



## CHAPTER III EXPERIMENTAL

### 3.1 Materials

#### 3.1.1 Polyamide 6 (PA6)

Polyamide 6 used for the study was an injection molding grade 1013B supplied by UBE Nylon (Thailand) Ltd. The properties of polyamide 6, 1013B, are given in Table 3.1.

**Table 3.1** Properties of polyamide 6

Properties	Units	Test results
Moisture content	wt%	0.03
Relative viscosity	-	2.43
Extractable content	wt%	0.15
Amino group	$\times 10^{-5}$ eq/g	4.5
Carboxyl group	$\times 10^{-5}$ eq/g	5.8
Melting point	$^{\circ}\text{C}$	215-225

#### 3.1.2 Low-Density Polyethylene

Low-Density Polyethylene, LD 1450J, was an injection molding grade polymer, graciously supplied by Thai Polyethylene Co., Ltd. The properties of Low-Density Polyethylene, LD 1450J, are given in Table 3.2

**Table 3.2** Properties of LDPE

Properties	Units	Test results
Density	g/cm <sup>3</sup>	0.914
Melt Flow Index	g/10min	50
Melting point	°C	103
T <sub>g</sub>	°C	(-130) - (-95)

### 3.1.3 Poly(ethylene-co-methacrylic acid)

Poly(ethylene-co-methacrylic acid) copolymer marketed under the trademark Nucrel<sup>®</sup> 0903, was supplied by DuPont (Thailand). The properties of (ethylene-co-methacrylic acid), Nucrel<sup>®</sup> 0903, are given in Table 3.3.

**Table 3.3** Properties of poly(ethylene-co-methacrylic acid)

Properties	Units	Test results
Density	g/cm <sup>3</sup>	0.93
Melt Flow Index	g/10min	2.5
Melting point	°C	101
Carboxyl group	wt%	9.0

### 3.1.4 Polypropylene

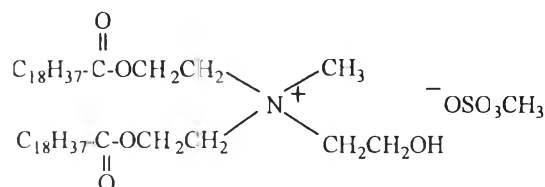
Polypropylene (MFI 11 dg/min) was obtained from IRPC Co., Ltd. Thailand, under the trade name polypropylene NK1126.

### 3.1.5 Clay

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

### 3.1.6 Surfactant

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.

### 3.1.7 Compatibilizer

Sodium-neutralized ethylene-co-methacrylic acid, Surlyn® PC350, (4.5 MFI, 15.2 wt% methacrylic acid, 1.99 wt% sodium, ~40% neutralization level), was purchased from DuPont Co., Ltd.

### 3.1.8 Dye

3.1.8.1 Acid dye : Lanaset Red 2B from Chiba Co., Ltd.

3.1.8.2 Basic dye : Maxilon Red GRL 200% from Chiba Co., Ltd.

3.1.8.3 Direct dye : Erionyl Red A-2BF from Chiba Co., Ltd.

## 3.2 Experimental

### 3.2.1 Blends of PA6/LDPE with/ without Compatibilizer

#### 3.2.1.1 *Scanning Electron Microscopy (SEM)*

A Scanning electron microscope (SEM), JEOL 5200-2AE (MP152001), was used to study phase morphologies of the blends. The specimens were fractured in liquid nitrogen and etched using (i) hot decalin (for LDPE minor phase blends) and (ii) formic acid (for PA6 minor phase blends). The specimens were then coated with gold under vacuum. All SEM images were obtained using a magnification of 1000x at 15 kV.

#### 3.2.1.2 *Dynamic Mechanical Analysis (DMA)*

A Solids Analyzer RSA II (Rheometric Scientific) was used to measure the storage and loss moduli as a function of temperature. Film geometry was used with 4°C temperature steps. Samples were molded to a thickness of around 0.5 mm. All experiments were performed with a 1 Hz frequency, 0.03% strain, and with static force tracking dynamic force.

#### 3.2.1.3 *Tensile Testing*

A D1708 microtensile die was used to cut the samples for tensile testing, and an Instron universal testing machine was used to measure the tensile strength using a crosshead speed of 1.30 mm/min. Samples were molded to a thickness of approximately 0.5 mm. At least 5 samples were used for each composition to determine the average and standard deviation.

#### 3.2.1.4 *Differential Scanning Calorimetry (DSC)*

The samples were cut from the same sheet used to cut samples for the tensile testing. For melting and glass transition temperature determination, samples were placed in aluminum DSC pans, and were scanned at a rate of 10°C/min. A TA

Instruments Q1000 differential scanning calorimeter with liquid nitrogen cooling was used for this study, and was routinely calibrated with four different standards (cyclopentane, biphenyl, indium, and tin) at a 10°C/minute heating rate. The melting characteristics of the two components were determined during this initial scan, while the glass transition temperature was determined during a second scan after the material was held at 250°C for 5 minutes and rapidly cooled to -100°C to assure good sample-pan contact and eliminate complicating enthalpy relaxation effects. The fractional crystallinity was determined by integrating the area under the respective melting exotherms, and converting these enthalpies to fractional crystallinities using a melting enthalpy of 282 J/g for polyethylene and 190 J/g for polyamide. Crystallinities were calculated by using Equation 1:

$$\chi_c = \frac{\Delta H \times 100\%}{\Delta H_f \times \text{wt. fraction}} \quad (1)$$

where  $\chi_c$  is % wt. fraction crystallinity

$\Delta H$  is melting enthalpy of the components present in the blend

$\Delta H_f$  is heat of fusion for 100% crystallinity of the pure component, (190 J/g for PA6, and 282 J/g for LDPE). [<http://web.utk.edu/~athas/databank>]

### 3.2.1.5 Dynamic Stress Rheometer

A Dynamic Stress Rheometer SR 5000 (Rheometric Scientific) was used to measure the steady shear viscosity  $\eta$  as a function of shear rate  $\dot{\gamma}$  at low shear rates. Cone and plate geometry was used with this experiment. Samples were molded to a thickness of around 0.5 mm and a plate diameter of 40 mm. All experiments were performed for 8 points of stress to get steady shear viscosity  $\eta$  as a function of shear rate  $\dot{\gamma}$ . The condition for nylon, LDPE, and EMAA was 230°C while that for the ionomers was 140°C.

### 3.2.1.6 Rheological and Extrudate Swell Measurements

A CEAST Rheologic 5000 twin-bore capillary rheometer was used to investigate the melt rheology of the as-prepared blends at high shear rates. The inner diameter and the length of the barrel used were 9.95 and 300 mm, respectively with a capillary diameter of 1 mm ( $L/D = 0.5$  and 20), and all measurements were made at 230°C. The apparent shear stress  $\tau_{app}$  is defined as:

$$\tau_{app} = \frac{R\Delta P}{2L} \quad (2)$$

R is the radius of the die,  $\Delta P$  the pressure drop across the die, and L is the length of the die; and the apparent shear rate  $\gamma_{app}$  is defined as:

$$\gamma_{app} = \frac{4Q}{\pi R^3} \quad (3)$$

Q is the volumetric flow rate. These quantities should be corrected using the procedures of Bagley and Rabinowitsch, respectively. According to these corrections, the actual shear stress is defined as:

$$\tau_{actual} = \frac{R\Delta P}{2(L + nR)} = \frac{\Delta P}{2(L/R + n)} \quad (4)$$

where n is a multiplication factor according to the Bagley correction; and the actual shear rate  $\gamma_{actual}$  is defined as

$$\gamma_{actual} = \frac{3n'+1}{4n'} \gamma_{app} \quad (5)$$

where  $n'$  is the slope from a plot (in a double logarithmic scale) between the apparent shear stress and the apparent shear rate that was fitted to the Rabinowitsch correction. According to these values, the actual shear viscosity  $\eta_{actual}$  is then defined as:

$$\eta_{actual} = \frac{\tau_{actual}}{\gamma_{actual}} \quad (6)$$

All quantities reported in this thesis have had both corrections applied.

The elongational contribution during the flow of the polymeric melt through a restricted die (i.e. converging flow) can also be evaluated using a well-known theory of Cogswell, according to which the important quantities can be summarized as follows:

$$N = \frac{\gamma_{app}}{4\gamma_{real} - 3\gamma_{app}}, \quad (7)$$

$$P_e = (\tau_{app} - \tau_{real}) \cdot \frac{4L}{D} \quad (8)$$

where  $N$  denotes an empirical constant,  $P_e$  an entry pressure, and  $D$  the inner diameter of the die. Quantities in Eqs. (7) and (8) reduce to

$$\varepsilon = \frac{4\tau_{app}}{3(N+1)P_e} \gamma_{app} \quad (9)$$

where  $\varepsilon$  is the elongational rate; and the elongational stress  $s$  can be expressed as:

$$\sigma = \frac{3(N+1)P_e}{8} \quad (10)$$

Finally, according to Eqs. (9) and (10), the elongational viscosity  $\eta_e$  is defined as:

$$\eta_e = \frac{\sigma}{\varepsilon} \quad (11)$$

Extrudate swell was measured using an attached KEYENCE VG laser analytical device, which comprises a laser light source and a light sensor. The extrudate swell ( $B$ ) is reported as in the following equation:

$$B = \frac{D_e}{D} \quad (12)$$

where  $D_e$  and  $D$  are the diameter of the extrudate and the die, respectively

### 3.2.2 Polypropylene Organoclay Nanocomposite Fiber

#### 3.2.2.1 *Thermogravimetric Analysis (TGA)*

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

#### 3.2.2.2 *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 indium. During the crystallization experiment, the specimens were first melted at 200°C, and then cooled to room temperature at 10°C/min. The specimens were subsequently heated at 10°C/min for the corresponding melting behavior investigations.

#### 3.2.2.3 *Dyeing Machine DAELIM Starlet model DL-6000*

The 5 g. fibers were dyed with acid, basic, disperse, and direct dye 250 ml. Each sample was put in the dye pot and placed in a dyeing machine (DAELIM Starlet model DL-6000). The temperature was raised to 50°C for 30 minutes and then raised to 100°C. The temperature was then kept constant at 100°C for 60 min. and was then decreased to 50°C. The fiber was washed with water for 30 min at room temperature and wash with tap water for 1 min.



#### 3.2.2.4 *Universal Testing Machine*

The polypropylene-organoclay nanocomposite fibers were tested mechanical properties with an Instron Universal Testing 4206 by follow ASTM D3822-01. The crosshead speed was 270 mm/min. The linear density of the polypropylene fibers ranged from  $1.85 \times 10^5$  to  $6.58 \times 10^6$  tex, depending on draw ratio from  $15 \times 10^3$  to  $47.6 \times 10^3$ . The gauge length was 20 mm. Each sample was tested 10 times.

#### 3.2.2.5 *UV-Visible Spectrophotometer (Shimadzu)*

The dye uptake (g/g fiber) was determined by UV-Visible spectrophotometer. The difference between the absorption of the initial and final dye solutions were reported as the dye uptake value. The initial dye concentration is 0.1 g/L.

$$\text{Dye uptake} = \text{initial dye concentration} - \text{final dye concentration}$$

#### 3.2.2.6 *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  $K_{\alpha}$  radiation operated at 40 kV and 30 mA. The powder samples were observed on the  $2\theta$  range of 1 to 40 degree with scan speed 2 degree/min and scan step 0.02 degree.

### 3.3 Methodology

#### 3.3.1 Ionomer Preparation

A 20 g. amount of EMAA was dissolved at 140°C in a 200 ml solution that contained toluene and n-butanol (3:1). A 25 ml amount of either sodium or lithium hydroxide (the concentration of the hydroxide was adjusted depending on the neutralization level desired) was added, and the system was refluxed at 140°C for 3

hours. The solvent was evaporated, and then 150 ml of fresh solvent was added and evaporated and then the fresh solvent addition and evaporation step was repeated two more times. The total time of the four evaporation steps and three addition steps was approximately 1 hour, i.e. the polymer was in contact with solvent for approximately 4 hours. The ionomer was dried overnight at 60°C.

For the zinc-neutralized materials, the appropriate amount of zinc acetate was mixed with 400g of EMAA by a tumble mixer for 10 minutes. The materials were then blended in a Collin D-8017 T-20 twin-screw extruder using a screw speed of 35 rpm, corresponding to a residence time of approximately 1 minute in the extruder.

To determine the neutralization level of the ionomers, the carboxyl contents of ethylene methacrylic acid were determined by a titration method<sup>15</sup> which involves the titration of a hot n-butanol and toluene solution containing polymer by 0.1N sodium hydroxide in aqueous solution with phenolphthalein as the indicator. Pure EMAA was also titrated to determine the starting carboxyl content of the material. The amount of acid monomer on the copolymer was 3.08 mol % (9 wt %) as determined by titration. Neutralization levels are 11, 33 and 55 wt% (+/- 0.5%) for the three cations.

### 3.3.2 Blend Preparation

#### 3.3.2.1 *Blends of PA6/LDPE with/ without Compatibilizer*

The pellets were mixed in a tumble mixer for 10 minutes, followed by drying under vacuum at 60°C for 24 hours. The materials were then blended in a Collin D-8017 T-20 twin-screw extruder using a screw speed of 55 rpm. The blends were extruded through a single strand die; the extrudates were cooled in a water bath, dried at ambient temperature and then pelletized. The pellets were dried and kept in sealed plastic bags prior to compression molding to minimize moisture absorption. For Chapter IV EMAA-compatible blends were extruded in one shot i.e. PA6, LDPE, EMAA. For Chapter V and VI, ionomer-compatible or EMAA-compatible blends were made in a two-step process: first the ionomer/EMAA and LDPE were extruded together as a 50/50 master batch, then the LDPE, PA6, and an appropriate

amount of the 50/50 master batch mix were extruded together. The temperature profile used was shown in Table 3.4. The composition of the blends is given in the Table 3.5.

**Table 3.4** Temperature profile of twin screw extruder

Extruder Zone	1	2	3	4	5	6
Temperature (°C)	75	200	215	220	230	230

**Table 3.5** Blend compositions

Blend systems	Concentration (wt%)		
	PA6	LDPE	Compatibilizer (phr)
PA6/LDPE	80	20	
	20	80	
PA6/LDPE/ EMAA	80	20	0.5,1.0, 5
	20	80	0.5,1.0, 5,10,20
PA6/LDPE/ 11,33,55%wt Na-EMAA	80	20	0.5,1.0, 5
	20	80	0.5,1.0, 5
PA6/LDPE/ 11,33,55%wt Zn-EMAA	80	20	0.5,1.0, 5
	20	80	0.5,1.0, 5
PA6/LDPE/ 11,33,55%wt Li-EMAA	80	20	0.5,1.0, 5
	20	80	0.5,1.0, 5,10,20

### 3.3.2.2 *Polypropylene Organoclay Nanocomposite Fiber*

#### 3.3.2.2.1 *Centrifugal Ball Mill*

The dried sediments were ground by a FRITSCH Peluerisette 6 Centrifugal Ball Mill with a rotational speed of 450 rpm in forward and reverse milling directions for 1 hr. The particle size of the powder was less than 44  $\mu\text{m}$ .

#### 3.3.2.2.2 *Twin Screw Extruder*

PP/organoclay nanocomposites were prepared by a Collin D-8017 T20 twin-screw extruder with an L/D ratio of 30 and 25-mm-diameter. Operating temperatures were maintained at 80/160/180/190/200/210°C with a screw speed of 50 rpm. The composites were made in a two-step process: first the sodium ionomer and organoclay were extruded together as a 50/50 master batch; then the PP, and an appropriate amount of the 50/50 master batch mix, was extruded together in composition of PP 81 wt%, Na-EMAA6 wt% and organoclay 5 wt%.

### 3.3.3 Specimen Preparation

#### 3.3.3.1 *Blends PA6/LDPE with/without Compatibilizer*

Test specimens were prepared using a Wabash V 50 H 50 ton compression molding machine. The pellets were placed in a picture frame mold and the mold was preheated at 240°C for 3 minutes in the press without application of pressure. The mold was then compressed under a force of 10 tons for a further 3 minutes, after which the mold is cooled to 40°C under a pressure of 10 tons. Test specimens were cut from the molded sheets using a die cutter.

#### 3.3.3.2 *Polypropylene Organoclay Nanocomposite Fiber*

##### 3.3.3.2.1 *Melt Spinning*

The polypropylene-organoclay nanocomposite fiber was prepared by melt spinning machine, as shown in Table 3.6. The as-spun filament was collected at a extruder speed of 1.68 m/min and drawn at 190 °C. The fiber was drawn with different speeds 9.1, 15.7, 21.8, and 28.3 m/min.

**Table 3.6** Draw ratio of fiber

<b>Roller speed (rpm)</b>	<b>Roller speed (measured) (m/min)</b>	<b>Draw ratio*</b>	<b>Cross section of fiber(mm<sup>2</sup>)</b>
30	15.3	9.1	0.0132
50	26.5	15.7	0.0132
70	36.6	21.8	0.0095
100	47.6	28.3	0.0063

\*Draw ratio = Roller speed/Extruded speed

Extruder speed = 1.68 m/min