

## CHAPTER III

### EXPERIMENTAL

#### 3.1 Materials

##### 3.1.1 Chemicals

- 3.1.1.1 Benzene (LOBA Chemie, ACS reagent, 99.5% purity)
- 3.1.1.2 Aluminum Chloride (Sigma Aldrich, Reagent grade, 98% purity, anhydrous)
- 3.1.1.3 Copper (II) Chloride (Aldrich, Reagent grade, 97% purity, anhydrous)
- 3.1.1.4 Iron (III) Chloride (Sigma Aldrich, Reagent grade, 97% purity, anhydrous)
- 3.1.1.5 Poly ( $\epsilon$ -caprolactone) (Aldrich,  $M_n \sim 70,000-90,000$ )
- 3.1.1.6 Luperox® A75 Benzoyl Peroxide (Aldrich, 75% remainder water)
- 3.1.1.7 18% Hydrochloric Acid (RCI Labscan, Reagent grade)
- 3.1.1.8 Absolute Ethanol (RCI Labscan, Reagent grade)

##### 3.1.2 Solvents

- 3.1.2.1 Benzene (LOBA Chemie, ACS reagent, 99.5% purity)
- 3.1.2.2 Absolute Ethanol (RCI Labscan, Reagent grade)

##### 3.1.3 Gas

- 3.1.3.1 Nitrogen gas (High purity grade)

#### 3.2 Equipment

- 3.2.1 FT-IR Spectrometer (Thermo Nicolet, Nexus 670)
- 3.2.2 Thermalgravimetric Analyzer (Perkin Elmer, TGA7)
- 3.2.3 Scanning Electron Microscopy or SEM (Hitachi, S4800)
- 3.2.4 Two-point Probe Couple with an Electrometer (Keithley, 6517A)

- 3.2.5 Particle Size Analyzer (Malvern, Masterizer X)
- 3.2.6 X-ray Fluorescence Spectrophotometer (PANalytical, Axios PW 4400)
- 3.2.7 Gas Pycnometer (Quantachrome Instrument, Ultrapycnometer 1000)
- 3.2.8 Melt Rheometer (Rheometric Scientific, Ares)
- 3.2.9 Digital Multimeter (Tektronix, CDM250)
- 3.2.10 Function Generator (Instek, GFG2816A)
- 3.2.11 DC Power Supply (Goldsun, GPS 3003D)
- 3.2.12 Vacuum Pump
- 3.2.13 Glasswares and Magnetic Stirrers

### 3.3 Methodology

#### 3.3.1) Poly(p-phenylene) (PPP) Synthesis

Poly (p-phenylene) was synthesized via the Kovacic method (Bonagamba *et al.*, 1995) by using benzene as monomer, anhydrous aluminium chloride ( $\text{AlCl}_3$ ), and anhydrous cupric chloride ( $\text{CuCl}_2$ ) with the mole ratio of 1:0.5:0.5, respectively. The reaction occurred in a 3-neck round-bottom flask at 37 °C for 4 hours. Then, the solution was filtered with 18% hot hydrochloric acid and finally in hot DI water, until it had a pH of 6.0. At last, undoped PPP (uPPP) was dried at 100 °C for 24 hours. Dried uPPP, the light brown solid powder, was obtained and stored in a glass desiccator (Kunanuraksapong *et al.*, 2007).

#### 3.3.2) PPP Doping Process

The PPP particle was immersed in  $\text{FeCl}_3$ -absolute ethanol mixtures at 60 °C in a 1:50, 1:30, 1:1, 30:1, 50:1 and 100:1 mole ratios between  $\text{FeCl}_3$  and PPP monomer. The mixtures were stirred for 48 hours before filtration by using a Büchner funnel and vacuum pump before dried at 100 °C for 24 hours and stored in a glass desiccators (Phumman *et al.*, 2009).

#### 3.3.3) Poly( $\epsilon$ -caprolactone) (PCL) Film Casting and Crosslinking

Poly( $\epsilon$ -caprolactone) ( $M_n$  70,000–90,000 by GPC), purchased from Sigma Aldrich, was dissolved in benzene under stirring for 2 hours at room temperature and cast on a glass plate and dried at room temperature for 24 hours. In case of

crosslinked PCL, 1, 3, 5, 7 and 10 wt% of benzoyl peroxide (BPO) were added in the solutions under stirring for 2 hours at room temperature. The solutions were cast on glass plates and dried at room temperature for 24 hours. The completely dried BPO-PCL was cured in an oven at 130 °C for 5 min to obtain crosslinked PCL film (Xiao *et al.*, 2010).

#### 3.3.4) PCL and PPP Composite Fabrication

uPPP and dPPP, were added in 0.01, 0.05, 0.1, 0.5, and 1%v/v into the solutions from 3.3.3. The particles were physically dispersed by vigorous stirring for 3 hours. Then they were dried at room temperature for 24 hours. Finally, the completely dried PCL was kept in an oven at 130 °C for 5 min as the curing temperature to obtain crosslinked PCL film embedded with PPP particles (Xiao *et al.*, 2010).

### 3.4 Testing and Characterization

#### 3.4.1) Undoped and Doped PPP Particle

- Size of PPP particle was measured by particle size analyzer (Malvern, Masterizer X) (Kunanuraksapong *et al.*, 2007).
- Chemical structures of uPPP and dPPP were investigated by Fourier transform infrared spectrometer (FT-IR) (Thermo Nicolet, Nexus 670). The spectrometer was operated in the transmission mode averaging 64 scans at a resolution of 4 cm<sup>-1</sup>, covering a wave number range of 4,000–400 cm<sup>-1</sup> (Kunanuraksapong *et al.*, 2007).
- Amount of dopant from doping process was carried out by X-ray fluorescence spectrophotometer (XRF) (PANalytical, PW 4400) (Plocharski *et al.*, 1999).
- Decomposition temperature of uPPP and dPPP were investigated by thermogravimetric analyzer (TGA) (Perkin Elmer, TGA7). The particle was weighed to 8–15 mg then pelletized and placed into a platinum pan. The experiment was operated from 30–900 °C with a heating rate of 10 °C/min under nitrogen atmosphere (Phumman *et al.*, 2009).

- Density of PPP particle was determined by a gas pycnometer (Quantachrome Instrument, Ultrapycnometer 1000). Density of the particle was measured under ultra high helium atmosphere with the flow purge of 1 minute (Sohn *et al.*, 2001).
- Electrical conductivity of uPPP and dPPP were measured by two-point probe connected with a voltage supplier (Keithley, 6517A). The polymers will be compressed into pellets at 10 tons with 1 cm diameter. A constant voltage was applied and the current will be simultaneously measured, then calculated into electrical conductivity. The electrical conductivity can be calculated from this equation:

$$\sigma = (I/KVt) \quad (\text{III-1})$$

where  $\sigma$  is the electrical conductivity (S/cm), I is the measured current (A), V is the applied voltage (V), t is the thickness of the pellet (cm), and K is the geometric correction factor of the two-point probe which can be determined by calibration of the probe with a silicon wafer possessing a known resistivity value (Phumman *et al.*, 2009).

- Morphology of PPP particle was observed by a using a scanning electron microscope (SEM) (Hitachi, S8400) (Sohn *et al.*, 2001).

#### 3.4.2) Uncrosslinked and Crosslinked PCL

- Electrical conductivity of uncrosslinked PCL and crosslinked PCL film were measured by two-point probe connected with a voltage supplier (Keithley, 6517A) (Xiao *et al.*, 2010).
- The electromechanical properties including storage modulus ( $G'$ ), storage modulus response ( $\Delta G'$ ) and storage modulus sensitivity ( $\Delta G'/G'_0$ ) under and not under electric field were measured by a melt rheometer (Rheometric Scientific, Ares) which has a custom-built copper parallel plate fixture (diameter 25 mm). DC voltage was supplied by a DC power supply (Tektronix, CDM250) that can provide up to 4 kV as the maximum voltage. Storage modulus was investigated as a function of electric field, which was

varied from and 0.1 kV to 2 kV, and frequency, was varied from 0.1 to 100 rad/s (Kunchornsup *et al.*, 2012)..

- Morphology of PCL film was observed by using scanning electron microscope (SEM) (Hitachi, S8400) (Xiao *et al.*, 2010).
- Young's modulus of the samples was measured by a universal testing machine (Lloyd,). The sample was cut into the rectangular shape before the test was accomplished with the crosshead speed of 30 mm/min and the gauge length of 30 mm, that were adapted from ASTM D882. Each experiment was repeated for 3 times.

#### 3.4.3) PCL/PPP Composite

- Electrical conductivity of uPPP and dPPP were measured by two-point probe connected with a voltage supplier (Keithley, 6517A) (Xiao *et al.*, 2010).
- Distribution of PPP in PCL matrix was observed by using scanning electron microscope (SEM) (Hitachi, S8400) (Xiao *et al.*, 2010).
- The electromechanical properties including storage modulus ( $G'$ ), storage modulus response ( $\Delta G'$ ) and storage modulus sensitivity ( $\Delta G'/G'_0$ ) under and not under electric field were measured by a melt rheometer (Rheometric Scientific, Ares) which has a custom-built copper parallel plate fixture (diameter 25 mm). DC voltage was supplied by a DC power supply (Tektronix, CDM250) that can provide up to 4 kV as the maximum voltage. Storage modulus was investigated as a function of electric field, which was varied from and 0.1 kV to 1.25 kV, and frequency, was varied from 0.1 to 100 rad/s (Kunchornsup *et al.*, 2012).
- The dielectrophoresis forces were determined the deflection distances in the vertical cantilever fixture under electric field. The specimens were vertically immersed in the silicone oil (viscosity=100 cSt) between parallel copper electrode plates (68 mm of length, 40 mm of width, and 2 mm of thickness). The gap between the pair of the electrodes will be 30 mm. 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. A CCD video camera was used to record the movement during the experiment. Pictures were captured from the video and the deflection distances in the x (d) and y axes (l) at the end of the specimen were determined by using the Scion Image software (version 4.0.3). The electric field strength was varied between 0 and 600 V/mm at room temperature. Both the voltage and the current were monitored. The resisting elastic force of the specimens was calculated under an electric field using the non-linear deflection theory of a cantilever, which can be obtained from the standard curve between  $(F_e l_0^2)/(EI)$  and  $d/l_0$  ( $l_0$  = initial length of specimens);  $F_e$  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  $I$  is the moment of inertia  $1/12t^3w$ , where  $t$  is the thickness of the sample and  $w$  is the width of the sample. The electrophoresis force can be calculated from the static horizontal force balance consisting of the elastic force and the corrective gravity force term ( $mg \sin \theta$ ), as shown in the following equations:

$$F_d = F_e + mg \sin \theta + \rho V g \sin \theta \quad (\text{III-2})$$

where  $g$  is  $9.8 \text{ ms}^{-2}$ ,  $m$  is the mass of the specimen,  $\rho$  is the density of the silicone oil (g/cm) and  $\theta$  is the deflection angle (Kunchornsup *et al.*, 2012).