



CHAPTER III EXPERIMENTAL

3.1 Materials

Diphenylamine, DPA (AR grade, Fluka), was used as a monomer. Hydrochloric acid, HCl (AR grade, Lab Scan), was used as a oxidant. Ammonium persulfate, $(\text{NH}_4)_2\text{S}_2\text{O}_8$ (AR grade, Riedel-de Haën), was used as a initiator. Toluene, C_7H_8 (Lab Scan, AR grade), was used as a solvent. Ammonium hydroxide solution, NH_4OH , (AR grade, Panreac), was used as a dedopant. Styrene-Isoprene-Styrene triblockcopolymer, Kraton D1162P 44%styrene, Kraton D1164P 29%styrene, and Kraton D1114P 19%styrene (Kraton Polymers U.S. LLC) were used as dielectric elastomers, and D1114P was specifically used as the polymer matrix for the polymer blend. Toluene (AR grade, Lab Scan) was used as a solvent.

3.2 Experimental procedures

3.2.1 Synthesis of Polydiphenylamine(PDPA)

Polydiphenylamine, PDPA was synthesized through the interfacial polymerization according to Orlov *et al.*,(2005) methods, A 0.2 M solution of diphenylamine in toluene, the monomer solution, and a 0.25 M solution of ammonium persulfate in the same volume of a 1 M solution of HCl, the oxidizer solution, were prepared. The solutions were first cooled to $-2 - 0^\circ\text{C}$ and then mixed momentarily. The reaction was carried out under intense stirring and temperature was remained at $-2 - 0^\circ\text{C}$, for 4 h. Reaction mixture was precipitated into a 5-fold excess of isopropyl alcohol, filtered and washed many times with distilled water to neutralize the reaction. After vacuum dried at 27°C for 24 h, the polymer obtained was a purple powder.

3.2.2 Doping of PDPA

Polydiphenylamine (PDPA) was dedoped by stirring 1 g of polymers powder in a 20 ml of 1 M ammonium hydroxide solution and a 5 ml of ethanol over night, washed with ethanol/H₂O (3/1 (v/v)), and then vacuum dried at room temperature. The polymer was doped with HCl solutions at room temperature by precisely controlling mole ratio between HCl and PDPA monomer ($N_{\text{acid}} : N_{\text{monomer}}$), the chosen values were 1:100, 1:10, 1:1, 10:1, 100:1, and 200:1. The mixture was stirred for 24 h. The doped Polydiphenylamine (D_PDPA) was filtered out by suction method and dried in vacuum oven at 27°C, 24 h (Hua and Ruckenstein., 2005). The obtained polymers are dark green powders, for higher HCl-doped PDPA, depended on degree of HCl doping.

3.2.3 Preparation of SIS Triblock Solution Casting

SIS triblock, Kraton D1162P 44%styrene, Kraton D1164P 29%styrene, and Kraton D1114P 19%styrene were used to prepare three different morphologies: lamella, cylindrical, and micellar, respectively. Using Winter *et al.* (1993) method, the films were casting from 10 % (w/v) toluene solution at room temperature for 1 week. To further remove toluene and to reduce stresses from solvent evaporation, the films were vacuum-dried at 120 °C for 24 h.

3.2.3 Preparation of De_PDPA/D1114P Blends Solution Casting

The blends were prepared by mechanical blending of dedoped Polydiphenylamine with an SIS triblock copolymer (D1114P) (Kunanuruksapong *et al.*, 2007). D1114P was dissolved in toluene and stirred for about 2 hours. Then De_PDPA powder was added to obtain 10 % (w/v) toluene solution and further stirred for 24 h. The dispersion of particle was random. Concentrations of De_PDPA in D1114P prepared were 5, 10, 20, and 30 %vol. The films were cast in a mold and allowed to dry in air to slowly remove the solvent, and then vacuum-dried to reduce stresses and residue solvent at 120°C for 24 hours (winter *et al.*, 1993).

3.3 Characterization and Testing

3.3.1 Characterizations

The identification of functional groups of the doped and dedoped polydiphenylamine was investigated by a Fourier Transform Infrared spectrophotometer or FT-IR (Thermo Nicolet, Nexus 670) operated in the absorption mode with 32 scans and a resolution of $\pm 4 \text{ cm}^{-1}$, covering a wavenumber range of $4000\text{--}400 \text{ cm}^{-1}$, using a deuterated triglycine sulfate detector. Optical grade KBr (Carlo Erba Reagent) was used as the background material. The synthesized PDPA particles were ground with a mortar, mixed with KBr at a ratio of PDPA:KBr = 1:20.

A thermal gravimetric analyzer (DuPont, model TGA 2950) was used to determine the amount of moisture content and the decomposition temperatures of dedoped polydiphenylamine 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.

Morphologies of SIS films (D1114P, D1164P, and D1162P) were observed by a polarizing optical microscope (Leica/DMRXP). The films were firstly cracked in liquid nitrogen and placed into microscope slides. Optical micrographs of the films were obtained with magnifications of 200 and 500 times.

Scanning electron micrographs were taken with a scanning electron microscope (JEOL, model JSM-5200) to determine the morphology of doped and dedoped polydiphenylamine in powder forms, SIS films, and De_PDPA/D1114P blends at various particle concentrations. The scanning electron micrographs of the conductive polymer and polymer blends were obtained by using an acceleration voltage of 15 kV with magnifications of 1500 and 2000 times.

The density of doped and dedoped polydiphenylamine was determined by using a ultrapycnometer (Ultrapycnometer 1000, V 2.4) with small cell size. The polymers were firstly vacuum-dried for 24 h and then weighted at ambient temperature, loaded the sample to the cell. Density determination was carried out 10 time for each sample for a run under flow purge mode, target gas pressure 17 psi, and calibration volumes: $V_{\text{added}} 12.4159 \text{ cm}^3$; $V_{\text{cell}} 20.8093 \text{ cm}^3$

Particle sizes of doped and dedoped polydiphenylamine were determined by using a particle size analyzer (Malvern Instruments Ltd. Masterizer X Version 2.15). The lens used in this experiment was 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.

3.3.2 Electrical Conductivity

Electrical conductivity of doped and dedoped polydiphenylamine was measured by using a custom-built two-point probe connected with a source power supplier (Keithley/ Model 6517A). The polymers were compressed into pellets at 10 tons with 1 cm diameter. A constant voltage was applied and the current was simultaneously measured.

According to the geometric effects of the probe, the geometrical correction factor depends on the configuration and probe tip spacing:

$$K = \frac{w}{l} \quad (3.1)$$

where K is the geometric correction factor, w is the probe width or the tip spacing (cm), and l is the probe length (cm).

The geometric correction factor can be determined by using standard materials whose specific resistivity values are known. In our case, silicon wafer chips were used as the standard materials. The resistance was measured by using our custom-made two-point probe, obtained by applying various voltages and simultaneously measuring currents. The geometric correction factor was calculated via the equation:

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

where ρ is the resistivity of a standard silicon wafer ($\Omega \cdot \text{cm}$), R is the resistance of film (Ω), t is the film thickness (cm), I is the measured current (A) and V is the applied voltage (V).

The conductivity measurement was performed under atmospheric pressure, 40-60 %RH and at 25-27°C. The regime where responsive current is linearly proportional to the applied voltage is called the linear Ohmic regime which can be identified by plotting the applied voltage against with the current. The voltage

and the current in the regime were converted to the electrical conductivity by following equation:

$$\sigma = \frac{1}{\rho} = \frac{1}{R_s \times t} = \frac{I}{K \times V \times t} \quad (3.3)$$

where σ is the specific conductivity (S/cm), ρ is the specific resistivity ($\Omega \cdot \text{cm}$), R_s is the sheet resistance (Ω/sq), t is the thickness of sample pellet (cm), V is the applied voltage (Voltage drop)(V), I is the measured current (A), and K is the geometric correction factor of the two-point probe meter. All sample thicknesses were measured by using a thickness gauge.

3.3.3 Electrorheological Property Measurement

The electrorheological properties were investigated by using a melt rheometer (Rheometric Scientific, ARES). 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. The oscillatory shear strain was applied and the dynamic moduli (G' and G'') were measured as functions of frequency, temperature, 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 strains of SISs films; D1114P, D1164P, and D1162P are 0.2, 0.1, and 0.2 %, respectively. For the De_PDPA/D1114P blends at 5, 10, 20, and 30 %vol the strains are 0.2, 0.3, 0.1, and 0.3 %, respectively. The frequency sweep tests were carried out to measure G' of each sample as functions of frequency, temperature, and electric fields (0, 1, and 2 kV/mm). The deformation frequency was varied from 0.1 to 100 rad/s. Each sample was presheared at a low frequency (0.039811 rad/s), and then the electric field was applied for 30 minutes to ensure the formation of equilibrium polarization before the G' measurements. Experiments were carried out at the temperature of 27 °C and repeated at least two or three times. The effect of temperature in SISs films and De_PDPA/D1114P blends was studied at various temperatures in the range of 27-117 °C. In the effect of electric field strength the experiments were taken with various electric fields (0, 1, and 2 kV/mm). Temporal response measurements of pure SIS films and the polymer blends were carried out at electric field strength 0 and 2 kV/mm.

3.3.4 Deflection Measurement

Deflection of SIS films and the polymer blends were carried out under various applied-electric strengths. One end of the sample was fixed with a tong suspended vertically in the chamber which consisted of two electrodes and poly(dimethylsiloxane). The input DC field was generated by a DC power supply (Gold Sun 3000, GPS 3003D) and a high voltage power supply (Gamma High Voltage, UC5-30P) which delivered to the electrodes various electric fields between 25 to 600 V/mm. A video recorder was used to record the displacement of the film made a model. The tip displacement was measured through a Scion Image (Beta 4.0.3) program. The theoretical force of sample displacement it can be regarded as a cantilever beam. It is assumed that the sample is symmetric with respect to the longitudinal direction and that a concentrated load is acting at the tip of an actuator. Then, the relation between tip displacements (d) and force (Fe) are calculated from the linear deflection and non-linear deflection models depending on their bending characteristic, as the following:

$$\text{(Linear deflection)} \quad Fe = \frac{3dEI}{l^3} \quad (3.4)$$

$$\text{(Non-linear deflection)} \quad Fe = \frac{dEI}{l^3} \quad (3.5)$$

where E is the modulus of elasticity (Pa), d is displacement distance in x axis (mm), I is the moment of inertia (m^4), and l is the deflection distance in y axis (mm). But, the absolute vertical deflection force at the free end of the sample does not only depend on Elastic force (Fe), but also depend on weight in deflection direction, ($mg \sin(\theta)$). Thus, the absolute deflection force of free end of sample beam or dielectrophoretic force is the sum of the elastic force (Fe) and $mg \sin(\theta)$, as in the following equation:

$$\text{(Dielectrophoretic force)} \quad Fd = Fe + mg \sin \theta \quad (3.6)$$