

## CHAPTER III EXPERIMENTAL



### 3.1 Materials

Low density polyethylene (LDPE) with the trade name LD 1905F supplied by the Cementhai Co., Ltd., Thailand with the melt flow index of 5 g/10 min was used as film matrix. The physical properties of the LDPE pellets are listed in Table 3.1.

**Table 3.1** Physical properties of LDPE with the trade name LD1905F.

Property	Test method	Value
Melt flow index (g/10 min)	ASTM D1238	5.0
Density (g/cm <sup>3</sup> )	ASTM D1505	0.919
Tensile strength at break (kg/cm <sup>2</sup> )	ASTM D 638	MD:210, TD: 170
Elongation at break (%)	ASTM D 638	MD: 320, TD: 680
Elmendorf tear strength (g/25 $\mu$ m)	ASTM D1922	MD: 370, TD: 210
Dart impact strength (g)	ASTM D1709	105
Haze (%)	ASTM D1003	5
Gloss (%)	ASTM D2457	100

Tapioca starch was obtained from the Siam Modified Starch Co., Ltd., Thailand with an average particle size of 14.84  $\mu$ m. The starch was heated in a hot-air circulating oven for 12 hours prior to blending with LDPE.

Three inorganic acids, hydrochloric acid (HCl 37%, Aldrich), sulfuric acid (H<sub>2</sub>SO<sub>4</sub> 95-97%, Merck), and nitric acid (HNO<sub>3</sub> 65%, Scharlau) were diluted to 5 N for acidic hydrolysis.

For enzymatic hydrolysis,  $\alpha$ -amylase (Termamyl Supra, 120 KNU/g, East Asiatic Co., Ltd., Thailand) was employed.

Calcium oxide (CaO) with specific gravity of 3.315 g/cm<sup>3</sup> was added to the LDPE/starch blends as a moisture adsorbent. Another additive was Irganox 1010, which acted as an antioxidant to the blends.

## 3.2 Experimental Procedure

### 3.2.1 Preparation of LDPE/starch Blends

Low density polyethylene, tapioca starch, CaO, and Irganox 1010 were mixed in plastic bags by manual shaking. The compositions of each blend are shown in Table 3.2.

**Table 3.2** Compositions of LDPE/starch blends.

Amount of starch in the blend	Composition of the blend			
	LDPE (g)	Starch (g)	CaO (g)	Irganox (g)
2 wt%	1960	40	3.2	9.8
4 wt%	1920	60	6.4	9.6
6 wt%	1880	120	9.6	9.4
8 wt%	1840	160	12.8	9.2
10 wt%	1800	200	16.0	9.0
12 wt%	1760	240	19.2	8.8

Then, each blend was melt extruded in a Collin ZX-25 twin-screw extruder. The twin-screw extruder was equipped with a single strand round die, water bath, and a pelletizer. The blends were manually fed into the hopper to prevent starch loss in the feed reservoir. The extrusion conditions

are summarized in Table 3.3. After extrusion, the LDPE/starch blends were kept sealed in plastic bags and placed in a desiccator.

**Table 3.3** Extrusion conditions for preparation of LDPE/starch blends.

Extrusion parameter	Value
Temperature profile from the feeding zone to the die (°C)	120, 125, 130, 135, and 135 (at the die)
Screw speed (rpm)	50

### 3.2.2 Film Preparation

Film processing was carried out in a chill roll cast film extruder (Collin D8017) to produce LDPE/starch films with thicknesses of 50, 80, and 100  $\mu\text{m}$ . The chill roll cast film extruder consists of a single screw, a hopper, a flat die, 2 chill rolls, and a winder. Each LDPE/starch blend was continuously fed into the hopper at the feed zone during extrusion. Temperature at the chill rolls was maintained constant at 36°C. Pure LDPE resin was used to clean the screw after each run was finished. The temperature profile and extrusion conditions are given in Table 3.4 and Table 3.5. Films containing 0-12 wt% starch were kept sealed in plastic bags and placed in a desiccator.

**Table 3.4** Extrusion conditions for preparation of LDPE/starch films.

Extrusion parameter	Value
Temperature profile from the feeding zone to the die (°C)	150, 155, 160, 165, 165, 170, and 170 (at the die)
Screw speed (rpm)	25

**Table 3.5** Chill roll speeds for the preparation of 0-12 wt% starch films.

Film composition	Film thickness ( $\mu\text{m}$ )	Chill roll speed (arbitrary unit)
0 wt% starch	50	2/40
2 wt% starch	50	2/60
4 wt% starch	50	2/65
6 wt% starch	50	2/95
8 wt% starch	50	3/10
10 wt% starch	50	3/35
12 wt% starch	50	3/40

(cont.)

Table 3.5 (Continued)

Film composition	Film thickness ( $\mu\text{m}$ )	Chill roll speed (arbitrary unit)
0 wt% starch	80	1/70
2 wt% starch	80	1/75
4 wt% starch	80	1/90
6 wt% starch	80	1/50
8 wt% starch	80	1/90
10 wt% starch	80	2/0
12 wt% starch	80	2/10
0 wt% starch	100	1/10
2 wt% starch	100	1/10
4 wt% starch	100	1/30
6 wt% starch	100	1/20
8 wt% starch	100	1/25
10 wt% starch	100	1/40
12 wt% starch	100	1/50

### 3.2.3 Porous Structure Formation by Acidic Hydrolysis

Porous structure of the LDPE/starch films was formed by removing starch particles with acid solutions. Specimens (15×15 mm) were cut from the films, preheated at 65°C for 6 hours to remove traces of moisture. The weights of specimens were recorded accurately before hydrolysis and were in the range of 6-9 mg. Five sets of experiments were conducted to investigate the effects of acid type, concentration, temperature, starch content, and film thickness.

### *3.2.3.1 Effect of Acid Type*

Film samples, 50  $\mu\text{m}$  in thickness, containing 12 wt% starch were immersed in 25 mL of each acid solution, namely HCl,  $\text{H}_2\text{SO}_4$ , and  $\text{HNO}_3$ . The concentration of each solution was 5 N. Acidic hydrolysis was carried out at 65°C for 30 hours in a water bath with continuous shaking. The film samples were removed every 2 hours, rinsed with distilled water, dried at 65 °C for 6 hours, and then weighed. A control sample having the same thickness and starch content as the test specimens was immersed in 25 mL of distilled water under the same conditions as the test specimens. The control sample was removed, dried, and weighed as for the test specimens.

### *3.2.3.2 Effect of Acid Concentration*

Nitric acid was diluted to 1 and 3 N concentrations. The same film samples as those in experiment (3.2.3.1) were immersed in the two solutions at 65°C for 15 hours. The samples were removed every 2 hours, dried, and weighed as described above.

### *3.2.3.3 Effect of Temperature*

Acidic hydrolysis was carried out using 5 N  $\text{HNO}_3$  solution for 15 hours at 25 and 45°C. Film samples with the same thickness and starch content as those used in experiment (3.2.3.1) were employed with the same weight checking procedure after every 2 hours.

### *3.2.3.4 Effect of Starch Content*

Different samples (50  $\mu\text{m}$  in thickness) with starch contents varying from 0-12 wt% were hydrolyzed in 5 N  $\text{HNO}_3$  at 65°C without weight checking every 2 hours. All samples were removed after hydrolysis had proceeded for 15 hours. The weights of these samples were accurately recorded after drying.

### 3.2.3.5 *Effect of Film Thickness*

The film samples containing 12 wt% starch with thicknesses of 80 and 100  $\mu\text{m}$  were used. Temperature in the water bath was maintained at 65°C from the beginning. The samples were hydrolyzed in 5 N  $\text{HNO}_3$  for 15 hours and weighed every 2 hours.

Film samples from each experiment were observed under SEM (Jeol, JSM-6400) in both surface and cross-sectional views. For mechanical testing and permeability measurements, film samples with starch contents 0-12 wt% and 50  $\mu\text{m}$  in thickness, were hydrolyzed in 5 N  $\text{HNO}_3$  at 65°C for 15 hours.

### 3.2.4 Porous Structure Formation by Enzymatic Hydrolysis

Film samples with 12 wt% starch and 50  $\mu\text{m}$  in thickness were immersed in 25 mL of a 2 vol% solution of  $\alpha$ -amylase in pH 6.5 acetate buffer containing 54 mM  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ . The enzymatic hydrolysis was allowed to proceed for 12 hours at a constant temperature of 80°C in a water bath with continuous shaking. Specimens were removed every 2 hours, washed and dried before weighing. A control sample of the same starch content and thickness was hydrolyzed in pH 6.5 acetate buffer without enzyme to determine weight loss without  $\alpha$ -amylase.

### 3.2.5 Mechanical Properties of Porous Films

Tensile stress at break and elongation at break of the porous films were measured based on ASTM D882 using a Lloyd universal testing machine (Model LRX). A load cell of 2.5 kN was used with a 125 mm/min cross-head speed and 250 mm gage length. The tensile properties could be determined only in the machine direction because the length of the film in transverse direction was shorter than the gage length. The tear resistance of film samples was determined both in machine and transverse direction using an SDL Elmendorf tear tester following ASTM D1922 test method. The gloss values

of films were determined based on ASTM D523-89 both machine and transverse direction. The measurement was made by Haze-Gloss (BYK Gardner) and the angle used was 60°.

### 3.2.6 Gas Permeability Measurements

Circular porous films prepared from 0-12 wt% starch films were used for these tests. A film sample of 7.5 cm in diameter was placed in a membrane test cell with porous support (Figure 3.1). The test gases were carbon dioxide (CO<sub>2</sub>), nitrogen (N<sub>2</sub>), ethylene (C<sub>2</sub>H<sub>4</sub>), propylene (C<sub>3</sub>H<sub>6</sub>), and propane (C<sub>3</sub>H<sub>8</sub>). The gas was let in on the upper side of the test cell at a pressure of 20 psig. The gas flux was measured by a bubble flow meter connected to the outlet of the test cell. The gas permeability was evaluated from Equation 3.1,

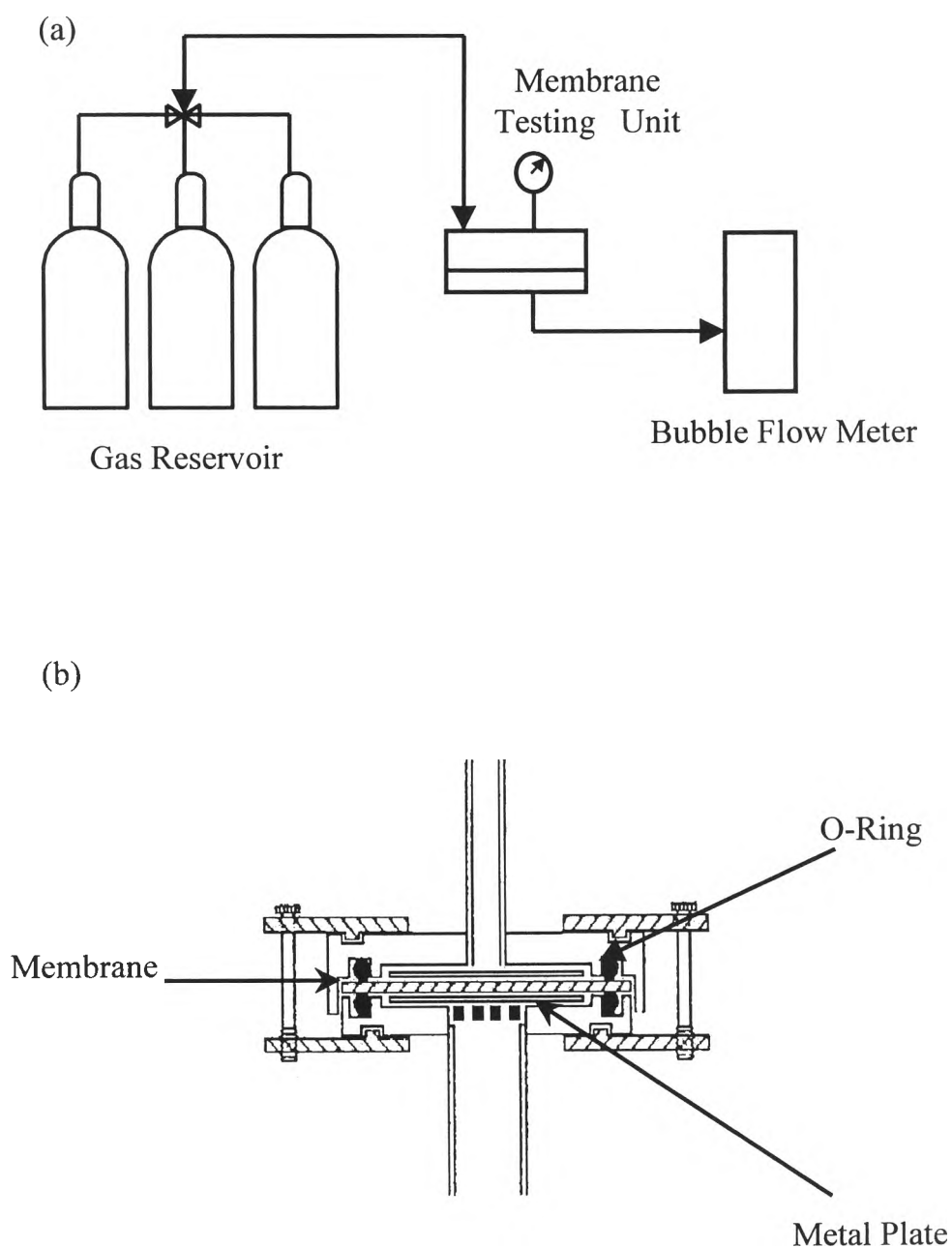
$$J_i = \frac{P_i \Delta p}{\delta} \quad (3.1)$$

where  $J_i$  is the flux,  $P_i$  the permeability of gas  $i$ ,  $\Delta p$  the pressure difference across the membrane, and  $\delta$  the membrane thickness. The separation factor (selectivity) was calculated from Equation 3.2,

$$\alpha = \frac{P_i}{P_j} \quad (3.2)$$

where  $\alpha$  is the selectivity and  $P_j$  the permeability of gas  $j$ .





**Figure 3.1** Membrane testing unit, (a) schematic diagram of experimental setup and (b) cross-section of membrane test cell.