

CHAPTER III

MATERIALS AND METHOD

3.1 Clay preparation and characterization

3.1.1 Materials

A bentonite, deposited at Lopburi province, was kindly supplied by Thai Nippon Chemical Industry Co.,Ltd. This clay is used throughout this study. Sodium chloride (NaCl) is purchased from BDH. Silver nitrate is purchased from Aldrich.

3.1.2 Equipment

3.1.2.1 X-ray diffractometer (XRD)

X-ray diffractogram was obtained by X-ray diffractometer, Phillips model X'perts PW3760 at Metallurgy and Materials Science Institute, Chulalongkorn University. X-ray of Cu-K alpha at 40 kV/30mA was used as source. The measurement was scanned in the range of 2 to 80 °2θ with scan speed 1 sec/step and step size 0.02 °2θ. The measurement were operated by PC-APD program and identified by PC-IDENTIFY program.

3.1.2.2 X-ray fluorescence spectrometer (XRF)

X-ray fluorescence spectrometer (Philips model PW2400) was used to analyze the chemical composition. The unit is located at Scientific and Technological Research Equipment Centre, Chulalongkorn University. It detected the wavelength which emission from the samples. The samples were mix with borate (H_3BO_4) and burning at 1000 °C

3.1.2.3 Thermalgravimetric analyzer (TGA)

Thermal gravimetric analysis was obtained by Netzsch STA 409 C which is located at Scientific and technological research equipment centre, Chulalongkorn University. The measurement was determined at temperature range of 25 -1000 °C

under N_2 atmosphere. The heating rate was $10\text{ }^\circ\text{C}/\text{min}$. Alumina crucible used as a reference material.

3.1.2.4 Particle analyzer

Particle size distributions were investigated by Mastersizer S Ver.2.19 at National Metal and Materials Technology Center (MTEC) with the detection range of $0.05\text{-}900.00\text{ }\mu\text{m}$. The measurement based on the scattering of the laser beam (He-Ne Laser). 1 g/L of Na-Hexametaphosphate, $(\text{NaPO}_3)_6$, was used as dispersion agent to prevent clay aggregation. The refractive index of clay and $(\text{NaPO}_3)_6$ are 1.5195 and 1.33, respectively.

3.1.2.5 Scanning electron microscope (SEM)

Micrograph of clay mineral was detected by Scanning electron microscope (SEM) of Philips model XL30 CP at Metallurgy and Materials Science Institute, Chulalongkorn University. There was operated at 25-30 kV, high vacuum and used back scattering mode.

3.1.3 Method

3.1.3.1 Clay mineral separation

Bentonite was dispersed in distilled water with 5 \%W/V , stirred at $1,000\text{ rpm}$ by mechanical stirrer with high shear propeller for one hour, and left to settle overnight in order to remove the fraction of the non clay mineral. The slurry was passed through sieve mesh no.325. The slurry was then dilute to 1 \%W/V with distilled water and centrifuged at 800 rpm for 15 minutes in order to separate the clay particle, having a particle size less than $2\text{ }\mu\text{m}$. This process has been shown in Figure 3.1 The clay suspension were collected for Na-montmorillonite preparation.

3.1.3.2 Na-montmorillonite preparation

Sodium chloride (NaCl) was added into the clay suspension until the concentration reaches 1.0 M . The suspension was stirred at $1,000\text{ rpm}$ by mechanical stirrer for one hour. The suspension of sodium saturated clay was centrifuged at $2,500\text{ rpm}$ for 30 minutes. The supernatant was discharged. The clay was redispersed in

distilled water and centrifuged at 2,500 rpm for another 30 minutes. The process was repeated until the clay starts to suspend in the supernatant. The clay was then separated and kept for a dialysis. The clay was dialyzed against distilled water. The water was constant changed until there is no white precipitate detected by 5% W/V of AgNO_3 solution. The Na-montmorillonite, free Cl^- , was dried at 110°C for three days. The powder was ground with alumina mortar and passed through sieve mesh no.180 as shown in Figure 3.1. This clay (SC1) was later used in all experiment.

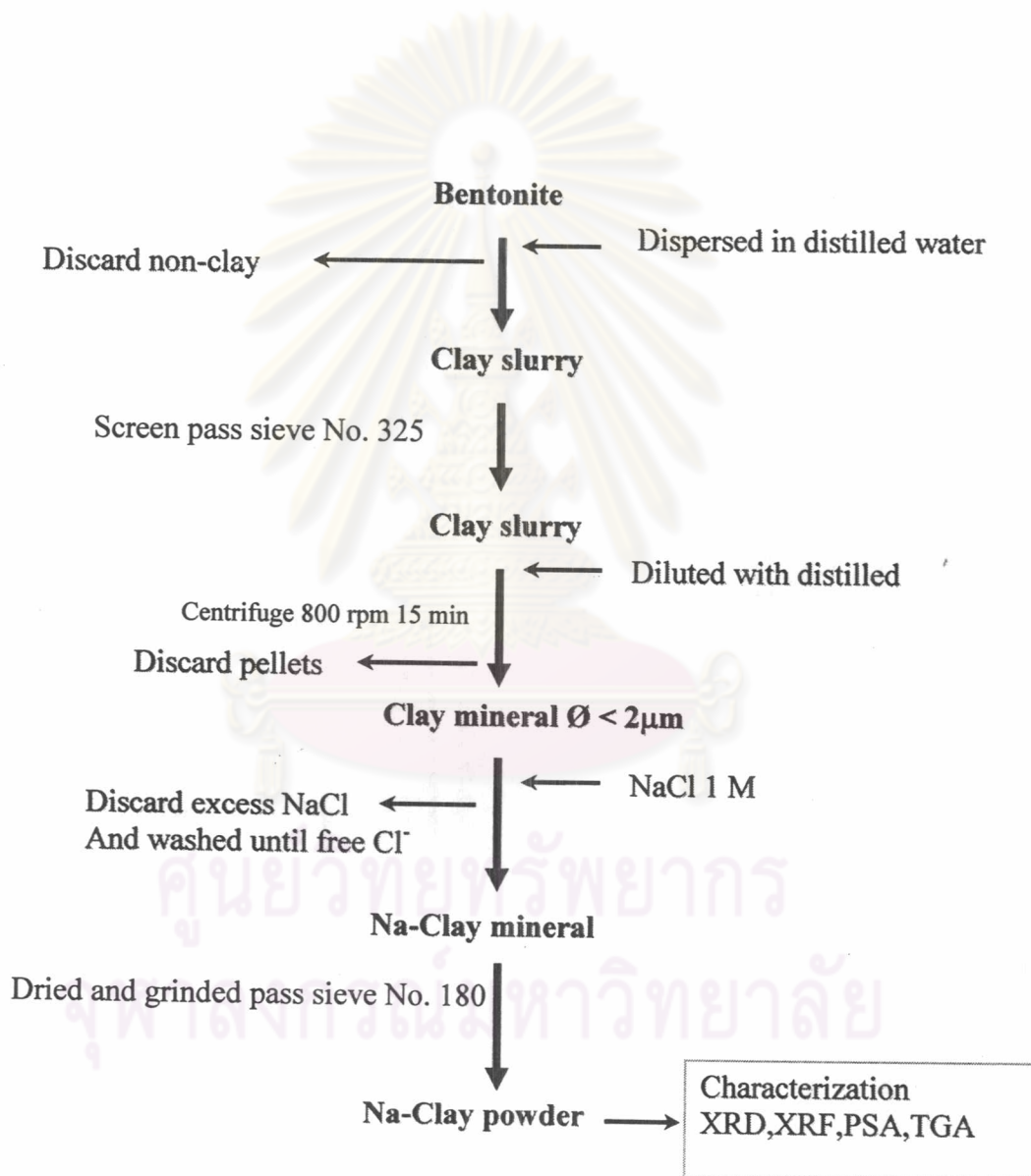


Figure 3.1 Flow chart of Na-clay preparation

3.1.3.3 Clay mineral identification by X-ray diffraction

Sample was detected by X-ray diffractometer of Phillips model X'perts PW3760, Cu anode, angle 2θ , scan speed 1 sec/step, step size $0.02^\circ 2\theta$, at Metallurgy and Materials Science Institute. All the peaks were identified by using the JCPDs powder diffraction cards.

3.1.3.4 Chemical composition investigation

6.0 g of powdered clay was mixed with borate (H_3BO_4) and melt at $1000^\circ C$ to burn out the organic parts. Then the sample was analyzed with X-ray fluorescence (XRF), at Scientific and Technological Research Equipment Centre, Chulalongkorn University.

3.1.3.5 Determination of cation exchange capacity (CEC) by methylene blue index

Cation exchange capacity was obtained by methylene blue index (MBI) followed ASTM C837-81 (1992). 2 grams of Na-montmorillonite (SC1) was dispersed in distilled water for 30 minutes at stirring speed 1000 rpm. The pH was kept in between pH 3-4 with a constant stirring of the suspension. 1.0 ml of 1.0 M methylene blue indicator was added into clay slurry and the solution was dropped onto a filter paper no.542. There will be a yellow ring appears around the dropped. The process was repeated until no yellow ring was detected. The MBI can be calculated by using the following equation (1)

$$MBI = \frac{\text{volume of methylene blue} \times 0.01 \times 100}{\text{Weight of montmorillonite}} \quad (1)$$

3.1.3.6 Particle size analysis

Sample, 10 %W/V swollen in deionized water, was investigated for particle size by Mastersizer S Ver.2.19. The machine has a detection range of 0.05-900.00 μm . The measurement based on the scattering of the laser beam (He-Ne Laser) by the clay particle. The experiment is carried out at National Metal and Materials

Technology Center (MTEC). 1 g/L of Na-Hexametaphosphate, $(\text{NaPO}_3)_6$, was used as dispersion agent which prevents clay aggregation during the experiment. The refractive index of clay and $(\text{NaPO}_3)_6$ are 1.5195 and 1.3300, respectively.

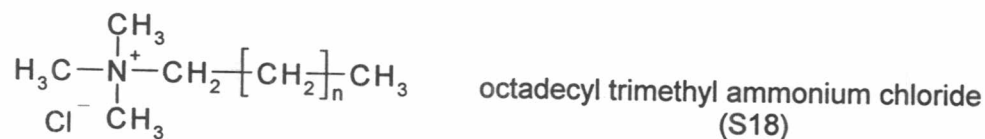
3.2 Organoclay preparation and characterization

3.2.1 Materials

In this experiment, there are four types of alkylammonium cations used in this study. Octadecyl trimethyl ammonium chloride (S18), dioctadecyl dimethyl ammonium chloride (D18), and methyl polyoxyethylene (15) octadecan ammonium chloride (EO18) were the product of Akzo Nobel Surface Chemistry in USA. They were supplied by Thai Specialty Chemical Co.,Ltd. Tricaprylyl methyl ammonium chloride (T8) was purchased from Aldrich. All chemical structures were shown in Figure 3.2



ศูนย์วิจัยทรัพยากร
จุฬาลงกรณ์มหาวิทยาลัย



$$n = 16 \sim 64 \% ; = 14 \sim 31 \% ; = 12 \sim 4 \% ; = 10 \sim 1 \%$$

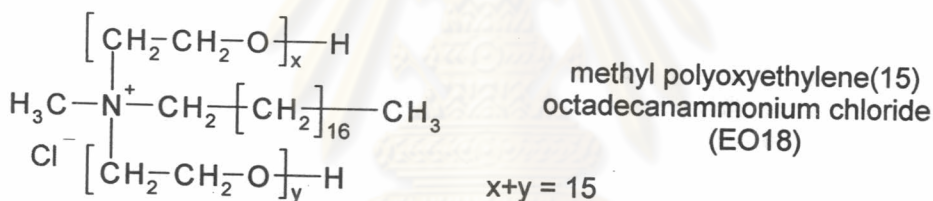
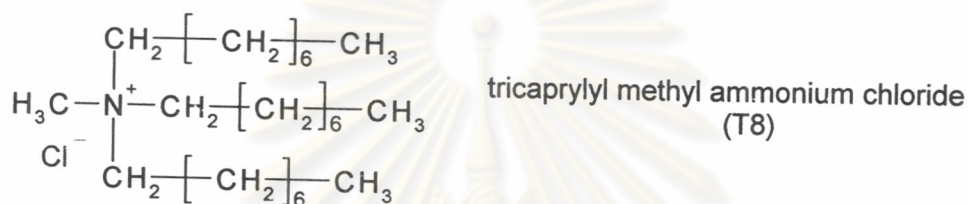
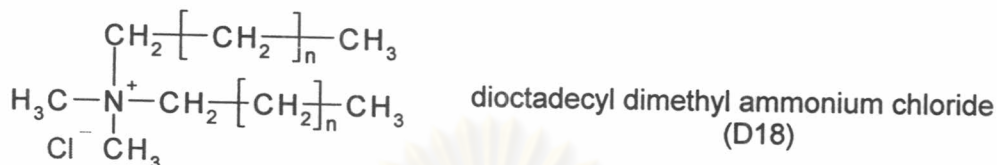


Figure 3.2 Chemical structure of Alkylammonium Salt

3.2.2 Equipment

3.2.2.1 X-ray diffractometer

X-ray diffractogram were obtained from Phillips model X'perts PW3760 diffractometer located at Metallurgy and Materials Science Institute, Chulalongkorn University. Cu-K alpha was used. The voltage and the current are 30 kV and 20 mA, respectively. The measurement was scanned in the range of 2.0° to $25.0^\circ 2\theta$ with scan speed 1.0 sec/step and step size $0.02^\circ 2\theta$. The measurements were operated by PC-APD program.

3.2.3 Method

3.2.3.1 Effect of loading concentration of surfactant

2% W/W of Na-clay was dispersed in distilled water. In a separated beaker, 0.25, 0.5, 1.0, 1.5 and 2.0 mmol alkylammonium salt in 50 ml of distilled water were prepared. Both clay and alkylammonium solution were heated to 70 °C for 30 min. The solution of alkylammonium was slowly poured into the clay suspension under a rigorous stir. The reaction was continued for another one hour. The stirring was stopped and the reaction was left overnight. The supernatant was carefully discarded. The precipitate was separated by filtration, using filter paper No.42. The organoclay precipitate was washed with 100 ml of distilled water for three times. The sample was dried at 110 °C. The organoclay was ground with mortar and passed through sieve mesh No.200 (Figure 3.3). The sample was kept in desiccator for further characterized and used as the organoclay.

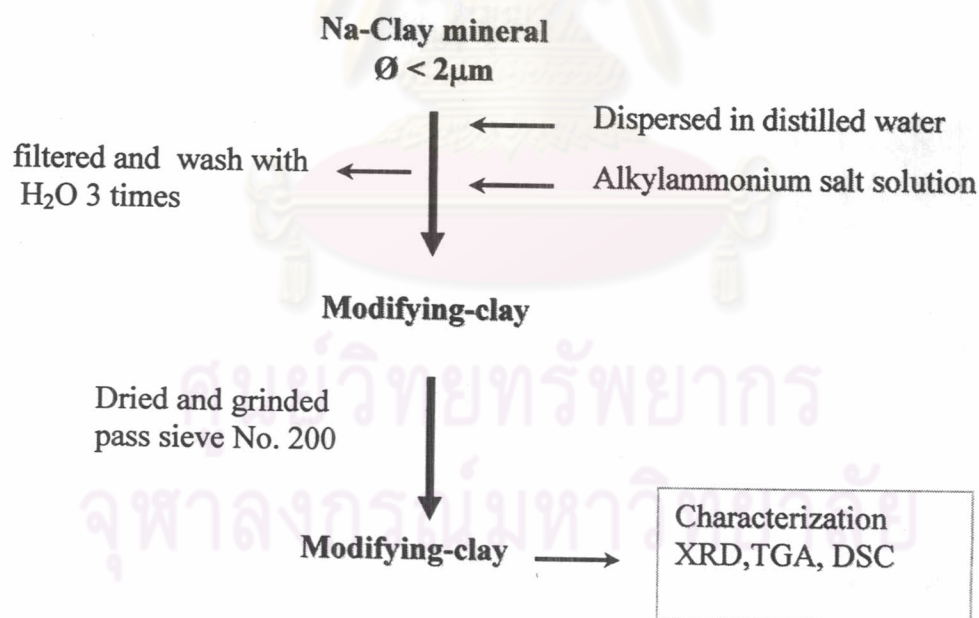


Figure 3.3 Flow chart of modifying montmorillonite

3.2.3.2 Washed the access of surfactant

The same procedure as 3.2.2.1 was carried out. After the organoclay was filtered with filter paper No.42, it was washed with distilled water until there were no white precipitates detected by a silver chloride solution. The organoclay was then washed with 100 ml of absolute ethanol for 2 times. The sample was dried at 110 °C, ground, and passed through the sieve.

3.3 Silane reaction and characterization

3.3.1 Materials

Octadecyl trimethoxysilane (OTMS) and Octadecyl dimethylchlorosilane (ODCS) has been used in this experiment was purchased from Fluka.

3.3.2 Equipment

3.3.2.1 Fourier transform infrared spectrophotometer (FTIR)

The spectra were obtained by a Nicolet Impact 400D FT-IR. The frequency range of measurement was 4000 - 400 cm^{-1} at a resolution of 4 cm^{-1} and the number of scans was 32. The measurement was controlled by Omnic software.

3.3.2.2 Viscometer

Brookfield Programmable DV-II + Viscometer was used to study the rheological behavior of modified clay at room temperature. The spin needles are No. 18 and No. 31 typed cylinder.

3.3.3 Method

3.3.3.1 Modification of clay with silane coupling agent

1 g. of clay was dispersed in 50 ml distilled water and stirred at 1000 rpm. for 1 hour. The reaction was heated to 70°C. The solution of octadecyl trimethoxy silane or octadecyl dimethylchlorosilane in 95% ethanol at desired concentration (0.5, 1.0, 1.5 and 2.0 mmol) was slowly dropped into the clay suspension. The reaction was stirred for another half an hour and was cooled down. The organoclay was filtered by Whatman filter paper no. 42. The precipitate was washed with mixed ethanol and

distilled water (1:1) for several times. The filtrate was dried at 110 °C in air oven, group with mortar and passed through sieve. The flow chart was shown in Figure 3.3

3.3.3.2 Characterize functional group by FTIR

FTIR is the simple technique to investigate the functional group of materials based on the interaction of infrared radiation with molecular dipole moment. The modifying clay was mixed with potassium bromide (KBr) by grinding in the agate mortar. The samples were compressed as a disc by hydraulic press. The sample was scanned from 4000 to 400 cm^{-1} with a resolution of 4 cm^{-1} for 32 scans.

3.3.3.3 Rheology of organoclay after modifying with octadecyl trimethoxy silane

1.0 g. of sample was dispersed in 20.0 ml of toluene by vortex mixer until no agglomerated is present. The sample was poured into the sample holder and measured the viscosity by Brookfield Programmable DV-II + Viscometer at room temperature, using needle No. 18 and 31.

3.4 **Polymer-clay nanocomposite preparation and characterization**

3.4.1 **Materials**

Polystyrene GP 110 was supported by Thai Petrochemical Industry Public Co.,Ltd. Thailand.

Nylon 6 under the polymer brand MAPEX N100N1 from Ginar Technology Co. Ltd., Taiwan was used. The polymer was purchased from FARCO International, Co., Ltd., Thailand.

3.4.2 **Equipment**

3.4.2.1 Internal mixer

Polymer-nanocomposites were prepared by melt intercalation with internal mixer of Barbender PL 2100 which located at Petroleum and Petrochemical College, Chulalongkorn University.

3.4.2.2 Extruder

The intercalation process was carried out by using a single screw extruder (Microtruder 0625 from Rancastle Extrusion Systems Inc, USA) located at Chemistry Department, Mahidol University. The three zone screw diameter was 0.625 inch and the length to diameter ratio was 24:1. The screw speed was 30 rpm. The temperature zone of 186, 231, 236 and 232 °C were employed in the study. Organoclay loading was varied from 1%wt to 5%wt.

3.4.2.3 Transmission electron microscope (TEM)

Transmission electron microscope (TEM), JEM-200-CX by JEOL was used to indicate the distribution and morphology of clay pellet in the polymer matrix. There was operated at high voltage of 100 kV, in the bright field mode. For high resolution, there was operated at 200 kV.

3.4.2.4 Differential scanning calorimeter (DSC)

Differential scanning calorimetry (DSC) is a thermal analysis techniques technique for measuring the energy necessary to establish a nearly zero temperature difference between a substance and an inert reference material, as the two specimens are subjected to identical temperature regimes in an environment heated or cooled at a controlled rate. DSC 550 from Instruments Specialists Incorporated, located at Physics Department, Mahidol University, was employed throughout this study.

3.4.3 **Method**

3.4.3.1 In situ polymerization of polymer-clay nanocomposite

Modified clay was dispersed in the styrene monomer by magnetic stirrer for 1 hour at room temperature. Then slowly added 1 %wt of initiator (benzoyl peroxide) into the suspension. The suspension was reacted in the oil bath at 110 °C for 18 hours. Polymer-clay composite was annealed in the air oven at 100 °C for 24 hours before characterization.

3.4.3.2 Melt blending of polymer-clay nanocomposite

Modified clay was dispersed in 20.0 ml toluene until the organoclay clay is nicely dispersed. The organoclay-toluene suspension was slowly coated onto 200 g of polystyrene, containing in a separate beaker, and dried in vacuum oven.

The organoclay-coated-polystyrene was poured into the internal mixer barbender and the mixing was done at 180 °C, 50 rpm. for 10 minutes.

3.4.3.3 Nylon nanocomposite

The organoclay was soaked with solvent and coated onto the nylon6 pellet to ensure a good dispersion of the organoclay while melt processing in the single screw extruder. Organoclays were dispersed in chloroform for D18 and in ethanol for EO18. The solution was mixed with the nylon 6 pellets until the pellet is throughout coated. The coated pellet was left till the solvent is evaporated and dried in the vacuum oven at 110 °C for 12 hr before processing.

3.4.3.4 Thermal analysis of polymer-clay nanocomposite

The composites have been cut in small pieces with weight of around 5.0 to 10.0 mg. The samples were placed in a aluminum based pan and closed with another aluminum lid. The experiment was done under nitrogen atmosphere. The heating and cooling are at 5°C/min.

3.4.3.5 Identify the type of nanocomposites by XRD

XRD was used to investigate the type of polymer-clay nanocomposite. The flat surface samples, cutting it, were scanned from 2-25 °2θ with scan speed 0.02 °2θ /sec at room temperature.

3.4.3.6 Distribution of clay filler in polymer-clay nanocomposite

The dispersion of clay platelet in the matrix of polymer has been investigate by TEM at high magnification. The samples were fixed on the resin and cut into thin section less than 100 nm. by ultramicrotrom with diamond knife.