

CHAPTER 3

EXPERIMENTAL

3.1 Chemicals, Equipment and Glassware

3.1.1 Chemicals

Cassava Starch was obtained from Thai Wah Co., Ltd. It was produced from *topioca* cultivated in summer. It contains 13% moisture, 0.15% ash, and has the pH value of 4.50-7.00 and viscosity of 600 BU.

Styrene, S, was obtained from HMT Polystyrene Co., Ltd. It was purified and fractional distilled at the atmospheric pressure and was stored under nitrogen gas in a refrigerator.

Polystyrene (GPPS grade, High-heat resins, G-150B) was obtained from HMT Polystyrene Co., Ltd. Physical properties of the material are listed in Table 3.1.

Zinc Stearate (light absorbent, prooxidant) was obtained from Coin Chemical (Thailand) Co., Ltd. Chemical and physical properties are listed in Table 3.2.

Epolene wax (E-43p, dispersing agent) was obtained from White Group Co., Ltd. The properties of Epolene wax are listed in Table 3.3.

3.1.2 Glassware and Equipment

3-necked round bottom flask, beakers, funnel, erlenmeyer flask, condenser, hot plate, magnetic stirrer, and water bath circulator.

Cobalt-60 source (Gamma cell 220 of 24,480 Curies from NORDIAN International Inc., Canada).

Two-roll mill compounding machine (Labtech Engineering Co., Ltd., Model LRM 110) and cutting machine.

Compression molding machine (Labtech Engineering Co., Ltd., Model LP 20).

Carbon Arc Lamp machine, continuous light ($\lambda = 320-390$ nm), (Suga Test Instruments Co., Ltd., Model FAL-5, Arc voltage/current = 135 V and 16 A)

LLOYD tensile tester model LR 100K.

FTIR Spectrophotometer (Perkin-Elmer, model 1760)

Scanning Electron Microscope, SEM (JEOL, model JSM-5410LV)

Thermogravimetric Analyzer, TGA (Perkin-Elmer, model 7)

Gel Permeation Chromatography, GPC (LC-10AD, CTO-10AC, C-R7A plus, Shimadzu, with an ultraviolet-visible detector, SPD-10AV)

3.2 Preparation Scheme

In order to ease understanding of the entire synthesis process, Figure 3.1 reveals the preparation of starch-g-polystyrene, characterization of the graft copolymer, their blends with polystyrene, physical, chemical and degradation properties testing of the blends.

Table 3.1 Properties of Polystyrene (GPPS grade)

Properties	ASTM Test Method	TYPE of GPPS		
		High Heat	Medium Flow	Easy Flow
Melt flow rate	D1238	1.6	8.5	21
Tensile properties	D638			
Strength at break, psi		8200	6000	5400
Elongation at break, %		2.4	1.5	1.4
Modulus at break, %		484	485	445
Flexural strength, psi	D790	12000	8700	7200
Flexural modulus, 10^3 psi	D790	457	465	455
Vicat softening temp., °C	D1525	108	93	85
Deflection temp., °C at 246 psi (annealed)	D648	103	85	77
Izod impact, ft-lb/in.	D256	0.45		

Table 3.2 Chemical and Physical properties of Zinc Stearate ($Zn(C_{17}H_{35}COO)_2$)

Properties	Apparent and Value
Appearance	White powder
Specific Gravity	1.09
Bulk Density	0.1-0.2 g/cm ³
Moisture	1.0% max
Melting Point	115-125°C
Metallic Content	9-11%
Free Fatty Acid	1.0% max
Particle Size	200 mesh 99% min. pass.

Table 3.3 Typical properties of Epolene Wax

Properties	Value
Ring and Ball Softening Point	157°C
Density	0.934 g/cm ³ at 25°C
Acid Number	47
Brookfield Thermosel Viscosity ^a (cP)	
At 140°C	Solid
At 150°C	Solid
At 190°C	400
Color, Gardner scale	11
Molecular Weight (GPC)	
\bar{M}_w	9100
\bar{M}_n	3900

^acP = centipoise

a = Conventional Brookfield viscosity

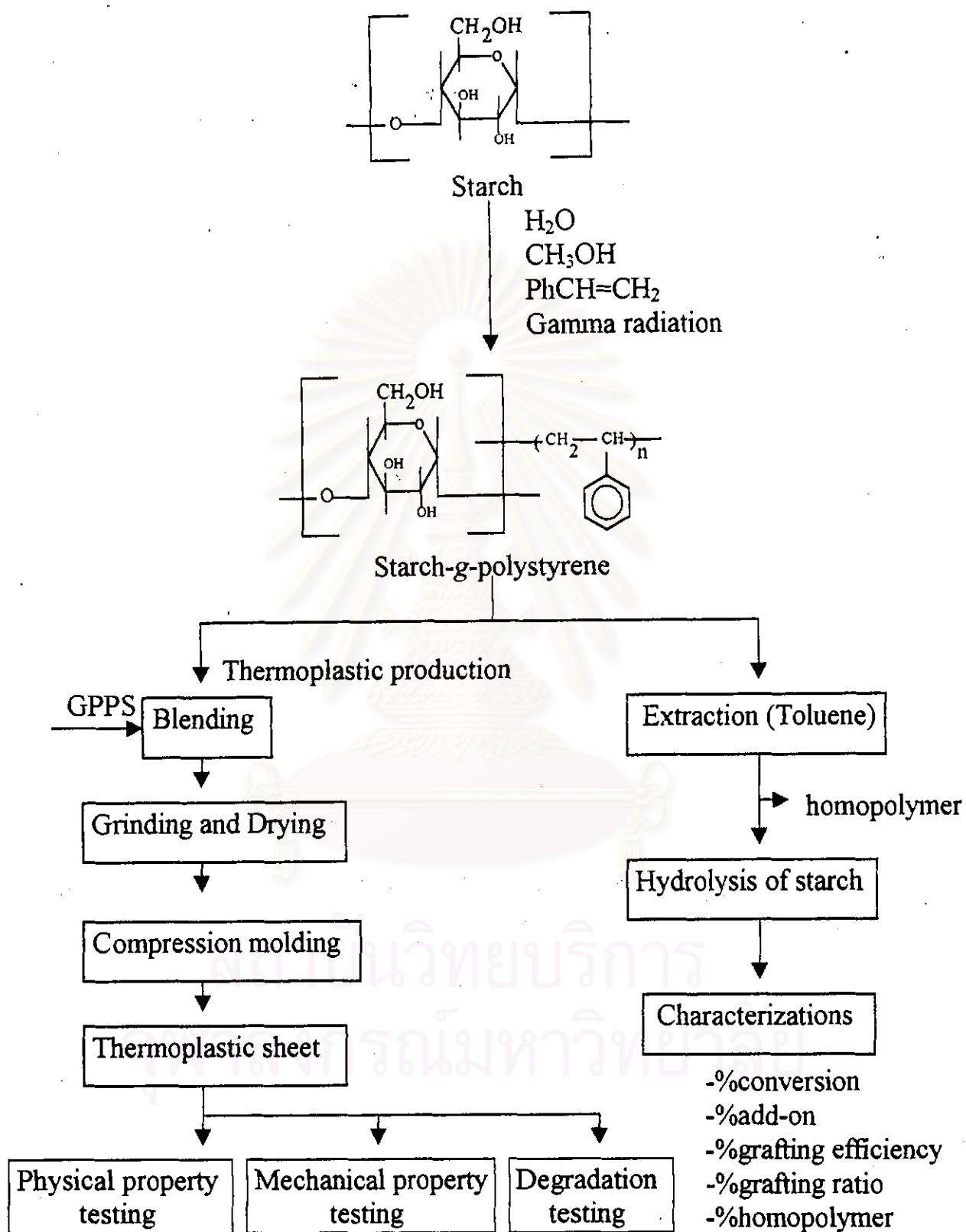


Figure 3.1 Overall schematic experimental process

3.3 Procedure

3.3.1 Grafting of Styrene onto Cassava Starch by simultaneous irradiation

In simultaneous grafting reactions, 4 g each of starch and styrene were blended with 1 cm³ water and 1.5 cm³ of methanol, the mixture was removed into the 250-cm³ tube and purged with nitrogen gas for 10 minutes. It was closed tightly with foil and parafin film, and then irradiated under gamma rays at various total doses. The reaction product was isolated by filtration, washed with methanol, and dried in a vacuum oven at 60°C for 24 hours.

To obtain a good yield of the copolymer, important reaction effects on graft copolymerization were carried out as follows:

3.3.1.1 Effect of Total Dose (kGy) on Graft Copolymerization

At a fixed dose rate of 2.5×10^{-3} kGy/sec, various quantities of total dose of 2, 4, 6, 8, 10, 12, 14, and 16 kGy of gamma rays were irradiated to the mixture of the starch-styrene as described in Section 3.3.1.

3.3.1.2 Effect of The Nitric Acid on Graft Copolymerization

One cm³ of 0.1-N HNO₃ was added to the mixture to investigate the effect of nitric acid on graft copolymerization. After gamma rays irradiation, the product was filtered and washed with methanol until the neutralized starch-polystyrene was obtained.

3.3.2 Homopolymer Extraction by Toluene

The total dried product (about 6 g) derived from Section 1 was extracted by Soxhlet extraction with toluene for 24 hours. The extracted product was filtered, washed with methanol and dried in a vacuum oven at 60°C for 24 hours and weighed to determine the amount of the homopolymer, polystyrene. All products were detected with an FTIR spectrophotometer (Perkin-Elmer model 1760).

3.3.3 Copolymer Characterization

3.3.3.1 Determination of Percent Add-on

In a 500-cm³ erlenmeyer flask equipped with a condenser, 3.00 g of the toluene-extracted polymer was stirred in 250 cm³ of 1.5 N HCl and the mixture was refluxed for 2 hours. The water-insoluble polymer was filtered, then washed until the pH of the washed solution was 7, and then it was dried. The weighed percentage polystyrene in the graft copolymer or the so called "percent add-on" was computed from the weight difference between the graft copolymer and the insoluble starch which was removed by acid hydrolysis.

3.3.3.2 Determination of Percent Conversion

The experimental procedures described in Section 3.3.1 was carried out. The weight of the graft copolymer along with homopolymer was regarded as the total amount of polymer obtained from the weight of monomer. Percent conversion was subsequently calculated.

3.3.3.3 Determination of Homopolymer Formation

The weight obtained from Section 3.3.2 was the amount of polystyrene produced as a by-product.

3.3.3.4 Determination of Grafting Efficiency

The experimental procedures of Sections 3.3.1 through 3.3.3.1, which gave the weight difference between the total weight of polymer and the weight of homopolymer produced were carried out to determine percentage grafting efficiency.

3.3.3.5 Determination of Grafting Ratio

The experimental procedures of Section 3.3.3.1 giving the weight of the polymer in grafts and the weight of substrate was regarded as the percentage grafting ratio.

3.3.4 Compounding of Plastic Materials

A two-roll mill compounding machine, Labtech Engineering Co., Ltd., Model LRM 110, was used. The temperature of the front roll was set at 180°C and the temperature at the back roll was 190°C. The temperatures of two clean rolls were maintained constantly for 60 minutes. The nip between the rolls was adjusted to be about 3-mm wide. The polystyrene resin was poured on the rolls and preheated for 3 minutes.

The rolls were allowed to move while the plastic was melting. Starch and graft copolymer were then mixed with a 2% (w/w) dispersing agent (Epolene wax, E-43p), specified amounts of soya oil and zinc stearate, and the mixture was gradually filled into the molten plastic. The composition of each compounding formula was shown in Table 3.4. A brass scraping knife and a wood-scraper were necessary for manual mixing so as to increase good homogeneity in all directions. The time for compounding was 20 minutes. After the compounding, the starch-polystyrene sheet formed was removed from the two-roll mill.

3.3.5 Compression Molding

The starch-polystyrene sheet was cut into small chips by a cutting machine. The mixture was placed in a mold whose dimension was 150 mm x 150 mm x 1 mm. Then, it was preheated on the heating part for about 5 minutes. Compression molding of the composite was done at 180°C. The molding time was 5 minutes and the pressure used was 6895 kN/m². Finally, the compressed sheet was transferred to the cooling part and cooled for 5 minutes with the constant pressure at 6895 kN/m² during the process. The sheet composite was cut to fit the standard test method for tensile property of plastics (ASTM D638M-91) [24] and hardness measurements (ASTM D2240-97) [25].

Table 3.4 The composition of starch-polystyrene sheets

Formula	Sample Code	Content (g)				
		PS	Starch	Starch-g-PS	Soya oil	Zinc stearate
1	PS	100	0	0	0	0
2	PS-S5-G5/1	100	5	5	2	0.1
3	PS-S5-G5/2	100	5	5	2	0.2
4	PS-S5-G5/3	100	5	5	2	0.4
5	PS-S5-G5/4	100	5	5	4	0.1
6	PS-S5-G5/5	100	5	5	4	0.2
7	PS-S5-G5/6	100	5	5	4	0.4
8	PS-S5-G5/7	100	5	5	8	0.1
9	PS-S5-G5/8	100	5	5	8	0.2
10	PS-S5-G5/9	100	5	5	8	0.4
11	PS-S5-G10/10	100	5	10	2	0.1
12	PS-S5-G10/11	100	5	10	2	0.2
13	PS-S5-G10/12	100	5	10	2	0.4
14	PS-S5-G10/13	100	5	10	4	0.1
15	PS-S5-G10/14	100	5	10	4	0.2
16	PS-S5-G10/15	100	5	10	4	0.4
17	PS-S5-G10/16	100	5	10	8	0.1
18	PS-S5-G10/17	100	5	10	8	0.2
19	PS-S5-G10/18	100	5	10	8	0.4
20	PS-S15/19	100	15	0	2	0.1
21	PS-S15/20	100	15	0	2	0.2
22	PS-S15/21	100	15	0	2	0.4
23	PS-S15/22	100	15	0	4	0.1
24	PS-S15/23	100	15	0	4	0.2
25	PS-S15/24	100	15	0	4	0.4
26	PS-S15/25	100	15	0	8	0.1
27	PS-S15/26	100	15	0	8	0.2
28	PS-S15/27	100	15	0	8	0.4
29	PS-G15/28	100	0	15	2	0.1
30	PS-G15/29	100	0	15	2	0.2
31	PS-G15/30	100	0	15	2	0.4
32	PS-G15/31	100	0	15	4	0.1
33	PS-G15/32	100	0	15	4	0.2
34	PS-G15/33	100	0	15	4	0.4
35	PS-G15/34	100	0	15	8	0.1
36	PS-G15/35	100	0	15	8	0.2
37	PS-G15/36	100	0	15	8	0.4

3.3.6 Outdoor Natural Exposure

Outdoor weathering test of the sheets composite was carried out. The natural exposures were carried out in Bangkok, Thailand, which is located at latitude 13° 44' N and longitude 100° 34' E. The exposed surfaces of the sample were mounted on racks. The tests were started in July 1997 and continued to December 1997 for 6 months. Samples were removed after 2 weeks, 1 month, 6 weeks, 2, 3, 4, 5 and 6 months. Plastic mechanical properties, molecular weight distribution and thermal property were determined. The meteorological and radiation data at the site were collected from the Monthly Report of the Climatology Division, Meteorological Department. The collected data, including the average of temperature, %relative humidity, total radiation, rainfall amount, are listed in Table 3.5 and shown in Figures 3.2-3.3.

Table 3.5 Meteorological data from July – December

Month	Temperature* (°C)	Relative* Humidity, (%)	Rainfall* Amount, mm	Radiation** MJ/m ²
July	29.7	69	34.0	16.61
August	29.5	70	122.6	18.19
September	28.7	76	360.3	14.45
October	28.9	75	218.8	16.39
November	29.0	69	31.6	15.83
December	29.1	65	28.5	33.35

*July 1997 – December 1997. The actual radiation dose for 1997 could not be obtained because the radiometers of the Meteorological Department were out of order which could not be repaired due to the country's economic crisis. They suggested to use the data of 1996 instead which was relatively reliable.

**July 1996 – December 1996.

3.3.7 Indoor Exposure Test

Indoor exposure test was used to compare with the outdoor exposure test. The tests were started in July 1997 and continued to December 1997 for 6 months. The plastic composite was removed every month for the mechanical property measurement.

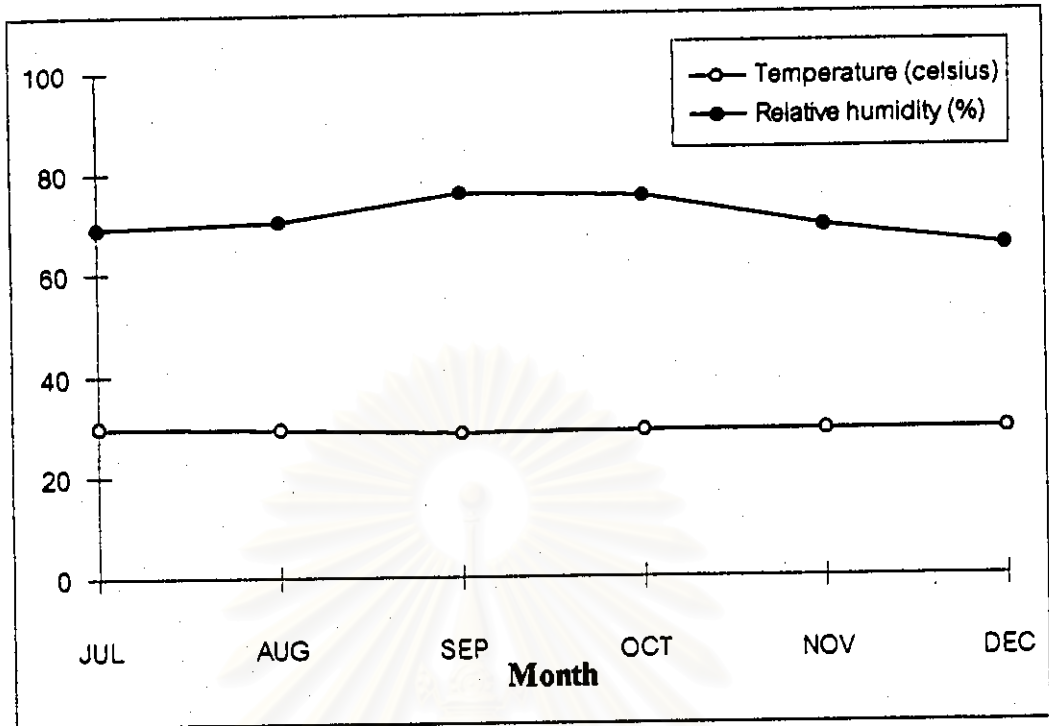


Figure 3.2 Average monthly temperature and relative humidity of Bangkok, Thailand, from July 1997 to December 1997.

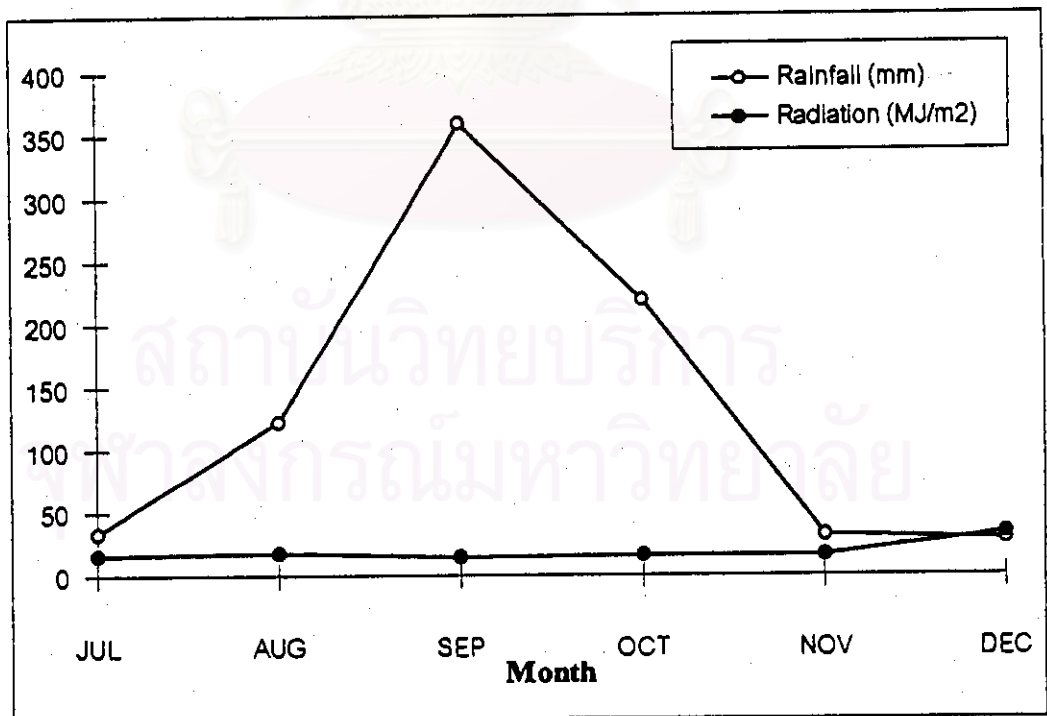


Figure 3.3 Total monthly rainfall (July 1997 to December 1997) and radiation (July 1996 to December 1996) of Bangkok, Thailand.

3.3.8 Soil Burial Test

A naturally soil burial experiment provides an realistic environment with seasonal changes in terms of soil wetness, temperature, and the presence of microorganisms. The tests was started in June 1997 and continued to November 1997 for 6 months. The soil were placed in a perforated plastic box to permit the access of microorganisms and moisture. The box was buried at a depth of 7-9 in. After sampling, the plastic sheets were stored in dark until testing. The plastic samples were removed every month. After removal, the samples were washed in distilled water and dried at 50°C in a vacuum oven for 24 hr and plastic mechanical properties were determined.

3.3.9 Gamma Radiation

The plastic samples were irradiated under gamma rays by Gamma cell 220 from NORDIAN International Inc., Canada, at a fixed dose rate of 2.5×10^{-3} kGy/sec to various quantities of total dose of 50, 100, 150, 200, 250, 300 kGy. Tensile property, hardness measurements (shore A), thermal properties, and molecular weight distribution were determined.

3.3.10 UV Irradiation Test

The Carbon Arc Lamp Machine, continuous light ($\lambda = 320-390$ nm), (Suga Test Instruments Co., Ltd., Model FAL-5, Arc voltage/current = 135 V and 16 A) was used to evaluate the photosensitivity of each plastic sheet. The plastic sheets were placed into the carbon arc lamp machine at a specific distance of 25.4 cm from the horizontal plane of the source and removed after 0.5, 5, 10 and 21 hours of exposure. Tensile property, hardness measurements, thermal property and molecular weight distributions of the exposed plastics were determined.

3.3.11 Determinating of the Bacteria Resistance of the Starch-PS sheets

The test of degradability resistance of starch-PS sheets were carried out in accordance with ASTM G22-76 [26].



3.3.11.1 Preparation of Bacteria Cell Suspension

Bacillus coagulans 352 was used in the experiment. The stock culture was used to prepare bacteria cell suspension. The suspensions were made by pouring 10 cm³ of 0.85% sodium chloride sterile solution into one subculture of bacteria. The bacteria cell suspension was diluted with the sterile salt solution in a manner that the resulting bacteria cell suspension was diluted to 2×10^4 to 15×10^4 cells/cm³, as determined by a Plate Count Technique.

3.3.11.2 Preparation of Mineral-salts Agar

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

Potassium monohydrogen orthophosphate (K ₂ HPO ₄)	0.7	g
Potassium dihydrogen orthophosphate (KH ₂ PO ₄)	0.7	g
Magnesium sulfate (MgSO ₄ .7H ₂ O)	0.7	g
Ammonium nitrate (NH ₄ NO ₃)	1.0	g
Sodium chloride (NaCl)	0.005	g
Ferrous sulfate (FeSO ₄ .7H ₂ O)	0.002	g
Zinc sulfate (ZnSO ₄ .7H ₂ O)	0.002	g
Manganeous sulfate (MnSO ₄ .H ₂ O)	0.001	g
Agar*	15.0	g

*In liquid media, the medium (without agar) was used.

The test medium was sterilized in an autoclave at 121°C for 20 minutes.

3.3.11.3 Preparation of Plastic Sample for Biodegradability Investigation

The plastic sheet (thickness = 0.423 mm) was sterilized by dipping in 95% ethanol for 10 minutes, the samples were then stored for cell inoculation.

3.3.11.4 Procedure A (Solid Media)

Sufficient sterile mineral-salts agar was melted and it was cooled to about 45°C. Sufficient seeded agar was poured into suitable sterile dishes to

provide an agar layer from 6 to 12 mm in depth and it was allowed to harden. After the agar is solidified, the medium was inoculated by spreading 0.5 cm³ of bacteria cell suspension (prepared in Section 3.3.10.1), throughout the surface of the agar. The plastic samples (2.5 x 5 cm) were then placed on the inoculated agar surface. The culture dishes were covered and sealed with a masking tape. It was incubated at 35 to 37°C (95 to 99°F) and in an environment which relative humidity was not less than 85% for 30 days.

3.3.11.5 Procedure B (Liquid Media)

The sterile mineral-salts (without agar) of 20 cm³ was pipetted into the tube. The medium was inoculated by pipetting 0.5 cm³ of bacteria cell suspension (prepared in Section 3.3.10.1) into the medium. The plastic samples (2 x 11 cm) were then placed in the tube and incubated at 35 to 37°C (95 to 99°F) for 30 days.

3.3.11.6 Observations

The samples free of growth were washed in an aqueous solution of mercuric chloride for at least 5 min before handling, rinsed in distilled water and air-dry overnight at room temperature. Examination of the surface microstructure of the samples was performed with a scanning electron microscope (JEOL, model JSM-5410LV).