



## CHAPTER III EXPERIMENTAL

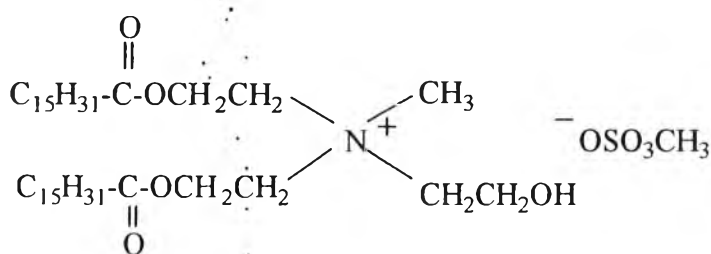
### 3.1 Materials

#### 3.1.1 Clay Mineral

Commercial sodium activated bentonite Mac-Gel<sup>®</sup> (GRADE SAC), Na-BTN, with cationic exchange capacitor (CEC) of 44.5 meq/100 g clay, was supplied by Thai Nippon Co., Ltd. Thailand.

#### 3.1.2 Surfactant

Dipalmitoylethyl Hydroxyethylmonium Methosulfate (Stepantex<sup>™</sup> SP-90) shown in figure 3.1 was received from Sunny World Co., Ltd.



**Figure 3.1** Chemical structure of Stepantex<sup>™</sup> SP-90

#### 3.1.3 Polymer

Polypropylene (Polene 1126 NK, 11 MFI dg/min) was purchased from Thai Petrochemical Industry Public Co., Ltd or IRPC Co., Ltd.

#### 3.1.4 Compatibilizer

Sodium-neutralized ethylene-co-methacrylic acid (Surlyn<sup>®</sup> PC350, 4.5 MFI dg/min) 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.

#### 3.1.6 Carbon Dioxide Scavenger

Calcium hydroxide (Ca(OH)<sub>2</sub>) was purchased from ACS Xenon Limited Partnership under trade name Fluka.

### 3.1.7 Solvent

Ethanol (C<sub>2</sub>H<sub>5</sub>OH) 98% v/v, AR, 2.5 L was purchased from Carlo Erba Reagent

### 3.1.8 Silane

3-aminopropyltrimethoxysilane was purchased from ACS Xenon Limited Partnership with trade name Fluka.

## 3.2 **Equipment**

### 3.2.1 X-ray Diffractometer (XRD)

X-ray diffraction (XRD) patterns of organomodified-BTN were obtained from a Rigaku Model Dmax 2002 diffractometer with Ni-filtered Cu K<sub>α</sub> ( $\lambda = 0.154$  nm) radiation operated at 40 kV and a tube current of 30 mA. The organoclay powder samples were measured in the  $2\theta$  range of 2-20 degrees with scan speed 2 degree/min and scan step 0.01 degree. For the nanocomposite film samples, the experiment was performed on a 2-40 degrees with scan speed 5 degrees/min and scan step 0.02 degree.

### 3.2.2 Thermogravimetric Analysis (TGA)

Thermal properties of specimens were investigated using TGA from Perkin-Elmer Pyris Diamond TG/DTA instrument under N<sub>2</sub> flow of 200 ml/min. The degradation temperature, initial degradation temperature, weight loss, and final degradation temperature of the samples were determined. The samples were loaded on platinum pan, which heating process was conducted from 30-900°C at a rate of 10°C/min and samples.

### 3.2.3 Differential Scanning Calorimeter (DSC)

The crystallization and melting behaviors of the PP/organoclay nanocomposites are measured from a Perkin-Elmer DSC 7 analyzer. The heat flow and temperature of the instrument are calibrated by indium which is a standard material. Nitrogen is consistently purged within the equipment to prevent specimens from thermal degradation. The specimens are first melted at 200°C, then, cooled down to 30°C at 10°C/min rate and they are subsequently heated at 10°C/min to 200°C for

the corresponding melting behavior investigations. The crystallinity of samples were calculated by this equation,

$$\%Crystallinity = \frac{\Delta H_{sample}}{\Delta H_{PP}^0} \times 100$$

where,  $\Delta H_{sample}$  = enthalpy of fusion of the sample (J/g)

$\Delta H_{PP}^0$  = enthalpy of fusion of completely crystalline PP (~ 209 J/g)

#### 3.2.4 Fourier Transform Infrared Spectrometer (FT-IR)

The FT-IR spectra of organoclay samples were collected from a Nicolet Nexus 670 FT-IR spectrometer with a wave number between 4,000-500  $\text{cm}^{-1}$  and 32 scans at a resolution of 2  $\text{cm}^{-1}$ . The samples were prepared with KBr pellets technique to observed the presence of alkylammonium cationic surfactant from clay layers.

#### 3.2.5 Lloyd Universal Testing Machine

Tensile test of PP/organoclay nanocomposites films were operated as ASTM D 882 with Lloyd Universal Testing Machine. The specimens were prepared by compression machine with thickness around 0.2 mm and cut into rectangular shape with 10x100mm. The crosshead speed was 50mm/min and the load cell was 500N

#### 3.2.6 Gas Chromatography (GC)

The ethylene adsorption capacity of the clay mineral was determined using Agilent Technologies 6890 N GC , with HP-PLOT Q column: 30 m x 0.32 mm ID and 20  $\mu\text{m}$  film thicknesses. A detector was FID type with He as the carrier gas. The initial temperature was 150  $^{\circ}\text{C}$ , and holding time was 10 minutes.

#### 3.2.7 Scannig Electron Microscope (SEM)

The dispersion of clay particles in the PP matrix was investigated by scanning electron microscopy using JEOL/JSM-5410 LV Model. The selected specimens, which were nanocomposite and PP pellets, were dipped and fractured in liquid nitrogen. Then, the specimens were coated with gold under vacuum to make them electrically conductive before viewing under a scanning electron microscope (SEM) operating at 15 kV.

### 3.2.8 Gas Permeability Testing

Oxygen permeability of nanocomposite films were measured according to ASTM D1434 by Oxygen Permeation Analyser Model 8000, Illinois Instrument Inc. , at 23°C with flow rate of N<sub>2</sub> 23 cc/min and O<sub>2</sub> 50 cc/min. The films were prepared from a compression-molded sheet with the same thickness of 150 μm and were cut into circular shape with 15 cm in diameter. The thickness of the films was measured by using the peacock digital thickness gauge model PDN 12N by reading 15 points at random position over tested area and the results were averaged.

### 3.2.9 Compression Molding Machine

PP/organomodified-BTN nanocomposites films were prepared using a Wabash V50H 50 ton compression molding machine. The sample pellets were preheated at 200°C for 5 min. Then, they were compressed under 10 tons for 10 minutes. After that, the molding was cooled to room temperature under the same pressure. These films were used to investigate oxygen permeability with 15 cm of circle and the thickness about 0.2 mm, and cut into rectangular shape with 2x2 cm for XRD analyzing.

### 3.2.10 Blow Film Extrusion Machine

PP/organomodified-BTN nanocomposites films are prepared by blow film extrusion machine at Tang Packaging Co., Ltd with screw speed 50 rpm, die diameter of 150 mm, screw diameter 45 mm, L/D ratio 26, at 210°C.

### 3.2.11 Centrifugal Ball Mill

FRITSCH Peluerisette 6 Centrifugal Ball Mill was used for grinding the dried organomodified-BTN into fine power with rotational speed of 450 rpm in forward and reverse milling directions for 20 min. The particle size of the power was less than 44 μm.

### 3.2.12 Twin Screw Extruder

PP/organoclay nanocomposites pallets were prepared by Colin D-8017, model T-20 corotating twin screw extruder with L/D ratio of 30 and with diameter 25mm. The operating temperatures were performed at 80/160/180/190/200/210°C from hopper to die, respectively. The screw speed was 50 rpm. The pellet samples were analyzed by TGA, DSC, and SEM.

### 3.3 Methodology

#### 3.3.1 Preparation of Organobentonite

350 g of Na-BTN was swollen in water for 24 hr. Alkyl ammonium ion (Stepantex<sup>TM</sup> SP-90, 2.0 CEC) is dissolved in ethanol at 70°C for 30 min. The swollen clay and alkyl ammonium ion solution are mixed together at 80°C for 1 hr with vigorously stirring, and follow by homogenized at 80°C for 2 hrs. After that, the mixture was filtrated and washed with hot water several times to remove the excess of surfactant. Then, it was dried in a vacuum oven at 100°C overnight, and ground into fine powder by centrifugal ball mill. After that, it was screened through a sieve, # 325 mesh. The ground powder was stirred within the solution of ethanol and water (75:25) for 2 hrs. Then, 3-aminopropyl trimethoxysilane is added into the system and refluxed at 70°C for 24 hrs. The organoclay is purified by washing several times to eliminate the physisorbed silane and than dried in the oven. The ethylene scavenger is aluminium hydroxide, and carbondioxide scavenger is calcium hydroxide. It was mixed with the organomodified bentonite by mechanical mixing.

#### 3.3.2 Characterizations of Organobentonite

The basal spacing of Na-BTN and organomodified bentonite were studied by X-ray diffraction (XRD). The intercalation of surfactant inside silica clay layer was studied using fourier transform infrared spectrometer (FT-IR). The thermal stability was observed by thermogravimetric analysis (TGA).

#### 3.3.3 Preparation of PP/Organobentonite Nanocomposite Films

The master batches containing 50 wt% organomodified clays with compatibilizer, Surlyn<sup>®</sup>, were firstly prepared by a Model T-20 co-rotating twin-screw extruder (Collin) with L/D=30 and D=25 mm. The operating temperatures of extruder were performed at 80, 170, 180, 190, 200, and 210°C from hopper to die, respectively, with 50 rpm of screw speed. Then, the master batch was compound with PP and Surlyn<sup>®</sup> in various contents to obtained 1%, 3%, and 5% wt of organoclay nanocomposites pellets. The compatibilizer was fixed with 6 wt%. Each composition was dried in a vacuum oven at 80°C for 12 h for moisture removal and then premixed by a tumble mixer for 10 min and used a Model T-20 co-rotating twin-screw extruder

(Collin) with  $L/D=30$  and  $D=25$  mm. The operating temperatures of extruder were performed at 80, 170, 180, 190, 200, and 210°C from hopper to die, respectively, with 50 rpm of screw speed. After that, these nanocomposites pellets were dried under vacuum at 80°C for 12 hr and fabricated into the nanocomposite packaging film by tubular blown film extrusion process. The screw speed was 50 rpm, screw diameter was 45 mm,  $L/D$  was 26 and the processing temperature were 210°C from hopper to die. The thickness of the films was controlled about 45  $\mu\text{m}$ .

#### 3.3.4 Characterizations of PP/Organobentonite Nanocomposite Films

The XRD patterns were used for investigate the crystal structure of PP and nanocomposites films.

The clay contents of the nanocomposite films are determined by Thermogravimetric Analysis (TGA). Moreover, crystallization and melting behavior of PP that incorporate with organoclay are investigated by Differential Scanning Calorimeter (DSC).

The tensile tests was conducted as ASTM D882 with Lloyd universal testing machine. The experiments are taken under room temperature without preconditioning of the samples.

The gas permeability constants of PP/organobentonite nanocomposite films were investigated using oxygen gas using gas permeability tester.

The dispersion of organomodified-BTN in PP/organobentonite nanocomposite films were observed by SEM.