CHAPTER III
EXPERIMENTAL

3.1 Materials

3.1.1 Clay Minerals

Montmorillonite (MMT) was obtained from Kunimine Industries Co., Ltd. and bentonite (BN) was supplied by Thai Nippon Chemical Industry Co., Ltd. The cation exchange capacity (CEC) of MMT and BN are 115 and 52 mmol/100g clay, respectively.

3.1.2 Surfactants

Alkyltrimethylammonium $[C_nH_{2n+1}N^+(CH_3)_3]$ bromide (n = 16) was supplied by Fluka and chloride (n = 12, 18) were obtained from Kao Industrial (Thailand) Ltd.

3.1.3 Co-surfactant

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

3.1.4 Silica Source

Tetraehtyl orthosilicate (TEOS), $Si(OC_2H_5)$, was supplied by Fluka.

3.1.5 Solvents

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

3.1.6 Polymer and Compatibilizer

Polypropylene (PP), under trademark Moplen HP550R, was obtained from HMC polymers Co., Ltd. Polypropylene grafted maleic anhydride (PP-g-MA), under trademark Polybond®3200 (1 wt% MA graft level), was supplied by Chemtula (Thailand) Ltd.

3.2 Equipment

3.2.1 X-ray Diffractometer (XRD)

X-ray diffractometer (XRD) was used to observe the d-value of organoclay and PCH and to investigate the crystal structure of nanocomposites. X-ray diffraction patterns were measured on a Rigaku Model Dmax 2002 diffractrometer with Ni-filtered Cu K_α radiation operated at 40 kV and 30 mA. The powder samples were observed on the 2θ 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°C on a Sorptomatic 1990 series ThermoFinnigan. Samples were degassed at 200°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 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°C to 900°C at a heating rate of 10°C/min under N_2 flow of 200 mL/min. For nanocomposites, the sample were heated from 30°C to 600°C at a heating rate of 10°C/min under N_2 flow of 200 mL/min.

3.2.4 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 250°C and cooled down at a rate of 10°C/min under a N_2 atmosphere with a flow rate of 60 ml/min. The sample was then reheated to 250°C at the same rate.

3.2.5 Scanning Electron Microscope (SEM)

Scanning electron microscopy was performed on JSM-6400 Model to observe surface morphology of PCH. The specimens were coated with gold under vacuum before observation.

3.2.6 Transmission Electron Microscope (TEM)

Transmission electron microscopy performed on JEOL JEM-2100 electron mocroscope 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.

3.2.7 Gas Permeability

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 desicator over $CaCl_2$ and kept for not less than 48 h prior to test.

3.3 Methodology

3.3.1 Purification of Bentonite

Bentonite was pulverized and screened with a sieve of 325 mesh. The 10 g of the passing part was treated with 100 mL of 0.5 M-HCl solution at room temperature for 24 h. The solid part was separated by centifugation and then washed with distilled water until the pH value is near 7. The purified-bentonite was dried in oven overnight and again pulverized in a mortar.

3.3.2 Synthesis of Porous Clay Heterostructure

3 g of clay was added to 50 mL of alkyltrimethylammonium cation and stirred at 50°C for 24 h. After the exchange reaction the solid was filtrated out,

washed with a mixture of methanol and water, and air-dried. The obtained organoclays are named MMT-C_n and BN-C_n (where n is the no. of carbon on the main alkyl chain) for organo-montmorillonite and organo-bentonite. Organoclay was stirred in dodecylamine for 30 min at room temperature after which TEOS was added. The resulting suspension was stirred for further 4 h at room temperature. The molar ratio of organoclay : dodecylamine : TEOS was 1 : 20 : 150. After reaction time 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 either by calcination or by solvent extraction. For calcination, the as-synthesized PCH was calcined at 600°C for 5 h using a temperature ramp rate of 1°C/min. The obtained PCH are named cal-PMH-C_n and cal-PBH-C_n for montmorillonite-PCH and bentonite-PCH, respectively. In the case of extraction, the surfactant was extracted from the as-synthesized PCH using HCl/methanol solution. Typically, 1 g of 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 air-dried at room temperature overnight. The obtained PCH are named ext-PMH-C_n and ext-PBH-C_n for montmorillonite-PCH and bentonite-PCH, respectively.

3.3.3 Preparation of Nanocomposites

1 wt% cal-PCH, 3 wt% PP-g-MA 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, 170, 180, 190, and 200 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 prior to compression molding.

3.3.4 Thin Film Preparation

Thin films of polymer nanocomposites were prepared by a Wabash V 50 H 50 ton compression molding machine. The pellets were placed in a mold and the mold was pre-heated at 200°C for 5 minutes without any applied force to allow fully melting. The mold was also compressed at 200°C for a further 5 minutes under a force of 30 tons after that the mold was cooled to 40°C under pressure.