



## CHAPTER III EXPERIMENTAL

### 3.1 Materials

#### 3.1.1 Synthesis of Alumalatrane and Silatrane

The starting material and products are slightly moisture and air sensitive. Therefore, all operations were carried out with careful exclusion of air by cleansing with nitrogen.

UHP grade nitrogen, 99.99% purity was obtained from Thai Industrial Gases Public Co., Ltd., Thailand. Aluminum hydroxide  $[Al(OH)_3 \cdot xH_2O]$  and silicon dioxide ( $SiO_2$ ) were purchased from Aldrich Chemical Co., Inc., USA. Triisopropanolamine (TRIS) and triethanolamine (TEA) were obtained from Fluka Chemical Co., Ltd., Switzerland and Union Carbide Co., Ltd., Thailand, respectively. All of them were used as received. Ethylene glycol (EG), used as a solvent in the reaction, was purchased from J.T. Baker Co., Ltd., USA and purified by fractional distillation at  $200^\circ C$ , under nitrogen prior to use. Triethylenetetramine (TETA), used as catalyst in the reaction, was obtained from Union Carbide Co., Ltd., Thailand. Acetonitrile was purchased from J.T. Baker Co., Ltd., USA and purified by standard techniques.

#### 3.1.2 Preparation of Organically Modified Montmorillonite

The polyamide 12 (PA12, Nylon12) is commercially available under the product named Grilamid L25 natural 6112, and was supplied by EMS-Chemie (ASIA) Co., Ltd. The polymer is in opaque-white pellet-bead form. The melt volume-flow rate is  $20 \text{ cm}^3/10 \text{ min}$  (at  $275^\circ C$ , load 5 kg), density is  $1.01 \text{ g/cm}^3$  and melting point is  $178^\circ C$ . The 258RB is the product name of a commercial polyvinyl chloride (PVC) that was supplied by VinyThai Public Co., Ltd., Thailand. The polymer is in white powder form. The viscosity index of PVC is 82 ml/g, density is  $0.56 \text{ g/cm}^3$  and melting point is  $175^\circ C$ . The stabilizer for PVC is Stabinex<sup>®</sup> OGP-101, was provided from Siam Stabilizers and Chemicals Co., Ltd., Thailand. The

stabilizer is in white powder form. The stabilizer has density of 1.00 g/ml and melting point of 98°C. The stabilizer (2 phr) was mixed with PVC to increase the thermal stability of PVC during processing.

Sodium-montmorillonite ( $\text{Na}^+$ -MMT) with cation exchange capacity (CEC) of 119 meq/100 g was supplied by Kunimine Industrial Co., Ltd., Japan. Octadecylamine, used as a modifying agent was purchased from Fluka Chemical, Switzerland. AR-grade hydrochloric acid (HCl) was purchased from J.T. Baker Co., Ltd., USA.

## 3.2 Equipment

### 3.2.1 Atomic Absorption Spectroscopy (AAS)

Varian SpectrAA-300 was applied to determine  $\text{Na}^+$ -exchanged percentage, using air and acetylene as supported gas and fuel gas, respectively. The sodium hollow cathode lamp with 5 mA was used to generate the wavelength of 589 nm. All of standard solutions were prepared by dilution technique from the 1000 ppm NaCl standard solution to create a calibration curve used to determine  $\text{Na}^+$  exchange of organically modified clay.

### 3.2.2 Bomb Calorimeter

Gross calorific value, the heat of combustion of nanocomposite materials, was obtained from Gallen Kamp Auto Bomb Calorimeter at King Mongkut's Institute of Technology Ladkrabang. The test was carried out according to ASTM D 2015.

### 3.2.3 Fourier Transform Infrared Spectroscopy (FTIR)

FTIR was used to verify the structure of metalatrane and the incorporation of modifying agent into the structure of clay. KBr pellet technique is used to prepare the sample. FTIR spectra were recorded from an Equinox 55 Bruker spectrophotometer at frequency range  $400\text{-}4000\text{ cm}^{-1}$  with 16 scans.

### 3.2.4 Mass Spectroscopy (MS)

A 707E-Fison Instrument (VG-Autospec, Manchester, England) with a VG data system was used to determine mass of synthesized metalatrane. Direct probe injection was used in the positive fast atomic bombardment (FAB<sup>+</sup>) mode. Cesium iodide was used as a standard for peak calibration. Samples were prepared using glycerol as a matrix. The range studied was set from m/e 20 to 1500.

### 3.2.5 Nuclear Magnetic Resonance Spectroscopy (NMR)

NMR was used to assay the structure of metalatrane. <sup>13</sup>C-NMR spectra were obtained from Bruker 300 MHz. spectrometer at King Mongkut's Institute of Technology Ladkrabang. <sup>13</sup>C-NMR spectrum of alumatrane was recorded at frequency of 75.5 MHz. and 10,000 scans, using chloroform (CDCl<sub>3</sub>) and tetramethylsilane (TMS) as the solvent and internal reference, respectively. <sup>13</sup>C-NMR spectrum of silatrane was obtained using solid-state NMR at frequency of 75.5 MHz. and 3169 scans.

### 3.2.6 Thermogravimetric Analysis (TGA)

A DuPont TGA was employed to determine thermal degradation temperature of metalatrane, materials used and product of organically-modified clay. The chamber inside the analyzer was continuously flushed with oxygen at flow rate of 20 ml/min and for balance chamber, it was set at 30 ml/min. The heating rate was set at 10°C/min and temperature program was started from 30° to 750°C.

### 3.2.7 Wide Angle X-ray Diffractometer (WAXD)

WAXD spectra were obtained from D/MAX-2000 series of Rigaku/X-ray Diffractometer system. X-ray of Cu-K<sub>α</sub> (0.154 nm) at 40 kV / 30 mA was used as the source. K<sub>β</sub> filter was used to eliminate interference peak. The standard sample holders were applied to both ground samples and composite films. The experiment was operated in the 2Theta range of 2-30 degrees at the scan speed of 5 deg/min and scan step of 0.02 degree.

### 3.2.8 Brabender Plasti-Corder (Twin-screw Extruder)

The polymers were mixed in a Brabender Plasti-Corder (twin-screw extruder) model PL 2000 at King Mongkut's Institute of Technology Ladkrabang. Blending condition for Nylon12 were made at 180°-185°-190°-195°C, 7 rpm and 160°-165°-170°-175°C, 15 rpm for PVC.

### 3.2.9 Compression Molding Machine

The blended samples were prepared by Wabash V50H compression press. The steps used in the process of Nylon12 and PVC were started by heating a mold at 190° and 170°C, subsequently without pressure for 5 min. Then, the mold was pressed by 10 tons force for 10 min. After that the mold was cooled under pressure to room temperature with cooling rate of 20°C/min. Thickness of mold cavity was 3 mm.

### 3.2.10 Limiting Oxygen Index Tester (LOI)

Fire retardancy was measured as Limiting Oxygen Index (LOI), the amount of oxygen required for combustible samples. All specimens were tested according to ASTM D 2863.

### 3.2.11 Shore D Hardness Tester

A Zwick Shore D Hardness Tester was employed to measure hardness of blended specimens. All specimens were tested according to ASTM D 2240.

### 3.2.12 Pendulum Impact Tester

A Zwick Pendulum Impact Tester model DXT-3 was used to investigate impact resistance of the blends. All specimens were tested according to ASTM D 256.

### 3.2.13 Universal Testing Machine

An Instron Universal Testing Machine model 4206 was carried out to test tensile properties of the blends. All specimens were tested according to ASTM D 638 at the gauge length of 50 mm, the load cell used was 100 kN and the crosshead speed was set at 10 mm/min.

## 3.3 Methodology

### 3.3.1 Synthesis of Alumatrane and Silatrane

Two types of metalatrane were prepared via the “Oxide One Pot Synthesis” Process.

#### 3.3.1.1 *Synthesis of Alumatrane*

Alumatrane was synthesized using conditions outlined by Opornsawad *et al.*, (2001). A typical synthesis was as follows:

3.55 g (45.5 mmol) of aluminum hydroxide, 13.39 g (70 mmol) of triisopropanolamine and 100 ml of ethylene glycol were added into a 250 ml two-necked round bottle flask. The reaction mixture was stirred and heated under nitrogen in a thermostat oil bath. When the oil bath temperature reached 200°C, the reaction was considered to commence until the reaction mixture turned clear, indicating complete reaction. Then the reaction mixture was left to stand overnight without stirring, the desired products were precipitated out and filtered. The precipitated products were stirred with acetonitrile to remove excess TRIS. The solid products were filtered off and dried under vacuum ( $10^{-2}$  Torr) at 120°C for 5 h. FAB<sup>+</sup>-MS, FTIR, TGA, DSC and XRD were used to characterize the obtained products.

#### 3.3.1.2 *Synthesis of Silatrane (Punchaipetch, 1995)*

Silatrane was synthesized using conditions studied by Punchaipetch (1995). A typical synthesis was as follows:

3.00 g (50 mmol) of fume silicon dioxide, 11.19 g (75 mmol) of triethanolamine, 3.65 g of triethylenetetramine (25 mmol) and 100 ml of ethylene

glycol were added into a 250 ml two-necked round bottle flask. The reaction mixture was stirred and heated under nitrogen in a thermostat oil bath. When the oil bath temperature reached 200°C, the reaction was considered to commence until the reaction mixture turned clear, indicating completed reaction. Then EG was removed by vacuum distillation ( $10^{-2}$  Torr) using a thermostat oil bath at 100°C until no more EG was removed. The precipitated products were stirred with acetonitrile to remove excess TEA. The solid products were filtered off and dried under high vacuum ( $10^{-2}$  Torr). FAB<sup>+</sup>-MS, FTIR, TGA, DSC and XRD were used to characterize the dried products.

### 3.3.2 Preparation of Organically Modified Montmorillonite

Na<sup>+</sup>-montmorillonite (Na<sup>+</sup>-MMT) was organically modified by ion-exchange reaction between Na<sup>+</sup> and alkylammonium ion, protonated from octadecylamine (OC), as shown in Scheme 3.1.



10 g of Na<sup>+</sup>-MMT in 300 ml of distilled water was stirred overnight to swell clay, followed by heating at 80°C for a half an hour. 100 ml of 1.5 equivalent octadecylamine in 3 equivalent of HCl solution was separately prepared. The alkylammonium solution was gradually added into the Na<sup>+</sup>-MMT suspension and temperature was kept at 80°C for 2 h with vigorous stirring. Then the product was separated and washed with 2L of hot distilled water. Filtrate was collected to determine Na<sup>+</sup> ion-exchanged percentage by AAS. The sediment of organically modified MMT was collected and dried overnight at 100°C. It was ground and kept in a bottle. Dried products were characterized using FTIR, TGA and WAXD.

### 3.3.3 Preparation of Polymer-Nanocomposite

A Brabender Plasti-Corder twin-screw extrusion type was used as a mixer in melt blending technique. The polymer (Nylon12 or PVC) and fillers (clay or metalatranes) were blended in a dry-mixer for 10 min. Then, the mixture was fed into the hopper of a twin-screw extruder. Different temperature profiles were used

for different polymers (Nylon12 was 180°-185°-190°-195°C, 7 rpm and 160°-165°-170°-175°C, 15 rpm for PVC). The composite products were cooled and cut into the pellet form. Sheets of the composites were formed by a Wabash V50H compression machine. The composite sheets were prepared with different thickness and shape according to the test methods.