

CHAPTER III

EXPERIMENTAL

3.1 Materials

3.1.1 Polymers

Commercial PLA (trade name 2003D) was purchased from NatureWorks LLC, the United State ($M_w = 287,900$, $M_n = 163,500$). Commercial PBS was purchased from the Mitsubishi Chemicals Co., Ltd, Japan ($M_w = 47,000$, $M_n = 37,000$). Tapioca starch was purchased from ETC International Trading Co., Ltd., Thailand.

3.1.2 Chemical Reagents

L-lactic acid (L-LA) was a gift from PURAC, Thailand, with 88 wt% aqueous solution. Analytical-grade 1,4-butanediol (with 99% purity) and tin(II)-2-ethylhexanoate ($\text{Sn}(\text{OCt}_2)_2$) (with 95% purity) was purchased from Sigma-Aldrich, the United state. Analytical-grade succinic acid (with 99% purity) was bought from Ajax, Australia. *N-N'*-dicyclohexylcarbodiimide (DCC) was purchased from Fluka, Germany. 4-Dimethylaminopyridine (DMAP) was bought from MERCK, Germany.

3.1.3 Solvents

Analytical-grade methanol (CH_3OH), chloroform (CHCl_3), dichloromethane (CH_2Cl_2), and HPLC-grade chloroform was purchased from RCI Labscan. Deuterated chloroform (CDCl_3) was purchased from Sigma-Aldrich, the United State.

3.2 Instruments and Equipment

3.2.1 Structural Characterization

3.2.1.1 *Fourier-transform Infrared Spectroscopy (FTIR)*

Architecture polymer was characterized by using an ALPHA Tensor series Bruker Fourier-transform infrared spectrometer. All FTIR spectra were measured under the room temperature over a scanning range of $4000\text{-}550\text{ cm}^{-1}$ with 32 scans and a resolution 4 cm^{-1} .

3.2.1.2 Nuclear Magnetic Resonance Spectroscopy (NMR)

^1H , ^{13}C , and HMBC 2D NMR analysis were obtained from an Ultrashield 500 Plus Bruker (500 MHz) at room temperature. CDCl_3 were used to dissolve the samples. The chemical shifts were calibrated by using the residual resonance of the solvent peak (7.26 ppm).

3.2.2 Thermal Analysis

Thermal properties were determined by using a DSC 200 F3 Maia NETZCH differential scanning calorimetry under a nitrogen atmosphere. The sample was weighed approximately 5 mg and sealed in an aluminum pan. The temperature ranged between -50 and +200 °C (PLA-based multi-layered films with PBS) and 0 and +200 °C (PLA-based multi-layered films with TPS).

The percent of crystallinity (X_c) is then calculated using the following equation 1 (Mathew *et al.*, 2006):

$$X_c = \frac{\Delta H_m - \Delta H_c}{\Delta H_m^0 \times f} \times 100\% \quad \text{eq. (1)}$$

where ΔH_m and ΔH_c are the enthalpy of melting and crystallization determined by integrating the areas (J/g) under the peaks. ΔH_m^0 is the reference value of melting enthalpy which represents the perfect crystalline PLA homopolymer (93.01 J/g) (Fischer *et al.*, 1973).

3.2.3 Mechanical Testing

Tensile strength, Young's modulus, and elongation at break of multi-layered films were carried out according to ASTM D 638M-91a on a LRX LLOYD universal testing machine with a 500 N load cell.

3.2.4 Compatibility Study

Compatibility of multi-layered films was investigated by a TM3000 Hitachi scanning electron microscope (SEM). The samples were coated with a thin layer of platinum. The accelerating voltage of machine was 15 kV.

3.2.5 Water Absorption

Multi-layered films were immersed in a water chamber at room temperature. After careful blotting of the surface liquid with paper, the samples were

weighed as quickly as possible, almost every day until the weight is constant. Water absorption values were calculated as a percentage of initial weight by the following equation 2 (Amalvy *et al.*, 2002):

$$\% \text{Water absorption} = \frac{W_a - W_i}{W_i} \times 100\% \quad \text{eq. (2)}$$

where W_a and W_i are the after weight and initial weight of samples, respectively.

3.2.6 Barrier Properties

Oxygen barrier testing was carried out in accordance with ASTM D3985-81. Oxygen permeation was measured by using an Ox-Tran 2/21 MOCON oxygen analyzer with an oxygen flow rate 20 cm³/min at 23 °C at 0% RH.

3.2.7 X-ray Diffraction

A Rigaku X-ray diffractometer was applied to determine crystalline pattern of the samples. X-ray diffraction (XRD) experiments were run using Cu K α radiation and operated at 40 kV/30 mA.

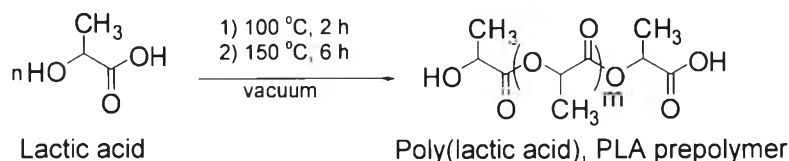
3.3 Methodology

3.3.1 PLA-based Multi-layered Films with PBS

3.3.1.1 *Poly(Lactic Acid) Prepolymer*

L-lactic acid (L-LA) (25.59 mL, 1 mol) in a three-necked round-bottom flask was heated at 100 °C for 2 h under high vacuum to eliminate initial water. After that the polymerization was occurred by adding SnOct₂ (0.1 mol% of L-LA) at 150 °C for 6 h to obtain a viscous product. The viscous product was dissolved in chloroform, precipitated in cold methanol and washed with methanol several times. The precipitate was dried under vacuum at 50 °C for 24 h.

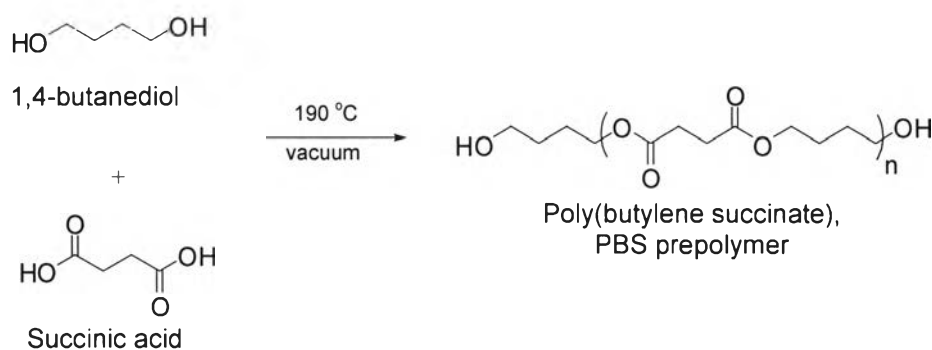
Scheme 3.1



3.3.1.2 Poly(Butylene Succinate) (PBS) Prepolymer

1,4-butane diol (9.75 mL, 0.11 mol) and succinic acid (11.81 g, 0.1 mol) were mixed into a three-necked round-bottom flask with a magnetic stirrer. The reaction was at 190 °C for 6 h under vacuum to obtain a viscous product. The product was collected in the same way as PLA prepolymer to obtain PBS prepolymer.

Scheme 3.2

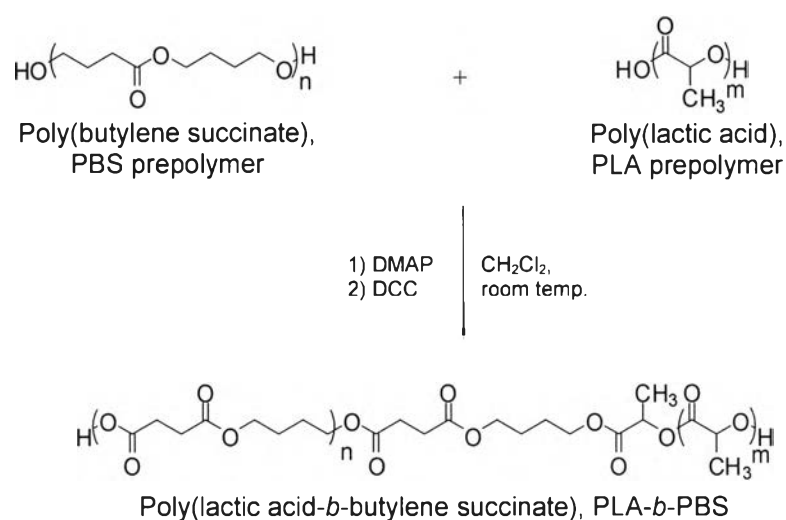


3.3.1.3 Poly(Lactic Acid-*b*-Butylene Succinate) (PLA-*b*-PBS)

PLA prepolymer (MW = 1200-2200) (12 g, 6 mmol) and 10 mol% DMAP (73.3 mg) was dissolved in 120 mL of CH₂Cl₂ by stirring for 10 min at room temperature. The solution of DCC (1.24 g, 6 mmol) which dissolved in 13 mL of CH₂Cl₂ was mixed into the reaction for 10 min. PBS prepolymer (MW = 2000-3000) (21.5 g, 10 mmol) was dissolved in 215 mL of CH₂Cl₂ and added into the reaction. The mixture solution was continued for 36 h at room temperature. The

precipitates were then filtered. The residual solution was heated to obtain viscous product. The viscous product was precipitated and washed in cold methanol several time. The product obtained was dried under vacuum at 50 °C for 24 h.

Scheme 3.3

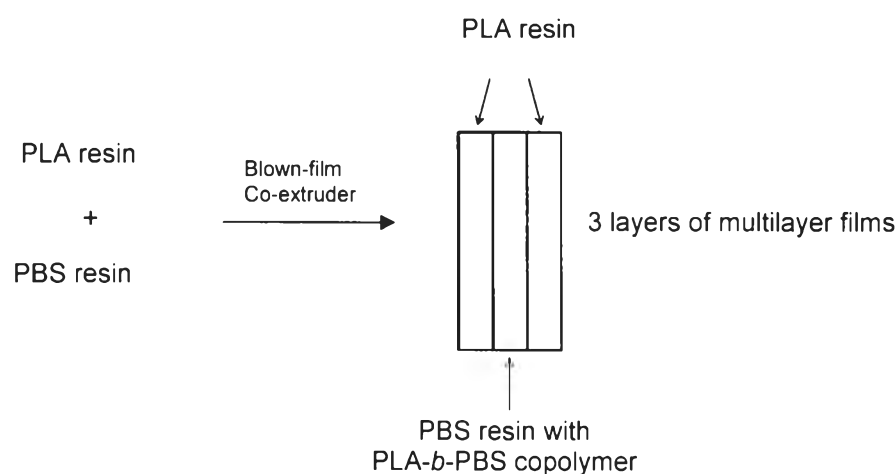


3.3.1.4 PLA/PBS/PLA Multi-layered Film

Three-layered films were formed as films with ~0.05 mm thickness by using a LBE12.5-30 Labtech Engineering multi-layered film blowing line. Temperature and screw speed settings were in range of 140-180 and 40-50 rpm, respectively. The structure of multi-layered films and composition of compatibilizer which was added into core (PBS) layer were shown in Table 3.1, including the sample name that will be used throughout this work.

Table 3.1 Structure of multi-layered films with various PLA-*b*-PBS in PBS phase

Multi-layered films	Content of PLA- <i>b</i> -PBS, phr
PLA/PLA/PLA	0
PLA/PBS/PLA	0
PLA/PBS+PLA- <i>b</i> -PBS0.5/PLA	0.5
PLA/PBS+PLA- <i>b</i> -PBS1/PLA	1.0
PLA/PBS+PLA- <i>b</i> -PBS3/PLA	3.0
PLA/PBS+PLA- <i>b</i> -PBS5/PLA	5.0

Scheme 3.4

3.3.2 PLA-based Multi-layered Films with TPS

3.3.2.1 *TPS Preparation*

Tapioca starch (70 %) and glycerol (30 %) was mixed and then extruded by using a LTE-20-40 Labtech Engineering counter-rotating twin screw extruder. Temperature and screw speed setting were in range of 130-170 °C and 40-50 rpm, respectively.

3.3.2.2 *TPS Blend Preparation*

TPS and PLA resin (2003D) were blended to obtain TPS blend resin in various weight ratios (TPS/PLA 90/10, 80/20, 70/30, 60/40, and 50/50

w/w) by a LTE-20-40 Labtech Engineering counter-rotating twin screw extruder. Temperature and screw speed were set at 140-170 °C and 20-30 rpm, respectively.

3.3.2.3 PLA/TPS/PLA Multi-layered Films

In the same way, PLA/TPS/PLA multi-layered films were blown by changing the layer of PBS to TPS blend. The procedure temperature and screw speed settings were 170-180 °C and 50-60 rpm, respectively. Table 3.2 shows the sample name, composition, and structure of multi-layered films.

Table 3.2 Structure of PLA-based multi-layered films with TPS

Multi-layered film	TPS/PLA blend ratio in core layer
PLA/PLA/PLA	-
PLA/TPS50/PLA	50/50
PLA/TPS60/PLA	60/40
PLA/TPS70/PLA	70/30
PLA/TPS80/PLA	80/20
PLA/TPS90/PLA	90/10
PLA/TPS100/PLA	100/0