CHAPTER III

EXPERIMENT

3.1 Materials and Chemicals

3.1.1 Poly(Ethylene Terephthalate)

Poly (ethylene terephthalate) (PET), PET film grade chip (5564F), used in this investigation was supplied by Thai Shinkong Industrial Co., Ltd. The properties of the PET chip used are summarized in Table 3.1.

Table 3.1 Characteristics of the PET chip [50]

Property	Unit	Testing method	Values
Type	-	-	Homopolymer
Intrinsic viscosity		ASTM D 2857	0.640-0.015
Moisture content	Wt%	ASTM D 4019	< 0.5
Melting point	°C	ASTM D 3418	252 minimum
Color	-	JIS Z 8722	4.0-2.0
Acid Value (COOH)	10-6 equ/g	Zimmer PV.07013.4	40 maximum
Pallet Shape	-	-	OVAL
Bulk Density	g/cm3	ASTM D 792	0.9
Molding Temperature	°C	-	265-285

3.1.2 Montmorillonite

Montmorillonite used in this study were classified into in two types: as received montmorillonite (KIE 02097) (unmodified montmorillonite) and montmorillonite modified with Dimethyl -dioctadecylammonium chloride (2C18) (KIE 02210) which its structure was shown in figure 3.1. They were both kindly provided by Kunimine Industries Co.,Ltd.

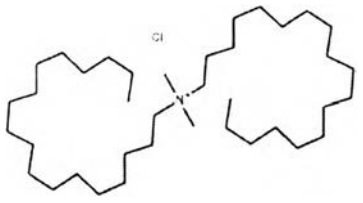

Figure 3.1 Chemical structure of dimethyl -dioctadecylammonium chloride [51]

3.1.3 Solvents

In this study mixed solvent of 50/50 by volume of phenol: 1,1,2,2 tetrachloroethane was used to dissolve and to disperse montmorillonite in poly (ethylene terephthalate) solution.

1,1,2,2 tetrachloroethane was purchased from Fluka Chemicals Ltd. (England), product number 86962, the boiling point is about 142-145 °C and the density is 1.595 g/mol.

Phenol AnalaR®, product code 101884Y, was purchased from BDH laboratory Supplies (England). The solidification point and boiling point of phenol are 41.0 °C and 180-182 °C, respectively.

3.2 Instruments

Details of each instrument are classified according to the experimental procedure as following and their features are exhibited in Appendix A.

3.2.1 Sample Preparation

a) Glass Mold (glass plate)

The glass plates were used to prepare the nanocomposite thin film by pouring the Poly (ethylene terephthalate)/MMT Nanocomposite solution directly onto a glass plate. The glass plates cut into 34 cm x 24 cm, 0.5 cm in thickness.

b) Ultrasonic Bath

The dispersion and compatibility of Poly (ethylene terephthalate) and montmorillonite was assisted by the sonication process using power ultrasound wave of the ultrasonic bath, CREST model 575 HT.

c) Automatic Film Applicator

An automatic Film Applicator machine, model PI-1210 with wire bar coating rod number 75 of Tester Sangyo Co., Ltd ,was used to prepare nanocomposite film by casting nanocomposite solution on the glass plate of the applicator. The final nanocomposite film thickness range between 20 and 30 μm. Coating speed was set at a level of 1.5 and the stop position was adjusted at a scale of 6 which is suitable to the length of glass plate

d) Vacuum Oven

The vacuum oven, Isotemp®Vacuum oven model 282A, Fisher Scientific, was used to evaporate the residue solvent from wet nanocomposite film.

3.2.2 Physical Properties Measurement

a) Viscosity

The Brookfield viscometer, model RVT, with spinner number 2 was used to measure the nanocomposite solution viscosity at a speed of 100 rpm.

b) Film Thickness

A micrometer (Peacock, Model G, Japan) was used to measure thickness of the film samples.

c) Scanning Electron Microscope (SEM)

Scanning electron microscope, JEOL JSM-5410LV, Japan, was used to observe the surface morphology of the samples.

d) UV/Visible Spectroscopy

Macbeth Color-Eye 7000 spectrophotometer from Kollmorgen instruments Corporation was employed to determine transparency of the film samples.

e) Wide-angle X-ray Diffraction (WAXD)

The WAXD is a technique commonly used to determine the basal spacing in nanocomposite materials. Wide-angle x-ray diffraction (XRD) experiments were performed on film specimens using Bruker D8 Advance diffractometer at 40 kv and 40 mA to characterize both basal spacing of dispersed montmorillonite and crystalline structure of PET/MMT nanocomposite film.

f) An Analytical Balance

An analytical balance, model AB204 from Mettler Toledo Ltd., capable of reading 0.0001 grams was used to measure the weight changes and determine the water absorption value of film samples.

3.2.3 Mechanical Properties Testing

Tensile Testing

Universal testing machine model LLOYD LR 100 K from LLOYD instruments was used to determine tensile properties of the film specimens.

3.2.4 Thermal Property Characterizations

a) Differential Scanning Calorimeter (DSC)

DSC measurements were performed using the DSC 822e supported by Mettler Toledo Ltd., Thailand. The melting temperature(T_m), the enthalpy of fusion (ΔH_f) and degree of crystallization (χ_c) of the PET/MMT nanocomposite films were analyzed.

b) Thermogravimetric Analysis (TGA)

The thermal stability of the PET/MMT nanocomposite film in terms of the onset of decomposition temperature (T_d') and the weight residue (%) was recorded using the TGA/SDTA 851^a (Mettler Toledo Ltd.)

3.3 Methodology

Flow chart of the experimental process is shown below in Figure 3.1.

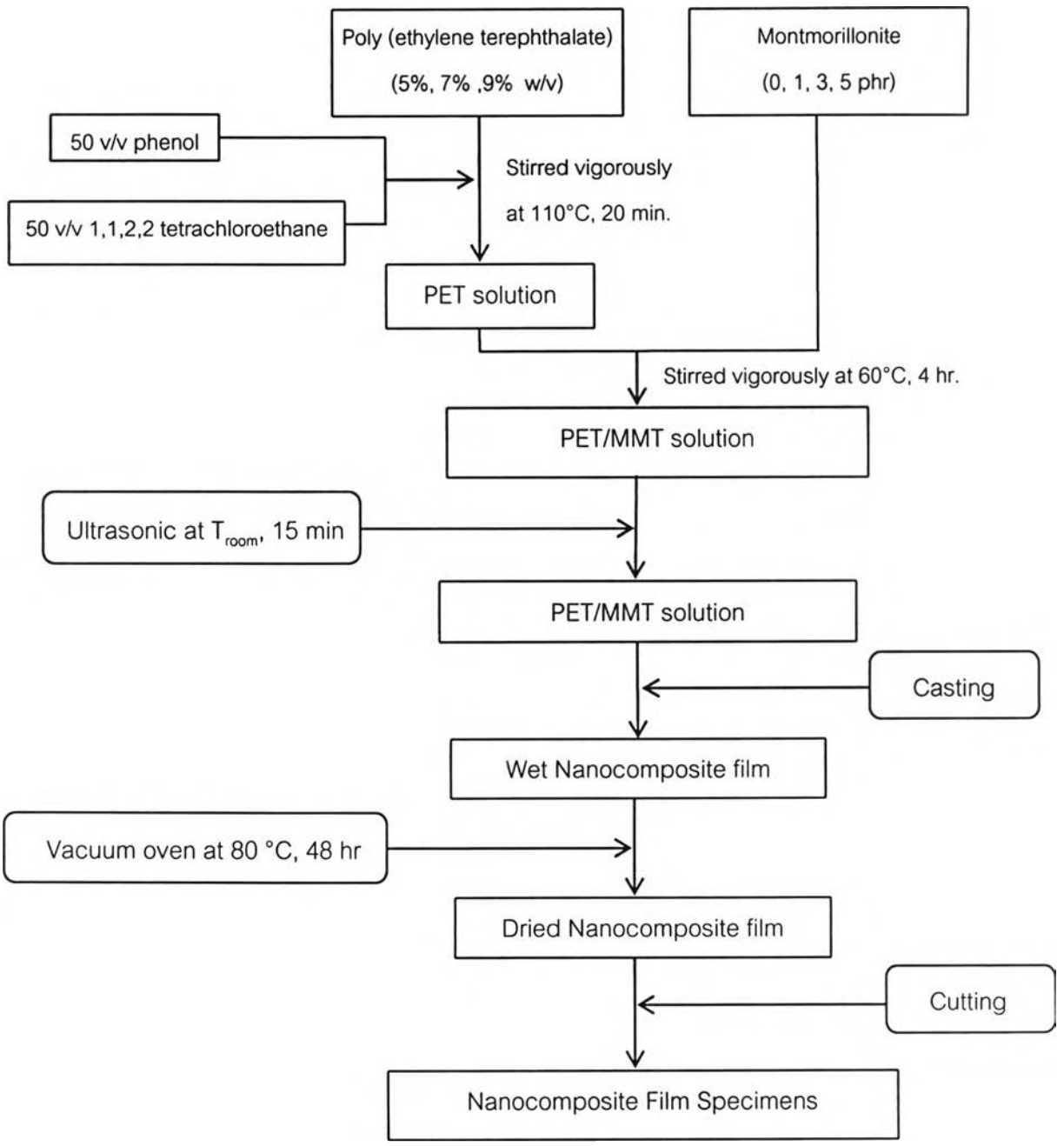

Figure 3.2 The flow chart of experimental procedure

3.3.1 PET/MMT Solution Preparation

Poly (ethylene terephthalate) solution (5, 7, 9% w/v) was prepared by dissolving PET in the mixed solvent of phenol: 1,1,2,2 tetrachloroethane (50/50 v/v) at 110°C and stirred vigorously for 20 min. After that, montmorillonite (1,3,5 phr) was slowly added into the PET solution. Table 3.2 summarizes the formula of PET/montmorillonite nanocomposite samples.

A mixture of PET solution and montmorillonite (MMT) was then stirred vigorously at 60°C for 4 hr to obtain PET/MMT solution. Finally, the PET/MMT solution was brought into an ultrasonic bath and shaken at room temperature for another 15 minutes to improve the compatibility between two components or to increase the dispersion of MMT in the PET solution, After 15 min, the homogenous solution can be observed. It should be noted that the PET chip and montmorillonite were dried in an oven at 80 °C for 48 h prior to use.

3.3.2 Sample Preparation

The nanocomposite films were prepared by casting method using the automatic film coater. The wet film on glass plate was dried in vacuum oven at 80°C for 48 h to remove any remaining solvent and to facilitate complete polymer intercalation between the silica layers. The dried nanocomposite film was removed from glass plate and cut into test piece specimen.

The specimens prepared for the mechanical properties were cut into a strip shape of 5 mm X 70 mm. Because this film formation method may lead to an anisotropic material, ten specimens were prepared for each sample, five for machine direction and five for transverse direction.

And the specimens for water absorption measurement were cut into rectangular shape of 76.2 mm long by 25.4 mm wide, according to ASTM D 570.

Table 3.2 Formula of the PET/MMT nanocomposite samples

Formula	Sample Code	PET (%w/v)	Unmodified-MMT (phr)	2C18-MMT (phr)
1	5PET-0	5	-	-
2	5PET-A1		1	-
3	5PET-A3		3	-
4	5PET-A5		5	-
5	5PET-B1		-	1
6	5PET-B3		-	3
7	5PET-B5		-	5
8	7PET-0	7	-	-
9	7PET-A1		1	-
10	7PET-A3		3	-
11	7PET-A5		5	-
12	7PET-B1		-	1
13	7PET-B3		-	3
14	7PET-B5		-	5
15	9PET-0	9	-	-
16	9PET-A1		1	-
17	9PET-A3		3	-
18	9PET-A5		5	-
19	9PET-B1		-	1
20	9PET-B3		-	3
21	9PET-B5		-	5

3.4 Characterization and Testing

3.4.1 Physical Properties

3.4.1.1 Rheological Property

The rheological property of nanocomposite solution for all formulas was studied by the Brookfield Viscometer. The viscosity measurement was performed at ambient temperature using spinner number 2 at a speed of 100 rpm.

3.4.1.2 Film Thickness Measurement

Film thickness was measured by a micrometer. Three thickness values were taken along the length of the film strip and the mean value was used for tensile strength calculation.

3.4.1.3 Structure Analysis

The basal spacing of (001) plan of used montmorillonite in PET/MMT nanocomposite films was analyzed by Bruker D8 Advance diffractometer. The CuKα radiation (λ = 1.542 Å) generated at 40 kV and 40 mA was monochromatized with a 15 μm Ni foil. The relative intensity was recorded in the scattering range *(2θ)* of 2.0-40.0 degree with scanning step of 2.00 deg min^{-1}.

Scanning electron microscope (SEM) was used to study the surface morphology of PET/MMT nanocomposite film. The film samples were sputter coated with gold to enhance their conductivity and scanned at an accelerating voltage of 15 kV for 2 min. Their images were scanned at an angle about 10 degrees.

3.4.1.4 Optical Properties Measurement

The transparency of PET/MMT film samples was measured by Macbeth Color-Eye 7000 spectrophotometer. The percent transmittance of calibrated white standard and film samples was measured in the wavelength of visible light about 400-750 nm.

3.4.1.5 Determination of Water Absorption

Water absorption of films was measured by twenty-four hour immersion method according to ASTM D 570 standard test, 1995. However, the PET/MMT nanocomposite films were immersed into the water longer than 24 hr until the water reached the equilibrium state. Film specimens were cut into rectangular shape of 76.2 mm long by 25.4 mm wide. The films were conditioned by drying in an oven at 50±3 °C for 24 hours, cooling in a desiccator, and weighing immediately to obtain the initial or dried weight. Then, the dried films were entirely immersed in a container of distilled water maintained at ambient temperature. At the end of 24 h, 48 h and 14 days, the films were removed from the water one at a time, their wet surfaces were wiped off with a dry cloth, and

weighed immediately to get the final or wet weight. The percentage of water absorbed, calculated from the difference in weight before and after immersion in water so called conditioned or dried weight and final or wet weight, respectively, was calculated using the following equation:

$$\text{Water absorption (\%)} = \frac{\text{wet weight} - \text{dried weight}}{\text{dried weight}} \times 100 \quad \text{.....(1)}$$

3.4.2 Mechanical Properties

Tensile testing was carried out according to the ASTM D 882-02 using the Universal Testing Machine model LLOYD LR 100K at a constant crosshead speed of 5 mm min^{-1}. The initial grip separation or gage length of 50.0 mm with load cell of 100 N was used. The air-actuated grips have been used to hold the film specimens. The film specimens, 5.0 mm X 70.0 mm in dimension, were conditioned at 23±2 °C and 50±5 % RH for 24 hours before testing.

In this study, the tensile strength (TS), tensile modulus, and percent elongation at break (%EB) were recorded. These properties were measured both in longitudinal direction (MD) and transverse direction (TD) to observe whether any difference in the orientation of polymer chain occurs.

3.4.3 Thermal Properties

The thermal properties of PET/MMT nanocomposite film can be performed using differential scanning calorimeter (DSC) and thermogravimetric analyzer (TGA).

DSC measurements were performed with DSC 822^e. Hermitically sealed aluminium pans were used to encapsulate the sample of approximately 10 mg and dried at 60 °C in oven before characterization. All measurements were carried out in nitrogen atmosphere (70 ml min^{-1}). The sample was heated first at 50 °C /min to 280 °C and kept for 3 min to remove the thermal history. The sample was then autocooled at 10°C /min to 50°C and reheated at 50 °C /min to 280°C. Both crystallization and melting parameters were obtained from the cooling and heating scans. The melting temperature(T_m) was considered to be the maximum of the endothermic meltig peak from heating scans and

T_c that of the exothermic peak of crystallization from the cooling scans. The degree of crystallization; χ_c (%) of the PET/MMT nanocomposite films were calculation by using the following equation;

$$\chi_c(\%) = \frac{\Delta H_f}{\Delta H_{f0}} \times 100 \quad \text{.....(2)}$$

where ΔH_f is the heat of fusion of sample which obtained from the area of the melting peak

ΔH_{f0} is the heat of fusion for 100% crystalline PET which is 140.1J/g [23]

TGA measurements were performed with TGA/SDTA 851[a]. The thermal stability of the PET/MMT nanocomposite film in terms of the onset of decomposition temperature (T_d) and the weight residue (%) were recorded. The approximately 5-7 mg of film samples were cut and put in the crucible weight. The sample were heated up from 30 °C to 1,000 °C at a heating rate of 10 °C /min under nitrogen atmosphere (70 ml min^{-1}).

Figure 3.3 presents the whole diagram of characterization and testing of Poly (ethylene terephthalate) / montmorillonite nanocomposite film

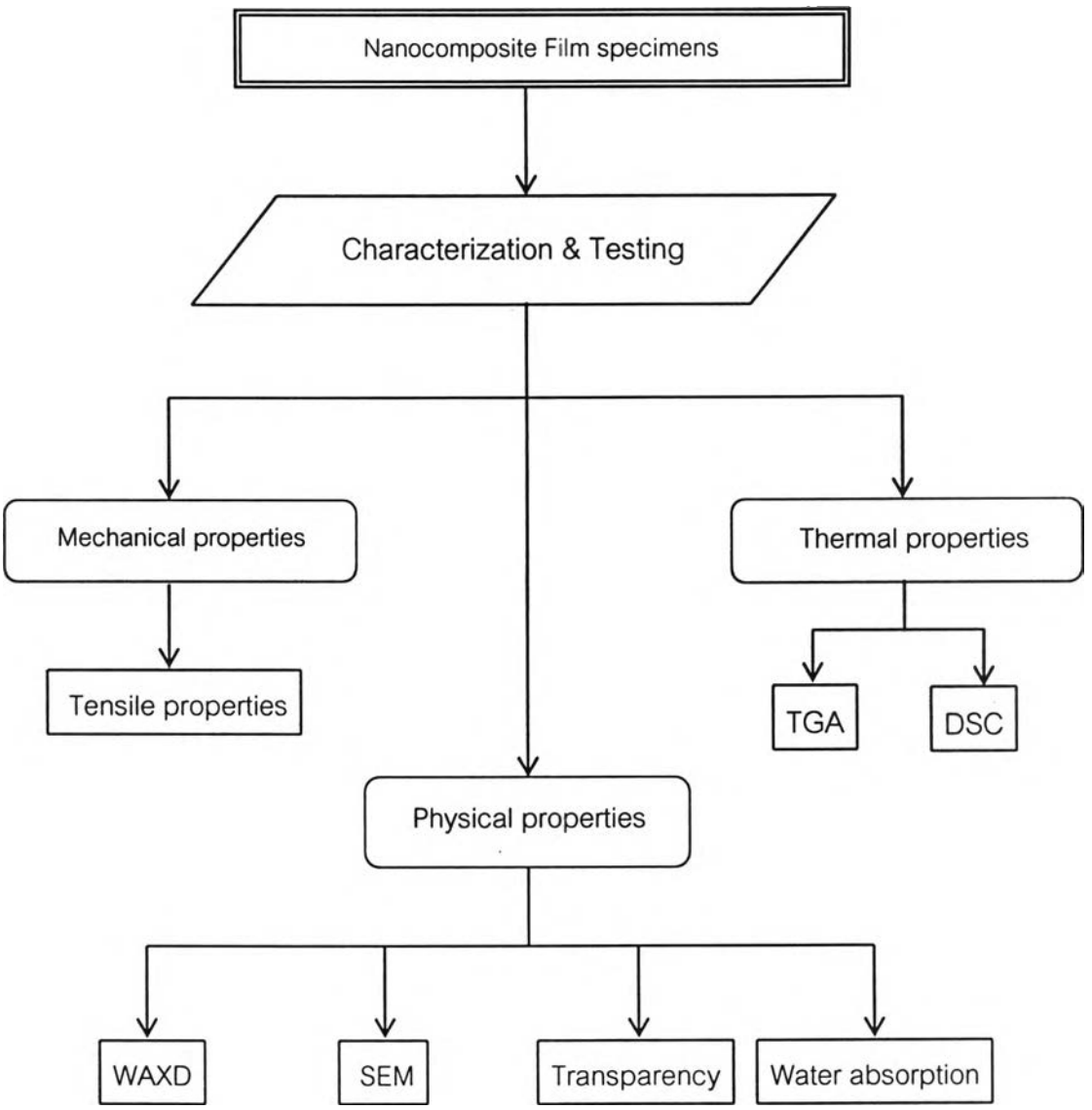

Figure 3.3 The diagram of characterization and testing of Poly (ethylene terephthalate) / montmorillonite nanocomposite films