

CHAPTER III EXPERIMENTAL

3.1 Materials

- 3.1.1 L-lactide monomer ((3*S*)-*cis*-3,6-Dimethyl-1,4-dioxane-2,5-dione),(CAS No. 4511-42-6) (99.5% purity) was purchased from Shenzhen Brightchina Industrial Co.,Ltd.
- 3.1.2 Epoxidized Natural Rubber (ENR) (25% epoxy group) (CAS No. 138009-59-3) was purchased from PARATHAI
- 3.1.3 Polylactide (PLA) (3052D) (CAS No. 33135-50-1) was purchased from B.C.Polymer Co., Ltd.
- 3.1.4 Catalyst (Stannous (II) octoate ($\text{Sn}(\text{Oct})_2$)) (CAS No. 301-10-0) was purchased from Sigma Aldrich.
- 3.1.5 Solvent : Tetrahydrofuran ($(\text{CH}_2)_4\text{O}$) , Chloroform (CHCl_3) (CAS No. 67-66-3) and Toluene ($\text{C}_6\text{H}_5\text{CH}_3$) (CAS No. 108-88-3) were purchased from Lab Scan Co.,Ltd.

3.2 Equipments

3.2.1 Brabender Mixer

The Brabender mixer was purchased from Melchers techexport (GMBH). For ring-opening polymerization, the blending between lactide monomer (50 wt%) and ENR (50 wt%) mixed with various catalyst concentration at 0.05 to 0.3 phr. First, ENR 25 g and stannous (II) octoate were added to the chamber for 5 minute. Then, lactide monomer 25 g was added and further mixed for 30 minute. The temperatures of mixing were varied at 160 to 200 °C. The rotor speeds were maintained at 20 rpm.

3.2.2 Twin Screw Extruder

The prepared mixture is transferred to a Labtech model LTE-20-32 & LTE-20-40 twin-screw extruder with screw diameter 20 mm and L/D of 40:1. The polymerization occurred during the barrel from hopper to die at the temperature around 150, 155, 160, 160, 160, 160, 165, 165, 165, and 170 °C respectively. The screw speed was around 30 rpm. The composition between lactide, PLA, and ENR content and catalyst concentration were varied.

3.2.3 Soxhlet extractor

The amount of copolymer and the grafting percentage were determined by Soxhlet extractor (VELP SCIENTIFICA, SER 148) with paper thimble. Chloroform and toluene were used to extract the copolymer at 180 °C for 3 hours. After that the resulting yields were dried in vacuum oven at 80 °C. The amount of copolymer and the grafting percentage were calculated as shown in Eq.3.1 and Eq.3.2 [Y. Liu] respectively.

$$\text{The amount of copolymer (\%)} = \frac{W_{\text{insoluble (g)}}}{W_{\text{crude (g)}}} \times 100\% \quad (\text{Eq. 3.1})$$

$$\text{Grafting percentage} = \frac{W_{\text{graft copolymer (g)}} - W_{\text{PLA (g)}}}{W_{\text{PLA (g)}}} \times 100\% \quad (\text{Eq. 3.2})$$

3.2.4 Compression Moulding

The copolymers obtained from twin-screw extruder were prepared into thin film with Labtech compression molding machine (maximum force is 150 kg, size of mold is 20x20 cm) with preheating 10 minute and heating for 5 minute with force 10 kN. The operating temperature is 180 °C and cool down to room temperature. The thickness of film was around 0.05 mm.

3.2.5 Injection Molding

The copolymers obtained from twin-screw extruder were prepared into specimen of dumbbell-shape with Battenfeld BA 250 CDC Injection molding with L/D is 88/22. The operating temperatures is 140 to 150 °C, pressure 95 bars and cool down at room temperature in dumbbell-shape mold. After that, the samples were used for investigating the impact strength and tensile properties.

3.2.6 Fourier Transform Infrared Spectroscopy (FTIR)

The functional groups of ENR-g-PLA copolymer were analyzed by Thermo Nicolet Nexus 670 FTIR spectrometer. The specimens were prepared by compression molding into film. The spectra will be record over the wave number range of 4000 - 400 cm^{-1} with 32 scans at a resolution of 4 cm^{-1} .

3.2.7 Gel permeation chromatography (GPC)

The molecular weight (MW) and molecular weight distribution index (MWD) were determined by gel permeation chromatography (GPC). GPC was carried out in Tetrahydrofuran (THF) solvent as the mobile phase using a Water Styragel HR 6E 0f 7.8mmID x 300 mm column packed. The conditions of this machine were temperature of 40 °C, flow rate of 1ml/min, and runtime of 15 minute. The molecular weight was calibrated according to polystyrene standards.

3.2.8 Dynamic mechanical analysis (DMA)

DMA analyzed was 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 set from -80 to 120 °C, 10 Hz for frequency. Static and dynamic strains were 10% and 5%, respectively. The tension mode was used.

3.2.9 Thermogravimetric-differential thermal analyzer (TG-DTA)

Thermal stability of copolymers was determined by Perkin-Elmer Pyris Daimond thermogravimetric analysis (maximum temperature is 1,000 °C). The weight of sample was in the range of 5-10 mg. and was heated at the heating rate of 10°C/min from 30-800°C in nitrogen atmosphere.

3.2.10 Differential Scanning Calorimetry (DSC)

Thermal properties analyses were carried out by using Mettler Toledo, DSC 822. The weight of sample was in the range of 4-10 mg. The samples were first heated from 30 °C to 200 °C and cooled down with a flow rate of 10 ml/min to -60 °C. The samples were then reheated to 200°C at the same rate.

3.2.11 Pendulum Impact Tester

The impact strengths were identified by Izod impact testing according to ASTM-D826 using the ZWICK 5113 Pendulum Impact Tester with the pendulum load of 21.6 J. The average values of five samples were reported.

3.2.12 Universal testing machine

The tensile properties were tested by using an Instron 4206 universal testing machine with cross-head speed of 10 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.

3.2.13 Field Emission Scanning Electron Microscopy (FE-SEM)

FE-SEM was performed on Hitachi, S-4800 Model. The extrudates obtained from twin-screw extruder were broken in liquid nitrogen. Then, the samples were atched by toluene around 10 minute and dried in vacuum oven at 80 °C overnight. After that, all of specimens were coated with platinum under vacuum.

3.2.14 Biodegradability testing

The copolymers were tested according to ASTM D5988 - 03 (Standard Test Method for Determining Aerobic Biodegradation in Soil of Plastic Materials or Residual Plastic Materials after Composting).

3.2.15 Melt Flow Indexer

The melt flow index of copolymer was measured by using Zwick, Model 4105 melt flow indexer. The weight of sample was in range of 5-8 g. The temperature processing was 150 °C. The melt was driven through a capillary die using a 1 kg piston, melting time 120 seconds, and cutting time 30 seconds. The average values of five samples were reported.

3.3 Methodology

3.3.1 Preparation ENR-g-PLA copolymer by using Brabender Mixer

3.3.1.1 In Brabender mixer, the optimum conditions in term of mixing temperature and the catalyst concentration were observed. In the method, the mixing temperature was varied around 160, 170, 180, and 200 °C and varied the amount of catalyst between 0.05 and 0.3 wt%. The mixtures are indicated in Table 3.1.

Table 3.1 The mixtures of ENR-g-PLA copolymerization in Brabender mixer

Materials	Quantity (wt%)			
	L-lactide monomer	50	50	50
ENR	50	50	50	50
Catalyst	0.05	0.1	0.2	0.3

3.3.1.2 The copolymers were extracted by soxhlet extractor. The solvents that used to extract copolymer are chloroform and toluene at 180 °C for 3 hours. After that, the resulting yield was dried in vacuum oven at 80 °C.

3.3.1.3 The functional group was characterized by using FT-IR and measured the molecular weight of copolymer by using GPC.

3.3.1.4 The optimum time and temperature of all samples from previous step were characterized and chosen for further studies by considering the percent yield and molecular weight of copolymer.

3.3.1.5 After we get an optimum condition in term of mixing temperature and time of reaction, we use this temperature and time in further process.

3.3.2 Preparation ENR-g-PLA copolymer by using twin-screw extruder.

3.3.2.1 In twin-screw extruder, the whole mass of LA/ENR copolymer (10/20, 10/15, 10/10, and 10/5 wt% of LA/ENR) from Brabender mixer was carried out and continuously blended with pure PLA by varying the amount of PLA/LA/ENR between 70/10/20, 75/10/15, 80/10/10, and 85/10/5 wt% and varying the amount of stannous (II) octoate between 0.1 and 0.3 wt%. The processing condition is shown in Table 3.2 and the mixtures are indicated in Table 3.3. The mechanical and thermal properties of copolymer were measured.

Table 3.2 Processing condition of PLA/LA/ENR copolymerization

Type	Temperature (°C)										Speed screw (rpm)
	Z1	Z2	Z3	Z4	Z5	Z6	Z7	Z8	Z9	Die	
PLA/LA/ENR copolymerization (0.1, 0.2, and 0.3 wt% Sn(Oct) ₂)	150	155	160	160	160	160	165	165	165	170	30

Table 3.3 The mixtures of PLA/LA/ENR copolymerization in twin-screw extruder

Ingredient	Quantity(wt%)			
Poly lactide	70	75	80	85
L-lactide monomer	10	10	10	10
ENR	20	15	10	5
Catalyst	0.1, 0.2 and 0.3	0.1, 0.2 and 0.3	0.1, 0.2 and 0.3	0.1, 0.2 and 0.3

3.3.2.2 The mechanical and thermal properties of copolymer were characterized.

3.3.3 Preparation specimen by Injection molding.

3.3.3.1 The copolymers obtained from twin-screw extruder were prepared into specimen of dumbbell-shape by using Battenfeld BA 250 CDC Injection molding with L/D is 88/22. The operating temperatures is 140 to 150 °C, pressure 95 bars and cool down in dumbbell-shape mold at room temperature.

3.3.3.2 The samples were used for investigating the impact strength and tensile properties.

3.3.4 Preparation thin film by compression molding

3.3.4.1 The copolymers obtained from twin-screw extruder were prepared into thin film with Labtech compression molding machine (maximum force is 150 kg, size of mold is 20x20 cm) with preheating 10 minute and heating for 5 minute with force 10 kN.

3.3.4.2 The operating temperature is 180 °C and cool down to room temperature.