CHAPTER III

EXPERIMENTAL

3.1   Materials and Chemicals

-    **Paper Mulberry**: Paper mulberry was purchased from Chitlada palace.
-    **Hydrogen peroxide (H₂O₂)**: Hydrogen peroxide was purchased from Merck Co.,Ltd., Germany.
-    **Hydrochloric acid (HCl)**: Hydrochloric acid was purchased from Merck Co.,Ltd., Germany.
-    **N, N-dimethylacetamide (DMAc)**: N, N-dimethylacetamide was purchased from Fluka Chemie A. G. Switzerland.
-    **Lithium Chloride (LiCl)**: Lithium Chloride was purchased from Fluka Chemie A. G. Switzerland.
-    **Lauroyl Chloride**: Lauroyl Chloride was purchased from Fluka Chemie A. G. Switzerland.
-    **N, N-dimethyl-4-aminopyridine (DMAP)**: N, N-dimethyl-4-aminopyridine was purchased from Fluka Chemie A. G. Switzerland.
-    **Chloroform**: Chloroform was purchased from Labscan Asia Co.Ltd., Thailand.
-    **Methanol**: Methanol was purchased from Labscan Asia Co.Ltd., Thailand.

3.2   Instruments

Details of each instrument are classified according to the experimental procedure as follows.

3.2.1 Sample Preparation

a. Glass Mold

Paper Mulberry film was prepared by pouring the cellulose ester solution directly onto a glass mold. The glass mold was composed of a set of glass pieces; i. e. 2 pieces of 0.3 cm × 1 cm × 27 cm plates, 2 pieces of 0.3 cm × 1 cm × 25 cm plates, and a 0.3 cm × 25 cm × 27 cm plates, as shown in Figure 3.1. The removable edges of the glass mold were intentionally made in order to allow the cellulose film to be detached from the mold easily after drying.

Figure 3.1 Glass mold.

b. Microwave oven

The esterification reaction of the cellulose was performed in a 2.45 GHz, household-Microwave oven (LG Intellowave).

Figure 3.2 LG Intellowave.

3.2.2 Physical Property Testing

a. Micrometer

A micrometer shown in Figure 3.3 (Peacock, Model G, Japan) was used to measure thickness of the film samples.

Figure 3. 3 Micrometer.

b. Gloss Meter

Micro-gloss 60° with standard holder of BYK-Gardner GmbH, Germany, presented in Figure 3.4, was employed to measure specular gloss of the film samples according to the ASTM D 523 standard method.
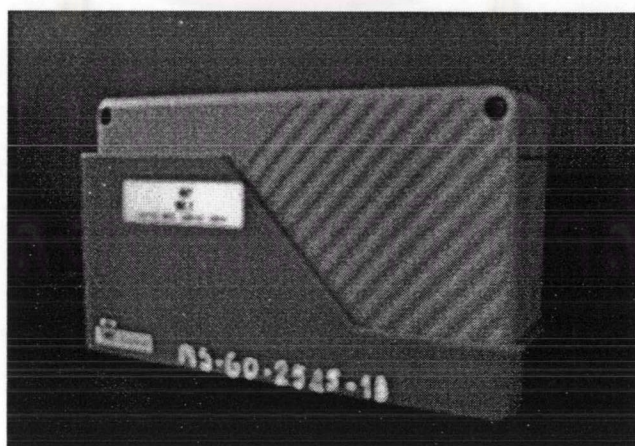

Figure 3. 4 BYK-Gardner Micro-gloss 60°.

c. Contact Angle Meter

A contact angle meter model CAM-PLUS MICRO (Tantec Inc., USA) (Figure 3.5) was used to determine the wettability of the film samples.
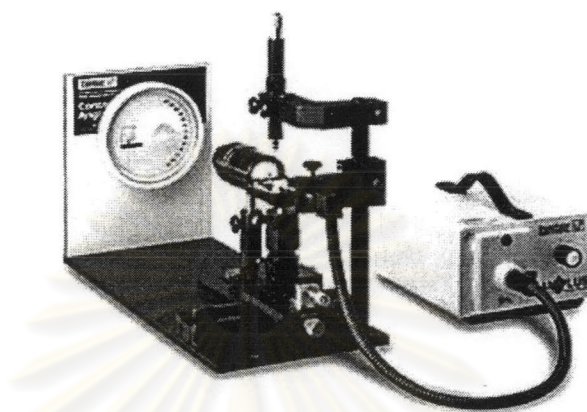

Figure 3. 5 Tantec CAM-PLUS MICRO contact angle meter.

d. Fourier Transform Infrared Spectrometer

Fourier Transform Infrared Spectrometer (Nicolet Impact 400D) shown in Figure 3.6 was used to determine the functional groups of cellulose and cellulose ester powder.

Figure 3. 6 FTIR: Nicolet Impact 400D.

e. Scanning Electron Microscope

The surface morphology of the different cellulose samples, unmodified cellulose, esterified cellulose powder, and cellulose film were analyzed using a scanning electron microscope. Figure 3.7 display SEM, JEOL: JSM-6400 employed in this research.
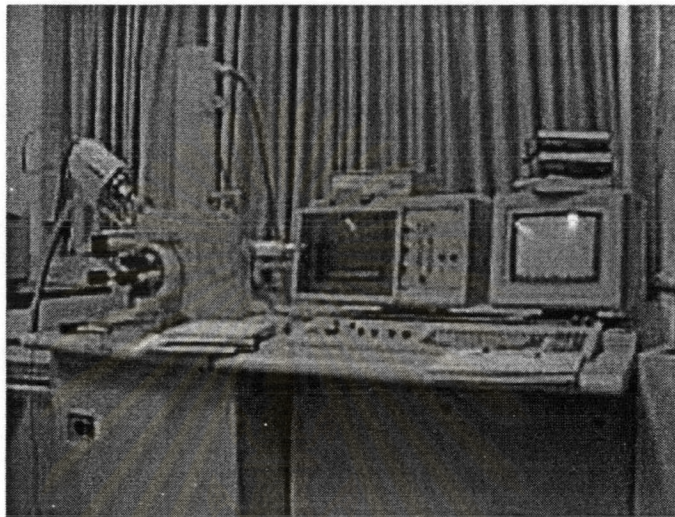

Figure 3. 7 SEM: JEOL: JSM-6400.

3.2.3 Thermal Property Characterization

a. Differential Scanning Calorimetry (DSC)

Thermal transition temperatures of the samples were characterized by a Differential Scanning Calorimetry (DSC), DSC822-e/400w, as presented in Figure 3.8
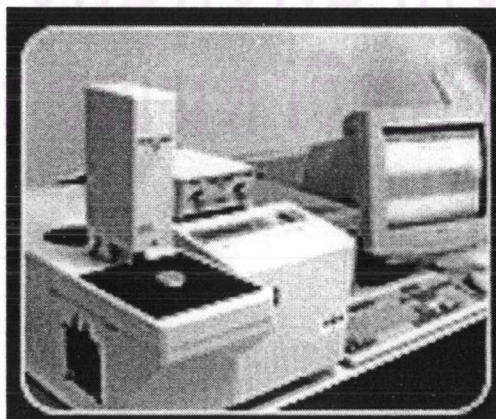

Figure 3. 8 DSC: DSC822-e/400w.

b. Thermogravimetric Analyzer (TGA)

Thermogravimetric analysis (TGA) was performed on samples using a Mettlor Toledo (TGA/SDTA851e/LS/1600) as shown in Figure 3.9.
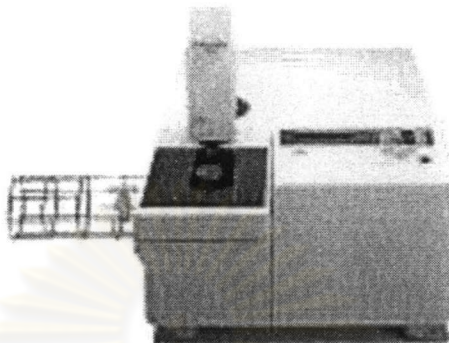

Figure 3. 9 TGA: TGA/SDTA851e/LS/1600.

3.2.4 Mechanical Property Testing

a. Tensile Testing Machine

Tensile properties of the film samples were tested by universal testing machine (LLOYD LR 100K) (Figure 3.10) according to the ASTM D 882.
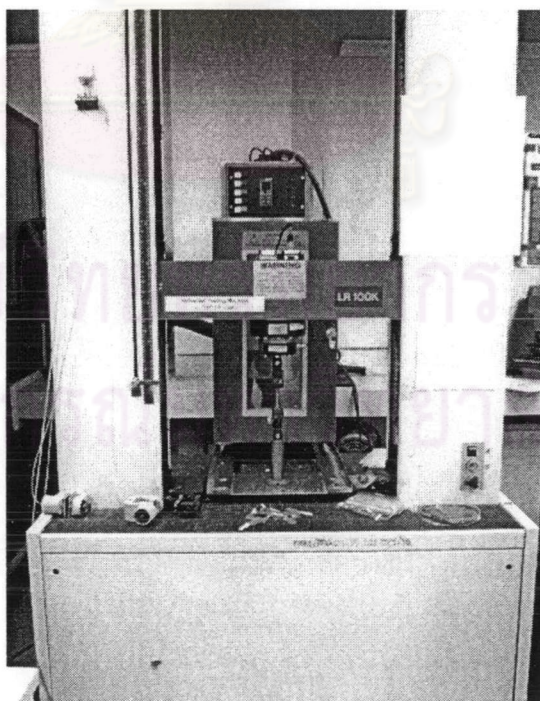

Figure 3.10 Universal Testing Machine LLOYD LR 100K.

3.2.5 Degradation Test

a. Xenotest Bata Lamp

The Photodegradation Test of film sample was performed by Xenotest Bata Lamp (HERDEUS BETA L M)(Figure 3.11) under simulated condition.

Figure 3. 11 Xeno Test: HERDEUS BETA L M.

3.3 Experimental Procedure

The experimental procedure for preparation of paper mulberry film is shown in Figure 3.12 and can be divided into 3 main steps as follow:

3.3.1 Preparation of paper mulberry powder

3.3.1.1 Delignification of paper mulberry

100 g of The paper mulberry bark was soaked in the1500 ml water for 24 hours in order to remove an impurity and to soften the bark. After 24 hours, the paper mulberry pulp was heated in distilled water until the temperature reached its boiling point and then sodium hydroxide (0.4 M) 1600 ml was added in order to remove lignin from the pulp. After 4 hours of extraction, the pulp was filtrated and washed with water until washing water reached pH 5.

3.3.1.2 Alkaline extraction (Bleaching)

The paper mulberry pulp was then bleached by hydrogen peroxide (1 M) 1800 ml at 100°C for 4 hours. After that the sample was filtrated and washed with water until washing water reached pH 5 [G. Chauvelon et al., 2000].

3.3.1.3 Hydrolysis of paper mulberry

The bleached-paper mulberry pulp was heated and stirred at 90°C in boiling 2.5 N hydrochloric acid for 2 hours. After that, the sample was transferred immediately to fritted-glass filters and washed acid with distilled water, followed by 5% (w/v) sodium hydroxide. Finally, the paper mulberry powder was obtained and then dried in vacuum oven for 5 hours at 60 °C.

3.3.2 Solubilization and Esterification of Paper Mulberry

3.3.2.1 Solubilization

In this experiment, the paper mulberry powder was dissolved in 8% (w/v) LiCl/DMAc. Firstly, 1 g of paper mulberry powder was mixed with DMAc (25 ml) and stirred for 2 hours at 120-130 °C. Then, LiCl (2 g) was added and maintained at 120-130 °C for another 20-30 min. After that, the solution was cooled down to 50°C and stirred overnight at the same temperature.

3.3.2.2 Esterification of paper mulberry

DMAP (0.1-1.2 equiv) and lauroyl chloride (5-14 equiv) were added to the cellulose solution, and this mixture was esterified under microwave energy in a household-microwave oven (LG Intellowave) at various times (30 s, 1.0, 1.30, 2.0 min) and power outputs (90, 180, 270, 360, 450, 540, 630 W). In this experiment, 1 g of cellulose was dissolved in 8 %(w/v) LiCl/DMAc. The esterified paper mulberry was precipitated by adding 98% ethanol (400 ml) for removing residual pyridine and lauroyl chloride.

3.3.3 Paper mulberry Film Casting

The esterified paper mulberry powder was solubilized in 30 ml chloroform, and then spreading evenly on a glass plate at room temperature under normal atmosphere. The solvent was completely evaporated and the paper mulberry film was finally obtained.
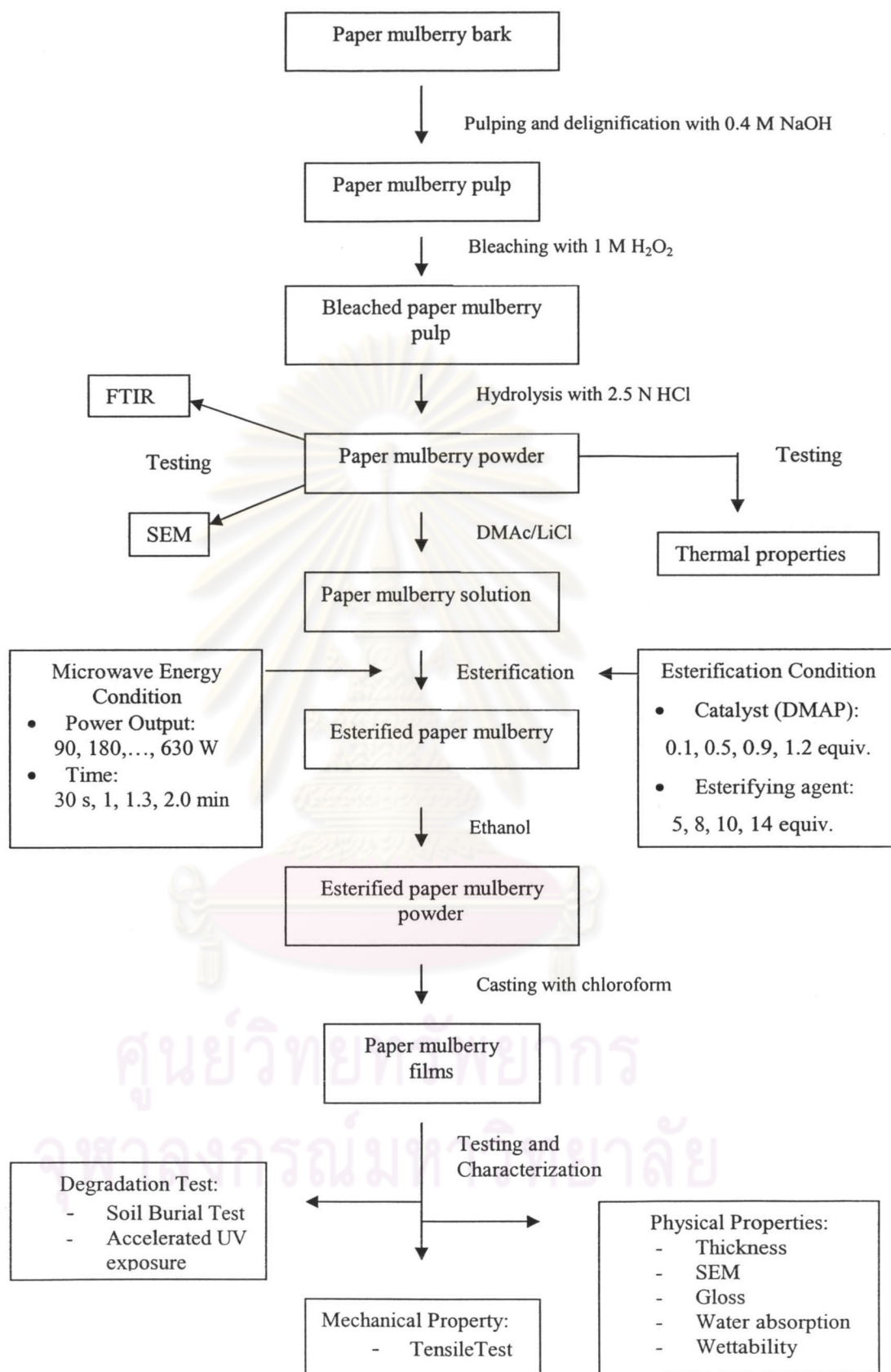
Figure 3.12 The experiment procedure for preparation of paper mulberry film.

3.4 Characterization and Testing

The paper mulberry sample was tested and characterized using various techniques as follows:

3.4.1 Physical Properties

3.4.1.1 Film Thickness Measurement

The tensile strength of samples is related to the thickness of film, the film thickness measurement was then conducted by using a micrometer. The average of four thickness values taken along the length of the film strip was used to calculate the tensile strength.

3.4.1.2 Functional groups and % esterification

Fourier Transform Infrared Spectrometer (FTIR) was used to investigate the functional groups of pure cellulose, cellulose ester and % esterification of cellulose. The Infrared spectra were recorded between 4000-400 cm^{-1}. % Esterification of cellulose was calculated from the peak height of hydroxyl group in the range of 3,000-3,300 cm^{-1}. Details of calculation were described in an Appendix c.

3.4.1.3 Morphological Studies

The surface morphology of various cellulose samples were analyzed using a scanning electronic microscope (JEOL: JSM-6400). The surface of the cellulose samples was coated with gold before being scanned.

3.4.1.4 Gloss Properties

Gloss or specular reflectance is defined as the degree to which the finished surface of the materials approaches that of the theoretical specular gloss standard, or the perfect mirror, which is assigned a value of 1000. In practice, gloss measurements are made in comparison to a black tile with a refractive index of 1.567 and assigned an arbitrary value of 100 gloss units. The amount of specular reflectance of the black tile at a given angle is dependent on the index of refraction of the glass.

In this study, the gloss of film samples was determined by micro-gloss 60° at 23 ± 2°C according to the ASTM D 523 standard method. Calibration of

dark standard holder was 95.1 units. Five positions of each film sample were tested and gloss values were averaged to obtain a mean value.

3.4.1.5 Surface Property Determination: Wettability

The contact angles of film samples were measured using a CAM-PLUS MICRO (Tantec, Inc.) according to Tantec's Half-Angle method. To calibrate the device, the height of the syringe was adjusted so that the needle tip image was at the lower border of the grid on the screen. The needle's image was then focused by moving the lens plate back and forth. The given specimen was placed onto the specimen holder under the syringe needle, and the knob was released clockwise to release the droplet of water. Bringing the specimen holder up slowly then down, one droplet of water was obtained, and was then focused. In this experiment, used three droplets of water/ one sample and five specimens for each film sample was calculated average value. The line was then adjusted so that it was lined up with the left edge of the droplet. The line was then moved till it cross the apex of the droplet, and the angle was measured on the protractor. A contact angle of zero results in wetting, while an angle between 0 and 90° results in spreading of the drop (due to molecular attraction). Angles greater than 90° indicate that the liquid tends to bead or shrink away from the solid surface.

3.4.1.6 Water Absorption

Water absorption of films was measured by twenty-four hours immersion method according to the ASTM D 570 standard test (1995). The films 25.4 mm × 76.2 mm were conditioned by drying in an oven at 50 ± 3°C for 24 hours, cooling in desiccator, and weighing immediately. Then, the conditioned films were entirely immersed in a container of distilled water maintained at ambient temperature. After 24 hours of exposure, the films were removed from the water one at a time, all surface water was wiped off with a dry cloth, and immediately weighed. The water absorption was calculated as the weight difference and reported as percentage of weight increase from the conditioned weight. The water absorption of films was calculated as follows:

$$\text{Water Absorption, \%} = \frac{\text{wet weight - conditioned weight}}{\text{conditioned weight}} \times 100 \quad \ldots\ldots \text{(Eq.3.1)}$$

Three specimens for each film samples were tested and the results were averaged to obtain a mean value.

3.4.2 Mechanical Properties

The tensile stress at maximum load, tensile modulus, and percent elongation at break of the film samples were measured by Universal Testing Machine (LLOYD LR 100K). The film samples in the size of 150 mm × 15 mm were conditioned for 24 hours at 25°C and 60% RH before testing. The test was carried out according to the ASTM D 882 standard method, with initial grip separation or gauge length of 100 mm, crosshead speed of 10 mm min^{-1}, and load cell of 100 N.

The tensile modulus is defined as the slope of the tangent to the stress-strain curve at low strain. Tensile stress at maximum load is the value of the stress on the stress-strain curve where the curve occurred at maximum load. The percent elongation at break is the maximum strain exhibited by the test sample at the point of breakage. Four specimens of each film samples were measured in longitudinal directions to obtain a mean value.

3.4.3 Thermal Analysis

3.4.3.1 Thermogravimetric analysis (TGA)

Thermal decomposition temperature of the cellulose ester was determined by the thermogravimetric analysis (TGA). 5 mg of the samples were heated at 10 °C/min from 0 °C to 500 °C under nitrogen atmosphere. The thermal decomposition temperature (T_d) was reported as the onset of significant weight loss from the heated sample.

3.4.3.2 Differential scanning calorimetry (DSC)

Measurements of calorimetric properties of the materials were performed by the differential scanning calorimetry (DSC). 5-10 mg of cellulose and cellulose ester samples were placed in aluminum DSC pans. Samples were heated from −50 °C to 250 °C at a heating rate of 10 °C/min and then cooling back to -50°C with the same rate. The second heating was also performed with the same condition as the first heating scan. Melting temperature (T_m) values were reported as the peak temperatures of melt endotherms recorded from the first heating scan. Glass transition temperature (T_g) values were recorded as the midpoint of the heat capacity change in the glass transition region during the first heating scan.

3.4.3 Degradation Tests

3.4.3.1 Soil burial test

The sample sized 1.5 cm x 2.0 cm was dried in an oven at 60 °C for 24 hr and weighed immediately as an initial weight (W_i). The sample were then buried is an aluminium tray contain soil with certain microorganisms at a depth of 1 cm from the surface. The soil was kept moist by watering its surface twice everyday. The sample was taken out from the soil every five days and carefully cleaned the soil left on the sample surface. Finally, the final weight of sample after degradation (W_f) was measured and weight loss of cellulose films was calculated as follows:

$$\text{Weight loss (\%)} = \frac{w_i - w_f}{w_i} \times 100 \qquad \text{............ (Eq. 3.2)}$$

By; w_i = initial weight of sample before degradation (g)
        w_f = final weight of sample after degradation (g)

Three film specimens for each condition were tested and the results were averaged to obtain a mean value. Besides weight loss measurement, physical appearance of the degraded film samples was also observed from SEM analysis. Electron micrograph of the exposed or degraded films was compared with the SEM micrograph of the as received film.

3.4.3.2 Accelerated UV exposure

Accelerated UV exposure was performed by using a xenon arc lamp in the Xenotest Beta Lamp chamber. Various parameters for simulating the weathering condition include time (h), temperature (°C), relative humidity (% RH), and irradiant intensity (E, W/m^2).

Film samples were cut into the size of 2.0 cm × 6.0 cm weighed (W_i), and placed into the Xenotest Beta lamp chamber. The samples were irradiated under UV radiation of 100 W/m^2 at 25 °C and 76 %RH for 72 hours. After that sample was removed from the chamber, dried in an oven at 60 °C for 24 hours, and then weighed (W_f). Weight loss of the films was also calculated using the above equation (Eq 3.2).