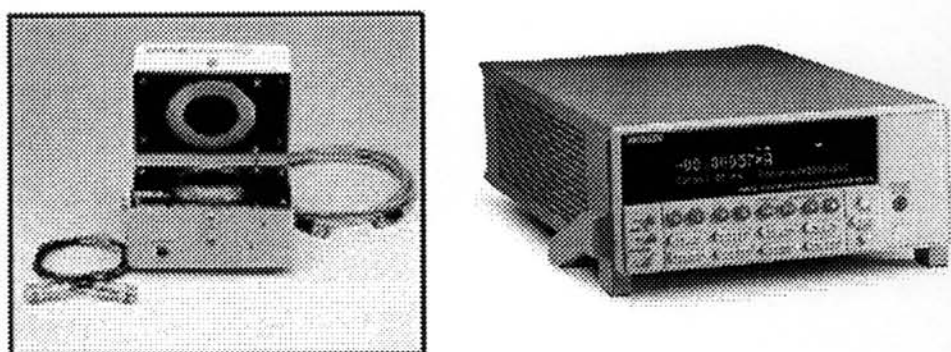

Figure 3.1 Images of Keithley 8009 Resistivity Test Fixture (lelf) and Keithley 6517A Electrometer/High Resistance Meter (right).

The resistance, R, of the films was calculated using Eq. (1), the volume resistivity, surface resistivity and the conductivity were found using Eq. (2), (3) and (4), respectively (see appendix B):

$$R = \frac{V}{I} \tag{1}$$

$$\rho_v = \frac{22.9V}{tI} \tag{2}$$

$$\rho_s = \frac{53.4V}{I} \tag{3}$$

$$\sigma = \frac{1}{\rho_v} \tag{4}$$

where R is the resistance (watts), V is the voltage (volts), I is the current (amperes), ρ_v is the volume resistivity (ohm centimeters), ρ_s is the surface resistivity (ohm), t is the film thickness (centimeters) and σ is the conductivity (siemens per centimeter).

The samples (original guage length = 90 mm, width = 20 mm, thickness = 0.3-0.8 mm) were stretched and measured conductivity by using two-point probe under N_2 atmosphere. The stretching increments were stepped to 0.80, 1.15, 1.90 and 2.75 mm, corresponding to strain 0.89, 1.28, 2.11 and 3.06%, respectively. The probes were connected to a source meter (Keithley, Model 6517A) for a constant voltage source and for reading current. The geometric correction factor was taken into account of geometric effects, depending on the configuration and probe tip spacing. The geometric correction determined by using standard material; silicon wafer chip (SiO_2) with known specific resistivity. The conductivity of the films was calculated using Eq. (5) and (6):

$$R_s = CF \times \frac{V}{I} \tag{5}$$

$$\sigma = \frac{1}{R_s \times \pi \times r} \tag{6}$$

where R_s is the sheet resistivity (ohms), CF is the correction factor which is 2.70 and r is the probe's radius which is 0.192 cm.
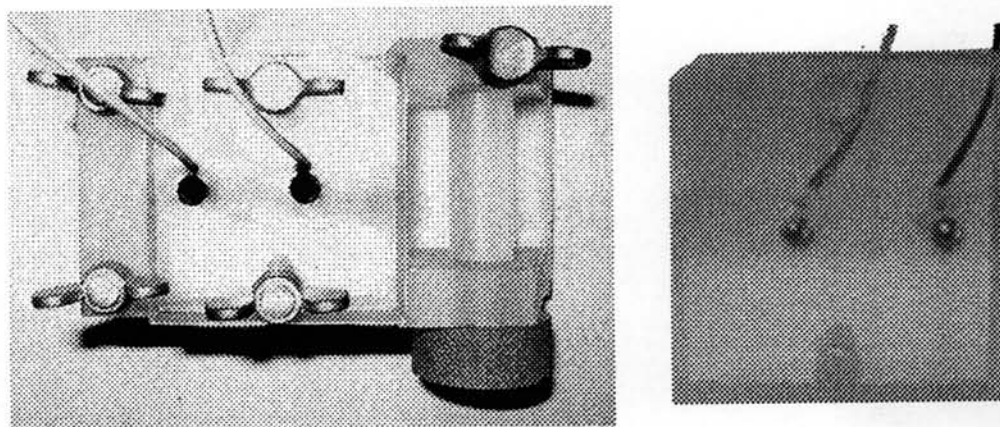

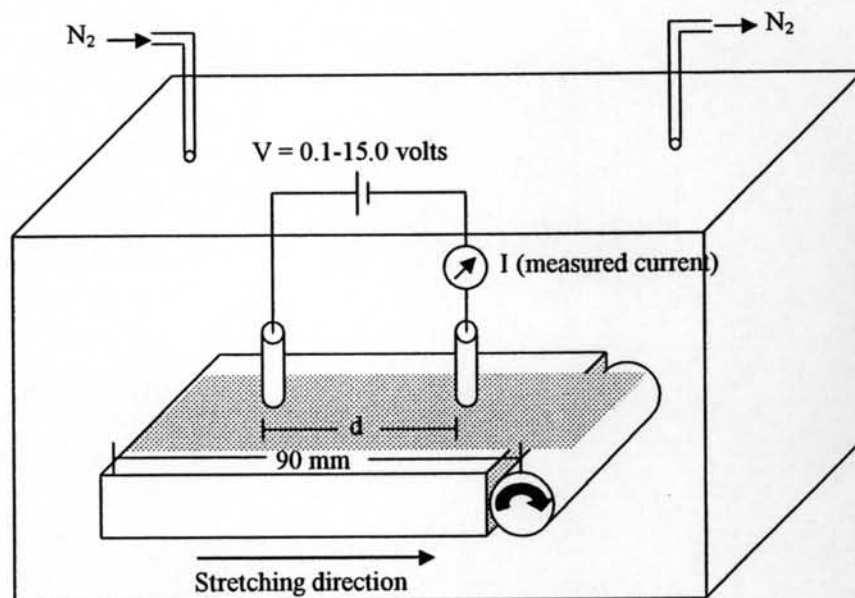**Figure 3.2** Schematics of a two-point probe base (left) and probes (right).

Figure 3.3 Diagram of a conductivity measurement using two-point probe.