

CHAPTER III EXPERIMENTAL

3.1 Materials

Commercial sodium activated bentonite Mac-Gel[®] (GRADE SAC), Na-BTN, with cationic exchange capacitor (CEC) of 50 meq/100 g clay, was supplied by Thai Nippon Co., Ltd. Thailand.

Methyl di-[(partially hydrogenated) tallow carboxyethyl]-2-dihydroxyethyl ammonium methyl sulfate (DOEM) under trade name Stepantex VP-85 shown in Figure 3.1 was received from Union Carbide Co., Ltd.

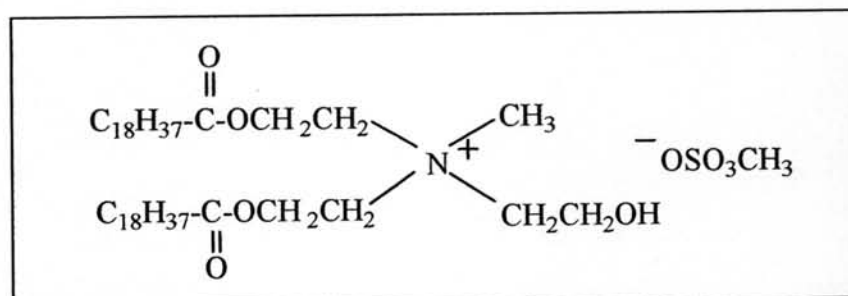


Figure 3.1 Chemical structure of DOEM.

Polypropylene (Moplen HP 400H, MFI of 2.1 g/10min at 200°C, 2.16 kg load cell) was purchased from HMC Polymer Co., Ltd.

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

Bromothymol blue (C₂₇H₂₈Br₂O₅S, MW 624.41) and bromocresol purple (C₂₁H₁₆Br₂O₅S, MW 540.24) were purchased from Labchem Chemical Co., Ltd.

The milk was obtained from CP-Meiji Co., Ltd. and tested 2 weeks before the expired date.

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)

The samples were analyzed by TGA using a Perkin-Elmer Pyris Diamond TG/DTA instrument under N_2 flow of 200 ml/min. The heating process was conducted from 30-900°C at a rate of 10°C/min.

3.2.3 Differential Scanning Calorimeter (DSC)

The crystallization and melting behaviors of the PP/organoclay nanocomposites were measured with a Perkin-Elmer DSC 7 analyzer. The heat flow and temperature of the instrument were calibrated with standard material, indium. Nitrogen was consistently purged into the equipment during the scan to prevent specimens from thermal degradation. During the crystallization experiment, the specimens were first melted at 200°C, and then cooled to room temperature at 10°C/min rate. The specimens were subsequently heated at 10°C/min for the corresponding melting behavior investigations.

3.2.4 Fourier Transform Infrared Spectrometer (FT-IR)

The FT-IR spectra of organoclay and nanocomposite film samples were collected by using a Nicolet Nexus 670 FT-IR spectrometer over a wave number range of 4,000-400 cm^{-1} with 32 scans at a resolution of 2 cm^{-1} .

3.2.5 Instron Universal Testing Machine

Mechanical properties test followed ASTM D 638 type I using Instron Universal Testing Machine model 4206. The dumbbell specimens prepared by injection molding machine were 3.9 mm wide and 10.4 mm thick. The tests were carried out at room temperature using crosshead speed of 50 mm/min and the load cell of 100 kN. The mean values were obtained from at least 5 separated tests.

3.2.6 Chroma Meter

The color changes of the indicator were measured through the lid with a Chroma Meter (ColorFlex[®] CX1034) and expressed as Hunter system (*L*, *a*, and *b*) values and total color difference (TCD).

3.2.7 Twin Screw Extruder

PP/organoclay nanocomposites were prepared by Colin D-8017 T20 twin screw extruder with L/D ratio of 30 and 25-mm-diameter. The operating temperatures were maintained at 80/160/180/190/200/210°C from feed to die with screw speed of 50 rpm.

3.2.9 Compression Molding Machine

PP/organoclay nanocomposites thin films were prepared by a Wabash V50H 50 ton compression molding machine. The mold containing the pellets was preheated at 200°C for 5 minutes, and then compressed under 10 tons of force for 5 minutes. After that the molding was cooling at 50°C under pressure.

3.2.10 Injection Molding Machine

Tensile (ASTM D 638) and Izod Impact (ASTM D 256) specimens were prepared by an Arburg Allrounder 270M-350-90 injection molding machine. The barrel temperature profiles were 200/190/180/170/160°C with injection pressure of 1,000 bar.

3.2.11 Centrifugal Ball Mill

Dried sediments were ground by FRITSCH Peluerisette 6 Centrifugal Ball Mill with rotational speed of 450 rpm in forward and reverse milling directions for 1 hr. The particle size of the powder was less than 44 μm.

3.2.12 UV-Vis Spectrometer

The indicator dyes were dissolved in water to prepare the standard solution of 1, 2, 5 and 10 ppm. The absorbance at 609 nm of the indicator dye standard solutions was observed by UV-vis spectroscopy (SHIMADZU model UV-2550) with medium scan rate and sampling the data every 1 nm.

3.3 Methodology

3.3.1 Preparation of Organomodified Bentonite

350 g of Na-bentonite, (Mac-Gel[®] GRADE SAC) supplied by Thai Nippon Co., Ltd. Thailand, was swollen in water 1.05 liter for 24 hr. DOEM _g as an alkyl ammonium ion (1.5CEC) was dissolved in the mixture of water and methanol (1:1 v/v) 1500 ml. The whole swollen clay was then mixed with DOEM solution with vigorous stirring for 2 hr at 80°C. After that the mixture was homogenized stirring for 20 min at 80°C. The sediment was filtrated and washed with hot water several times to remove to excess salts. It was dried in a vacuum oven at 100 °C overnight and ground into powder using centrifugal ball mill (FRITSCH Peluerisette 6) before being screened through a mesh #325.

3.3.2 Characterizations of Organomodified Bentonite

The variations of the interlayer spacing of Na-BTN and organobentonite were studied by wide-angle X-ray scattering. The thermal stability was determined by thermogravimetric analysis. The intercalation of the cationic surfactant was studied using infrared spectra collected using an FTIR spectrometer.

3.3.3 Preparation of PP/Organoclay Nanocomposites

The polypropylene nanocomposites were prepared as a two-step compounding process. First, polypropylene was blending with 6%wt of compatibilizer, Surlyn[®] using twin screw extruder as a masterbatch. The organoclay and the master batch were dried in a vacuum oven at 80°C for 12 h for moisture removal. Then, PP masterbatch was first dried-mixing with organoclay in tumble mixer for 30 min, then melt compounding using a twin screw extruder.

For polypropylene nanocomposites with indicator dye, bromothymol blue (BMB) and bromocresol purple (BP), the organoclay and indicator dye

were mixed in the weight ratio of 10:1, then the mixture was incorporated into the PP masterbatch at 3% by weight.

3.3.4 Characterizations of PP/Organoclay Nanocomposites

The clay contents of the nanocomposites were measured by burning the sample in a Thermogravimetric Analyzer.

Crystallization and melting behavior of PP changed with the addition of the organoclay were investigated by Differential Scanning Calorimeter (DSC).

After being dried, the pellets of the nanocomposites were injection molded into test pieces for the mechanical tests by injection molder. The temperature of the cylinders was 200°C and that of the mold was 40°C.

The tensile tests were conducted according to ASTM D638 using an Instron model 4206 machine. Modulus was measured using extensometer at a cross-head speed at 50 mm/min. The data were taken at room temperature without preconditioning of the samples.

3.3.5 Evaluation of PP/Organoclay Nanocomposites with Indicator Dye

The degree of spoilage of fresh milk was assessed for titratable acidity (TA), which was compared with Hunter color values of the indicators. Color changes of the indicator were measured through the lid with a Chroma Meter and expressed as Hunter system (L , a and b) values and total color difference (TCD). The TCD value (ΔE) was calculated by the following equation (Francis, 1983):

$$\Delta E = \left[(\Delta L)^2 + (\Delta a)^2 + (\Delta b)^2 \right]^{1/2} \quad (1)$$

Here, ΔL is the brightness difference between sample and target, Δa the redness difference between sample and target, and Δb is the yellowness difference between sample and target. The target color is (93.13, -0.96, 1.69) corresponding to (L , a , b) for white standard color in Hunter system. The TA was assessed by titrating 25 ml of the milk sample kept at difference storage times with 0.1 N NaOH solution to reach end point at pH 8.3, and converting as lactic acid content (g/l) following by equation (2):

$$\text{TA (g/l)} = \frac{\text{ml NaOH} \times \text{normality NaOH} \times \text{eq. wt of lactic acid} \times 100}{\text{Sample volume (ml)}} \quad (2)$$