

# CHAPTER III

## EXPERIMENTAL

### 3.1 Materials and Chemicals

The chemicals used in this experiment were normal analytical grade, and listed as follows.

1. Bleached knitted cotton fabric, (single jersey , yarn count (50/1))
2. Hydrochloric acid (37%) was manufactured by Merck Ltd., Germany.
3. *N,N*-Dimethyl acetamide ( $\geq 98.0\%$ ) was manufactured by Fluka Chemie A. G. Switzerland.
4. Lithium chloride was manufactured by Fluka Chemie A. G. Switzerland.
5. Toluene sulfonyl chloride was manufactured by Fluka Chemie A. G. Switzerland.
6. Stearic acid was manufactured by Merck Ltd., Germany.
7. Pyridine was manufactured by Merck Ltd., Germany.
8. Ethanol was manufactured by Labscan Asia Co.Ltd., Thailand.
9. Chloroform was manufactured by Labscan Asia Co.Ltd., Thailand.

### 3.2 Equipments and Instrument

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

#### 3.2.1 Synthesis Equipments

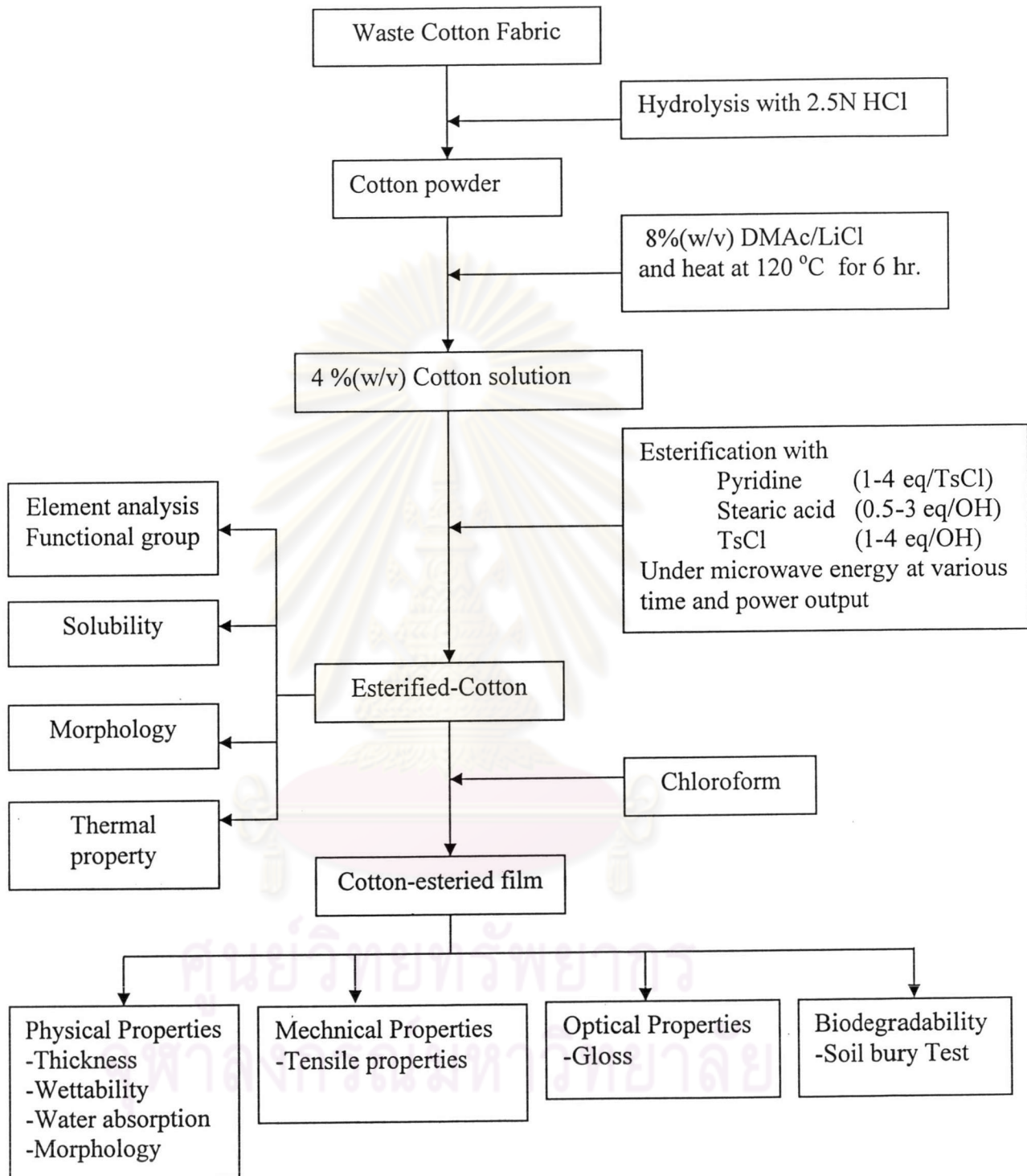
1. Hotplate and Magnetic Stirrer
2. 50 ml-Beaker
3. 50 ml-Cylinder
4. 200 °c-Thermometer

### Step 3: Film elaboration

The esterified-cotton or cotton-stearate powder was solubilized in chloroform, and then a film of cellulosic ester was fabricated by casting method. The esterified-cotton solubilized in chloroform was evenly spread on a glass plate maintained at room temperature until the solvent was totally evaporated from the film.

The experimental flow diagram for esterification of waste cotton fabric under microwave is shown below in Figure 3.12





**Figure 3.12** The flow diagram of experimental procedure

## 3.7 Characterization and Testing

Sample was tested and characterized using various techniques as follows:

### 3.7.1 Physical Properties

#### 3.7.1.1 Film Thickness Measurement

The tensile properties of film samples are related to the thickness of film, therefore, the film thickness measurement was conducted by using a micrometer. The average of five thickness values taken along the length of the filmstrip was used to calculate the tensile strength.

#### 3.7.1.2 Optical 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 depends on the index of refraction of the glass.

In this study, the gloss of film samples was determined by a micro-gloss 60° at  $23 \pm 2^\circ\text{C}$  according to ASTM D 523 standard method. Calibration of dark standard holder was 95.1 units. Five positions of each film sample were tested to obtain the average gloss values.

#### 3.7.1.3 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 film 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. 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.

#### 3.7.1.4 Water Absorption

Water absorption of films was measured by twenty-four hours immersion method according to the ASTM D 570 standard test (1995). The 25.4 mm × 76.2 mm film samples 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, 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:

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

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

#### 3.7.1.5 Solubility

To determine the solubility of esterified cotton, one gram of samples were dropped into 25 ml of variety of solvent (as show in list below) at room temperature. If sample insoluble at room temperature, then it was heated up to 100 °C or to boiling point of solvent for 30 min.

List of solvent :

Chloroform	<i>N,N</i> - dimethyl formamide
Toluene	Dimethyl sulphoxide
Acetone	Tetrahydrofuran
H <sub>2</sub> O	

### 3.7.2 Functional group

Fourier transform infrared spectroscopy (FTIR) was used to characterize the functional group of esterified cotton and the percent esterification or degree of esterification. % Esterification of cellulose was calculated from the height of IR peak in the range 3000-3200 cm<sup>-1</sup> as follows :

$$A = \text{Log } I_0 / I \quad (3.2)$$

$$\frac{A_C - A_S}{A_C} \times 100 = C_S \quad (3.3)$$

where

- $A_C$  is Absorbance of cellulose
- $A_S$  is Absorbance of cellulose stearate sample
- $I$  is % transmittance of OH functional group at maximum
- $I_0$  is % transmittance of OH functional group at baseline
- $C_S$  is % esterification of cellulose sample

Details of calculation can be found in Appendix A. For each spectrum, 32 consecutive scans with 4 cm<sup>-1</sup> resolution were used. The samples were scanned at frequency range of 4000-400 cm<sup>-1</sup>.

### 3.7.3 Chemical Analysis

#### Elemental Analysis

The elemental composition of cotton-esterified powder product was measured by XRF analysis. The XRF was used to study the composition of sulfur and chlorine in sample product.

### 3.7.4 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 (Model LLOYD LR 100K). The film samples in the size of 150 mm × 20 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 gage length of 100 mm, crosshead speed of 10 mm min<sup>-1</sup>, 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. These values were measured in longitudinal directions. Five specimens of each sample were tested and averaged to obtain a mean value.

### 3.7.5 Thermal Properties

#### (a) Thermogravimetric Analysis(TGA)

TGA analysis of sample was carried out under nitrogen atmosphere from 25°C at 300 °C with a heating rate of 10 °C/min. Prior to do the experiment, the samples were dried in oven at 60°C overnight. The thermal degradation temperature ( $T_d$ ) was reported as the onset of weight loss of heated sample.

#### (b) Differential scanning calorimeter (DSC)

Esterified cotton and unmodified powder with an average weight of 5-10 mg were placed in hermetically sealed aluminium pans. Two consecutive heating and cooling cycle were performed in order to obtain the melting and glass transition temperatures of the samples clearly. First, the samples were heated from 10 °C to 180 °C at a heating rate of 20°C/min, and then cooling back to 10°C with same the rate. For the second cycle, the heating and cooling temperature profiles were carried out with same condition as the first cycle. Melting temperature ( $T_m$ ) values were reported as the peak temperature of melting endotherm recorded from the 4<sup>th</sup> heating scan. Glass transition temperature ( $T_g$ ) values were aslo recorded

as the midpoint of heat capacity change in the glass transition region during the 4<sup>th</sup> heating scan.

### 3.7.6 Degradability

#### Soil bury test

The cellulosic film samples were cut into the size of 2 cm x 1 cm and then transferred to on aluminum tray containing soil. The samples were buried in soil at a depth of 4 cm from bottom and 2 cm from surface. 50g of water was sprayed all over the surface of soil twice a day. The samples were removed from soil every 5 days, after cleaning the soil on the surfaces of sample with dry cloth and dring a film in oven at 60 °C overnight, the degead film sample were weighed ( $w_f$ ) and calculated as follows:

$$\% \text{ Weight loss} = \frac{W_i - W_f}{W_i} \times 100 \quad (3.4)$$

where  $W_i$  is weight of sample before degradation test (g)  
 $W_f$  is weight of sample after degradation test (g)

Besides weight loss measurement, physical appearance of the exposed or degraded film samples was aslo observed from SEM analysis. Electron micrograph of the unexposed film was compared to those of exposed films. Similar to weight loss determination, prior to do so, each film sample was also cleaned the soil on the surfaces of sample with dry cloth and drying a film in oven at 60 °C overnight

### 3.7.7 Morphological Studies

The morphology of esterified-cotton film was characterized by scanning electron microscope (JEOL:JSM-6400). The scanning electron microscopy was operated at 15 KV. The surface of the sample was sputter-coated with a thin layer of gold before being scanned to avoid surface charing under electron beam.