

## CHAPTER III

### EXPERIMENTAL

#### 3.1. Materials

- Bentonite H (BNH) was supported by Ceramic “R” us (Bangkok, Thailand).
- Sodium chloride (NaCl) was purchased from BDH.
- Silver nitrate (AgNO<sub>3</sub>) was purchased from Aldrich.
- Semi-permeable membrane was (size #9 with 28.6 mm in diameter) purchased from Semiper Medicell International Ltd (distributed by Becthai, Bangkok, Thailand).
- Tallowtrimethylammonium chloride (TTM) was supported by Thai Spacialty Chemical Co., Ltd.
- Oleylmethylbis(2-hydroxyethyl)ammonium chloride (OMH) was supported by Thai Spacialty Chemical Co., Ltd.
- Octadecylmethyl[ethoxylate(15)]-ammonium chloride (ODMH) was supported by Thai Spacialty Chemical Co., Ltd.
- Methyl methacrylate (MMA) monomer; a commercial grade, was supported by PAN Industrial Co., Ltd., Thailand.
- 2,2'-Azobisisobutyronitrile (AIBN), a commercial grade, was supported by Pan Asia Industrial Co., Ltd., Thailand.
- 2,2'-Azobis(2,4-dimethyl valeronitrile) (ADVN); a commercial grade, was supported by Pan Asia Industrial Co., Ltd., Thailand.

#### 3.2 Equipment

##### Fourier Transform Infrared Spectrophotometer (FTIR)

The spectra were obtained by a Nicolet-Magna 750 Series II FT-IR Spectrometer. The frequency range of measurement was 4000-400 cm<sup>-1</sup> at a resolution of 4.0 cm<sup>-1</sup> and the number of scans was 32. The measurement controlled by Omnic software.

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

X-ray diffractometer used in this study is Bruker model D8 ADVANCE with CuK $\alpha$  radiation (1.5406 Å). The voltage and the current of X-ray tubes were 40 kV and 30 mA respectively. The scanning was done by step scanning with a step size of 0.05 degree 2 theta and integration time of 0.1 deg/step.

### **Thermal Gravimetric Analyzer**

The thermal gravimetric analysis (TGA) was conducted on a Perkin-Elmer Pyris Diamond TG-DTA under N<sub>2</sub> flow from 30 °C to the temperature 800 °C. The heating rate was 10 °C/min.

### **Glass Mold and PVC Gasket**

Glass molds were the temper glass from the Thai-Asahi Co., Ltd. and PVC gaskets were produced by extruded in PAN Asia Co., Ltd.

### **Transmission Electron Microscope (TEM)**

The microscopic investigation of the clay microstructure is performed by JEOL 2010 TEM at an acceleration voltage of 200 kV. All the sample are cut by Ultramicrotome (locate at Mahidol University) with a diamond knife. The thickness is set at 100 nm.

### **Differential Scanning Calorimeter (DSC)**

Differential scanning calorimetry (DSC) was carried out on a Mettler Toledo DSC822<sup>o</sup> at a heating rate of 5 °C/min under N<sub>2</sub> flow from 40 °C to the temperature 200 °C.

### **Zwick Pendulum Impact Tester**

Impact properties of the PMMA casted sheet were performed by Zwick pendulum impact tester model 5113. Using pendant load of 2.7 N, and the release angle was 124.4 degrees. The specimen size was 62 mm long and 12.7 mm width.

### **Hardness Measurement**

Surface hardness of the PMMA casted sheet was measured by Rockwell Hardness tester in scale-M (Ball  $\frac{1}{4}$  inch and load 100 kg).

## **3.3 Methodology**

### **3.3.1 Preparation of Organoclay and characterization**

#### **3.3.1.1 Preparation of Na-clay**

Clay was stirred vigorously in water until homogeneous and left overnight without stirring. Supernatant was separated and added 1 M of sodium chloride (NaCl). Solution was stirred overnight at room temperature to ensure a complete exchanged reaction. An excess sodium ion was removed centrifuged at 2500 rpm for 10 minutes. A chloride ion was removed from the clay suspension by diffused throughout semipermeable membrane until no appeared white precipitate of silver chloride (AgCl) was detected with silver nitrate (AgNO<sub>3</sub>) solution. The particle size separation, for particle size smaller than 2  $\mu\text{m}$ , was carried out at the spinning speed of 800 rpm for 15 minutes at room temperature. The supernatant, the clay portion, is carefully separated. The water was evaporated by rotary evaporator at 60 °C at 100 mbar yielding clay power. Na-Clay is dried in a vacuum oven at 110 C for 3 day, and ground with mortar, and then passed through sieve mesh no.180. Cation Exchange Capacity (CEC) of Na-Clay determine by methylene blue index as follow as ASTM C837-81 (1992). The samples were characterized by XRD.

#### **3.3.1.2 Preparation of Organoclay**

The Na-clay was dispersed in distilled water with 1% wt. In a separated beaker, quaternary ammonium salt was dispersed in distilled water at various concentration; 0.5, 1.0 and 1.5 mmol. Both solutions were heated to 70 °C for 20 min. The intercalation was achieved by pouring surfactant solution into the clay dispersion. The reaction was stirred at 70 °C for another 2 hr. And then turn off the

stirrer and left its overnight to keep it to equilibrium state. The solution was filtered and washed chloride ion from organoclay. The organoclay is dried in a vacuum at 75 °C and ground with mortar then passed through sieve mesh no. 325. The samples were characterized by FTIR, XRD and TGA.

### 3.3.1.3 Characterization of Organoclay

The organoclay prepared from Na-BNH and three quaternary ammonium salt were characterized to verify the structure and composition by using these following techniques:

#### XRD

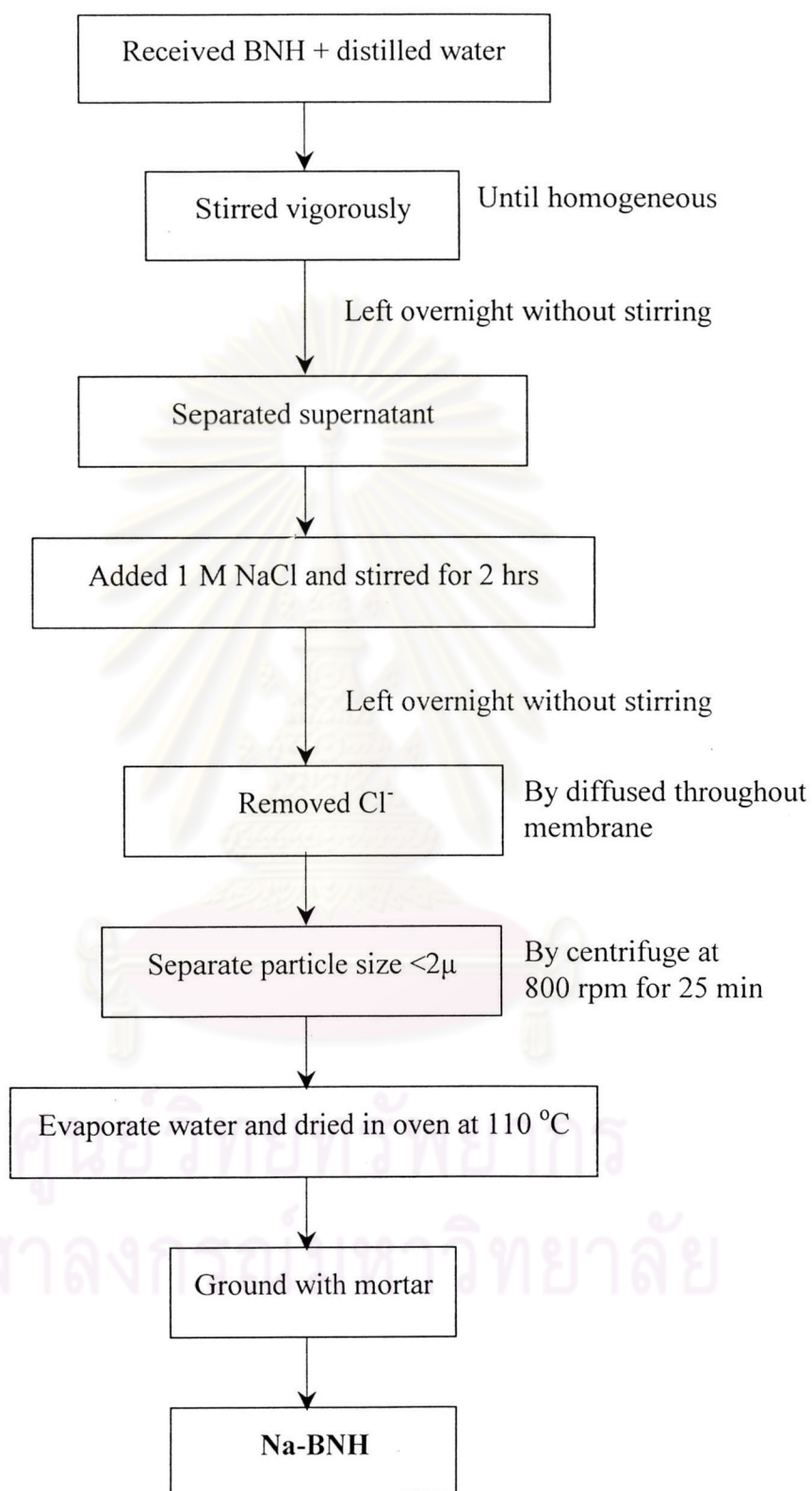
Sample was detected by X-ray diffractometer of Bruker model D8 ADVANCE with CuK  $\alpha$  radiation (1.5406 Å). The voltage and the current are 40 kV and 30 mA, respectively. The measurement was scanned in rang of 1.0 to 25.0 °2 $\theta$  with scan speed 2.0 sec/step and step size 0.05 °2 $\theta$ . The measurements were operated by EVA program.

#### FT-IR

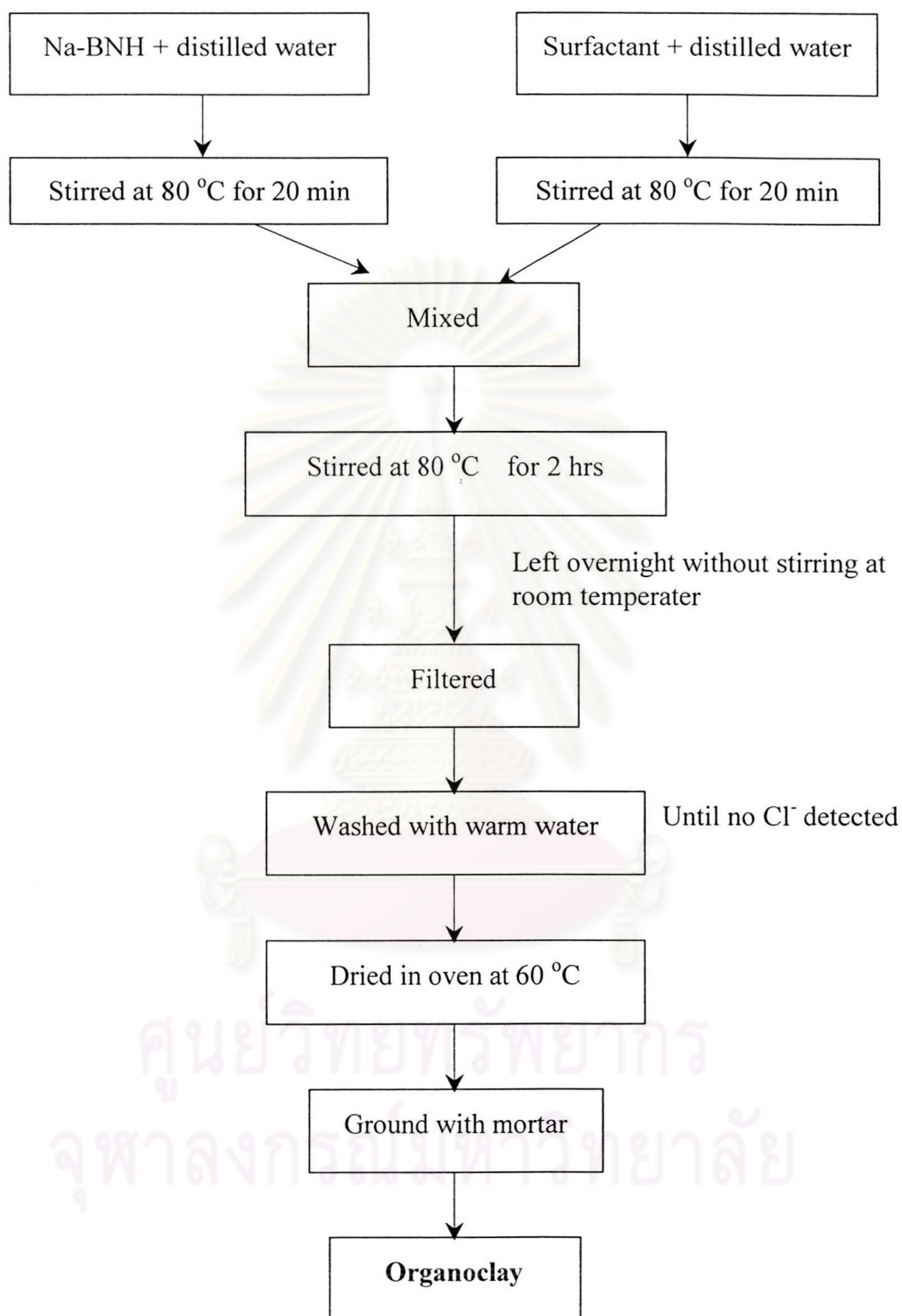
FT-IR is the simple technique to investigate the characteristic group frequencies of Na-BNH, TTM-BNH, OMH-BNH and ODMHBNH. In this experiment, characteristics of the organoclay were obtained using a transmission mode of FTIR with potassium bromide (KBr) disc. The organoclay was mixed with KBr by grinding in the agate mortar. The sample was compressed as a disc by hydraulic press. The sample was scanned from 4000-400 cm<sup>-1</sup> with a resolution of 4 cm<sup>-1</sup> for 32 scans.

#### TGA

Thermogravimetric analysis technique was used to determine thermal stability of Na-BNH and organoclay by putting dried powder in a small disc inside the heater chamber under nitrogen atmosphere. The heating rate was 10 °C/min.



**Scheme 3.1** The diagram of process for Na-BNH preparation



**Scheme 3.2** The diagram of process for organoclay preparation

### 3.3.2 Dispersion of Organoclay in MMA Monomer

Study of compatibility of organoclay and MMA monomer was performed by the observation dispersion of organoclay in MMA monomer. In cylinder, organoclay 200 mg was dispersed in 5 mL of MMA monomer. The mixer was stirred 1 hr and left it for 24 hr. The observation dispersion was recorded.

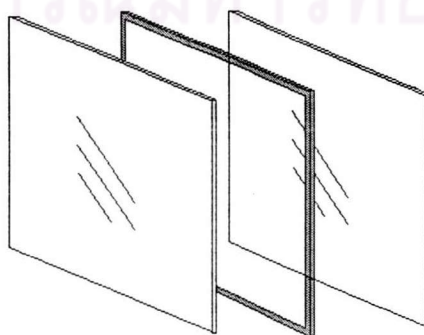
### 3.3.3 Preparation of PMMA/clay Nanocomposite Casted Sheet

#### 3.3.3.1 Preparation of PMMA/clay Syrup Solution

The PMMA/clay syrup was prepared by mixing MMA monomer with organoclay at 2, 4 and 6 %w/w loading in round bottom flask and stirred for 5 minutes by homogenizer. 0.0018 %wt of 2,2'-azobisisobutyronitrile (AIBN) was filled in the mixture and stirred for 30 minutes at polymerization temperature of 95°C. The syrup was controlled a percent conversion of about 7-10 %.

#### 3.3.3.2 Preparation of Glass Mold

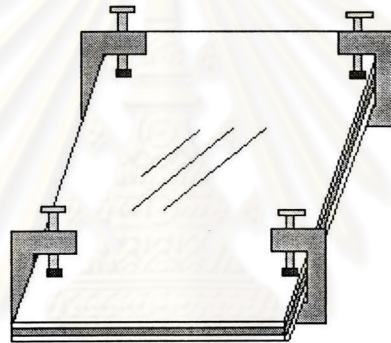
Glass molds were polished and inspected some defects such as scratches before use while PVC gaskets were prepared suitable thickness by using extruder. The PVC gasket and two glass molds were assembled that they were like a sandwich, as shown in Figure 3.1.



**Figure 3.1** The molds and the PVC gaskets before clamping

### 3.3.3.3 Preparation of PMMA/Clay Nanocomposite Sheet

PMMA/clay syrup (from 3.3.3.1.) was mixed with 0.038 %wt of 2,2'-Azobis-(2,4-dimethyl valeronitrile) (ADV N) for 20 minutes and dried under vacuum to eliminate contaminations and bubbles before using. The mixture was mixed into the glass mold in a certain dimension and was clamped by C-clamps, shown in Figure 3.2. The mold was put into the water bath for 3 hours at 60°C and annealed at temperature range at 110°C. After that, PMMA sheet was taken out from the mold by releasing the clamps. The samples were characterized by XRD and TEM.



**Figure 3.2** The mold after assembly

### 3.3.4 Characterization

#### XRD

Interlayer spacing of organoclay in nanocomposite was investigated by XRD. Sample was detected by X-ray diffractometer of Bruker model D8 ADVANCE with CuK  $\alpha$  radiation (1.5406 Å). The voltage and the current are 40 kV and 30 mA, respectively. The measurement was scanned in rang of 1.0 to 25.0 °2 $\theta$  with scan speed 30.0 sec/step and step size 0.05 °2 $\theta$ . The measurements were operated by EVA program.



## TEM

Morphology of composite was study by TEM. . The samples were cut by Ultramicrotome with a diamond knife. The thickness is set at 100 nm. The samples were dried in oven at 50 °C for 2 hr.

### 3.3.5 Mechanical Property

To investigate mechanical properties of the blends, the final PMMA cast sheet from each condition was cut into specific size for each measurement. Zwick pendulum impact tester using 2.7 Joules striker measured impact resistance using unnotched Izod test method following ASTM D256. Surface hardness of the PMMA sheet was measured using Rockwell Hardness Tester following ASTM D2240. In each case, at ten sample specimens were used to calculate the mean values.

### 3.3.6 Thermal Property

The glass transition temperatures ( $T_g$ ) of various materials were evaluated using Mettler Toledo DSC822<sup>e</sup> under N<sub>2</sub> flow. A scan rate of 5 °C/min and temperature in the range 40-200 °C were used.

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