

## CHAPTER III EXPERIMENTAL

### 3.1 Materials

#### 3.1.1 Clay Mineral

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

#### 3.1.2 Surfactant

Methyl di-[(partially hydrogenated) tallow carboxyethyl]-2-dihydroxyethyl ammonium methyl sulfate (DOEM) shown in figure 3.1 was received from Union Carbide Co., Ltd.

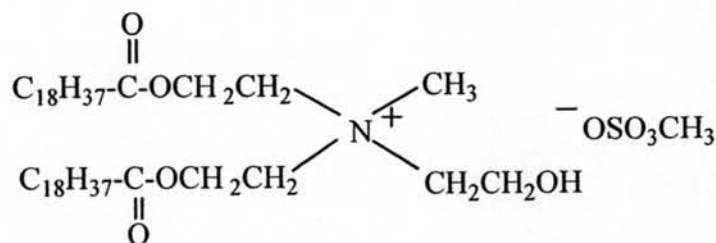


Figure 3.1 Chemical structure of DOEM.

#### 3.1.3 Polymer

Polypropylene (Polene 1126 NK, 11 MFI) was purchased from Thai Petrochemical Industry Public Co., Ltd.

#### 3.1.4 Compatibilizer

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

#### 3.1.5 Ethylene Scavenger

Aluminium hydroxide (Al(OH)<sub>3</sub>) was purchased from LabScan Asia Co., Ltd. and aluminium acetate, basic from Sigma Co., Ltd.

## 3.2 Equipment

### 3.2.1 X-ray Diffractometer (XRD)

Wide angle X-ray diffraction (WAXD) patterns of organomodified bentonite were obtained using a Rigaku Model Dmax 2002 diffractometer with Ni-filtered Cu  $K_{\alpha}$  radiation operated at 40 kV and 30 mA. The experiment was performed in the  $2\theta$  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  $K_{\alpha}$  radiation operated at 40 kV and 40 mA. The experiment was performed in the  $2\theta$  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 30-800°C at a rate of 10°C/min.

### 3.2.3 Differential Scanning Calorimeter (DSC)

The crystallization and melting behaviors of the PP/organomodified bentonite 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 250 °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 organomodified bentonite 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 Lloyd Universal Testing Machine

Tensile test of PP/organomodified bentonite nanocomposites films samples operated according to ASTM D 882 was carried out by Lloyd Universal Testing Machine. The specimen dimension is 10x100 mm. Crosshead speed is 50 mm/min

### 3.2.6 Surface Area Analyser (SAA)

The surface area of clay mineral was observed by using Thermo Finnigan, Sotomatic 1990 from Quanta Chrom Company.

### 3.2.7 Atomic Adsorption Spectroscopy (AAS)

The nanocomposite films were heat at 400 °C. The residual was digested by hydrofluoric acid (HF) to prepare the sample solution the analyzed by using Varian, StractAA 300.

### 3.2.8 Gas Chromatography (GC)

The ethylene adsorption capacity of the clay mineral was determined by using Agilent Technologies 6890 N GC system. The used condition, initial temperature is 150 °C and holding time is 10 minute.

### 3.2.9 Scanning Electron Microscope

The dispersion of organomodified bentonite in polymer matrix was determined by using SEM (JEOL/JEM 5800 LV).

### 3.2.10 Twin Screw Extruder

PP/organomodified bentonite 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 80/170/180/190/200/210°C with screw speed of 50 rpm.

### 3.2.11 Blow Film Extrusion Machine

PP/organomodified bentonite nanocomposite films were prepared by blow film extrusion machine at Tang Packaging Co., Ltd. The screw speed was 50 rpm, screw diameter was 45 mm, L/D was 26 and the processing temperature was 210 °C

### 3.2.12 Gas Permeability Testing

Ethylene gas permeability were measured according to ASTM D1434 by using GDP/E Brugger Munchen.

### 3.2.13 Centrifugal Ball Mill

Dried organomodified bentonite were ground by FRITSCH Peluette 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  $\mu\text{m}$ .

## 3.3 Methodology

### 3.3.1 Preparation of Organomodified Bentonite

In container, 350 g of Na-bentonite was swollen in 10 L of water for 24 hr, and in another container DOEM as an alkyl ammonium ion (1.5CEC) was dissolved in 1600 ml of water/ethanol (1/1, v/v) solution. Then, the solution was heated at 80 °C until it became transparent. Then solutions of two containers were vigorously mixed for 2 hr at 80 °C 1000 rpm and homogenized at 600 rpm for 30 min. The organo-modified bentonite was filtered and washed with hot water several times. It was dried in a vacuum oven at 100 °C overnight and ground into 325 mesh under [5].

The ethylene scavenger chemicals are aluminium trihydroxide (ATH) and aluminium acetate (AlAc). Aluminium hydroxide 5, 10, and 15% wt of 3%wt organomodified bentonite in the nanocomposite were mixed with the organomodified bentonite by mechanical mixing.

### 3.3.2 Characterizations of Organomodified Bentonite

The variation of the interlayer spacing of Na-BTN and organo-bentonite 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. Surface area analyzer was used to determine the surface area of the clay mineral. The ethylene gas adsorption capacity was determined by GC.

### 3.3.3 Preparation of PP/Organomodified Bentonite Nanocomposite Films

The polypropylene nanocomposites were prepared as a two-step compounding process. First, polypropylene was blended with 6%wt of compatibilizer, Surlyn<sup>®</sup> using twin screw extruder as a masterbatch. The organomodified bentonite 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 1, 3, 5 and 7% wt

organomodified bentonite in tumble mixer for 30 min, and then the compounded pellet was obtained by using twin screw extruder.

For polypropylene nanocomposites with aluminium hydroxide, the amount of aluminium hydroxide which was 5%, 10% and 15% by weight of 3% organomodified bentonite then the mixture was incorporated into the PP masterbatch. The compounded pellet was use to prepared PP/organomodified bentonite nanocomposite films by the using blow film extrusion machine.

### 3.3.4 Characterizations of PP/Organomodified Bentonite Nanocomposite

#### Films

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

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

The tensile tests were conducted according to ASTM D882 using Lloyd universal testing machine. Modulus was measured using extensometer at a crosshead speed at 50 mm/min, load cell 500 N. The data were taken at room temperature without preconditioning of the samples.

The gas permeability constants of PP/organobentonite nanocomposite films were determined by using ethylene gas.

The dispersion of organomodified bentonite in PP/organobentonite nanocomposite films were observed by SEM and TEM.