CHAPTER III
EXPERIMENTAL

3.1 Materials

Commercial sodium montmorillonite, MMT (Kunipia F®), was supplied by Kunimine Industries Co,Ltd in Japan. Commercial sodium activated bentonite, BEN (Mac-Gel® wn-02), was supplied by Thai Nippon Chemical Industry Co,Ltd.

Stearylamine (SA) was purchased from Fluka. Dimethyl Stearylammonium Bromide (DMS), Trimethyl octadecylammonium Bromide (TMS) and Dimethyl Distearylammonium Bromide (DMDS) were supplied by Kao Industrial Co,Ltd in Thailand. (Chemical structures of surfactants are shown in Figure 3.1)

SA : $CH_3\text{-}(CH_2)_{17}NH_2$ DMS : $CH_3(CH_2)_{17}N(CH_3)_2$

TMS : $CH_3(CH_2)_{17}N^+(CH_3)_3\ Br^-$ DMDS : $[CH_3(CH_2)_{17}]_2N^+(CH_3)_2\ Br^-$

Figure 3.1 Chemical structures of surfactants.

Methacrylic acid (MAA) was purchased from ACROS (99.5%). Dicumyl peroxide (DCP) was purchased from Aldrich (98%). Hydrocholic acid (HCl) was purchased from CARLO ERBA (37%).

PP (HP 500N) was supplied by HMC Polymer Company limited.

3.2 Instruments

3.2.1 X-ray Diffractometer (XRD)

XRD spectra were recorded by using a D/MAX-2000 series of Rigaku/X-ray Diffratometer that provides X-ray of Cu K-alpha at 40 kV/30 mA. The experiment was operated at scan speed 2 degree/min with the 0.01-degree 2θ-stepwise increment. The standard sample holders were applied to both ground samples and composite film.

3.2.2 Thermogravimetric Analysis (TGA)

TGA was performed by High Resolution TG-DTA Pyris Diamond (Perkin Elmer) with a heating rate of 10°C/min with resolution 6.0°C from room temperature to 900°C using a nitrogen purge with a purge rate of 200 ml/min.

3.2.3 Differential Scanning Calorimeter (DSC)

DSC analysis was performed by differential scanning calorimeter Perkin-Elmer DSC 7 with nitrogen purge with a purge rate of 60 ml/min. The rates of cooling and reheating were 10°C /min and temperature range varied from room temperature to 250°C.

3.2.4 Instron Universal Testing Machine

Tensile test of PP/clay nanocomposite samples were carried out by an Instron Universal Testing Machine model 4206. The test was operated according to an ASTM D 638. A gauge length of 50 mm was employed with a crosshead speed of 50 mm/min. Width and thickness of specimens at gauge length were about 10.4 and 3.9 mm, respectively.

3.2.5 Melt Flow Index (MFI) Tester

MFI was performed by Zwick model 4105. The test was operated following ASTM D1238. The temperature was set at 230°C and load was 2.16 kg.

3.2.6 Thumber Mixer

Physical mixing of materials was produced by a thumber mixer.

3.2.7 Twin Screw Extruder

PP/clay nanocomposites and PP-graft-modified organoclay were preparation by Collin D-8017 T20 twin screw extruder. The screw speed was set at 50 rpm, and the barrel temperature profiles were 90/160/170/180/190/200°C.

3.2.8 Compression Molding Machine

Film specimens were prepared by Wabash V50H compression molding machine. The pressure acting on the mold was set at 10 tons and the temperature was set at 200°C. Film specimens were shaped by preheating for 5 minutes, compression and cooling under pressure for 5 minutes.

3.2.9 Centrifugal Ball Mill

Dried sediments were ground by Peluerisette 6. The particle size of powder was less than 44 μm (sieve 325 mesh).

3.2.10 Injection Molding Machine

Dumbbell shape specimens for tensile testing were produced by Arburg Allrounder 270M 350-90. The pressure was set at 1000 bar, and the barrel temperature profiles were 160/170/180/190/200°C.

3.3 Methodology

3.3.1 Organomodification of Nanoclays

Two different nanoclays are organically modified via ion exchange reaction between Na^+ and cationic surfactant (alkylammonium ion) by using four different types of alkylammonium cationic surfactant [Stearylamine (SA), Dimethyl Stearylammonium Bromide (DMS), Trimethyl Octadecylammonium Bromide (TMS), Dimethyl Distearylammonium Bromide (DMDS)].

Sieved nanoclay with 325 meshes ($\leq$44μm) 10 g was swollen in distilled water 300 ml and stirred overnight. Alkylammonium ion solution was prepared by dissolution 1.5CEC of alkylammonium ion in distilled water 100 ml, in alkylammine added 3CEC of HCl solution. The swollen clay was mixed with alkylammonium ion solution. Then the mixing was kept at 80°C for 2 hours with stirring. After that the mixing was homogenized at 80°C for 20 minutes. The sediment of organoclay was filtrated with filter paper, Whatman@ grade 2, and washed with hot distilled water.

3.3.2 Characterization of Organoclays

XRD was used to characterize d-spacing of organoclays. Thermogravimetric Analysis (TGA) was used to study the intercalated alkylammonium ion into silicate clay layers.

3.3.3 Modified Organoclays

Organoclay 10 g was swollen in distilled water 100 ml overnight. Then swollen organoclay was modified with 0.5CEC of methacrylic acid. The sediment of modified organoclay was filtrated, washed with distilled water and dried at 100°C. Finally dried sediment was ground in centrifugal agate ball mill and sieved with 325 meshes to obtain modified organoclay.

3.3.4 Characterization of Modified Organoclays

XRD was used to characterize d-spacing of modified organoclays. Thermogravimetric Analysis (TGA) was used to study the intercalated the co-intercalation monomer into silicate clay layers

3.3.5 Preparation of PP/Clays Nanocomposites

Modified organoclays were blended with PP in twin screw extruder to generate PP-graft-modified organoclays as a master batch. Before blending in twin screw extruder, the initiator of grafting reaction, DCP (0.1 %wt), was mixed with modified organoclay in thumber mixer for 10 minutes, and then PP was mixed with them in thumber mixer for 30 minutes. The modified organoclay content of the composites was about 6%. Then, PP was mixed with PP-graft-modified organoclays in twin screw extruder, at ratio PP: PP-graft-modified organoclays; 50:50, to obtain PP/clay nanocomposites (modified organoclay content 3%), before blending in twin screw extruder PP and PP-graft-modified organoclays were mixed in the thumber mixer for 30 minutes.

PP was mixed with initiator in thumber mixer for 30 minutes, and then they were blended in twin screw extruder to generate PP-DCP. PP was mixed with PP-DCP in thumber mixer for 30 minutes, after that they were blended in twin screw extruder to obtain PP-PP/DCP which was blank in this research.

3.3.5 Characterization of PP/Clays Nanocomposites

X-ray Diffractometer was used to determine dispersion of silicate clay layers in PP matrix and crystal structure of PP/clay nanocomposites. Film specimens were prepared by compression molding machine.

Decomposition temperature of PP/clay nanocomposites was investigated by TGA. Melting temperature (T_m) and crystallization temperature (T_c) of nanocomposites was determined by using DSC. MFI of PP/clay nanocomposites were also determined.

Tensile testing of PP/clay nanocomposites were carried out by Instron Universal Testing Machine. A gauge length of 50 mm was employed with a crosshead speed of 50 mm/min in accordance with ASTM D 638. Five dumbbell shape specimens which were shaped by an inject molding machine were tested.