

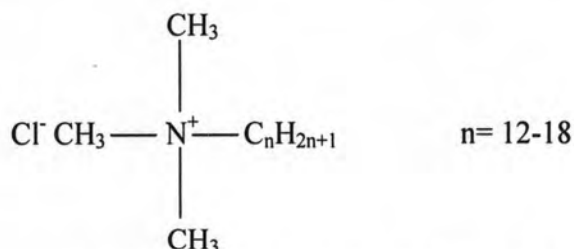
CHAPTER IV

EXPERIMENTS

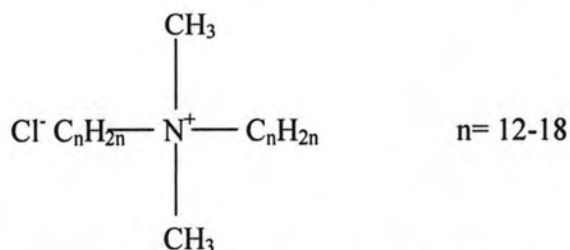


4.1. Materials

Nylon 6 was obtained from UBE NYLON, Thailand. It has molecular weight (MW) of 22,000 g/mol and specific gravity of 1.14 as listed in Table 4.1. Sodium bentonite with cation exchange capacity (CEC) of 90 meq/100g (ASTM C 837) of clay was supplied by Kunimine Industrial Co., Ltd., Japan. Surfactants that were used for ion-exchanged reaction in this study were trimethyl tallow quaternary ammonium chloride ($M_3TN^+Cl^-$) (MW = 347.5 g/mol and 50 %assay) and dimethyl bis (hydrogenated-tallow) ammonium chloride ($M_2 (HT)_2N^+Cl^-$) (585.5 g/mol and 75 %assay). Their structures were shown in figure 4.1. They were supplied by Akzo Nobel Co., Ltd., Thailand.



Trimethyl tallow quaternary ammonium chloride (ARQUAD ®T-50)



Dimethyl bis (hydrogenated-tallow) ammonium chloride (ARQUAD ®2HT-75)

Figure 4.1: Molecular structure of amine salts.

Table 4.1: Physical properties of nylon 6 (Data from UBE NYLON, Thailand).

Properties	Nylon 6 (1022B)
1. Melting point (°C)	215-225
2. Tensile Strength at yield (MPa)	74 (Dry as Mold at 23 °C)
3. Elongation at yield (%)	8 (Dry as Mold at 23 °C)
4. Flexural modulus (GPa)	2.5 (Dry as Mold at 23 °C)
5. Impact Strength (Izod, Notched) (J/m)	68.7 (Dry as Mold at 23 °C)
6. Density (g/cm ³)	1.14
7. Heat distortion Temperature (°C) (ASTM D-648)	170 (4.6 kgf/cm ²)

4.2 Preparation of Nylon 6/Clay Nanocomposite Films

4.2.1 Preparation of Modified Clay

Sodium bentonite, which was used in this research, is hydrophilic pristine clay. To obtain organophilic clays, sodium bentonite must be treated with surfactant to convert hydrophilic clays to hydrophobic or organophilic clays. The procedures of modification of sodium bentonite were shown as follows:

- 1) 20L distilled water was poured into a tank.
- 2) 400g sodium bentonite was put into a tank and stirred intensively for 3hours to disperse sodium bentonite into homogeneous phase. A tank was then heated up to 70°C.
- 3) 20L distilled water was added into another tank and heated up to 70°C. After that trimethyl tallow quaternary ammonium chloride was put into a tank and stirred intensively to dissolve it. The calculation of surfactant loading that was added into distilled water to form as a solution was summarized in appendix B.
- 4) The solution of ammonium salt of trimethyl tallow quaternary ammonium chloride was added into dispersed sodium bentonite and stirred vigorously at 70°C for a hour.
- 5) The solid part was filtered and washed by distilled water for several times.

- 6) The solid part was dried in an oven at 80°C until it dried and was then mortared and sieved respectively.
- 7) Step 1 to 6 was repeated with dimethyl bis (hydrogenated-tallow) ammonium chloride surfactant.

4.2.2 Preparation of Nylon 6/Clay Nanocomposite Films via Melt Processing Method

Organoclay powder and nylon 6 were dried at 80°C for at least 24 hours in the vacuum oven to remove the absorbed water due to the high moisture absorption of nylon 6. Organoclay powder and nylon 6 were through mixed and then placed into a hopper of screw feeder at the different organoclay loading (1, 3, 5 and 7 wt%). Melt blended nylon 6/clay nanocomposite films were formed by using a twin screw extruder attached blown film die (Thermo Haake Rheomex, Germany) with a barrel temperature set at 250°C and a screw speed of 200 rpm.

4.3 Specimen Characterizations

4.3.1 X-ray Diffraction (XRD)

XRD patterns of pristine clay, organoclay powder and nylon 6/clay nanocomposite films were obtained by using D8 discover, BRUKER AXS MODEL, with CuK α radiation of wavelength 1.542 Å. An angle value (2θ) in the range of $2\theta = 1-10^\circ$ and $2\theta = 18-28^\circ$ was scanned at rate of 0.0125 degree/min. The voltage and current used in this analysis were 40 kV and 40 mA respectively. The interlayer spacing of pristine clay, organoclay powder and the crystalline phase of nylon 6 matrix was determined by means of XRD according to Bragg's equation (see Appendix A).

4.3.2 Transmission Electron Microscope (TEM)

Dispersion of layered silicates in the nylon 6/clay nanocomposite films was observed by means of transmission electron microscopy (TEM), JEOL JEM-2010, at an accelerating voltage of 200 kV. Before observing the dispersion of layered silicates in nylon 6/clay nanocomposite films, nylon 6/clay nanocomposite films were embedded in epoxy resin. Ultra-thin sections of 80 nm in thickness of nylon 6/clay nanocomposite films were then obtained under cryogenic condition (-10°C), using cryoultramicrotome.

4.3.3 Differential Scanning Calorimetry (DSC)

Thermal transitions of neat nylon 6 and nylon 6/clay nanocomposite films were determined by means of differential scanning calorimetry (DSC). All of the nanocomposite films were heated from 40 to 240°C at heating rate 10°C/min and then stayed at this temperature (240°C) for at least a minute to remove the thermal history of nylon 6 matrix. After that nanocomposite films were cooled at the same scanning rate of 10°C/min until their temperature approached to 40°C. In this process, all nanocomposite films were analyzed under nitrogen atmosphere. The values of crystallization temperature (T_c), melting temperature (T_m), melting enthalpies (ΔH) and percent crystallinity (see Appendix H) were measured over the same temperature range of 40 to 240°C.

4.3.4 Tensile Measurement

Tensile tests were performed by using Universal Testing Machine (Instron 5567, NY, USA), which was used to determine tensile modulus, percent of elongation at break and yield strength of neat nylon 6 and nylon 6/clay nanocomposite films according to ASTM D 882. All tested specimens were required in rectangular shape with the width of 10 mm, the length of 150 mm. In this standard, initial grip separation of 50 mm and rate of grip separation of 500 mm/min were used for nylon 6/clay nanocomposite films whose percent elongation at break was greater than 100.

On the other hand, initial grip separation of 100 mm and rate of grip separation of 50 mm/min were set for nylon 6/clay nanocomposite films whose percent elongation at break was between 50 and 100. Moreover, twenty five samples were repeated in the each of composition in order to reduce the standard deviation (SD) and approach the accurate value.

4.3.5 Oxygen Permeability Analysis

Oxygen permeability analysis of nylon 6/clay nanocomposite films and neat nylon 6 films has been investigated by using oxygen permeation analyzer, Illinois 8000 (0 %RH). All of nanocomposite films were required in circular shape with diameter of 15 cm. Two nanocomposite films were repeated for the each of batch in order to obtain the accurate value. Nanocomposite film was attached to a diffusion chamber. Pure oxygen (99.9%) was then introduced into the upper half of chamber at rate of 40 cc/min, chamber temperature of 23 °C and atmospheric pressure. After that oxygen passed through nanocomposite films together with pure nitrogen carrier gas at the lower half of chamber. The measured amounts of oxygen which passed through nanocomposite films were detected and displayed in unit of $\text{cc}/(\text{m}^2.\text{day}.\text{atm})$ according to ASTM D 3985.

4.3.6 Determination of Inorganic Content

Inorganic content in pristine clay, organoclays and all nanocomposite films was determined by placing all samples into a furnace at 1000°C for 4 hours. Before taking all samples into a furnace, the absorbed water should be removed by using dried oven at 80°C for at least 24 hrs. The remained ash in each crucible was weighed to determine inorganic content. Inorganic content of pristine clay, organoclays and nanocomposite films were summarized in appendix D and F.