



CHAPTER III EXPERIMENTAL

3.1 Materials

Benzene solution (AR grade, Thai aromatic Co.,LTD) was used as the monomer. Aluminium chloride, AlCl_3 (AR grade, Riedel-delHean) was used as the oxidant. Cupric chloride, CuCl_2 (AR grade, Fluka-Aldrich) was used as the catalyst. The sulphuric acid dopant, H_2SO_4 (AR grade, Fluka-Aldrich) was used as received.

Nipol AR71 ($T_g = 258 \text{ K}$) and AR72HF (AR72) ($T_g = 245 \text{ K}$) are acrylic elastomers produced by Nippon Zeon Polymix Advance Co., Ltd. Acrylic elastomer AR7018 (AR70), Styrene-Butadiene rubber latex (UCAR DL849, $T_g = 312 \text{ K}$), and Styrene-Acrylic-copolymer latex (UCAR DA27, $T_g = 297 \text{ K}$) were provided by Dow Chemical Co., Ltd. Styrene-isoprene-styrene triblock copolymer (Kraton D1112P) was obtained from Shell in Thailand Co., Ltd. The chemical structures of all elastomers are shown in Figures 5.1(a)-(d).

The silicone oil, poly(dimethylsiloxane) 200® fluid, was supplied by Dow Corning Corp. The oil had a kinematic viscosity of 100 cSt, and was used as the medium in the deflection experiments.

3.2 Synthesis and Doping of Poly(p-phenylene)

We followed the poly(p-phenylene) synthesis procedure of Kovacic (Kovacic *et al.*, 1961) using benzene, AlCl_3 , and CuCl_2 . The reaction was carried out under nitrogen in a 3-neck flask equipped with a paddle stirrer. After the dropwise addition of benzene (1 mole) and aluminum chloride (0.5 mole), cupric chloride (0.5 mole) was introduced into the solution. Temperature was raised to 35-37°C, and the reaction was allowed to proceed for 3 hours. Then the solution was cooled to 5°C and filtered with 18% HCl solution. The obtained poly(p-phenylene) powder was washed with boiling 18% HCl solutions until the washing solutions were colorless. The poly(p-phenylene) powder was finally washed with hot water until the washings had a pH of 7.0. After drying at 27°C under vacuum for 12 hours, the final

obtained product was in the form of a finely divided, light brown solid powder. Great care was taken to avoid contamination from moisture (Kovacic *et al.*, 1961).

A suspension of dried poly(p-phenylene) powder in sulphuric acid was prepared in a sealed flask. The mole of sulphuric acid (N_{acid}) was varied vs. the mole of monomer (N_{monomer}). $N_{\text{acid}} : N_{\text{monomer}}$ values chosen were 1:100, 1:10, 1:1, 10:1 and 100:1. The mixture was stirred for 2 hour, at temperature of 5°C, under nitrogen atmosphere. The doped poly(p-phenylene) was filtered out by a funnel. After drying at 27°C under vacuum for 12 hr, the obtained products were dark brown powders whose color depended on the degree of doping.

3.3 Sample Preparations

3.3.1 Preparation of Acrylic Elastomers and Styrene Copolymers Films

All elastomer specimens were fabricated through solution casting. The AR70, SAR, and SBR specimens were formed by water evaporation; SIS D1112P, AR71, and AR72 specimens were dissolved in toluene at 30 % vol/vol. The solutions were cast onto a mold (diameter 25 mm, thickness 1 mm) and the solvent was eliminated under a vacuum atmosphere at 300 K for 72 hours.

3.3.2 Preparation of Acrylic Elastomers and Undoped Poly(p-phenylene) Blends

The blends were prepared by mechanical blending of undoped Poly(p-phenylene) with an acrylic elastomer. We dissolved 7 cm³ of acrylic elastomer (Nipol AR71) in 70 cm³ of toluene at 30 % vol/vol and stirred for about 10 hours. Then the undoped PPP powder was added and the mixture was stirred over night. The dispersion of particle is randomly. Concentrations of PPP in AR71 prepared were 5, 10, 15, 20, 25, 30, and 40% vol. We cast the sheets in a mold and left them in a vacuum oven to remove bubbles at 27°C for 24 hours.

3.3.3 Preparation of Specimens for Bending Test under DC Field

All elastomer specimens were fabricated through solution casting. AR70, SAR, and SBR specimens were formed by water evaporation; the SIS

D1112P, AR71, and AR72 specimens were dissolved in toluene at 30 % vol/vol. The solutions were cast onto a mold and the solvent was eliminated under a vacuum atmosphere at 300 K for 72 hours. Each sample was cut into a thin ribbon (length \approx 23 mm, width \approx 2.5 mm, and thickness \approx 0.5 mm). The specimens were immersed in the silicone oil 200® fluid overnight before testing.

3.3.4 Preparation of Specimens for Bending Test under AC Field

All elastomer specimens were fabricated through solution casting. SAR and SBR specimens were formed by water evaporation; the AR71 specimens were dissolved in toluene at 30 % vol/vol. The solutions were cast onto a mold and the solvent was eliminated under a vacuum atmosphere at 300 K for 72 hours. Each sample was cut into a thin ribbon (length \approx 15 mm, width \approx 2.2 mm, and thickness \approx 0.1-0.9 mm). The specimens were immersed in the silicone oil 200® fluid overnight before testing.

The blends were prepared by mechanical blending of doped Poly(p-phenylene) ($N_{\text{acid}} : N_{\text{monomer}} = 100:1$) with an acrylic elastomer. We dissolved 7 cm³ of acrylic elastomer (Nipol AR71) in 70 cm³ of toluene at 30 % vol/vol and stirred for about 10 hours. Then the undoped PPP powder was added and the mixture was stirred over night. The dispersion of particle is randomly. Concentrations of PPP in AR71 prepared were 1, 10, and 20% vol. The sheets were cast in a mold and left them in a vacuum oven to remove bubbles at 27°C for 24 hours.

3.4 Characterization Method

The undoped and doped poly(p-phenylene) (PPP) were characterized by a FT-IR spectrometer in order to identify their functional groups. The FT-IR spectrometer (Thermo Nicolet, Nexus 670) was operated in the absorption mode with 32 scans and a resolution of ± 4 cm⁻¹, covering a wavenumber range between 400 to 4,000 cm⁻¹, using a deuterated triglycine sulfate detector. Optical grade KBr (Carlo Erba Reagent) was used as the background material. The synthesized PPP was intimately mixed with dried KBr at a ratio of PPP:KBr = 1:20

The six elastomers were characterized by an FT-IR spectrometer in order to identify their functional groups. The FT-IR spectrometer (Thermo Nicolet, Nexus 670) was operated in absorption mode with 32 scans at resolution of $\pm 4 \text{ cm}^{-1}$, covering a wavenumber range between 400 and 4.000 cm^{-1} , using a deuterated triglycine sulfate detector. The specimens were prepared as thin films (thickness $\approx 0.5 \text{ mm}$).

The UV-Visible spectra of undoped and doped Poly(p-phenylene) were recorded with a UV-Vis absorption spectrometer (Perkin-Elmer, Lambda 10). Measurements were taken in the reflectance mode in the wavelength range between 200-900 nm. Synthesized PPP was grinded into a fine powder and put into a sample holder. The scan speed was 100 mm/min, and a slit width of 5.0 nm using a deuterium lamp as the light source.

A thermal gravimetric analyzer (DuPont, model TGA 2950) was used to determine the amount of moisture content and the decomposition temperatures of undoped and doped poly(p-phenylene) at various mole ratios of dopant to poly(p-phenylene) with the temperature scan from 30 to 900°C , and with a heating rate of $10^\circ\text{C}/\text{min}$. The samples were weighted in the range of 5-10 mg and loaded into a platinum pan, and then heated it under a nitrogen gas flow.

Scanning electron micrographs were taken with a scanning electron microscope (JEOL, model JSM-5200) to determine the morphology of poly(p-phenylene) in powder forms and PPP/AR71 blends at various particle concentrations. The scanning electron micrographs of poly(p-phenylene) and polymer blends were obtained by using an acceleration voltage of 20 kV with magnifications of 350 and 1500 times. The percentages of elements (Cu, Zn, Fe, Cl, Na, C, and O) in the elastomers were characterized and determined by an EDX (Energy Dispersive X-Ray Fluorescence Spectrometer, OXFORD Pentafet, model 6111); it was also connected to a scanning electron microscope (JEOL, model JSM-5200).

X-rays diffraction patterns as recorded by a diffractometer (Phillips PW 1830/00 No.DF 1241) between angles of $5\text{-}35^\circ$ were used to study the atomic arrangements and the degree of crystallinity of undoped poly(p-phenylene) and doped poly(p-phenylene). Samples were prepared in a pellet form from the compression.

Particle sizes of poly(p-phenylene) were determined by using a particle size analyzer (Malvern Instruments Ltd. Masterizer X Version 2.15). The lenses used in this experiment were 30 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.

Electrical conductivity was measured by a meter which consists of two probes making contact with the surface of a film sample. The probes were connected to a source meter (Keithley, Model 6517A) for a constant voltage source and for reading current. The applied voltage and the current change in the linear Ohmic regime were converted to the electrical conductivity of polymer using equation (3.1) as follows:

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

where σ is specific conductivity (S/cm), ρ is the specific resistivity ($\Omega \cdot \text{cm}$), R_s is the sheet resistivity (Ω), I is the measured current (A), K is the geometric correction factor, V is the applied voltage (voltage drop) (V), and t is the pellet 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 (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:

$$K = \frac{\rho}{R \times t} = \frac{I \times \rho}{V \times t} \quad (3.2)$$

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

The dielectric constant values of all elastomers and blends were measured by an LCR meter (HP, model 4284A) connected to the rheometer (Rheometric Scientific, ARES) with a 25 mm parallel plate fixture. The thickness of the specimens is typically 1 mm and the diameter is about 25 mm. The top and bottom sides of the specimens were coated with silver adhesive to improve the electrical contact between the specimens and the electrodes. The measurements were carried at temperatures between 300 and 370 K. AC voltage applied was varied between 1 and 10 V, depending on materials. The dielectric constant at a frequency of 20 Hz will be referred to as the dielectric constant of the materials.

3.5 Electromechanical Properties Measurements

A melt rheometer (Rheometric Scientific, ARES) was used to measure rheological properties of all elastomers and blends. 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 the 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 strains to measure G' and G'' in the linear viscoelastic regime. The appropriate strain was determined to be 0.1% for pure AR71 and for the undoped poly(p-phenylene) blended with AR71 matrix, respectively. 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. Before each measurement, pure elastomers and poly(p-phenylene)/AR71 blends samples were presheared at a low frequency (0.039811 rad/s), and then the electric field was applied for 13-30 minutes to ensure the formation of equilibrium polarization before the G' and G'' measurements. Experiments were carried out at the temperature of 300 K and repeated at least two or three times. The effect of temperature was studied at various temperatures between 300-370 K for the elastomers and polymer blend PPP/AR71 at 30%vol. The

temporal response experiments were carried out at 1 and 2 kV/mm for pure AR71, AR70, SAR and the polymer blend PPP/AR71 at 30%vol.

3.6 Deflection Measurement under DC and AC Field

The dielectrophoresis forces were determined by measuring the deflection distances of the elastomers in the vertical cantilever fixture under DC and AC electric field. (The experimental setup is shown in Figure 6.1.) The specimens were vertically immersed in the silicone oil (viscosity = 100 cSt) between parallel copper electrode plates (40 mm long, 30 mm width, and 1 mm thick). The gap between the pair of electrodes was 30 mm for DC mode and 10 mm for AC mode. A DC voltage was applied with a DC power supply (Goldsun, GPS 3003B) connected to a high voltage power supply (Gamma High Voltage, model UC5-30P and UC5-30N) which can deliver an electric field up to 25 kV. The output voltage from the high voltage power supply was calibrated using a Fluke 40 kV High Voltage Probe. An AC voltage was applied with function generator (Trektonix, model CFG253) connected to high voltage power supply (Instek, GFG 8216A) which can deliver an electric field up to 4 kV. The amplitude and the frequency of AC field were varied.

We used a CCD video camera to record the movement during the experiment. Still pictures were captured from the video and the deflection distances in x (d) and y axes (l) at the ends of the specimen were determined by using Scion Image software (version 4.0.3). The DC electric field strength was varied between 0–600 V/mm and the AC electric field was varied from 0 – 800 V/mm, $f = 0-60$ Hz at room temperature, 300 ± 1 K. We calculated the resisting elastic force of the specimens under electric field using the non-linear deflection theory of a cantilever (Timoshenko et al.) and (Kim et al., 2007), which can be calculated from the standard curve between $\frac{F_e l_0^2}{EI}$ and $\frac{d}{l_0}$ (l_0 = initial length of specimens) (Timoshenko et al.).

where F_e is the elastic force, d is the deflection distance in the horizontal axis, l is the deflection distance in the vertical axis, E is the Young's modulus —which is equal to

$2G(1+\nu)$, where G is the shear storage modulus taken to be $G'(\omega = 1 \text{ rad/s})$ at various electric field strengths and, ν is the Poisson's ratio (0.5 for an incompressible sample)— and I is the moment of inertia $\frac{1}{12}t^3w$, where t is the thickness of the film and w is the width of the film. The dielectrophoresis force can be calculated from the static horizontal force balance consisting of the elastic force and the corrective gravity force term ($mg\sin\theta$):

$$F_d = F_e + mg \sin \theta , \quad (3.3)$$

where $g = 9.8 \text{ m.s}^{-2}$, $m = \text{mass of the specimen}$, and θ is the deflection angle.

To investigate the materials as potential actuators, the energy density, force density, mechanical power, power density, the electromechanical efficiency of the elastomers are important factors for comparison. These factors were calculated using equations 5 to 10, respectively (Timoshenko et al.):

$$\text{Energy density} = \frac{1}{2} E \theta^2 \text{ (J)} , \quad (3.4)$$

$$\text{Force density} = \frac{F_d}{\text{volume}} \text{ (N.cm}^{-3}\text{)} , \quad (3.5)$$

$$\text{Mechanical power} = \frac{1}{4} F_d \frac{d}{\tau_i} \text{ (W)} , \quad (3.6)$$

$$\text{Power or work density} = \frac{\text{mechanical power}}{\text{volume}} \text{ (W.cm}^{-3}\text{)} , \quad (3.7)$$

$$\begin{aligned} \text{Electromechanical coupling efficiency} &= \frac{\text{mechanical power}}{\text{power consumption}} \times 100\% = \\ &= \frac{(1/4) * F_d * d}{\text{inductiontime} * \text{power consumption}} \times 100\% , \end{aligned} \quad (3.8)$$

where τ_i is the induction time.