

CHAPTER II

EXPERIMENTAL SECTION

2.1 Materials

In this study, high-density polyethylene (HDPE) of film extrusion grade (Polene A3355, TPI Co., Ltd.) was used as the polymer matrix. Some physical properties are listed in Table 2.1 below.

Table 2.1 Physical properties of high-density polyethylene

Property	Value
MFI (g/10min.)	0.06
Density (g/cm ³)	0.95
Melt density (g/cm ³)	0.77 at 150°C , 0.75 at 190°C
Tensile strength (N/mm ²)	> 40
Yield strength (N/mm ²)	> 28.0
Ultimate elongation (%)	> 1700
Notched impact strength (mJ/mm ²)	> 12.0

Two types of starch were used as filler, namely native rice starch and native tapioca starch. The starches were kindly supplied by Siam Modified Starch Co., Ltd.

Diethyl ether (C₂H₅OC₂H₅) was used as the non-solvent for measuring the specific gravity of the rice starch and the tapioca starch by the pycnometric technique.

Calcium oxide (CaO), having the specific gravity of 3.315 g/cm^3 , was used as a desiccant.

2.2 Experimental Procedure

2.2.1 Pretreatment of starch

In order to determine the decomposition temperature and the water content of the rice starch and the tapioca starch used in this study, thermogravimetric analysis was conducted by heating the starches from 24°C to 500°C at a heating rate of $10^\circ\text{C}/\text{min}$ using a NETZSCH TG209 TGA analyzer.

Suitable drying time was determined by constructing drying curves of the starches. Weight loss was plotted against drying time until no significant change in weight was observed. The starches were weighed prior to being heated in a hot-air oven at 100°C and periodically removed to determine progressive weight loss. The starches were immediately placed back in the oven after being weighed.

2.2.2 Starch density measurement

The densities of the starches were measured using the pycnometric technique. The method involves the use of a pycnometer of known volume. The starch to be evaluated was weighed and put into the pycnometer. The pycnometer containing the starch was then filled with diethyl ether of known density and reweighed. The weight and thus the volume of diethyl ether could then be found from the weight difference. The densities of the starches could then be determined from the following equation:

$$\rho_{st} = [W_{st}/(V_{pyc}-(W_{ether}/\rho_{ether}))]$$

where:

ρ_{st} is the density of the starch

W_{st} is the weight of the starch contained in the pycnometer

V_{pyc} is the volume of the pycnometer = 25.04 cm³

W_{ether} is the weight of diethyl ether contained in the pycnometer

ρ_{ether} is the density on diethyl ether = 0.7079 g/cm³

2.2.3 Processability of starch-based HDPE blends

2.2.3.1 Mixing process of starch-based HDPE blends. Mixing was studied using a Brabender Plasti-Corder, PL-2100, equipped with a cam-type mixer-measuring head. The mixer-measuring head consists of an intra-connected, figure-eight-shaped chamber, having a capacity of 55 cm³, in which two sigmoid, counter-rotating blades turn. A rotor speed of 50 rpm and an oil bath temperature of 160°C were used. All runs were carried out on Heat and Shear Stability mode and a fill factor of 0.90 was used. Starch contents were varied from 0 to 40%. Calcium oxide was added in an amount of 8.0% to the weight of starch. An average value of HDPE melt density of 0.76 g/cm³ was used, based on a melt density of 0.75 g/cm³ at 200°C and 0.77 g/cm³ at 150°C. The starches were dried for 2.5 hours in a hot-air oven at 100°C and kept in sealed containers until used. Batch sizes were calculated from the following equation:

$$\text{Batch size (g)} = \text{Volume of chamber (cm}^3\text{)} \times \text{Density of the blend (g/cm}^3\text{)} \\ \times \text{Fill factor}$$

The batch size calculations for the starches are summarized in Table 2.2 and Table 2.3.

Table 2.2 Batch size calculation of rice starch

Starch content (%)	Total weight of ingredient(s) (g)	HDPE (g)	Rice starch (g)	Calcium oxide (g)
0	37.62	37.62	0	0
10	39.82	35.52	3.98	0.32
20	42.30	33.17	8.46	0.68
30	45.11	30.50	13.53	1.08
40	48.32	27.45	19.32	1.55

Table 2.3 Batch size calculation of tapioca starch

Starch content (%)	Total weight of ingredient(s) (g)	HDPE (g)	Rice starch (g)	Calcium oxide (g)
0	37.62	37.62	0	0
10	39.72	35.43	3.97	0.32
20	42.06	32.97	8.41	0.67
30	44.69	30.21	13.41	1.07
40	47.68	27.08	19.07	1.53

The ingredients were physically premixed -except for the study on the effect of starch where HDPE was masticated for three minutes before the starch and the calcium oxide were added- before being added to the mixer-measuring head. The torque required to turn the blades at the set rotation speed was transmitted from the dynamometer housing to the computer to record the torque value as a function of time. The stock temperature was measured by a thermocouple positioned inside the chamber.

The effects of mixing conditions on dispersion and distribution of starch particles in the starch-based HDPE blends were studied using a Joel Scanning Electron Microscope (SEM), model JSM-35CF. Samples of the blends were collected from the Brabender mixer-measuring head at one-minute intervals. The cooled and hardened samples were notched, dipped in liquid nitrogen, broken off, and surface-coated with gold. A Semafore program was used to measure the size of the starch particles and agglomerates in the starch-based HDPE blends.

2.2.3.2 Sample preparation. Starch masterbatch containing 20% by weight starch was prepared on a Collin ZX-25 counter-rotating twin screw extruder equipped with a single strand round die. The starches were dried in a hot-air oven at 100°C for 2.5 hours before being tumble-mixed with HDPE. The mixture was put into the hopper of a single screw feeder from which the mixture was fed into the twin screw extruder. The extrudate strand, exiting from the die, was air-cooled and fed into a pelletizer to obtain starch masterbatch pellets. The extrusion conditions used in preparing the starch materbatch are summarized in Table 2.4.

Table 2.4 Extrusion conditions used in preparing starch materbatch

Extrusion parameter	Value
Temperature profile from the feeding zone to the die (°C)	145, 155, 160, 160, 160, and 160 (die)
Screw speed (rpm)	50
Single screw feeder speed (arbitrary units)	200

Starch-based HDPE film with thickness of 80 to 90µm were prepared on a Betol single screw blown film extruder equipped with a 50mm annular blown film die. Films with varying starch contents of 0, 2.5, 5.0,

7.5, 10.0, and 12.5% were prepared. HDPE and an appropriate amount of starch masterbatch were tumble-mixed and the mixture fed into the blown film extruder to obtain the film. The extrusion conditions used in preparing the starch-based HDPE blown film are summarized in Table 2.5.

Table 2.5 Extrusion conditions used in preparing the starch-based HDPE blown film.

Extrusion parameter	Value
Temperature profile from the feeding zone to the die (°C)	150, 175, 185, 200, 200, and 200 (die)
Screw speed (rpm)	75
Blow-up ratio	2.5
Take-up ratio	4.5
Frost line height (mm)	135

The blow-up ratio (BUR) is defined as the ratio of the bubble diameter to the die diameter, the take-up ratio (TUR) as the take-up velocity to the extrudate velocity at the die exit, and the frost line height (FLH) as the distance from the die to the point where the extrudate changes from the amorphous (transparent) state to the crystalline (hazy) state.

2.2.4 Mechanical properties of starch-based HDPE blown film

Films prepared by the blown film extrusion process are biaxially orientated in the axial or machine direction (MD) and the radial or transverse direction (TD). This orientation is made permanent by the combined effects of crystallization and cooling, which freezes the orientation in place. Therefore, mechanical properties testing of the film needed to be conducted in both directions.

2.2.4.1 Tear resistance testing. The force required to propagate tearing across starch-based HDPE film was measured using an Elmendorf 2000 tear tester with an ‘A’ pendulum (8000 mN full-scale load). This test was conducted according to ASTM D1922. Test specimens were cut, as shown in Fig. 2.1, to form a constant-radius testing length to compensate for oblique tearing. Two sets of specimens were cut – one set which was torn parallel to the machine direction (MD) and the other set torn parallel to the transverse direction (TD). In this test, four plies of film were used for each test run. Ten measurements were conducted for each sample, and the results were averaged to obtain a mean value.

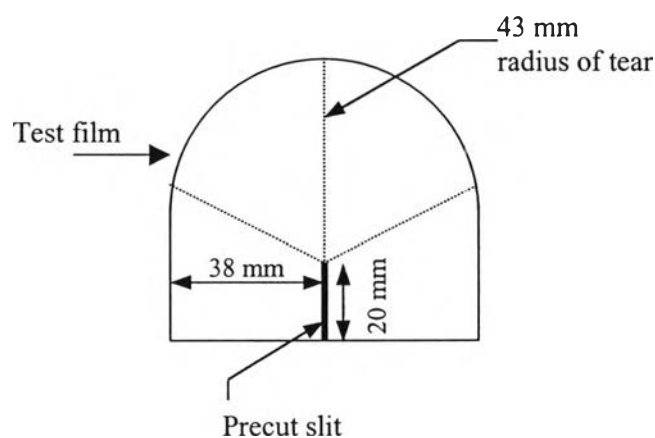


Figure 2.1 Constant-radius test specimen for tear resistance test.

2.2.4.2 Tensile properties Testing. Tensile strength and elongation at yield of starch-based HDPE blown film in both the MD and TD were measured using a Lloyd universal testing machine. The test was conducted according to ASTM D882. The test specimens were prepared by cutting strips of uniform width and thickness from the film samples. The specimens used were 150 mm in length, 20mm in width, and 80 to 90 μm in thickness. Ten

specimens, five MD and five TD, were tested for each sample and the results were averaged to obtain a mean value. Test conditions are summarized in Table 2.6.

Table 2.6 Tensile testing conditions

Test parameter	Value
Load cell (N)	500.0
Initial grip separation (mm)	50.0
Crosshead speed (mm/min)	10.0
Initial strain rate (mm/mm.min)	2.0

2.2.5 Water and moisture absorption of starch-based HDPE blown film

Water absorption was measured according to ASTM D570. The test specimens were in the form of bars 76.2 mm long by 25.4 mm wide by the thickness of the film. The test specimens were dried in a hot-air oven for 24 hours at 50°C, cooled in a desiccator, and immediately weighed. The test specimens were then immersed in distilled water. At regular time intervals, a specimen was removed, wipe-dried with blotting paper, and then weighed to determine the water uptake. The specimens were immediately placed back in the water after each measurement. The water absorption was calculated as the weight difference and reported as the percent increase of the initial weight. Three specimens were measured for each sample and the results averaged to obtain a mean value.

Tensile strength of water-saturated starch-based HDPE blown film was determined according to ASTM D882. The specimens were immersed in distilled water for five days in order for the saturation point to be established. The specimens were then removed from water, wipe-dried, and tested for

tensile strength. The dimension of the specimens and the test conditions were the same as in part 3.3.4.2.

For moisture absorption measurements, specimens were prepared and conditioned in the same way as in the water-absorption study. The dried specimens were placed in an enclosure containing an aqueous solution of 33.2% sulfuric acid at 25°C in order to maintain a relative humidity of 70%. The moisture absorption was calculated as the weight difference and reported as the percent increase of the initial weight. Three specimens were measured for each sample and the results averaged to obtain a mean value.