

## CHAPTER III EXPERIMENTAL

### 3.1 Materials

#### 3.1.1 Clay Minerals

Bentonite (BN) was supplied by Thai Nippon Chemical Industry Co., Ltd. The cation exchange capacity (CEC) of BTN is 43 mmol/100g of clay.

#### 3.1.2 Surfactants

Cetyltrimethylammonium [ $C_{16}H_{33}N^+(CH_3)_3$ ] bromide was supplied by Fluka.

#### 3.1.3 Co-surfactant

Dodecylamine,  $C_{12}H_{27}N$ , (98% purified) was supplied by Aldrich.

#### 3.1.4 Silica Sources

Tetraethyl orthosilicate (TEOS),  $Si(OC_2H_5)_4$  and Methyltriethyl orthosilicate (MTS),  $CH_3Si(OC_2H_5)_3$ , was supplied by Fluka.

#### 3.1.5 Solvents

Methanol ( $CH_3OH$ ) was supplied by Lab Scan and Hydrochloric acid (HCl) was supplied by Carlo Erba.

#### 3.1.6 Polymer

Polypropylene (PP), under trademark Moplen HP550R, was supplied by HMC polymers Co., Ltd.

#### 3.1.7 Compatibilizer

Sodium- neutralized ethylene-co-methacrylic acid (Surlyn<sup>®</sup> PC350, 4.5 MFI) was purchased from DuPont Co Ltd.

## 3.2 Equipment

### 3.2.1 X-ray Diffractometer (XRD)

X-ray diffractometer (XRD) was used to observe the d-value of organoclay, PCH and HPCH and to investigate the crystal structure of nanocomposites. X-ray diffraction patterns were measured on a Rigaku Model Dmax 2002 diffractometer with Ni-filtered Cu  $K_{\alpha}$  radiation operated at 40 kV and 30 mA. The powder samples were observed on the  $2\theta$  range of 1.2-20 degree with scan speed 2 degree/min and scan step 0.01 degree. For the film samples, the experiment was performed on a 10-30 degree with scan speed 5 degree/min and scan step 0.02 degree.

### 3.2.2 Surface Area Analyzer (SAA)

$N_2$  adsorption-desorption isotherms were obtained at  $-196^{\circ}\text{C}$  on a Quantachrome Autosorb-1. Samples were degassed at  $150^{\circ}\text{C}$  during 12 h in a vacuum furnace prior to analysis. Surface areas were calculated using the BET equation. The pore size distributions were constructed based on Barrett, Joyner and Halenda (BJH) method using the adsorption branch of the nitrogen isotherm.

### 3.2.3 Fourier Transform Infrared Spectroscopy (FT-IR)

The FT-IR spectra of organoclays, PCHs, HPCHs and nanocomposites film were obtained using a Nicolet Nexus 670 FT-IR spectrometer in the frequency range of  $4000\text{-}400\text{ cm}^{-1}$  with 32 scans at a resolution of  $2\text{ cm}^{-1}$ . KBr pellet technique was applied in the preparation of powder samples. The incorporation of organic group into silicate network is investigated by using FTIR.

### 3.2.4 Thermogravimetric Analysis (TGA)

TG-DTA curves were collected on a Perkin-Elmer Pyris Diamond TG/DTA instrument. The clay sample was loaded on the platinum pan and heated from  $30^{\circ}\text{C}$  to  $900^{\circ}\text{C}$  at a heating rate of  $10^{\circ}\text{C}/\text{min}$  under  $N_2$  flow of 100 mL/min. For nanocomposites, the sample were heated from  $30^{\circ}\text{C}$  to  $600^{\circ}\text{C}$  at a heating rate of  $10^{\circ}\text{C}/\text{min}$  under  $N_2$  flow of 100 mL/min.

### 3.2.5 Differential Scanning Calorimetry (DSC)

DSC analyses were carried out using a Perkin-Elmer DSC 7 instrument. The sample was first heated from 30°C to 200°C and cooled down at a rate of 10°C/min under a N<sub>2</sub> atmosphere with a flow rate of 10 ml/min. The sample was then reheated to 200°C at the same rate.

### 3.2.6 Scanning Electron Microscope (SEM)

Scanning electron microscopy was performed on JEOL JSM-5410 lv Model to observe surface morphology of PCH. The specimens were coated with gold under vacuum before observation to make them electrically conductive.

### 3.2.7 Transmission Electron Microscope (TEM)

Transmission electron microscopy performed on JEOL JEM-2100 electron microscope with an accelerating voltage of 160 kV was used to observe the structure of pores and the dispersion of PCH in polymer matrix of nanocomposites. TEM samples were prepared by embedding the powder in resin and sectioning on a ultramicrotome. The thin sections were supported on 300 mesh copper grids.

### 3.2.8 Gas Permeability Tester

Gas permeation experiments were investigated by Brugger Gas Permeability Tester. The sample films were cut into circular shape with 110 mm in diameter according to ASTM 1434-82. The thickness of the films was measured with the peacock digital thickness gauge model PDN 12N by reading ten points at random position over the entire test area and the results were averaged. The films were placed in a desiccator over NaCl and kept for not less than 3 days prior to test.

### 3.2.9 Twin Screw Extruder

PP/ Clay nanocomposites were prepared using a Colin D-8017 Model T-20 corotating twin-screw extruder with L/D=30 and D=25 mm. The operating temperatures of extruder were maintained at 80, 160, 180, 195, 205, and 215 °C from hopper to die, respectively. The screw speed was maintained at 50 rpm.

### 3.2.10 Blow Film Extrusion Machine

PP/Clay nanocomposites films were prepared by using blow film extrusion machine with screw diameter of 45 mm, die diameter of 150 mm, L/D=26, The rotation speed of screw less than 50 rpm and blowing ratio of 0.65. The barrel and mold temperature were 210 °C.

### 3.2.11 Gas Chromatography

Gas chromatography with flame ionization detector was utilized to examine ethylene adsorption capacity of the porous clays. Ethylene adsorption was measured by placing each product in a jar (0.6 l), then sealing with a screw-cap lid. Ethylene was injected into a jar to give a specific concentration of 500 ppm. Ethylene concentration in the jar was measured periodically about once an hour. The ethylene adsorption was calculated by taking the difference between the amount of ethylene added and the amount of remaining in the headspace.

## 3.3 Methodology

### 3.3.1 Purification and pH Adjustment of Bentonite

Bentonite was pulverized and sieve through 325 mesh. Four 10-g of the passing part were purified by centrifugation and then washed with distilled water several time until pH value was near 9. After that, centrifugation was applied. Again, the same amount of distilled water was added, and then the pH of three samples was adjusted to 3, 5, and 7 by using dilute HCl solution. This procedure was repeated for three days to equilibrate the pH of each sample. The samples were air-dried overnight and again pulverized in a mortar.

### 3.3.2 Synthesis of Porous Clay Heterostructures (PCHs)

Each pH-adjusted bentonite was converted into a quaternary ammonium form by ion exchange with cetyltrimethylammonium bromide and stirred at 50 °C for 24 h. After the reaction time, the solid was filtered out, washed with a mixture of methanol and water and then air-dried. The obtained organoclay was stirred in dodecylamine for 30 min at 50°C. In addition, TEOS (at molar ratio of

organoclay:dodecylamine:TEOS was 1:20:150) was added and the resulting suspension was stirred for further 4 h at room temperature. The solid was separated from solution again by filtration and air-dried overnight at room temperature to form the as-synthesized PCH. The surfactant was removed from the as-synthesized PCH by solvent extraction using methanol/HCL solution. Typically, 1 g of the as-synthesized PCH material has been added to 45 mL of methanol and 5 mL of HCl and refluxed for 2 h. The solid was subsequently filtrated out and washed with a mixture of methanol and water and dried at 70°C under vacuum for 2 hr. The obtained PCH are named PCH-n (n denotes the pH value of pH-adjusted bentonite clay).

### 3.3.3 Modification of Hybrid Organic-Inorganic PCHs (HPCHs)

The pH-adjusted bentonite was converted into a quaternary ammonium exchange form to obtained organoclay and reacted with dodecylamine according to a PCH formation procedure previously. Then a mixture of TEOS and MTS in a mole fraction of 1:1 was added and stirred for further 12 h at 35 °C. The obtained as-synthesized organic modified PCH was collected by centrifugation and air-dried overnight at room temperature. The surfactant was removed from the as-synthesized HPCH by solvent extraction using methanol/HCL solution as same procedure as in case of PCH formation. The obtained HPCH are named HPCH-n (n denotes the pH value of pH-adjusted bentonite clay).

### 3.3.4 Preparation of Nanocomposites

1 wt% PCH-n or HPCH-n, 2 wt% Surlyn ionomer and PP were melt blended in a Model T-20 co-rotating twin-screw extruder (Collin) with L/D=30 and D=25 mm; the processing conditions were the following: temperature (°C): 80, 160, 180, 195, 205, and 215 from hopper to die, respectively and the screw rotation is 50 rpm. Each composition was premixed in a tumble mixer before introducing into the twin-screw extruder to be well mixed and extruded through a single strand die, and solidified with cold water and pelletized. The obtained pellet was dried in oven.

### 3.3.5 Preparation of Nanocomposites Films

The nanocomposites films were prepared by blown film extrusion machine. The nanocomposites pellets were dried in oven prior to blowing. Following extrusion conditions were employed, the rotation speed of screw less than 50 rpm and blowing ratio of 1.52. The barrel and mold temperature were 210 °C. The thickness of the films was controlled to about 30  $\mu\text{m}$ .