CHAPTER III
EXPERIMENTAL

3.1 Materials

Poly(lactic acid) (PLA) under the trade name of NatureWorks® PLA polymer 4042D (cost = 120 baht/kg), Poly(butylene succinate adipate) (PBSA) under the trade name of Bionolle® 3001G), and Poly(butylene adipate terephthalate) (PBAT) under the trade name of Ecoflex® (cost = 170 baht/kg) were supplied from Thantawan Industry Public Co., Ltd. Native tapioca starch (10-20 μm particle size) was supplied from Thai Wah Public Co., Ltd. 3-Glycidoxypropyltrimethoxysilane was received from Dow Corning Toray Co., Ltd. Methylenedi-p-phenyl diisocyanate (MDI), glycerol and polyethylene glycol (PEG) (MW 200) were purchased from ACROS Organics (Belgium), Merck KGaA (Germany) and Sigma-Aldrich, Inc. (USA), respectively. Maleic anhydride and succinic acid were purchased from Fluka Chemika, Switzerland. Cloisite Na^+ was supplied from Southern Clay Products, Inc. Polyethylene glycol with average molecular weight of 6,000 and 20,000, talc and polyoxymethylene in commercial grade were supplied from Thai Polyacetal Public Co., Ltd.

3.2 Equipment

3.2.1 Twin Screw Extruder

PLA blends were prepared by using a twin screw extruder, Colin D-8017 T20. The barrel length to diameter ratio (L/D) is 30 and is divided into six zones. The temperature in each zone was controlled and adjusted to a specified level. For blends of PLA, the temperature profile from the feed to die section was 80°C, 165°C, 175°C, 185°C, 190°C and 175°C, respectively. For blends containing PBSA, the temperature profile was 80°C, 155°C, 155°C, 160°C, 165°C and 150°C. The speed of screw was used at 30 rpm.

3.2.2 Compression Molding

The compression molding was performed by using a Wabash V50H Press, at 180°C for 15 minutes and at 10 tons compression force for 3 minutes before being cooled down to 50°C.

3.2.3 Film Casting

The film casting was done by using a Brabender PL 2100. The temperature profile from the feed to die section was 90°C, 160°C, 175°C, and 160°C, respectively.

3.2.4 Blown Film Extruder

The film was done by using film blowing machine with an extruder model THIP MT3 02. The temperature of feed, compression 1, compression 2, metering and die zones were 140°C, 145°C, 140°C, 135°C and 130°C, respectively.

3.2.5 Scanning Electron Microscope (SEM)

The morphology of the blends, especially the starch distribution and the bonding quality between the starch filler and polymer matrix, was observed by a SEM in JEOL JSM 5200.

3.2.6 Differential Scanning Calorimeter (DSC)

The thermal properties, including glass transition temperature (T_g), crystallization temperature (T_c) and melting temperature (T_m) were determined by a Perkin-Elmer DSC-7 and a Mettler-Toledo DSC-822 instrument. The sample (7-10 mg) was sealed in an aluminum pan. For the analysis using a Perkin-Elmer DSC-7, the thermal history of a sample was erased by heating it from -20°C to 180°C at a rate of 10°C/min under nitrogen gas, and then cooling it to -20°C at the same rate. The thermal behavior was recorded by the reheating of the sample from -20°C to 180°C and recooling of the sample from 180°C to -20°C at 10°C/min. For Mettler-Toledo DSC-822, the sample was heated from -60°C to 180°C and cooled from 180°C to -60°C at a rate of 10°C/min under protection of nitrogen flow. The thermal behavior was recorded by reheating the sample from -60°C to 180°C and recooling the sample at 10°C/min.

3.2.7 Fourier Transform Infrared Spectroscopy (FT-IR)

The structural characterization was done by a Nicolet/Nexus 670 FT-IR with 32 scans at a resolution of 4 cm^{-1} and recorded from 4000 to 400 cm^{-1}.

3.2.8 Polarizing Optical Microscope

The morphology of spherulites was observed using a Leica/DMRXP polarizing optical microscope. The samples were prepared by pressing the samples between two cover glasses at 200°C using a hot plate. The polarizing optical microscope observation was carried out at room temperature and from 180°C to 30°C.

3.2.9 Mechanical Testing

Tensile strength, Young's modulus and percentage elongation at break were measured according to ASTM D 882-91 using a LLOYD Model LRX Mechanical Universal Testing Machine with a 500 N load cell, a crosshead speed of 20.00 mm/min and a 50 mm gauge length. Test samples were cut into rectangular shape with a size of 10 x 100 mm and the thickness are in the range between 0.1 mm and 0.2 mm for the films from compression molding and the range between 0.05 mm and 0.1 mm for the films from blown film extruder. The results are the average of ten specimens.

3.3 Methodology

3.3.1 Study on Properties of Commercial Biodegradable Plastic Bags

The commercial biodegradable plastic bags, i.e, Terramac®, Lacea® and Bioplast®, were characterized by FT-IR, DSC, polarizing optical microscope and SEM.

3.3.2 Sample Preparation

A series of compounding conditions were considered as summarized in Table 3.1.

3.3.2.1 PLA Compounding by Twin Screw Extruder

Twin screw extruder was applied in order to find the optimum for the film production. For **1-6** and **17-19**, PLA, PBSA and PBAT pellets were vacuum-dried at 50°C for 4 hours, whereas starch was oven-dried at 110°C for 2 hours prior to use in order to remove the moisture. After mixing, the blends were fed into twin screw extruder. The extruded pellets were vacuum-dried at 50°C for 4 hours to remove water. For **2-5**, **17-18** and **19**, the films were prepared by compression molding, film casting and blown film extruder, respectively.

3.3.2.2 PLA Compounding by Mixing in Hot Plate

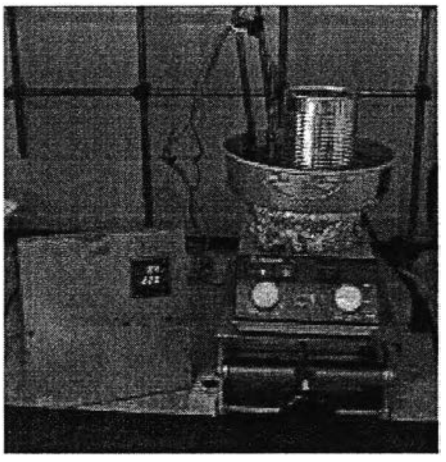

Figure 3.1 Hot plate for blend preparation.

To prepare a certain amount (5 mg) and simplify the compounding preparation steps, a simple hand mixing in hot plate was used (Figure 3.1). For **7-16,** PLA containing different additives were the ones prepared by mixing in the hot plate to study the effect of each additive.

Table 3.1 Components of blends

Sample	PLA	Filler	Plasticizers						Nucleating agents				Compatibilizers			Estimated
		Tapioca starch	PBSA	PBAT	GLY[1]	PEG[2] 200	PEG 6,000	PEG 20,000	Talc	Cloisite Na+	POM[3]	Succinic acid	MA[4]	ES[5]	MDI[6]	cost (baht/kg)
1	70%	30%	-	-	-	-	-	-	-	-	-	-	-	-	-	87
2	60%	30%	10%	-	-	-	-	-	-	-	-	-	-	-	-	92
3	60%	30%	10%	-	-	-	-	-	-	-	-	-	1phr	-	-	151.9
4	60%	30%	10%	-	-	-	-	-	-	-	-	-	-	1phr	-	157.4
5	55%	30%	10%	-	5%	-	-	-	-	-	-	-	-	-	-	107
6	55%	30%	10%	-	-	5%	-	-	-	-	-	-	-	-	-	208
7	80%	-	20%	-	-	-	-	-	-	-	-	-	-	-	-	-
8	80%	-	-	-	-	-	20%	-	-	-	-	-	-	-	-	-
9	80%	-	-	-	-	-	-	20%	-	-	-	-	-	-	-	-
10	100%	-	-	-	-	-	-	-	1phr	-	-	-	-	-	-	-
11	100%	-	-	-	-	-	-	-	-	1phr	-	-	-	-	-	-
12	100%	-	-	-	-	-	-	-	-	-	1phr	-	-	-	-	-
13	100%	-	-	-	-	-	-	-	-	-	-	1phr	-	-	-	-
14	55%	45%	-	-	-	-	-	-	-	-	-	-	-	-	-	-
15	55%	45%	-	-	-	-	-	-	-	-	-	-	-	1phr	-	-
16	55%	45%	-	-	-	-	-	-	-	-	-	-	-	-	0.5phr	-
17	50%	40%	-	-	-	-	10%	-	-	-	-	-	-	1phr	-	149.4
18	50%	40%	-	-	-	-	10%	-	-	-	-	-	-	-	1phr	136.4
19	50%	10%	-	20%	-	-	20%	-	-	-	-	-	-	0.1phr	-	141.5

[1]GLY : Glycerol

[2]PEG : Polyethylene glycol

[3]POM : Polyoxymethylene

[4]MA : Maleic anhydride

[5]ES : 3-Glycidoxypropyltrimethoxysilane

[6]MDI : Methylenedi-p-phenyl diisocyanate