# CHAPTER III

# EXPERIMENTAL SECTION

## 3.1 Materials

### 3.1.1 Polymer Matrix

Low-density polyethylene (LDPE) extrusion film grade LD1902F, supplied by Thai Polyethylene Co, Ltd. was used as a polymer matrix. The melt flow index was 2.0 g/10 min and the density was 0.919 g/cm$^3$.

### 3.1.2 Compatibilizer

Polyethylene/maleic anhydride graft copolymer (PE-g-MA), obtained from DuPont Co., Ltd., USA under trade name Fusabond was used as a compatibilizer. The graft level was 0.5-1 wt%.

### 3.1.3 Photosensitizer

ZnO and Benzophenone purchased from A.C.S. Xenon Limited Partnership were used as photosensitizers.

### 3.1.4 Biodegradable Additive

Banana starch was used as a biodegradable additive. Preparation of banana starch will be described in the next section.

## 3.2 Instrument

Table 3.1 shows the instruments listed consecutively based on the experimental procedure. The detail of each step will be further described in next section.

Table 3.1 Experimental instruments

| Instruments | Model | Manufacturer |
|---|---|---|
| Twin screw extruder | DSR-28 | Thermoprism |
| Chill roll cast film | ECS-T10 | Collin |
| Fourier transform infrared spectroscopy | Impact 400D | Nicolet |
| Thermogravimetric analyzer | TGA 7 | Perkin Elmer |
| Differential scanning calorimeter | Dimond DSC | Perkin Elmer |
| Universal testing machine | LR 100k | LLOYD |
| Scanning electron microscope | JSM-5410 LV | Jeol |

## 3.3 Experimental Procedure

The flow chart of the entire manufacturing process is shown in Figure 3.1

### 3.3.1 Banana Starch Preparation

Green banana was peeled and sliced into small pieces. It was suspended in 0.05N solution. The mixture was ground in a mixer until it was homogenized. The slurry was filtered through sieve (120 μm pore size). Prime starch was sedimented from the filtrate. The starch was washed several times with distilled water until the supernatant layer was substantially free of color. Finally, starch was dried in an air oven at 80°C and kept in a dessicator until being used.

3.3.2 Film Preparation

A twin screw extruder was used to mix the blend composition. Prior to mixing, banana starch was dried in an air oven at 80°C for 24 hours. The constituents, LDPE, banana starch, PE-g-MA, and photosensitizer, were physically premixed before being fed into the extruder. Temperature profile of five zone extruder was 100, 135, 140, 145 and 150°C, respectively. The screw speed was kept at 25 rpm. Starch content was 5, 10, 15, and 20 wt%. In these blends, PE-g-MA was used as compatibilizer at an amount of 10 wt% based upon starch content. The photosensitizer concentration was varied in three different levels, 0.25, 0.50 and 1.0 wt%. The amount of both starch and photosensitizer was varied based on LDPE content.

After mixing into the pellet form, starch based LDPE films were prepared using a chill roll cast film. Barrel temperature was in the range of 100-160°C and the screw speed was 25 rpm.

## 3.4 Selection of Photosensitizer

Two types of a photosensitizer, 1% benzophenone and 1% ZnO, were used to mix with LDPE using a twin screw extruder and then the films were prepared by a chill roll cast film. Photodegradation test of LDPE/benzophenone and LDPE/ZnO films was performed by outdoor exposure. Carbonyl index and tensile properties of the films were tested. The most effective photosensitizer to accelerate photodegradation of the films was chosen to blend with LDPE-starch base films in a various content.

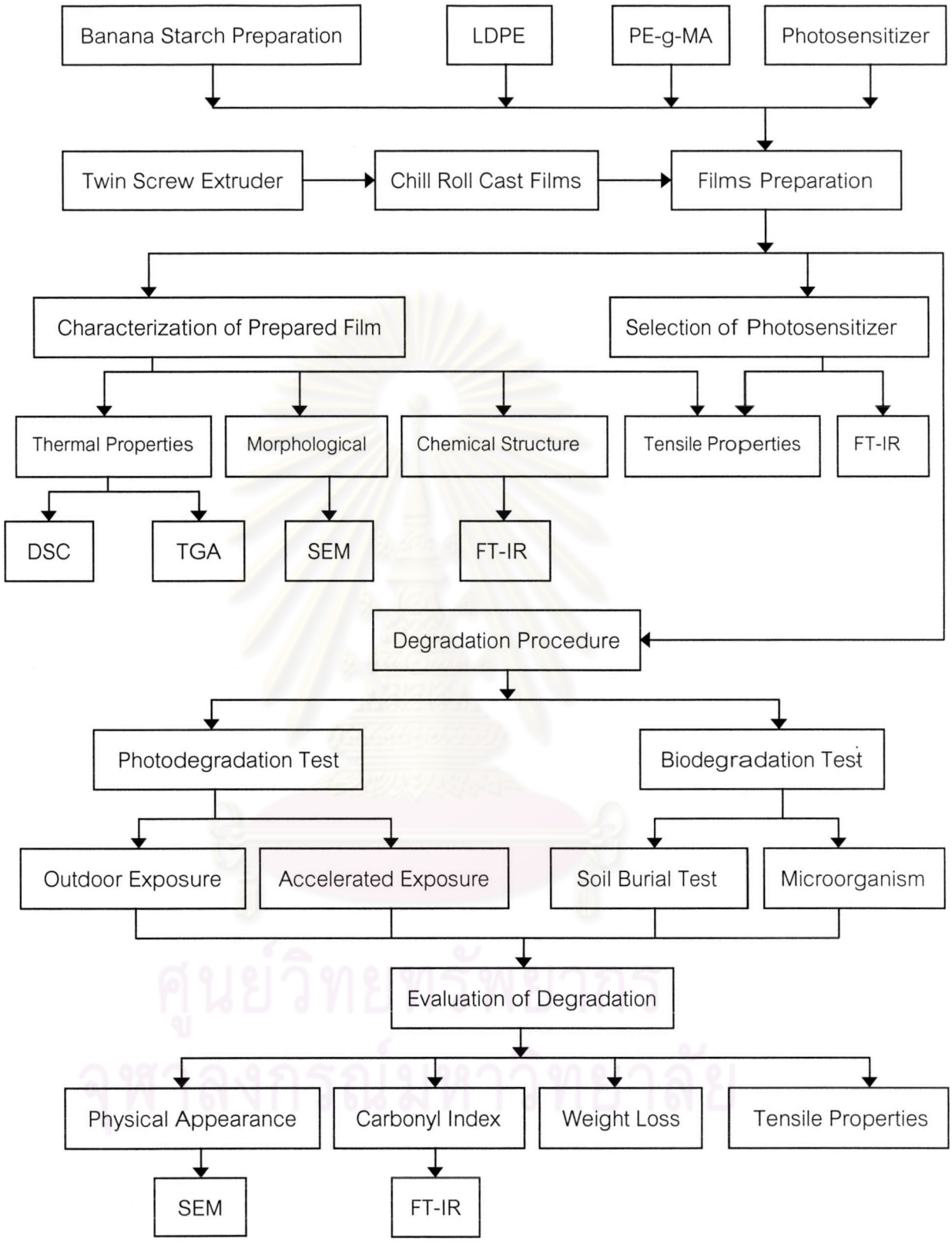


Figure 3.1 Flow chart of manufacturing process.

## 3.5 Characterization of Blend Films

### 3.5.1 Chemical Structure of Films

Fourier Transform Infrared Spectroscopy (FTIR) was used to study the structure and functional group of the blend films. For each spectrum, 32 consecutive scans with 4 $cm^{-1}$ resolution were used. The samples were scanned at a frequency range of 4000-400 $cm^{-1}$.

### 3.5.2 Morphological Studies

Scanning Electron Microscope (SEM) was used to examine the surface of blend films. The surface of the sample was coated with a thin layer of gold before being scanned.

### 3.5.3 Thermal Properties

#### 3.5.3.1 Thermogravimetric Analyzer (TGA)

TGA analysis was carried out under nitrogen atmosphere at a heating rate of 10°C/min from 20°C to 650°C. Prior to do the experiment, the samples were dried in a vacuum oven at 60°C for 24 hours. The onset of degradation temperature ($T_d$) for each sample was recorded.

#### 3.5.3.2 Differential Scanning Calorimeter (DSC)

Sample size with an average weight of 4 mg encapsulated in a hermitically sealed aluminium pan was prepared for each sample. The same temperature history was applied to all samples: first heating from 20°C to 200°C, followed by quenching the sample to 20°C to remove any previous thermal history, and finally heating again to 200°C at a heating and cooling rate of 10°C/min. The melting temperature ($T_m$) and

heat of fusion ($\Delta H_f^*$) of the samples were obtained from the maximum peak and the area under the peak, respectively. The percent crystallinity of the LDPE phase was calculated using the following equation.

$$\% \text{ Crystallinity} = \frac{\Delta H_f^*}{\Delta H_f^o} \times 100$$

where :

$\Delta H_f^o$ = heat of fusion for 100% crystalline LDPE

$\Delta H_f^*$ = heat of fusion of the semi-crystalline LDPE blend

### 3.6 Tensile Properties

Tensile test of rectangular film specimens with the size of 1.5 cm wide, 20 cm long and about 100 μm thickness shaped specimens were conducted using a crosshead speed of 50 mm/min and a gauge length of 10 cm, according to the ASTM D882. At least five specimens of each films were tested and the results were averaged to obtain a mean value.

### 3.7 Photodegradation Procedure



#### 3.7.1 Outdoor exposure



Outdoor exposure of LDPE films containing banana starch and photosensitizer was carried out in Bangkok, Thailand for 4 months. The natural exposure was started from September, 2002 to December, 2002. The samples were prepared in rectangular shape with the size of 25×30 cm, and then fixed on the exposure racks with 45 degree angle to the horizontal. The racks were designed in accordance with the ASTM D1435-94 as shown in Figure 3.2. The tensile properties and carbonyl index of the film samples were tested at every 1 month of an exposure.

Figure 3.2 The exposure racks for outdoor exposure study

Exposure condition for the testing method of photodegradation was based on the report of Thailand weathering climate at Bangkok Metropolis. The weathering climate data were received from the Meteorological Department. The collected data, including average of temperature, %relative humidity (%RH), total radiation and rainfall amount, are shown in Table 3.2.

Table 3.2 Data of Thailand weathering climate (at Bangkok Metropolis)

| Month (in 2002) | Temperature ($^{o}$C) | %RH | Rainfall amount (mm) | Radiation (MJ/m$^{2}$) |
|---|---|---|---|---|
| September | 28.7 | 77 | 197.6 | 472.67 |
| October | 28.6 | 76 | 346.6 | 433.98 |
| November | 28.3 | 73 | 135.9 | 516.53 |
| December | 28.7 | 71 | 54.1 | 502.03 |



3.7.2 Accelerated UV Exposure

Accelerated UV exposure was carried out by using a xenon arc lamp in the Xenotest Beta Lamp chamber as seen in Figure 3.3. This approach is used for evaluating the degradation of plastics exposed in a machine that produces simulated sunlight irradiance and controls temperature and relative humidity.

Figure 3.3 The Xenotest Beta Lamp chamber for accelerated UV

The Xenotest operation program was based on standard method ISO 4892 under the following parameters as shown in Table 3.3

Table 3.3 Xenotest operation parameters

| Parameter | Phase 1 | Phase 2 |
|---|---|---|
| Filter system | Xenochrome 320 | Xenochrome 320 |
| Irradiance (E, $W/m^2$) | 100 | 100 |
| Temperature ($^oC$) | 29* | 27* |
| Rain | no | yes |
| %RH | 76* | - |
| Phase time (minute) | 51 | 9 |



The film samples were collected at every 5,10,15 and 20 hours, respectively. The change in tensile properties and carbonyl index of the films were investigated.

* Average data of temperature and %RH in Bangkok recorded during 1992-2001 by the Meteorological Department.

## 3.8 Biodegradation Procedure

### 3.8.1 Soil Burial Test

Biodegradation of the blends was followed during soil burial for four months. The samples in the form of thin films were cut into size of 1.5 cm × 20 cm. Soil was placed into plastic box (35 × 45 × 35 cm) with tiny holes at the bottom and on each sides of the box to increase air and water circulation. Soil was kept moist with water and stored outside the room at ambient humidity (69-73%) and temperature (26-30$^{o}$C). Samples were buried in soil at a depth of 30 cm. The samples were removed for testing their biodegradation at every one month. After removal, samples were washed with distilled water and dried under vacuum oven at 60$^{o}$C for 24 hours before testing. Measurement performed to follow the biodegradation of sample was the percentage weight loss, tensile properties, and SEM analysis.

### 3.8.2 Determination of Film Resistance to Fungi

The test of degradability resistance of the blend films was carried out according to the ASTM G21-96.

1. Preparation of Fungus Spore Suspension

A strain of fungi, Aspergillus niger, was used in this experiment. The stock culture of strain was used to prepare spore suspension. The suspension was made by pouring 10 ml of 0.85% sodium chloride sterile solution into subculture of fungus. The spore suspension was diluted with the sterile salt solution in a manner that the resulting spore suspension was diluted to $1\times10^{7}$ to $2\times10^{7}$ 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 ($MgSO_4.7H_2O$) | 0.7 g |
| Ammonium nitrate ($NH_4NO_3$) | 1.0 g |
| Sodium chloride (NaCl) | 0.005 g |
| Ferrous sulfate ($ZnSO_4.7H_2O$) | 0.002 g |
| Zinc sulfate ($ZnSO_4.7H_2O$) | 0.002 g |
| Manganous sulfate ($MnSO_4.H_2O$) | 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. 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 thin film plastics of 2.5×5 cm were sterilized by dipping in 95% ethyl alcohol for 10 minutes and then placed on the inoculated agar surface.

4. Incubation of Inoculated Samples

Each inoculated test specimens were covered with a cover dish and incubated in an incubator at 28-30°C and not less than 85% relative humidity. The test

specimens were incubated at such condition for 28 days according to the standard test method.

5. Observation for Visible Effects

After a specific of period of incubation, the specimens were removed from the incubator and the growth rate of the fungi on the films surface was rate followed the Table 3.4. Growth rates are classified according to the film surface covered with colonies of Fungi. A rating of trace or no growth (one or less) must be confirmed by microscopic observation.

Table 3.4 The growth rate of inoculated fungi

| Observed growth on specimens | Rating |
|---|---|
| None | 0 |
| Traces of growth (less than 10% covered) | 1 |
| Light growth (10 to 30% covered) | 2 |
| Medium growth (30 to 60% covered) | 3 |
| Heavy growth (60% to complete coverage) | 4 |

## 3.9 Evaluation of Degradation

### 3.9.1 Tensile Properties

Determination of tensile strength and elongation at break were carried out according to the ASTM D882 method using universal testing machine. Measurement was performed before and after degradation testing with a crosshead speed of 50 mm/min. The dimension of film specimens was 1.5 cm wide, 20 cm long, and about 100 μm thickness. The gauge length of specimens was 10 cm. An average of five specimens was reported as a representative value.

3.9.2 Weight Loss

The weight loss of the films was measured by weighing the sample before and after biodegradation. The percentage weight loss of the film samples was calculated using the following equation:

$$\text{Weight loss (\%)} = \frac{w_i - w_f}{w_i} \times 100$$

where:

$W_i$ = initial weight of sample before degradation (g)

$W_f$ = final weight of sample after degradation (g)

3.9.3 Physical Appearance

Electron micrographs were obtained from the film samples collected before and after biodegradation testing. Each samples were washed with distillated water and dried in a vacuum oven at 60°C for 24 hours. The scanning electron microscope was operated at 15 kV. The surface of films were coated with gold prior to investigation to avoid surface charging under electron beam.

3.9.4 Carbonyl Index

Fourier Transform Infrared Spectroscopy (FTIR) technique was used to monitor the damage caused by UV radiation on the chemical structure change in the films. Film samples were measured before and after the photodegradation testing.

The band index is obtained by peak ratioing of a variable intensity peak against a peak which does not appreciably change after the sample has been exposed to UV radiation. The carbonyl index is a measurement of the amount of oxidation which

occurs in a polymer during UV exposure. The maximum intensity of the peak at 1715 $cm^{-1}$ represented the carbonyl peak measures the amount of oxidation and the maximum intensity of the peak at 1467 $cm^{-1}$ is the characteristic of the polyolefins that was used as a reference peak since its height remains constant during UV exposure. The carbonyl index is therefore the ratio of the absorbance of these two peaks.

The equation for the carbonyl index (I) is

$$I = \frac{\text{Absorbance peak height at 1715 } cm^{-1}}{\text{Absorbance peak height at 1467 } cm^{-1}}$$

Since, the carbonyl index is a measure of the amount of oxidation which happens in a polymer during UV exposure. Therefore, the high value of carbonyl index indicated that the high efficiency in photodegradation.