



## CHAPTER III METHODOLOGY

### 3.1 Materials

#### 3.1.1. Polymer Chemicals

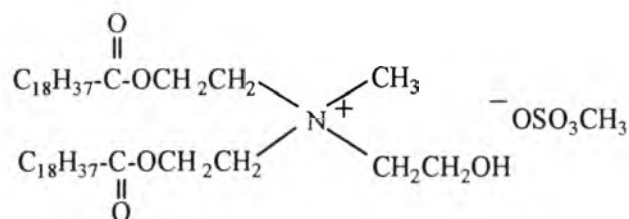
Polypropylene (MFI 11 dg/min) was obtained from IRPC Co., Ltd. Thailand under trade name polypropylene NK1126.

#### 3.1.2. Clay

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.

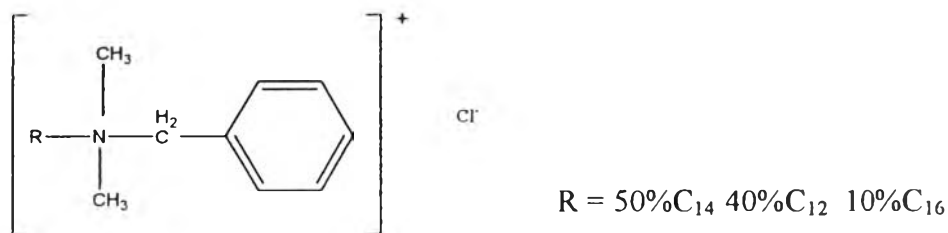
#### 3.1.3. Surfactants

3.1.3.1 *Methyl di-[(partially hydrogenated) tallow carboxyethyl]-2-Dihydroxyethyl Ammonium Methyl Sulfate (DOEM)* shown in Figure 3.1 was received from Union Compound Co., Ltd.



**Figure 3.1** Structure of DOEM

3.1.3.2 *N-alkyl Dimethyl Ammonium Chloride (BTC 8358<sup>®</sup>)* was obtained from Sunny World Co., Ltd.



**Figure 3.2** Structure of BTC 8358<sup>®</sup>

### 3.1.4. Compatibilizers

Polypropylene grafted maleic anhydride (PP-g-MAH), Polybond®3200 (1 wt% MA grafted level) was purchased from Chemtula Co., Ltd. Thailand

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

### 3.1.5. Dyes

The following dyes were used in the study of dyeability of polypropylene organoclay fibers

- 1) *Acid dye : Lanaset Red 2B* from Ciba Co., Ltd.
- 2) *Basic dye : Maxilon Red GRL 200%* from Ciba Co., Ltd.
- 3) *Disperse dye : Terasil Red SD* from Ciba Co., Ltd.
- 4) *Direct dye : Erionyl Red A-2BF* from Ciba Co., Ltd.

## 3.2 **Equipment**

### 3.2.1 X-ray Diffractometer (XRD)

X-ray diffractometer (XRD) was used to observe the d-value of organoclay and to investigate the crystal structure of fiber nanocomposites. X-ray diffraction patterns were measured on a Rigaku Model Dmax 2002 diffractometer with Ni-filtered Cu K<sub>α</sub> radiation operated at 40 kV and 30 mA. The powder samples were observed on the 2θ range of 1.5-20 degree with scan speed 2 degree/min and scan step 0.02 degree. The crystal size can be determined by the Scherrer equation

$$L = K\lambda/B\cos\theta$$

Where L = average crystal size

K = full width at half maximum of the peak

### 3.2.2 Thermogravimetric Analysis (TGA)

The samples were analyzed by TGA using a Perkin-Elmer Pyris Diamond TG/DTA instrument under N<sub>2</sub> flow of 200 ml/min. The heating process was conducted from 30-700°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. The crystallinity can be calculated with the following formula

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

$\Delta H$  = enthalpy of fusion of the sample (J/g)

$\Delta H$  = enthalpy of fusion of completely crystalline PP (~ 209 J/g) [15]

### 3.2.4 Twin Screw Extruder

PP/organoclay nanocomposites were prepared by Collin 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 with screw speed of 50 rpm.

### 3.2.5 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.

### 3.2.6 UV-Visible spectrophotometer (Shimadzu)

Dye solutions from the dye baths before and after dyeing process were used to determine the content of % dye exhaustion by UV-Visible absorption. For the acid, basic direct, and disperse dyes, the absorbance were measure at wave-

length 525, 530, 500, and 490 nm respectively ( these are  $\lambda_{\max}$  of acid, basic, direct, and disperse dye) respectively.

$$\% \text{ Dye exhaustion} = \frac{(C_f - C_i)}{C_i} \times 100$$

Where  $C_i$  = concentration of dye solution before dyeing process

$C_f$  = concentration of dye solution after dyeing process

The color intensity of fiber (measure of dye absorption) was measured by reflectance mode of UV-Visible Absorption. K/S (absorption to scattering coefficient) values of dyed samples were calculated by the measuring their reflectance (R) in visible spectrum (200-800 nm).

$$K/S = (1-R)^2/2R$$

Where K/S = absorption to scattering coefficient

R = reflectance

### 3.2.7 Chroma Meter

The color of the dyed samples were measured with a Chroma Meter (ColorFlex<sup>®</sup> CX1034) and expressed as Hunter system (*L, a, and b*). The color intensity was represent by the following parameters and equation.

$$\Delta E = \sqrt{\Delta L^{2*} + \Delta a^{2*} + \Delta b^{2*}}$$

$\Delta E$  = The difference in color (Eab) between any two points in the color space

$\Delta L^*$  = The brightness difference between sample and control sample

$\Delta a^*$  = The redness difference between sample and control sample

$\Delta b^*$  = The yellowness difference between sample and control sample

### 3.2.8 Melt spinning machine

Polypropylene–organoclay nanocomposite fiber was prepared by melt spinning machine (see Figure 3.1). The as-spun filament was collected at a take up speed of 1 mm/min and draw at 190 °C. The fiber was drawn with different speed 15.3, 26.5, 36.6, and 47.6 m/min, see Table 3.1.

**Table 3.1** Draw ratio of fiber

Roller speed (m/min)	Draw ratio*
15.3	$15.3 \times 10^3$
26.5	$26.5 \times 10^3$
36.6	$36.6 \times 10^3$
47.6	$47.6 \times 10^3$

\*Draw ratio = Roller speed/Extruded speed

Extruder speed = 1 mm/min

### 3.2.9 Dyeing machine DAELIM Starlet model DL-6000

Fibers were dyed with acid, basic, disperse, and direct dye. Sample was put into the dye pot and placed in dyeing machine (DAELIM Starlet model DL-6000). Dye bath temperature was raised to 50 °C 30 minutes and then to 100 °C. Temperature was kept constant at 100 °C for 60 min. Then, temperature was decreased to 50 °C. Fiber was washed with water for 30 min at room temperature and wash with tap water for 1 min.

### 3.2.10 Universal Testing Machine

Polypropylene-organoclay nanocomposite fibers were tested mechanical properties with Lloyd Universal Testing 4206 by follow procedure outline in ASTM D3822-01. Crosshead speed of 270 mm/min was used. Linear density of polypropylene fibers were ranged from  $1.85 \times 10^5$  to  $6.58 \times 10^6$  tex depended on draw ratio from  $15.3 \times 10^3$  to  $47.6 \times 10^3$ . The gauge length was 20 mm. Results were obtained from an average of ten samples.

### 3.2.11 Fourier Transform Infrared Spectroscopy (FT-IR)

FT-IR spectra of PP and modified PP fiber were obtained using a Nicolet Nexus 670 FT-IR spectrometer in the frequency range of  $4000-400 \text{ cm}^{-1}$  with 128 scans at a resolution of  $4 \text{ cm}^{-1}$ . The spectra were recorded with the polarization

radiation parallel and perpendicular to the draw direction to investigate the orientation of the fibers. The dichroic ratio and angle of orientation were calculated from the following equations.

$$\text{Dichroic ratio } D = A_{\parallel}/A_{\perp}$$

where  $A_{\parallel}$  = Intensity of light polarized parallel to fiber axis after passing through the material

$A_{\perp}$  = Intensity of light polarized perpendicular to fiber axis after passing through the material

$$D_0 = 2 \cot^2 \alpha$$

where  $D_0$  = the value of the dichroic ratio corresponding to a perfectly oriented sample

$\alpha$  = angle between the transition moment of vibration of this group and the axis of the polymer chain

$$f = \overline{(3 \cos^2 \theta - 1)} / 2$$

where  $f$  = Herman Orientation Function

### 3.2.12 Scanning Electron Microscope (SEM)

Scanning electron microscope on (JEOL JSM-6400 scanning electron microscope (SEM)) was used to study the surface morphology of the obtained fiber and the Si species were identified by LINK ISIS series 300 for energy dispersive X-ray (EDX) analysis.

### 3.2.13 Scanning Probe Microscope

Scanning probe microscope, Nanoscope IV scanning probe microscope, by silicon probe with tapping mode was also used to study the surface morphology of the obtained fiber.

### 3.3 Methodology

#### 3.3.1 Preparation of Organo-Modified Clay

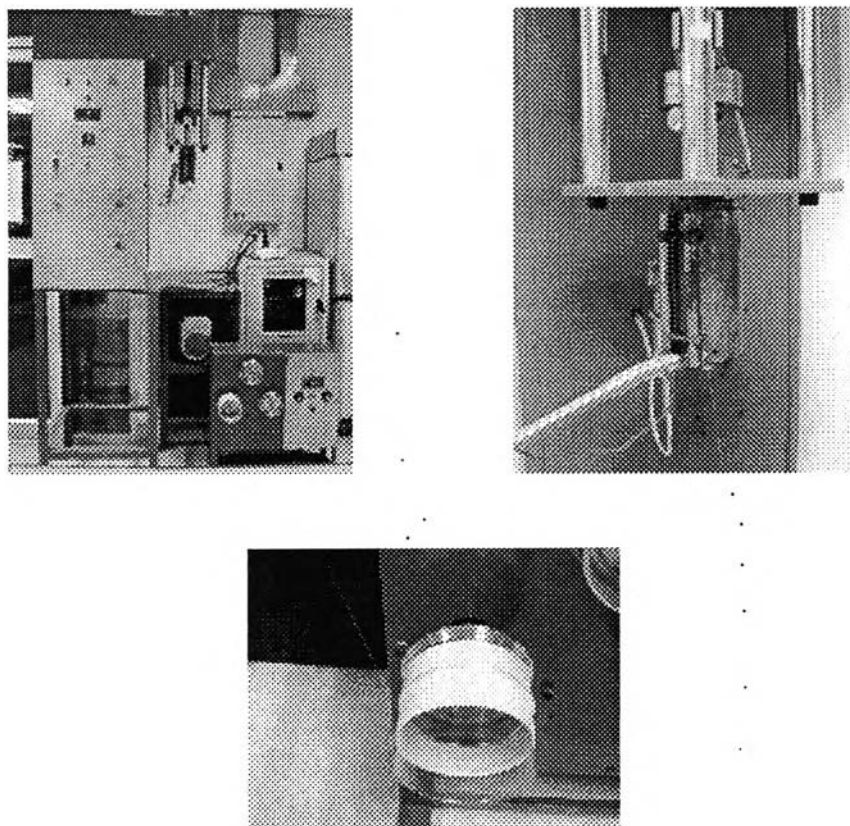
Preparation of organo-modified clay was carried out following the experiment procedure established by Sakkarin (2007). 300 g of Na-Bentonite was swollen in 1500 ml water for 24 hr. 100 g surfactant was added to 500 ml water at 80 °C for 30 min. The whole swollen clay suspension was mixed with the 500 ml surfactant solution in 5 L mixer and kept with vigorously stirring at 80 °C for 2 hr. After that the mixture was homogenized at 80 °C for 1 hr. The sediment was filtered and washed several time with hot water several times to remove the excess salts until the washed water turn from basic to neutral. The organo-modified clay was then dried in a vacuum oven at 100 °C overnight. The dried sample was ground to powder and screened through a mesh #325.

#### 3.3.2 Preparation of organo-modified clay/polypropylene nanocomposites

Preparation of organo-modified clay/polypropylene nanocomposites was carried out by following the experiment established by Sakkarin (2007). The polypropylene nanocomposites were prepared as a two-step compounding process. First, 60%wt organoclay was blended with 40%wt compatibilizers (PP-g-MAH and Surlyn<sup>®</sup>) using twin screw extruder as a masterbatch. The operating temperatures were maintained at 80/160/180/190/200/210°C with screw speed of 50 rpm. The masterbatch were dried in a vacuum oven at 80 °C for 12 hr for moisture removal. Then, the masterbatch was mixed with polypropylene pellets in a tumble dry mixer for 10 min, then the melt compounding of the premix was carried out by using a twin screw extruder to produce 3, 5, and 7 phr organoclay/polypropylene nanocomposites. The operating temperatures were maintained at 80/160/180/190/200/210°C with screw speed of 50 rpm; the extrudate strand was cooled in a water bath and palletized.

### 3.3.3 Spinning Process

Before undergo melt spinning, polypropylene and polypropylene/organoclay nanocomposites were dried in a vacuum oven for 4 hr at 80 °C to remove any moisture on the polypropylene pellets. Melt spinning was performed on a melt spinning machine (see Figure 3.3).



**Figure 3.3** Melt Spinning Machine



### 3.3.4 Dyeing Process

#### 3.3.4.1 *Acid dye*

Fiber 5 g was dyed in the 250 ml dye pot. dyeing condition is outline below. (see Table 3.2)

**Table 3.2** Dyeing condition for acid dye

Reagent	Amount	
	% o.w.f.*	Volume of solution in a 250 ml dye pot (ml)
0.4% Lanaset red 2B	2	25
10% Glauber's salt	10	5
2% Acetic acid	1	2.5
Water		267.5

material to liquor ratio 1: 50

\* o.w.f. = on weight of fiber ( the amount of reagent per mass of textile material)

\*\* Volume of solution in 250 ml dye pot can be calculated by

$$\text{No. of ml stock solution required} = \frac{WP}{C}$$

where W = weight of sample to be dyed, g

P = amount of dye or assistant to be used, % o.w.f.

C = concentration of stock solution, %

### 3.3.4.2 Basic dye

Fiber 5 g was dyed in the 250 ml dye pot, dyeing condition is outline below. (see Table 3.3)

**Table 3.3** Dyeing condition for basic dye

Reagent	Amount	
	% o.w.f.	Volume of solution in a 250 ml dye pot (ml)
0.4% Maxilon Red GRL 200%	2	25
2% Sodium acetate	10	25
2% Acetic acid	1	2.5
Water		197.5

material to liquor ratio 1: 50

### 3.3.4.3 Disperse dye

Fiber 5 g was dyed in the 250 ml dye pot, dyeing condition is outline below. (see Table 3.4)

**Table 3.4** Dyeing condition for disperse dye

Reagent	Amount	
	Concentration	Volume of solution in a 250 ml dye pot
0.4% Terasil red SD	2 % o.w.f.	25 ml
Dispersing agent	2 g/l	0.5 g
Water		225 ml

material to liquor ratio 1: 50

### 3.3.4.4 Direct dye

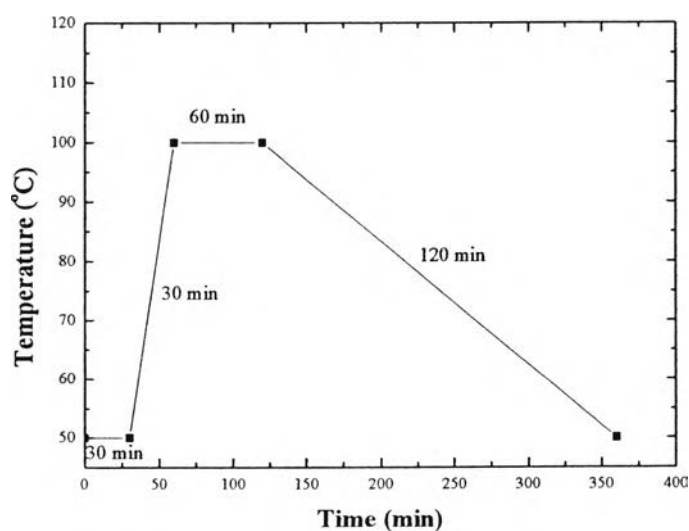
Fiber 5 g was dyed in the 250 ml dye pot, dyeing condition is outline below. (see Table 3.5)

**Table 3.5** Dyeing condition for direct dye

Reagent	Amount	
	Concentration	amount in a 250 ml dye pot
0.4% Erionyl Red A-2BF	2 % o.w.f.	25 ml
Sodium chloride	20 g/l	5 g
Water		225

material to liquor ratio 1: 50

The dyed pot was placed in dyeing machine (DAELIM Starlet model DL-6000). Temperature was raised to 50 °C 30 minutes and raised up to 100 °C. Temperature was kept constant at 100 °C for 60 min. Then, temperature was decreased to 50 °C (Fig. 3.4). Fiber was washed with water 30 min at room temperature and wash with tap water for 1 min.



**Figure 3.4** Time-temperature profile for dyeing process

### 3.3.5 Characterization of Fiber

- a. The dispersibility of organoclay in PP/organoclay was determined by X-ray Diffractometer (XRD).
- b. Crystallization behavior was investigated by Differential Scanning Calorimetry (DSC).
- c. Mechanical properties were determined by universal testing machine.
- d. Dyeing properties was analyzed by UV-visible spectrophotometry and CIE colorimetry.
- e. Surface morphology was observed by Scanning Electron Microscopy (SEM) and Scanning Probe Microscopy (SPM)