

CHAPTER III

EXPERIMENTAL

This chapter described the preparation of encapsulated benzophenone by the simple coacervation technique, the preparation of LDPE films containing various types and amount of additives, and the characterization of LDPE films and their photodegradation behavior. The ratios of benzophenone and gelatin, used in simple coacervation, were 1:0.5, 1:1, and 1:2, whereas the amount of hardening agent was 1, 2, and 4 ml. The amount of benzophenone, gelatin, and encapsulated benzophenone, blended with LDPE, was varied from 0 – 5 % by weight of LDPE. The photodegradation was estimated by outdoor exposure test and accelerated weathering test. The degradation behavior was followed by observing the changes in weight loss, tensile properties, and carbonyl index of the films. The morphological changes of film surface were characterized by scanning electron microscopy (SEM).

3.1 Materials

Materials used in this research are as follow.

1. Low-density polyethylene (LDPE) powder grade LD 1902F, supplied by Thai Polyethylene Co, Ltd., was used as a polymer matrix. The melt flow index was 2.0 g/10min and the density was 0.919 g/cm³.

2. Gelatin supplied by Kodak Company (USA) was used as a coating material of encapsulated particles.

3. Benzophenone purchased from A.C.S. Xenon Limited Partnership, Thailand, was used as a photosensitizer and core particle of encapsulated particles.

4. Sodium sulphate purchased from APS Finechem, Thailand, was used in microencapsulation technique for coacervating of gelatin.

5. Formaldehyde (40% v/v) purchased from AJAX Chemicals, Thailand, was used as a hardening agent for encapsulated capsules.

3.2 Instruments

Table 3.1 shows the instruments used in this research, listed consecutively based on the experimental procedure.

Table 3.1 Experimental instruments

Instruments	Model	Manufacturer
Compression molding	-	-
Freeze dryer	Lyopro 6000	Heto
Accelerated Weathering Tester (QUV)	Solar Eye	Q - Panel
Fourier transform infrared spectroscopy	Impact 400D	Nicolet
Thermogravimetric analyzer	TGA 7	Perkin Elmer
Universal testing machine	LR 100k	LLOYD
Scanning electron microscope	Jsm-5410 LV	Jeol

3.3 Procedure

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

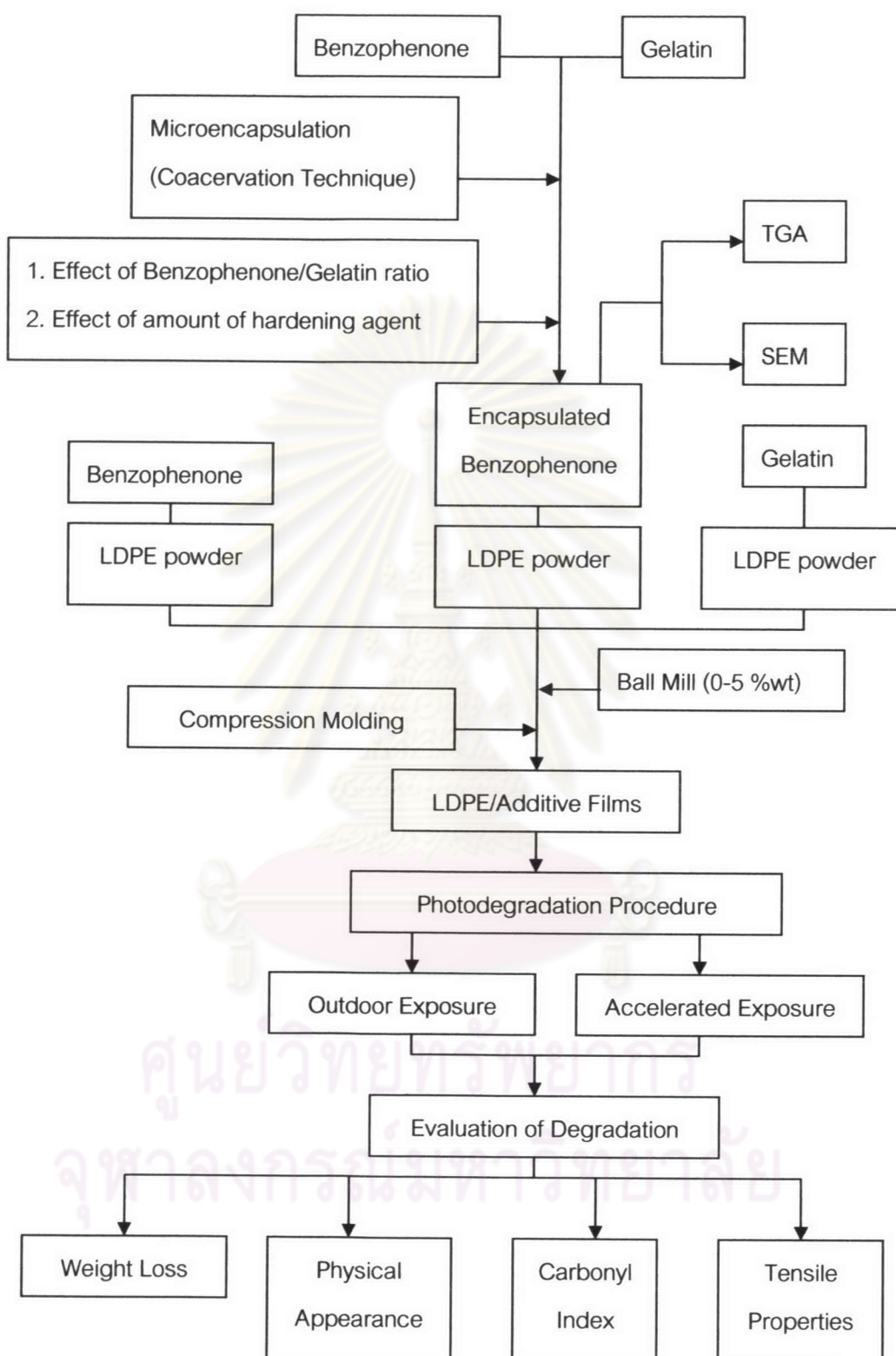


Figure 3.1 Flow chart of the entire manufacturing process

3.3.1 Benzophenone and Gelatin Powder Preparation

Benzophenone and gelatin were prepared into powder by using ball mill. They were ground in the ball mill for 1 day. The ground powder was filtered through the sieve no. 100 in order to receive the homogeneous powder of approximately less than 150 μm .

3.3.2 Preparation of Benzophenone Microcapsules

The microcapsules of benzophenone were prepared by simple coacervation technique [24]. First, benzophenone powder was added to the gelatin solution, prepared by dissolving gelatin in water at room temperature, in which its temperature was adjusted to 35 ± 1 $^{\circ}\text{C}$. The system was homogenized at 1,000 rpm for 15 minutes. After that, the sodium sulphate solution (20 % w/v) was added into the system and the temperature was adjusted to 47 ± 1 $^{\circ}\text{C}$, while the stirring was maintained for another 15 minutes. Then, the formaldehyde (40 %v/v) was added and agitation had been continued for 60 minutes. After that, the ethanol solution was added to remove the unreacted benzophenone and the remaining system was stirred for 15 minutes. Then, microcapsules were washed by distilled water and dried by freeze-drying for 24 hours. The freeze dryer is shown in Figure 3.2. Finally, the microcapsules were filtered through the sieve in order to receive the homogeneous encapsulated capsules before being characterized by scanning electron microscopy and thermogravimetric analyzer. Figure 3.3 presents the flow chart of the microencapsulation technique.

The degradation of LDPE was controlled by varying not only the amount of microencapsulated particles but also the thickness of coating material of the microencapsulated particles. In order to obtain encapsulated benzophenone particles with various wall or coated thickness, the ratio of core to wall or benzophenone to gelatin ratio and the amount of hardening agent were studied.

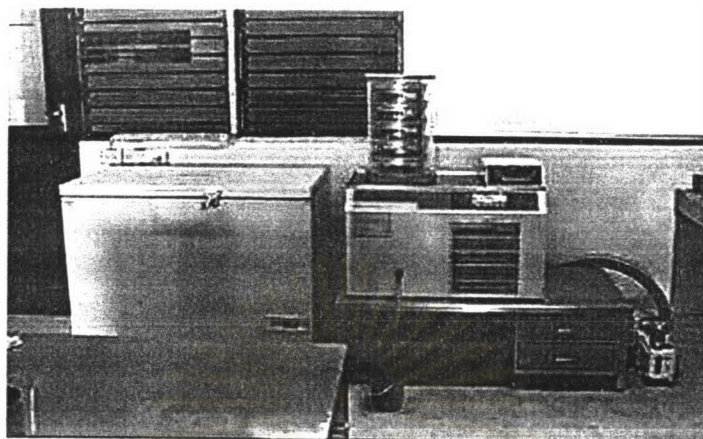


Figure 3.2 The freeze dryer for drying microcapsules

3.3.2.1 Effect of Benzophenone to Gelatin Ratio

Encapsulated benzophenone was prepared at various core to wall ratio (i.e. 1:0.5, 1:1, 1:2), whereas the amount of hardening agent, formaldehyde, was maintained at 2 ml, as shown in Table 3.2. The gelatin solution was prepared by dissolving gelatin powder in water at room temperature.

Table 3.2 The formulation of various core to wall ratio of encapsulated benzophenone

Formulation	Benzophenone (g)	Gelatin (g)	Formaldehyde (ml)
EN1	1	0.5	2
EN2	1	1	2
EN3	1	2	2

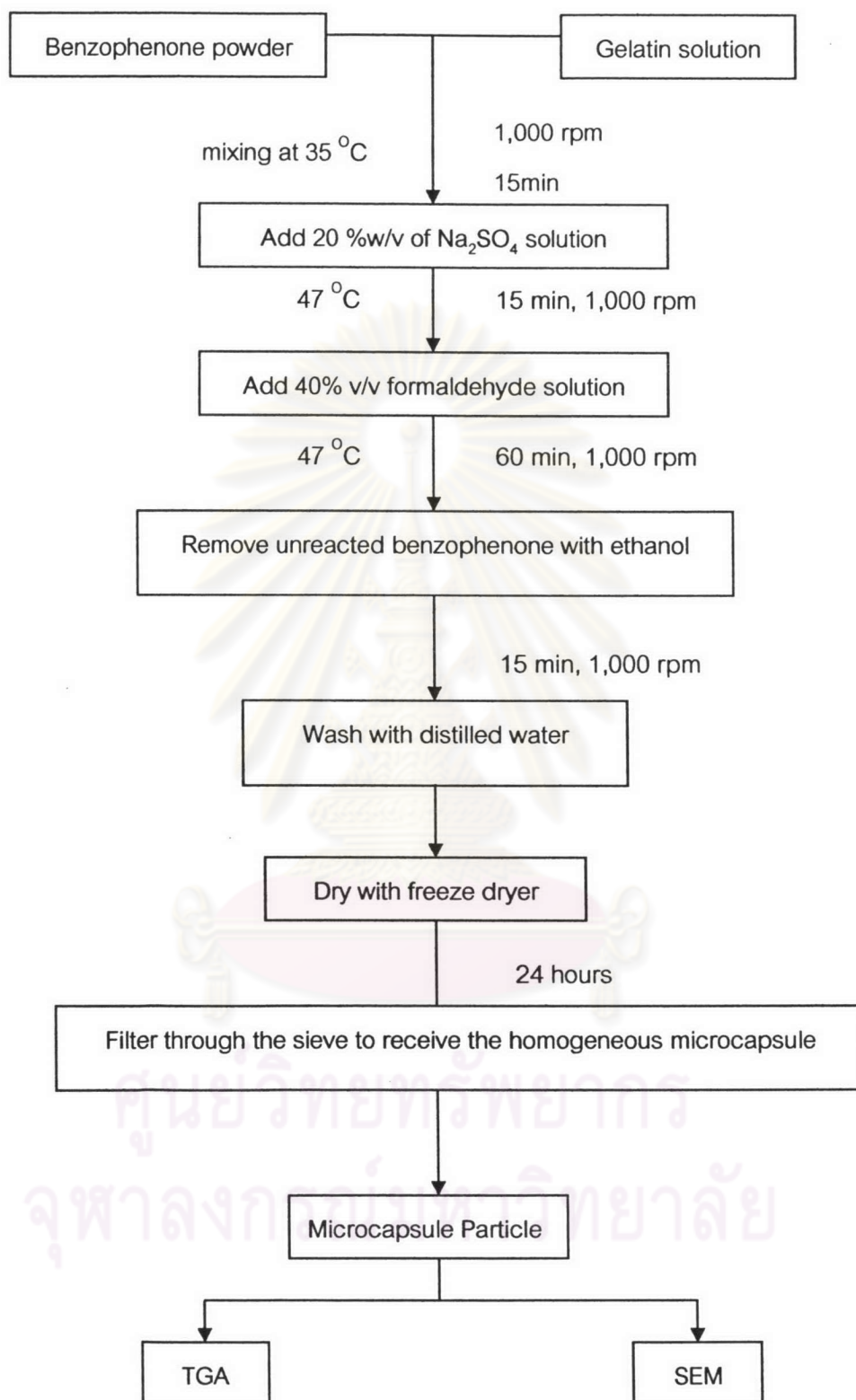


Figure 3.3 Flow chart of the simple coacervation technique

3.3.2.2 Effect of Amount of Hardening Agent

Encapsulated benzophenone was prepared at various concentration of hardening agent i.e., 1, 2, 4 ml, while the benzophenone to gelatin ratio was kept constant at 1:1. The formulation was shown in Table 3.3

Table 3.3 The formulation of various amount of hardening agent of encapsulated benzophenone

Formulation	Benzophenone (g)	Gelatin (g)	Formaldehyde (ml)
EN4	1	1	1
EN5	1	1	2
EN6	1	1	4

3.3.3 Film Preparation

LDPE films were prepared using the compression molding. Prior to do so, the constituents, LDPE and benzophenone, gelatin, or encapsulated benzophenone, were physically premixed in the ball mill for 1 day. The amount of benzophenone, gelatin, or encapsulated benzophenone was varied in four different levels; 0.5, 1, 3, and 5 %w/w of LDPE. Appendix E listed all the formula used in preparation of LDPE films.

The temperature of compression molding was set at 190 °C. Each film was then prepared by compressing the compositions at 4,000 Psi for 2 minutes. The compressed films were suddenly cooled in the air after opening the molds. The dimension of the obtained films was 9 cm x 20 cm with approximately 80 µm thickness.

3.4 Characterization of Encapsulated Benzophenone

3.4.1 Morphological Studies

Scanning Electron Microscope (SEM) was used to examine the surface morphology of microcapsule. The surface of the samples was coated with a thin layer of gold before being scanned. The scanning electron microscope was operated at 15 kV.

3.4.2 Thermal Properties

Thermogravimetric Analyzer (TGA) was carried out under nitrogen atmosphere at a heating rate of 20 °C/min from 20 °C to 600 °C. The onset of degradation temperature (T_d) and the thermal degradation behavior for each sample were recorded.

3.5 Photodegradation Procedure

3.5.1 Outdoor Exposure

Outdoor exposure of LDPE films and LDPE films containing benzophenone powder, gelatin powder, or encapsulated benzophenone were carried out in Bangkok, Thailand for 4 months. The natural exposure was started from October, 2004 to January, 2005. The samples were prepared in rectangular shape with the size of 9x20 cm, and 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 3.4. The tensile properties and carbonyl index including other properties of the film samples were tested at every 1 month of an exposure.

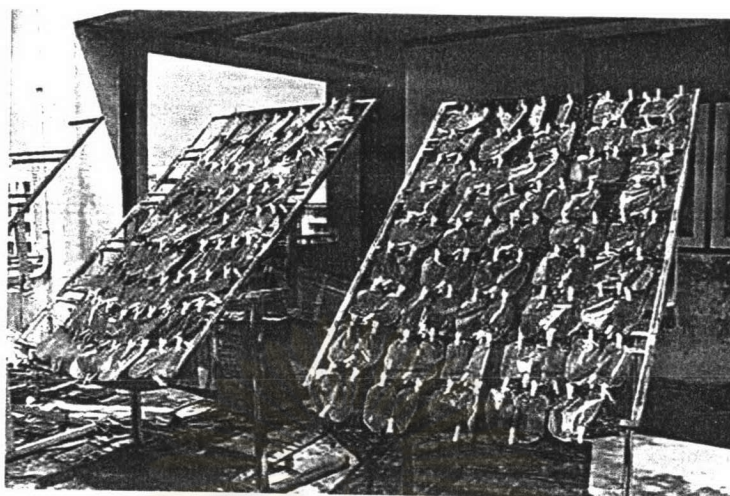


Figure 3.4 the exposure racks for outdoor exposure study

Exposure condition during 4 months of photodegradation testing was based on the weathering climate at Bangkok Metropolis, Thailand. The weathering climate data were received from the Meteorological Department. The collected data, including average of temperature, %relative humidity (%RH), total UV radiation, and amount of rainfall, are shown in Table 3.4

Table 3.4 Data of Thailand weathering climate (at Bangkok Metropolis)

Month (in 2004 – 2005)	Temperature (°C)	%RH	Rainfall amount (mm)	Radiation (MJ/m ²)
October (2004)	30.2	77	50.1	453.78
November (2004)	30.2	76	5.0	535.23
December (2004)	30.2	73	5.0	512.95
January (2005)	28.3	71	46.4	498.67

3.5.2 Accelerated UV Exposure

Accelerated UV exposure was carried out using a 6 as shown in Figure 3.5. It is used to predict the relative durability of materials exposed to the outdoor environment. The damaging effects of sunlight were simulated by fluorescent UVB-313 lamps. Humidity was simulated by a revolutionary condensation system.

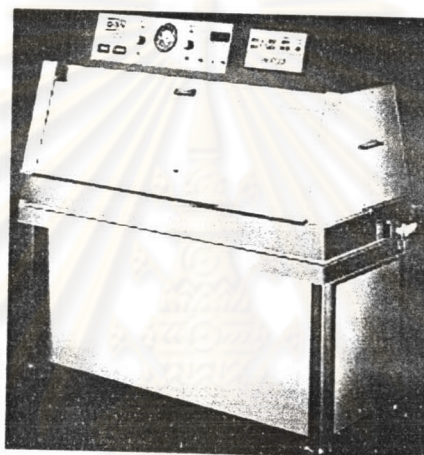


Figure 3.5 The QUV Accelerated Weathering Tester

The QUV operation program was based on ASTM G154 under the following parameters as shown in Table 3.5.

Table 3.5 QUV operation parameters

Parameter	Phase 1	Phase 2
Irradiance (E,W/m ²)	394.4	-
Temperature (°C)	60	50
Condensation system	no	yes
Phase time (hrs.)	8	4

The comparison between outdoor exposure time and accelerated exposure time was calculated as follow:

Thailand UV radiation in 1 year	= $348.34 \times 10^6 \text{ Watt sec/m}^2$
Radiation of 2 UVB lamps	= 197.19 Watt/m^2
Radiation of 4 UVB lamps	= 394.4 Watt/m^2
1 year of outdoor exposure equivalent to	= $(348.34 \times 10^6 \text{ Watt sec/m}^2) / (394.4 \text{ Watt/m}^2)$ = $0.88 \times 10^6 \text{ sec in UVB lamps}$ = 245.34 hrs. in UVB lamps
1 month of outdoor exposure equivalent to	20.5 hrs. in UVB lamps

* Average data of UV radiation in 1 year recorded during 1998-2003 by the Meteorological Department

From the calculating, 1, 2, 3, 4 months of the outdoor exposure time are equivalent to 20.5, 41, 61.5, 82 hours, so the film samples were collected at every 20.5, 41, 61.5, 82 hours, respectively. The tensile properties and carbonyl index including other properties of the film samples were investigated as a function of exposure time.

3.6 Evaluation of Degradation

3.6.1 Weight Loss

Weight loss of films was measured by weighing the sample before and after photodegradation. The percentage weight loss of the film samples was calculated at every 1 month of an exposure using the following equation;

$$\text{Weight loss (\%)} = \frac{W_i - W_f}{W_i} \times 100 \quad (3.1)$$

where

W_i = initial weight of sample before degradation (g)

W_f = final weight of sample after degradation (g)

3.6.2 Physical Appearance

Electron micrographs were obtained from the film samples collected before and after photodegradation. Before investigating the surface morphology of the film samples, each sample was washed with distilled water and dried in an oven at 50°C for 24 hours. The scanning electron microscope was operated at 15 kV. The film surface was coated with gold prior to investigation to avoid surface charging under electron beam.

3.6.3 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. The films samples were scanned at a frequency range of 4,000 – 400 cm^{-1} .

The carbonyl index (CI) is a measurement of the amount of oxidation which occurs in a polymer during UV exposure. 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 maximum intensity of the peak at 1715 cm^{-1} represented the carbonyl peak measured the amount of oxidation and the maximum intensity of the peak at 1467 cm^{-1} is the characteristic of the polyolefin 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 as shown in Equation 3.2

$$CI = \frac{A_{1715}}{A_{1467}} \quad (3.2)$$

where

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

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

3.6.4 Tensile Properties

Determination of tensile strength and elongation at break was 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 approximately 80 μm thicknesses. The gauge length of specimens was 10 cm. An average of five specimens was reported as a representative value.

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