CHAPTER III
EXPERIMENTAL

3.1 Materials

3.1.1 Clay Minerals

Sodium bentonite (Na-BN), with cation exchange capacity (CEC) of 52.55 meq/100 g and particle size 200 meshes (<74 μm), was supplied by Thai Nippon Co Ltd, Thailand. It was screened with a sieve of 325 meshes. Montmorillonite (Na-MMT), with cation exchange capacity (CEC) of 115 meq/100 g and particle size 325 meshes (<45 μm), was supplied by Kunimine Industries Co Ltd, Tokyo, Japan.

3.1.2 Polymer

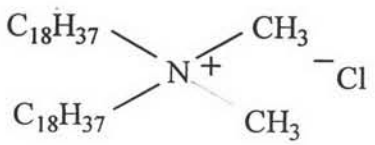
Polypropylene (Moplen HP500N, 12.0 MFI) was supplied by HMC Polymer Co Ltd, Rayong, Thailand.

3.1.3 Compatibilizer

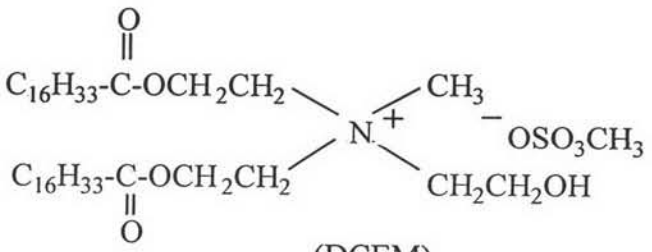
Sodium- neutralized ethylene-co-methacrylic acid (Surlyn® PC350, 4.5 MFI) was purchased from DuPont Co Ltd.

3.1.4 Surfactants

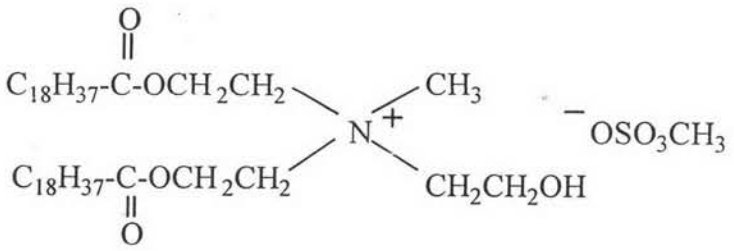
Dihydrogenated tallow dimethylammonium chloride (DTDM) was supplied by V.P.C.Group Co, Ltd. Methyl di-(palm carboxyethyl)-2-hydroxyethyl-ammonium methylsulfate (DCEM) was obtained from JJ degussa Co, Ltd. Methyl di-[(partially hydrogenated) tallow carboxyethyl]-2-hydroxyethyl ammonium methyl-sulfate (DOEM) and methyl bis-(soya amidoethyl)-2-hydroxyethylammonium methylsulfate (DOAM) were received from Union Compound Co, Ltd. The chemical structures of them were shown in Fig. 3.1.



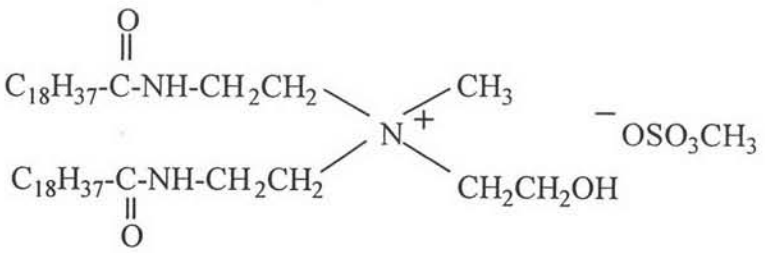
(DTDM)



(DCEM)



(DOEM)



(DOAM)

Figure 3.1 Chemical structures of surfactants.

3.2 Equipment

3.2.1 X-ray Diffractometer (XRD)

Wide angle X-ray diffraction (WAXD) patterns of organoclay were obtained using a Rigaku Model Dmax 2002 diffractometer with Ni-filtered Cu K_α radiation operated at 40 kV and 30 mA. The experiment was performed in the 2θ range of 1.2-20 degrees with scan speed 2 degree/min and scan step 0.01 degree. For the nanocomposites film samples, the experiment was performed on a 10-40 degree with scan speed 5 degree/min and scan step 0.02 degree. Small angle X-ray

diffraction (SAX) patterns of nanocomposites film samples were conducted using a Bruker AXS Model D8 Discover with Cu K_α radiation operated at 40 kV and 40 mA. The experiment was performed in the 2θ range of 0.2-10 degrees with scan speed 1 sec/step and scan step 0.02 degree.

3.2.2 Thermogravimetric Analysis (TGA)

TG-DTA curves were collected on a Perkin-Elmer Pyris Diamond TG/DTA instrument. The samples were heated from 30°C to 900°C at 10°C/min heating rate under the protective N_2 atmosphere (200 ml/min). The initial degradation temperature, weight loss and final degradation temperature of the samples were measured.

3.2.3 Differential Scanning Calorimetry (DSC)

Melting point and crystallization temperature of the nanocomposites as well as virgin PP were carried out by Differential Scanning Calorimeter (Perkin Elmer-DSC-7). The sample was heated from room 30°C to 250°C at the rate of 10°C min^{-1} in order to remove the thermal history and then allowed to cool from 250°C to 30°C at the rate of 10°C min^{-1} under N_2 atmosphere to get the crystallization temperature. Finally the samples were reheated from 30°C to 250°C at the rate of 10°C min^{-1} to get the melting point.

3.2.4 Fourier Transform Infrared Spectroscopy (FTIR)

The FT-IR spectra of organoclays and nanocomposites film were obtained using a Nicolet Nexus 670 FT-IR spectrometer in the frequency range of 4000-400 cm^{-1} with 32 scans at a resolution of 2 cm^{-1}. KBr pellet technique was applied in the preparation of samples. Intercalation of alkylammonium cationic surfactant into silicate clay layers is investigated by using FTIR.

3.2.5 Instron Universal Testing Machine

Tensile properties were measured as per ASTM-D-638 with cross-head speed of 50 mm/min by using an Instron 4206 Universal Testing Machine. The

sample size was prepared according to ASTM-D-638 type I. The data reported were the average of five tests of the same test for each composition.

3.2.6 Impact Tester

The notched izod impact strength of the specimens was measured by using Zwick Impact Tester with 2.70 J hammer according to ASTM-D-256. The data reported were the average of five tests of the same test for each composition.

3.2.7 Twin Screw Extruder

PP/ Clay nanocomposites were prepared using a Model T-20 co-rotating twin-screw extruder (Collin) with L/D=30 and D=25 mm. The operating temperatures of extruder were maintained at 80, 160, 170, 180, 190, and 200°C from hopper to die, respectively. The screw speed was maintained at 50 rpm.

3.2.8 Injection Molding

Tensile (ASTM D638 type I) and Izod (ASTM D256) specimens were prepared by injection molding using an Arburg Allrounder 270M-350-90 injection molding machine using a barrel temperature of 160/170/180/190/200°C, mold temperature of 45°C, injection pressure of 1000 bar.

3.2.9 Compression Molding Machine

Polymer nanocomposites thin films of 2 mm. thick were prepared by a Wabash V50 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 10 tons after that the mold was cooled at 50°C under pressure.

3.3 Methodology

3.3.1 Preparation of Organomodified Bentonite and Montmorillonite

In a container, 10 g of Na-BN or Na-MMT was swelled in 300 ml of water/ethanol (4/1, v/v) solution for 24 h, and in another container, alkylammonium

(1.5 times of the exchange capacity) was dissolved in 200 ml of water/ethanol (1/1, v/v) solution at 80°C for 30 min. Then, the solutions of two containers were mixed together and the mixture was vigorously stirred for 2 h at 80°C follow by homogenizer stirred for 20 min at 80°C. The resulting organoclays were filtered and washed with the water and ethanol for several times to remove excess salts. After the product was dried at 100°C in vacuum for 24 h, it was ground into powder, and finally screened through a 325 meshes sieve.

3.3.2 Characterization of Organomodified Bentonite and Montmorillonite

The change of interlayer distance was measured by wide-angle X-ray Diffractometer (WAXD, D/MAX2200, Rigaku) The X-ray beam was nickel-filtered Cu K-alpha1 (λ = 0.154 nm) radiation operated at a tube voltage of 40 kV and tube current of 30 mA. The scanning range was 2θ = 1.2-20° with a rate of 2° min^{-1}. To calculate the exchanged content of surfactant; Thermo Gravimetric Analysis (TGA), was carried out from 50°C to 900°C at a heating rate of 10°C min^{-1} in the nitrogen atmosphere of 80 ml min^{-i}. Infrared spectra (IR) of organoclays were obtained using a Nicolet Nexus 670 FT-IR spectrometer by standard KBr disk method.

3.3.3 Preparation of PP/ Clay Nanocomposites

The three components of 3 wt% organoclays, PP, and Surlyn® ionomer with the designed contents were dry-mixed by shaking them in an internal-mixer. PP/Clay nanocomposites were prepared using a Model T-20 corotating twin-screw extruder (Collin) with L/D=30 and D=25 mm. The operating temperatures of extruder were maintained at 80, 160, 170, 180, 190, and 200°C from hopper to die, respectively. The screw speed was maintained at 50 rpm. Surlyn® materials were dried in a vacuum oven at 65°C for a minimum of 48 hours prior to compounding while the organoclays were predried in vacuum oven at 80°C for 2h to remove the absorbed moisture. The mixture was melt-blended to yield strands of the nanocomposites. The obtained strands were palletized and dried under vacuum at 80^0C. Resulting nanocomposites and virgin polypropylene were molded separately into sheets in compression molding machine for 10 min. at 200°C for material property evaluation. Tensile (ASTM D638) and Izod (ASTM D256) specimens were

prepared by injection molding using an Arburg Allrounder 270M-350-90 injection molding machine using a barrel temperature of 200°C, mold temperature of 45°C, injection pressure of 1000 bar. After molding, the samples were immediately sealed in a polyethylene bag and placed in a vacuum desiccator for a minimum of 24 h prior to testing.

3.3.4 Characterization of Nanocomposites

The change of interlayer distance was measured by small angle X-ray diffraction (SAX, Bruker AXS Model D8 Discover) with Cu K_α radiation operated at 40 kV and 40 mA. The experiment was performed in the 2θ range of 0.2-10 degrees with scan speed 1 sec/step and scan step 0.02 degree. Wide-angle X-ray Diffracto-meter was performed by D/MAX2002, Rigaku in order to investigate the crystal structure of PP matrix. The X-ray beam was nickel-filtered Cu K-alpha1 (λ = 0.154 nm) radiation operated at a tube voltage of 40 kV and tube current of 30 mA. The scanning range was 2θ = 10-40 degrees with a rate of 2° min^{-1}.

Thermogravimetric Analysis (Perkin-Elmer Pyris Diamond TG/DTA) was carried out from 30°C to 900°C at a heating rate of 10°C min^{-1} in the nitrogen atmosphere of 200 ml min^{-1}. The initial degradation temperature, weight loss and final degradation temperature of the samples were measured.

Melting point and crystallization temperature of the nanocomposites as well as virgin PP were carried out by Differential Scanning Calorimeter (Perkin Elmer-DSC-7). The sample was heated from room 30°C to 250°C at the rate of 10°C min^{-1} in order to remove the thermal history and then allowed to cool from 250°C to 30°C at the rate of 10°C min^{-1} under N_2 atmosphere to get the crystallization temperature. Finally the samples were reheated from 30°C to 250°C at the rate of 10°C min^{-1} to get the melting point.

Tensile tests were performed at room temperature according to ASTM D638 using an Instron model 4206 with digital data acquisition. Yield strength and strain at break were measured using an extensometer at a crosshead speed of 50 mm/min. Notch Izod impact tests were performed by using Zwick Impact Tester with 2.70 J hammer at room temperature. Standard notches were made according to ASTM-D-256 while sharp notches were made by tapping a razor blade

into the center of the machined standard notch. The data reported from five specimens were averaged to determine mechanical properties.