

CHAPTER III EXPERIMENTAL

3.1 Materials

Materials used in this study were as follow:

3.1.1 Sodium Montmorillonite ($\text{Na}_{0.6}[(\text{Mg}_{0.6}\text{Al}_{3.4})\text{Si}_8\text{O}_{20}(\text{OH})_4]$)

Sodium montmorillonite (Kunipia-F) with cation exchange capacity (CEC) of 119 meq/100 g was provided by Kunimine Industrial Co., Ltd., Japan.

3.1.2 Bis (Hydrogenated tallowalkyl) Dimethyl Quaternary Ammonium Chloride

Bis (hydrogenated tallowalkyl) dimethyl quaternary ammonium chloride was kindly supplied by Unilever Thai Holdings Co., Ltd. It was used as a modifying agent. The melting range is 56-61 °C.

3.1.3 *p*-xylylene Bis(tetrahydrothiophenium) Chloride was purchased from Aldrich Co., Ltd.

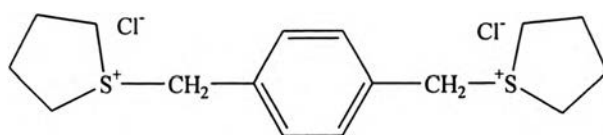


Figure 3.1 Chemical structure of *p*-xylylene bis(tetrahydrothiophenium) chloride.

3.1.4 The Scales of Seabass was kindly supported by The Department of Chemical Technology, Faculty of Science, Chulalongkorn University.

3.1.5 Methanol (CH₃OH) was purchased from Carlo Erba Reagenti.

3.1.6 Chloroform (CHCl₃) was obtained from Lab-Scan Analytical Sciences.

3.1.7 Hydrochloric Acid (HCl) was purchased from Carlo Erba Reagenti.

3.1.8 Dialysis Tube

Seamless cellulose tube was obtained from Sigma. The cut off molecular weight of dialysis membrane is 6000. The capacity is approximately 150 ml/ft.

3.1.9 Indium Tin Oxide (ITO) Coated Glass

ITO substrates (Corning 1737) were kindly supported by Thin Film Devices, Incorporated. The surface resistivity of the ITO is 250 ohm/square.

3.2 Equipment

3.2.1 Wide Angle X-ray Diffractometer (WAXD)

The WAXD is a technique commonly used to study structure at and below the nanometer scale. Therefore, this technique can be used to confirm results obtained by WAXD about the organization of the clay layers in polymer-clay nanocomposites. WAXD spectra were performed at room temperature by a Rigaku Model D/MAX 2000 diffractometer. The Cu K-alpha radiation source was operated at 40 kV/ 30 mA. K-beta filter was used to eliminate interference peak. Divergence slit and scattering slit at $\frac{1}{2}$ deg together with 0.3 mm of receiving slit were set on the instrument. The powder was placed into a sample holder and the measurement was continuously run. The experiment was recorded by monitoring the diffraction appeared in the 2θ range from 2° to 30° with scan speed 5 deg/min and scan step 0.02 deg.

3.2.2 Fourier Transform Infrared Spectrophotometer (FTIR)

The FTIR spectra were obtained on an Equinox 55 BRUKER spectrometer with 32 scans at a resolution of 2 cm^{-1} . A frequency range of $4000\text{-}400\text{ cm}^{-1}$ was observed using a deuterated triglycinesulfate detector (DTGS) with a

specific detectivity, D^* , of $1 \times 10^9 \text{ cm.Hz}^{1/2}.\text{W}^{-1}$. Both neat techniques on ZnSe plate and KBr pellet were used.

3.2.3 Atomic Absorption Spectrophotometer (AAS)

The % ion exchange was determined by an atomic absorption spectrometer Varian SpectrAA-300 that acetylene was used as fuel and air was used as supported gas. The hollow cathode lamps used were sodium cathode lamps for sodium ion with 5 mA lamp current. Ion solution standard 1000 ppm was prepared according to the analytical method of Varian. The wavelength at 589.0 nm was used to determine the absorbance of sodium ion.

3.2.4 Thermogravimetric Analysis (TGA)

Thermogravimetric analysis technique is used to determine thermal stability and the decomposition temperature of both ordinary polymers and their nanocomposites. Using a Dupont 2950 thermogravimetric analyzer, characterization of polymer-clay nanocomposites was performed by heating about 10 mg of each sample up to 750°C at the heating rate 10°C/min under the nitrogen atmosphere. The mass change with increasing temperature was monitored and recorded. The decomposition temperature (T_d) was obtained from the derivative TGA thermogram.

3.2.5 Transmission Electron Microscope (TEM)

Transmission Electron Microscope is a particular instrument used to evaluate the basal spacing between the clay layers. In this experiment, a thin section of TEM specimen was prepared by cutting with a diamond knife of an LKB Bromma 2088 Ultratome® V. The knife in water through was used for collecting a 100 nm thick slice of material and the sample was moved up and down with a small advance for each cut. The sections were picked up from the water surface on a copper supporting grid and stained with saturated vapor of 0.2 g of ruthenium chloride in 5 wt % of aqueous sodium hypochlorite for 1 hour to enhance the phase contrast of the images. The micrographs were produced using a JEOL-200 CX Electron Microscope with an acceleration voltage of 100 kV. The magnification of all images was adjusted at 100000X.

3.2.6 Photoluminescence Setup

The Stellarnet spectrometer is a fiber optic instrument for UV and VIS measurement. Figure 3.2 shows the apparatus of photoluminescence measurement. The SpectraWiz® operating software is included with the Stellarnet miniature fiber optic spectrometer system. Polymer-clay nanocomposites were excited with monochromatic light at 410 nm from a laser diode (Power Technology, maximum optical power at 25 milliwatts). Typical optical power measured at the output of the fiber-optic delivery system is 10 milliwatts.

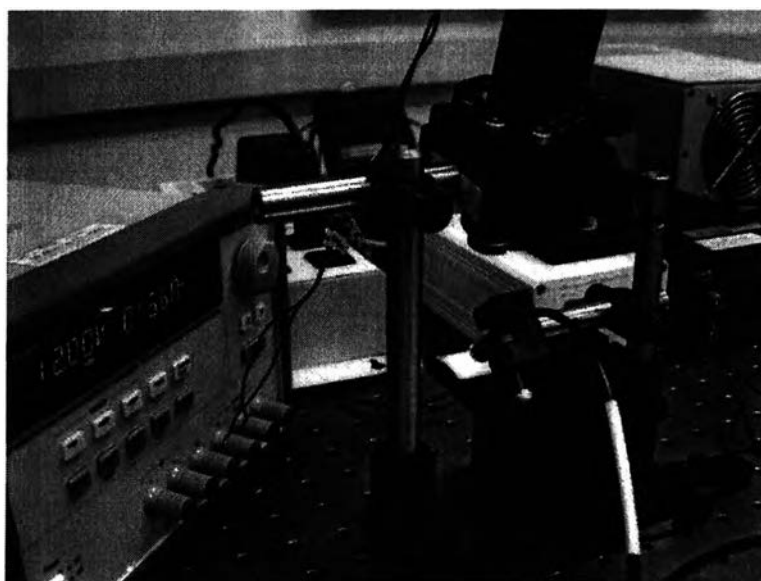


Figure 3.2 Photoluminescence setup.

3.2.7 Current-Voltage Measurement Unit

For the measurement of device properties, current-voltage (I-V) characteristics were measured using the current/voltage source (Figure 3.3) which consisted of Keithley 196 system digital multimeter, Advantest TR 6120A programmable DC standard, and Advantest TR 1161 GP-IB adapter. The injected current of polymer/layered silicate nanocomposites sandwiched devices was measured by the voltage supply while applying the bias and recorded by computer. Adjustable voltage is measured in the range of 0 to 5 volts. Upon application of an electrical voltage to an LED device, electrons from the low work junction cathode were injected into the lowest unoccupied molecular orbital (LUMO) of the organic

semiconductors, whereas holes from the high work function were injected into the highest occupied molecular orbital (HOMO). These injected charges migrated under the influence of the applied field and combined in the bandgap of the polymer layer. The current-voltage characterizations of Al/polymer-clay nanocomposites/ITO done in a vacuum chamber at pressure less than 0.1 mbar were monitored and recorded by the controller software.



Figure 3.3 Current/voltage source unit.

3.3 Methodology

3.3.1 Preparation of Organically Modified Montmorillonite

Na-montmorillonite (Na-MMT) is organically modified by means of ion-exchange reaction between Na^+ and alkylammonium ion. The ion exchange reaction could be done by stirring 10 g of Na-MMT in 300 ml of distilled water at room temperature overnight. The resulting swollen clay and the separated 10 g of bis (hydrogenated tallowalkyl) dimethyl quaternary ammonium chloride in 100 ml of distilled water were, at the same time, heated at 80°C for half an hour. Then, the alkylammonium solution was gradually added into the Na-MMT suspension, and temperature was kept at 80°C for another 2 h with vigorous stirring. The sediment of organically modified MMT was isolated by filtering and washing with 2 L of hot distilled water to remove the residue of ammonium salt of bis (hydrogenated

tallowalkyl) dimethyl quaternary ammonium chloride. After that, the collected sediment was dried overnight at 100°C, and it was then ground with mortar and kept in a bottle. The flow chart for this preparation is shown in Figure 3.4.

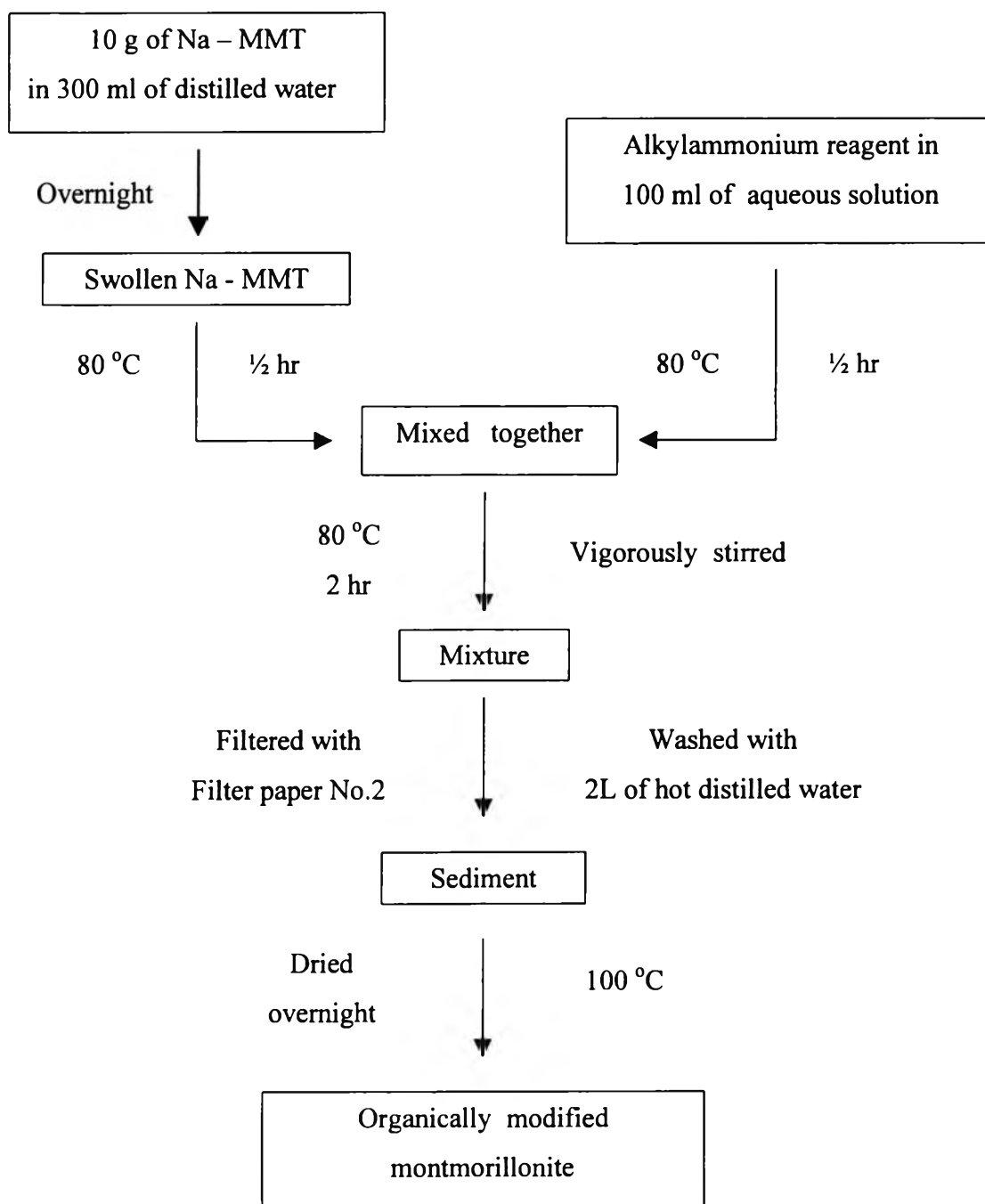


Figure 3.4 Flow diagram of organically modified clay preparation.

3.3.2 Synthesis of Poly(*p*-phenylene vinylene) (PPV)

In this work, poly(*p*-phenylene vinylene) was synthesized by the method of Burn *et al.* (1992).

3.3.2.1 *Preparation of Tetrahydrothiophenium Precursor Polymer*

To a solution of the salt, *p*-xylylenebis (tetrahydro thiopheniumchloride), 1.0 g (2.6 mmol) in methanol 7.5 cm³ cooled to 0°C, was added dropwise into an aqueous sodium hydroxide 6.3 cm³ (0.4 M, 2.5 mmol). The reaction mixture was stirred for a further 120 min at 0°C and slightly acidified with hydrochloric acid 1 cm³ (0.4 M). The solution 14.8 cm³ was then dialysed against a water-methanol mixture (1:1, 3x1000 cm³) over 3 days after which the solvent was completely removed. The residue was redissolved in methanol.

3.3.2.2 *Thermal Conversion of Tetrahydrothiophenium Precursor Polymer into PPV*

After cooling, the aqueous solution of poly [*p*-xylylenebis (tetrahydrothiopheniumchloride)] was poured onto glass and allowed to evaporate at room temperature in a free air stream, avoiding dust as much as possible. After 24 hours, the yellowish-green precursor films were heated at 200°C for 16 hours in vacuum oven to form PPV.

3.3.3 Preparation of Protein Extracted from the Scales of Seabass

The scales on the dried skin of seabass were removed with a razor cutter. Then, the seabass scales were ground to powder with mortar and sieved with 38 micron mesh size. The procedure was as following: 15 g of the grounded scale powder was leached in 300 ml of chloroform. The solution was placed in 500 ml three-necked round bottom flask equipped with thermometer, condenser and mixer. It was heated by oil bath and the temperature was kept at 50°C. The solution was stirred vigorously for 1.5 day. After mixing, the scales were recovered by filtering. The photoluminescence extraction from the scales of seabass was collected from the supernatant part.

3.3.4 Preparation of PPV/Layered Silicate Nanocomposites

A dispersion of organophilic montmorillonite in butanol was stirred vigorously using magnetic stirrer for 48 hours. Next, the solution was sonicated for 6 hours. poly [*p*-xylylenebis (tetrahydrothiopheniumchloride)] solution was blended with organophilic clay solution and mixed together. Contents of modified montmorillonite were varied from 30-60 wt % in pure PPV. After mixing, the solution was stirred for 18 hours. Since the photoluminescence intensity of PPV films spin coated on glass decreased with increasing conversion temperature (Herold *et al.*, 1996), the low conversion temperature at 110°C was chosen.

3.3.5 Preparation of Protein/Layered Silicate Nanocomposites

The organically modified montmorillonite dispersed in chloroform solvent was stirred for 24 hours. Protein extracted from the scales of seabass dissolved in butanol was sonicated for 6 hours at room temperature. Each polymer solution and various contents of clay dispersed in chloroform were mixed together and then stirred for an additional 12 hours. The clay filler contents were also varied at 30 wt %, 40 wt %, 50 wt %, and 60 wt %.

3.3.6 Spin-coating of Polymer/Layered Silicate Nanocomposites

Before photoluminescence measurement, polymer-clay nanocomposites were spin-coated on glass substrates. The glass substrates had been cleaned satisfactorily. In this process, glass slides were placed on the spinning apparatus, Spin-coater P6708 (Figure 3.5), which held the glass down by using the generated by a vacuum pump. Next, several drops of polymeric matter were smeared over the surface. If polymer is too thick on the surface, the spin rate is speeded up to make it thinner. If it is too thin, the rate is slowed down so the material has greater thickness on the ITO. PPV, protein, and their nanocomposites were spread on the surface by the determined spin rate at 1000 rpm for 120 seconds. After spinning was complete, the samples were visually inspected for homogeneity and imperfection.



Figure 3.5 Spin-coater model P6708.

3.3.7 Sample Preparation for Color Tunability and Environmental Stability Measurement

After spin-coating method, photoluminescence spectra were measured by exciting 410 nm monochromatic light. The environmental stability was investigated by the decay of photoluminescence intensity as a function of time while irradiating polymer-clay nanocomposites films with an excitation light source at 410 nm. All experiment data were obtained under an air ambient condition.

3.3.8 Sample Preparation for Water Absorption Measurement

Water absorption in conducting polymer is generally important, since it can deteriorate environmental stability of the material. The extent of water absorption was determined by measuring percent mass loss of the material between room temperature and 100°C. All samples were left at room temperature, 75 % relative humidity for 48 hours prior to the test. Thermogravimetric analysis was used for study on water absorption of PPV, protein, and their nanocomposites by TGA Dupont 510 with a heating rate of 10°C/min. The chamber inside the instrument was exposed to nitrogen as a purge gas at flow rate of 20 ml/min. The mass changes

during temperature increase were monitored and recorded using the controller software.

3.3.9 Fabrication of Light-Emitting Devices

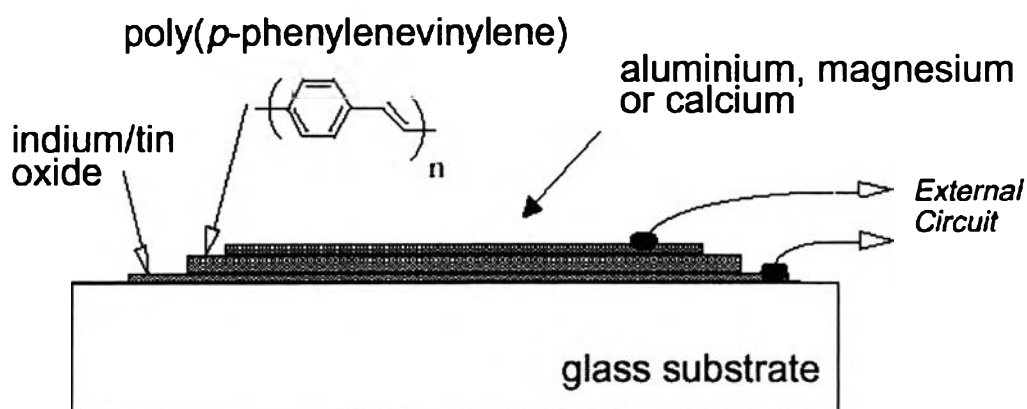


Figure 3.6 Typical structure of a single-layer polymer light-emitting diode device.

The layout of a typical single-layer light-emitting diode based on polymer-clay nanocomposites thin film was schematically shown in Figure 3.6. Out of the two electrodes at least one should be transparent or semitransparent. In practice, transparent indium tin oxide (ITO) coated glass is often used as the anode and a layer of low work function metal is used as the cathode. ITO substrates were cleaned in ultrasonic baths of acetone and then propanol and finally dried under nitrogen flow. The polymer materials were spin-coated on ITO-coated glass substrates. Baking of the spin-coated thin film was done at 50°C and 110°C in vacuum oven for protein-clay nanocomposites and PPV-clay nanocomposites, respectively. Aluminum as a cathode was deposited under a high vacuum (10^{-4} torr).