

CHAPTER 3

EXPERIMENTAL

Reagents and Materials

Blown film grade low density polyethylene (JJ4324) was obtained from Thai Petrochemical Industry Co.,Ltd. (TPI). Physical properties of the material are listed in Table 3.1. Cassava starch for this experiment was supplied by Thai Wah Co.,Ltd., while Epolene E-43p, dispersing agent, was obtained from White Group Co.,Ltd. The other chemicals, iron stearate and soya oil were used as prooxidant and lubricant, respectively.

Table 3.1 Physical properties of low density polyethylene (JJ4324)

Physical properties	Test method	Unit	JJ4324 (LDPE)
Melt index (2.16 kg/190°C)	ASTM D1238	g/10 min	5.50
Density	ASTM D1238	g/cm ³	0.922
Tensile strength	ASTM D1238	N/mm ²	>11.0
Yield strength	ASTM D1238	N/mm ²	>11.0
Ultimate elongation	ASTM D1238	%	>600
Vicat softening temperature	ASTM D1238	°C	95
Haze	ASTM D1238	%max	<6.5
Gloss	ASTM D1238	%min	>95
Impact strength	ASTM D1238	g	>160

Sample Preparation

1. Filler Preparation

Thai cassava starch was used as filler. Since polyethylene is hydrophobic and starch is hydrophilic, these two material are naturally

incompatible. In order to improve the homogeneous properties of both materials, the starch was then mixed with a 2% (w/w) dispersing agent (Epolene wax E-43p) in a dry blend mixer at 70 °C. A mixing time was 15 minutes.

2. Compounding of Plastic Material

A two roll-mill compounding machine, Labtech Engineering Co., Ltd., Model LRM 110, was used. The temperature of the front roll was set at 140 °C and the temperature at the back roll was 135 °C. The temperature of two clean rolls were maintained constantly for 30 minutes. The nip between the rolls was adjusted to be about 3 mm. The polyethylene resin was poured on the rolls and preheated for 3 minutes.

The rolls were allowed to move while the plastic was melting. The starch mixed with Epolene wax, soya oil and iron stearate were gradually filled into the molten plastic in order to get a good compatibility between starch and polyethylene. The composition of each compounding formula was shown in Table 3.2. A trowel was used during mixing in order to spread the material on the rolls. The time for compounding was 15 minutes. After the compounding operation, the starch-polyethylene sheet formed was removed from the two roll-mill.

3. Film Preparation

The starch-polyethylene sheets were cut into small chips by a cutting machine, Model LRM 110, Labtech Engineering Co.,Ltd. The starch-polyethylene films of average thickness 0.055 ± 0.05 mm. was obtained by extruding the chips in Film Blowing machine with an extruder Model PE-142 from Numchai Plastic Machinery. The temperature of feed, compression, metering and die zones were 140, 145, 150 and 155 °C, respectively.

Table 3.1 The composition of starch-LDPE films.

Formula	Abbreviation	Content (g)			
		LDPE	Starch	Soya oil	Iron stearate
1	PE	100	0	0	0
2	PE-S5	100	5	2	0
3	PE-S10	100	10	2	0
4	PE-S15	100	15	2	0
5	PE-S20	100	20	2	0
6	PE-5S/F	100	5	2	0.1
7	PE-10S/F	100	10	2	0.1
8	PE-15S/F	100	15	2	0.1
9	PE-20S/F	100	20	2	0.1

Sample Natural Exposure

Outdoor weathering of the unfilled LDPE and starch-LDPE films was carried out. The natural exposures were carried out in Bangkok, Thailand, which is located at latitude $13^{\circ} 44' N$ and longitude $100^{\circ} 34' E$. The exposed surface of samples were mounted on racks. The tests were started in September 1994 and continued to February 1995 for 6 months. The meteorological and radiation data at the site were collected from the Monthly Report of the Climatology Division, Meteorological Department. The collected data, including average of temperature, %relative humidity, total radiation, rainfall amount, are listed in Table 3.2 and shown in Figures 3.1- 3.2.

Table 3.3 Meteorological data

Month	Temperature (°C)	% R.H.	Rainfall amount, mm	Radiation MJ/M ²
1994 September	28.0	80.0	375.0	20.31
October	27.1	75.0	155.8	19.05
November	27.8	66.0	4.3	16.98
December	26.8	67.0	5.3	20.22
1995 January	26.2	69.0	0.0	21.24
February	27.0	71.0	0.1	35.30

Soil Burial Test

A naturally soil burial experiment provides an realistic environment with seasonal changes in term of soil wetness, temperature, and the presence of microorganisms. The thin film samples of $10 \times 2.5 \text{ cm}^2$, and the soil were placed in a perforated plastic box to permit the access of macroorganisms and moisture. The box that was buried at a depth of 6-8 in. After sampling, the films were stored in dark until testing.

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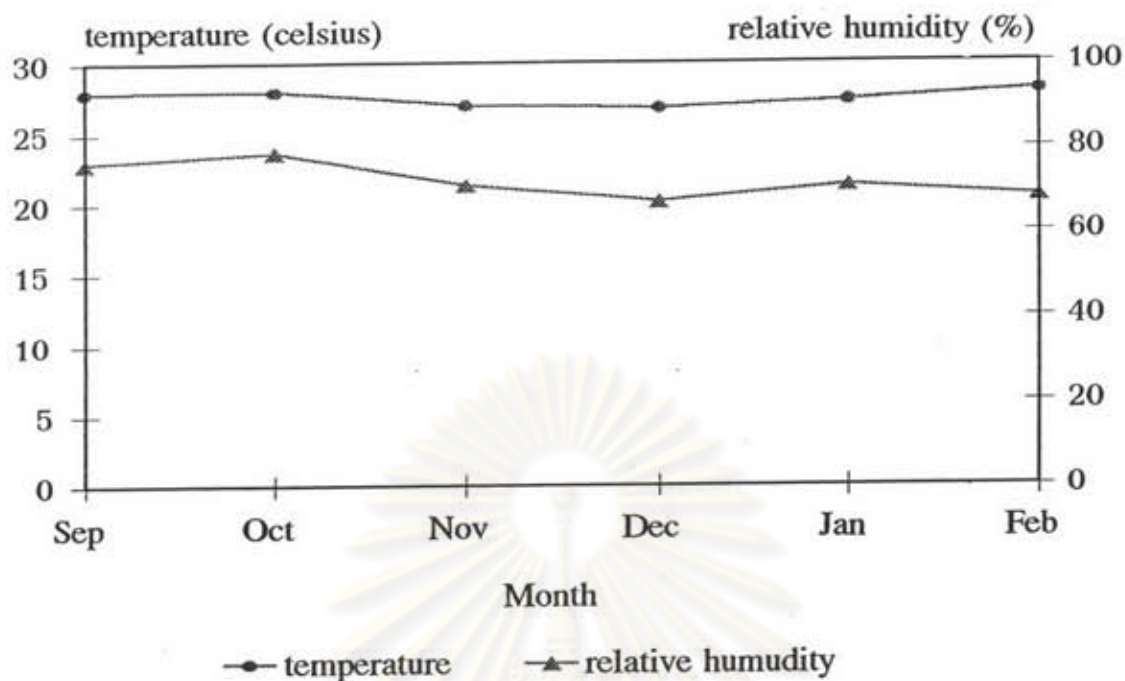


Figure 3.1 Average monthly temperature and relative humidity of Bangkok, Thailand, from September 1994 to February 1995

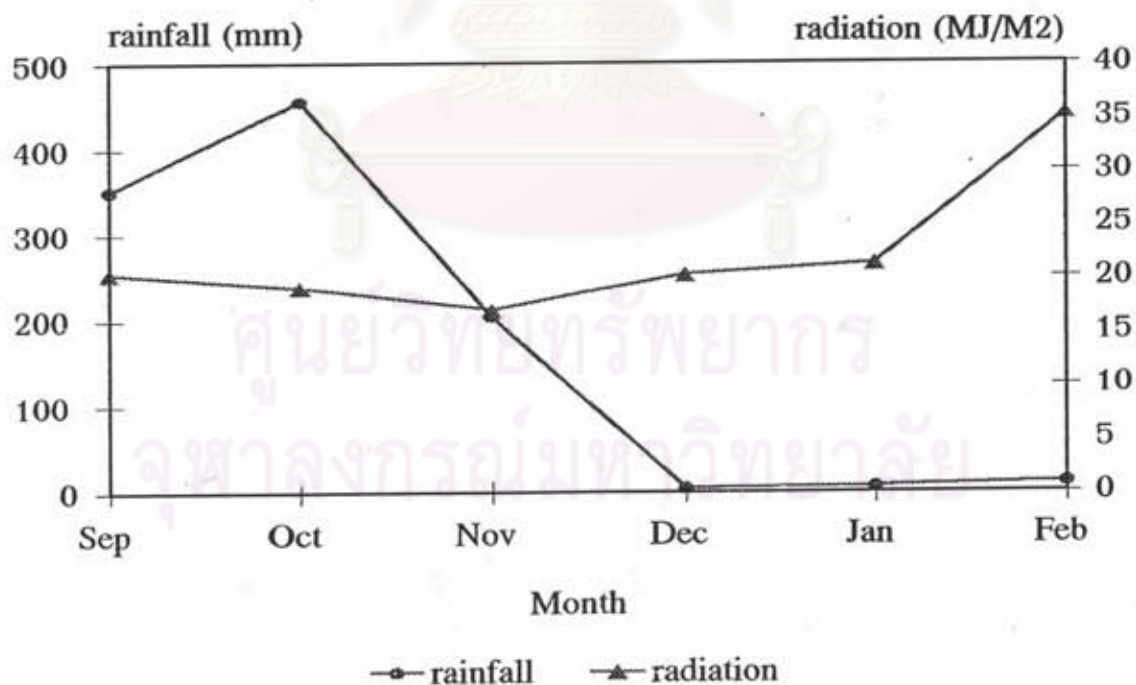


Figure 3.2 Total monthly rainfall and radiation of Bangkok, Thailand, from September 1994 to February 1995

Determination of Tensile Strength and Elongation at Break

The samples were collected at an interval for mechanical testing. According to the ASTM D882, the specimens for tensile testing were cut out along the machine direction, into strips of 25.4 mm wide with a gauge length of 50 mm. Tensile strength was measured by means of INSTRON tensile tester model 1123 with a cross head speed of 100 mm/min. in the test condition of 27±2 °C and 65±2% relative humidity. The thickness of test specimens were measured with a micrometer to the nearest of 0.001 mm. An average of five specimens was reported as a representative value. The resulting stress-strain traces were determined as an average. The tensile strength(σ) was calculated as:

$$\sigma = F/A \quad (3.1)$$

where σ = tensile strength at breaking, N/mm²

F = load at breaking, N

A = cross section area of gauge length section, mm²

The elongation at break was calculated as follows:

$$\% \epsilon = \frac{(L - L_0) \times 100}{L_0} \quad (3.2)$$

where $\% \epsilon$ = elongation at break, %

L = stretched length at break of the specimen, cm

L₀ = original length of the specimen (gauge length), cm

FTIR measurements

The FTIR adsorption spectra of the PE films were recorded on an FTIR spectrophotometer, Perkin-Elmer model 1720, that were used for estimating the changes in the carbonyl group C=O, in the chain at 1715 cm⁻¹. The polyethylene band at 1465 cm⁻¹ served as an internal standard to which the

absorbances of the other bands were related. The results were expressed by the carbonyl index defined as follows (Sung and Nikolov, 1992)

$$I_{CO} = A_{1715} / A_{1465} \quad (3.3)$$

where I_{CO} = Carbonyl index
 A_{1715} = Absorbance of the carbonyl group at 1715 cm^{-1}
 A_{1465} = Internal standard band in PE chain at 1465 cm^{-1}

Molecular Weight Measurements

Molecular weights of the LDPE were determined by the viscosity method, using decahydronaphthalene solution and calculated from the Mark-Houwink-Sakurada equation:

$$[\eta] = kM^a \quad (3.4)$$

where $[\eta]$ = intrinsic viscosity
 M = viscosity average molecular weight
 k, a = constant that can be obtained from the literature for a given polymer-solvent system (Brandup and Immergut, 1975). At temperature 70 °C, k and a are 38.73×10^3 and 0.738, respectively.

Approximately 15 ml of decahydronaphthalene was transferred by a syringe into an Ubbelohde viscometer, which is permanently positioned in the oil bath which was kept at a constant given temperature until the solution attained thermal equilibrium (about 5 min.). The liquid level was brought about approximately 10 mm above the upper graduation mark in the viscometer capillary. As the meniscus passed this point, the timer was started and the interval for the solution to drain to the lower mark in the capillary was tuned. The efflux time of the solution was measured at least three times. Three consecutive readings should agree within 0.2 second. The solution was then removed from the viscometer.

The samples were weight and dissolved with hot decahydronaphthalene. The solution were made up to the 50 ml mark with solvent maintained at a given temperature by means of a syringe, and the flasks were shaken once again. In the same manner as decahydronaphthalene, three consecutive efflux times of the first LDPE solution were transferred respectively into three 25 ml volumetric flasks, and then all solutions were made up to the 25 ml mark with the solvent maintained at the given temperature.

Determination of the Resistance of the Starch-LDPE Films to Fungi

The test of degradability resistance of starch-LDPE films was carried out according to ASTM G21-90.

1. Preparation of Fungus Spore Suspension

Two strains of fungi: *Aspergillus niger* and *Penicillium pinophilum* were used in the experiment. The stock cultures of each strain were used to prepare spore suspensions. The suspensions were made by pouring 10 ml. of 0.85% sodium chloride sterile solution into one subculture of each fungus. The spore suspension was diluted with the sterile salt solution in a manner that the resulting spore suspension was diluted to 1×10^7 to 2×10^7 spores/ml, as determined by a counting chamber.

2. Preparation of Nutrient-salts Agar

A nutrient-salt agar, a medium without a carbon source, was prepared according to the following formula by dissolving in 1 L of water:

Potassium dihydrogen orthophosphate (KH_2PO_4)	0.7 g
Magnesium sulfate ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$)	0.7 g
Ammonium nitrate (NH_4NO_3)	1.0 g
Sodium chloride (NaCl)	0.005 g
Ferrous sulfate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$)	0.002 g
Zinc sulfate ($\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$)	0.002 g
Manganeous sulfate ($\text{MnSO}_4 \cdot \text{H}_2\text{O}$)	0.001 g
Agar	15.0 g
Potassium monohydrogen orthophosphate (K_2HPO_4)	0.7 g

The test medium was sterilized in an autoclave at 121 °C for 20 minutes. The medium was then kept in a 100 ml. bottle for use in the next step.

3. Preparation of Plastic Sample for Biodegradability Investigation

The thin film plastic of 2.5×5 cm. were sterilized by dipping in 95% ethyl alcohol for 10 minutes, the samples were then stored for spore inoculation.

4. Inoculation

Sufficient nutrient-salt agar was poured onto the sterile dishes to provide a solidified agar layer with 3 to 6 mm in depth. After the agar solidified, the medium was inoculated by spreading 0.1 ml of the fungus spore suspension (prepared in 1.), throughout the surface of the agar. The plastic samples were then placed on the inoculated agar surface.

5. Incubation of Inoculated Samples

The inoculated test specimens were covered and incubated in an incubator at 30 °C, for 30 days. The growth of fungi was recorded after 1 month.

Dispersibility Measurement

A Polarized Light Microscope, Model AFXII, with camera, Nikon CO.,Ltd., Japan, was used to observe the cassava starch granules and their dispersibility in the LDPE matrix.

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