



CHAPTER III EXPERIMENTAL

3.1 Materials

3.1.1 L-lactide ((3S)-cis-3,6-Dimethyl-1,4-dioxane-2,5-dione) (99.5% in water)

L-lactide was purchased from Bio Invigor Corporation Co., Ltd.

3.1.2 32 mol% Ethylene Vinyl Alcohol Copolymer (EVAL F171, 1.8 MFI)

32 mol% Ethylene Vinyl Alcohol Copolymer was purchased from Kurarey.

3.1.3 Catalyst

2-ethylhexanoic acid Tin (II) ($\text{Sn}(\text{Oct})_2$) was purchased from Sigma.

3.1.4 Stabilizers

Zinc Stearate ($\text{Zn}(\text{C}_{17}\text{H}_{35}\text{COO})_2$) and Calcium Stearate ($\text{Ca}(\text{C}_{17}\text{H}_{35}\text{COO})_2$) were ordered from Imperial Industrial Chemical Co., Ltd.

3.1.5 Solvents

Chloroform (CHCl_3), isopropyl alcohol, and dimethylformamide (DMF) were purchased from Lab Scan Co., Ltd.

3.2 Equipments

3.2.1 Brabender Mixer

For ring-opening polymerization, the mixture of lactide monomer (50 wt %) and EVOH (50 wt %) mixed with 0.1 wt % of $\text{Sn}(\text{Oct})_2$ and 5 wt % of Zn/Ca stearate stabilizer was placed in the chamber used as polymerization reactor with purged with N_2 gas. Firstly, 25 g EVOH and $\text{Sn}(\text{Oct})_2$ were added to the chamber and mixed for 3 min. Then the 25 g lactide and Zn/Ca were added and mixed further for 30 min. The operating temperatures were varied at 185, 195, and 205 °C. The rotor speeds were maintained at 40 and 60 rpm.

3.2.2 Twin Screw Extruder

For reactive extrusion polymerization, the lactide monomer and EVOH are used as received without further purification. A mixture of lactide and EVOH mixed with 0.1 wt% of Sn(Oct)₂ catalyst and 5 wt% of Zn/Ca stearate stabilizer. The prepared mixture is transferred into a Colin D-8017 T20 twin-screw extruder having a screw diameter of 25 mm and a L/D ratio 30 used as polymerization device. The polymerization occurs during the barrel from hopper to die at the temperature of about 80, 160, 190, 220, 220, and 220 °C, respectively. The polymer is extruded through a strand die and pelletised. The screw speed (30, 40, 50, and 60 rpm), monomer to polymer ratio (50/50, 60/40, 70/30, and 80/20 wt %), and monomer to catalyst ratio (0.1, 0.3, and 0.5 wt %) are varied.

3.2.3 Soxhlet extraction

The resulting polymers received in the reactive extrusion were purified by extraction with isopropyl alcohol at the temperature of about 183 °C for 3 h and with chloroform at the temperature about 160 °C for 3 h. After that the resulting yields were dried in vacuum oven at the temperature of 85 °C for the extracted polymer with isopropyl alcohol and 60 °C for the extracted polymer with chloroform. Then the extracted polymers were characterized by FTIR spectrometer and NMR for studying the chemical structure and calculating the amount of the graft copolymer and homopolymer, conversion, and degree of grafting.

3.2.4 Compression Moulding

The crude graft copolymers obtained from bulk twin screw extruder were prepared into thin film with 0.35 mm thickness by using a Labtech compression moulding machine with preheating for 5 min, followed by heating for 20 min at a force of 25 kN. The operating temperatures of mould were maintained at 200 °C and cooled down to room temperature. Then these thin films were used to study the color intensity. Moreover, the crude polymers were prepared into the sheet with 3 mm thickness by using a Labtech compression moulding machine with the method which was similar to the former method. After that, these sheets were cut into dumbbell-shape for investigating the tensile properties.

3.2.5 Fourier Transform Infrared Spectroscopy (FT-IR)

Infrared spectra of isopropyl alcohol and chloroform extracted EVOH-g-PLA copolymers were recorded on a Nicolet Nexus 670 FT-IR spectrometer in the frequency range of 4000-400 cm^{-1} with 32 scans at a resolution of 4 cm^{-1} . Samples were prepared by casting 0.5 wt % chloroform solutions on KBr pellets, followed by vacuum drying at 50 °C for 48 h. The conversion and degree of grafting are calculated by using FTIR.

3.2.6 Nuclear Magnetic Resonance Spectroscopy (NMR)

^1H NMR measurement, the samples were dissolved in DMSO- d_6 in 5 mm NMR tubes at room temperature. The sample concentration was about 1.0 % by weight. NMR spectra were recorded on a Varian XL-300 NMR spectrometer working at 300.032 MHz for protons.

3.2.7 Thermogravimetric Analysis (TGA)

TG-DTA curves were collected on a Perkin-Elmer Pyris Diamond TG/DTA instrument. The samples were loaded on the platinum pan and heated from 50°C to 550 °C at a heating rate of 10°C/min under N_2 flow of 100 mL/min.

3.2.8 Differential Scanning Calorimetry (DSC)

DSC analyses were carried out by using a Perkin-Elmer DSC 7 instrument. The samples were first heated from 20°C to 200 °C and cooled down with a flow rate of 10 ml/min. The samples was then reheated to 200°C at the same rate.

3.2.9 X-ray Diffraction

X-ray diffraction profiles were measured on a Rigaku Model Dmax 2002 diffractometer with Ni-filtered $\text{Cu K}\alpha$ radiation operated at 40 kV and 30 mA. The film samples were observed on the 2θ range of 2-30 degree with a scan speed of 2 degree/min and a scan step of 0.02 degree.

3.2.10 Scanning Electron Microscopy (SEM)

Scanning electron microscopy was performed on JEOL JSM-5410 Model to observe the morphology of the samples. The extrudates obtained from twin-screw extruder were broken in liquid nitrogen. All of the specimens were coated with gold under vacuum before observation to make them electrically conductive.

3.2.11 Gel Permeation Chromatography (GPC)

Gel Permeation Chromatography (GPC) was carried out in DMF solvent as the mobile phase using KD-806 M column and RID-10A detector. The DMF solvent was filtrated with MN 615 Ø 155 mm filter paper under the vacuum. The crude polymers were dissolved in DMF at the concentration 0.5 wt % and filtrated with 0.45 mm diameter of filter before injecting into the column. The conditions of this machine were 40-85 °C column temperature, 1 ml/min flow rate, and 30 min run time. Molecular weight and molecular weight distribution of PLA were calculated in reference to a polystyrene calibration.

3.2.12 Dynamic Mechanical Analysis (DMA)

DMA analyse were carried out by using a dynamic-mechanical analyzer GABO EPLEXOR QC 25 instrument. The samples were 13 mm x 55 mm x 3 mm (width x length x thickness). The testing temperature was -30 to 100 °C, 10 Hz for frequency. Static and dynamic strains were 3 % and 1.5 %, respectively. The tension mode was used.

3.2.13 Universal Testing Machine

The tensile properties were tested by using an Instron 4206 Universal Testing Machine with cross-head speed of 50 mm/min. The samples were in the dumbbell-shape. The size of sample specimen was 13 mm width of narrow section, 90 mm length of narrow section, and 3 mm thickness.

3.3 Methodology

3.3.1 Synthesis of PLA with EVOH by solution ring-opening polymerization

Ring-opening polymerization of lactide was conducted using stannous octoate ($\text{Sn}(\text{Oct})_2$) as catalyst. The 10 g EVOH was dissolved in 40 ml toluene and heat at 185 °C. This mixture was placed in a round bottom flask, together with 15 g lactide monomer and solution of 0.1 wt%. $\text{Sn}(\text{Oct})_2$ catalyst. The round bottom flask was sealed and conditioned in oil bath kept at a temperature of 200 °C and vigorously shaken until the monomer was melted and the catalyst was completely mixed with the molten monomer. Then the reaction was operated about 24 h. After that the

reaction was stopped by quenching to room temperature. The reacted solution was opaque. The polymerization product was precipitated with dichloromethane for chemical analysis by FTIR spectrometer.

3.3.2 Synthesis of PLA with EVOH by using Brabender Mixer W50

For ring-opening polymerization, the mixture of lactide (50 wt %) and EVOH (50 wt %) mixed with 0.1 wt % of $\text{Sn}(\text{Oct})_2$ and 5 wt % of Zn/Ca stearate stabilizer was taken in the chamber used as polymerization reactor with purged with N_2 gas. The operating temperatures were varied at 185, 195, and 205 °C. The rotor speeds were maintained at 40 and 60 rpm.

3.3.3 Synthesis of PLA with EVOH by using Twin-screw Extruder

For reactive extrusion polymerization, the lactide monomer and EVOH are used as received without further purification. A mixture of lactide and EVOH mixed with 0.1 wt% of $\text{Sn}(\text{Oct})_2$ catalyst and 5 wt% of Zn/Ca stearate stabilizer. The prepared mixture is transferred into a Colin D-8017 T20 twin-screw extruder having a screw diameter of 25 mm and a L/D ratio 30 used as polymerization device. The polymerization occurs during the barrel from hopper to die at the temperature of about 80, 160, 190, 220, 220, and 220 °C, respectively. The polymer is extruded through a strand die and pelletised. The screw speed (30, 40, 50, and 60 rpm), monomer to polymer ratio (50/50, 60/40, 70/30, and 80/20 wt %), and monomer to catalyst ratio (0.1, 0.3, and 0.5 wt %) are varied.

3.3.4 Soxhlet Extraction

The crude graft copolymers were purified by extraction with isopropyl alcohol at the temperature of about 183 °C for 3 h. After that the resulting yields were dried in vacuum oven at the temperature of 85 °C.

3.3.5 Preparation of Bioplastic Film

The crude graft copolymers obtained from bulk twin screw extruder were prepared into thin film with 0.35 mm thickness by using a Labtech compression moulding machine with preheating for 5 min, followed by heating for 20 min at a force of 25 kN. The operating temperatures of mould were maintained at 200 °C and cooled down to room temperature. Then these thin films were used to study the color intensity. Moreover, the crude polymers were prepared into the sheet with 3 mm thickness by using a Labtech compression moulding machine with the method which

was similar to the former method. After that, these sheets were cut into dumbbell-shape for investigating the tensile properties.