

CHAPTER IV

THE EFFECT OF TEMPERATURE AND CATALYST CONCENTRATION ON EPOXIDIZED NATURAL RUBBER-g-POLYLACTIDE

4.1 ABSTRACT

This research has an aim to prepare copolymer between lactide monomer and epoxidized natural rubber (ENR) via ring-opening polymerization by using stannous (II) octoate as an catalyst. First, epoxidized natural rubber-g-poly lactide copolymer (ENR-g-PLA) was prepared by varying the amounts of catalyst at 0.1, 0.2, and 0.3 wt% and varying the temperatures of mixing at 160, 170, and 180 °C in the Brabender mixer. The chemical structure of ENR-g-PLA copolymer was characterized by FT-IR. The FT-IR spectrum show the strong peak at 1740 cm^{-1} in copolymer and pure PLA that attributed to carbonyl group (C=O). Furthermore, the amount of copolymer was determined by a Soxhlet extractor. The amount of copolymer shows a maximum %yield at an optimum temperature around 160 °C and a catalyst concentration around 0.2 wt%. Moreover, the number average molecular weight (M_n), the weight average molecular weight (M_w), and the molecular weight distribution (MWD) were investigated by a gel permeation chromatography (GPC). The highest molecular weight was around 2.78×10^4 g/mol. The suitable temperature and catalyst concentration were 160 °C and 0.2 wt% respectively.

Keywords: Epoxidized natural rubber, Lactide monomer, Polylactide, Ring-opening polymerization, Stannous (II) octoate.

4.2 INTRODUCTION

Poly lactide (PLA) is hydrophobic aliphatic polyester that the mechanical and thermal properties are comparable with the traditional thermoplastics. PLA is prepared by two ways, the polycondensation polymerization of lactic acid and the ring-opening polymerization of lactide. The ring-opening polymerization of lactide is the way to get high molecular weight of PLA. Not only the polymerization method, but the temperature of mixing and the catalyst content also affect to molecular weight. Hyon *et al.* synthesized poly lactide with different molecular weight. They found that the increase of temperature and catalyst content resulted in the decrease in molecular weight [1]. Moreover, PLA is being commercially produced for commodity application [2]. For example, fibers produced from PLA exhibit low odor retention and excellent moisture absorption properties [3], the internal fixation of bone fractures were produced from PLA for medical application [4], and PLA can be formed by injection molding as several objects. Eventhrough, PLA has many advantage properties but it has some disadvantages such as, rigidity, slow crystallization and heat deflection temperature.

There are several methods to overcome the limitation of PLA such as processing, plasticization, blending, and copolymerization. The great method to improve limitation of PLA is copolymerization of lactide or lactic acid monomer with the other monomers because it is not occurred phase separation. Nooeaid *et al.* successfully synthesized the EVOH-g-PLA copolymer in Barbender mixer. The composition of EVOH/LA at 50/50 wt% gave the highest molecular weight ($M_w = 36.6 \times 10^4$ g/mol) and the amount of graft copolymer. Furthermore, the optimum of mechanical properties was found in this composition [5].

Epoxidized Natural Rubber (ENR) is the natural rubber that some part of double bonds is replaced by epoxide groups. ENR has many good mechanical and thermal properties offering high strength, due to their ability to undergo strain crystallization, along with increase glass transition temperature and high degree of damping [6]. There are many researchers studied ENR blending with other polymers to improve mechanical and thermal properties of each polymer. For example, Charøen Nakason *et al.* blended ENR with poly(methyl methacrylate) to improve the

mechanical, thermal and morphological properties [7]. Moreover, G.H. Yew *et al.* blended ENR with poly(lactic acid)/rice starch to improve brittleness of poly(lactic acid), the result showed that poly (lactic acid) had more rubbery behavior [8].

The purpose of this research is to synthesis copolymer between epoxidized natural rubber (ENR) and lactide monomer using stannous (II) octoate ($\text{Sn}(\text{Oct})_2$) as an catalyst. The epoxy group in ENR can initiate the ring-opening polymerization of lactide monomer. This leads to high molecular weight of PLA. The focus of this work is to study the effect of the catalyst content and temperature of mixing on molecular weight of the graft copolymer.

4.3 EXPERIMENTAL

4.3.1 Materials

L-lactide monomer ((*3S*)-*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. Epoxidized Natural Rubber (ENR) (25% epoxy group) (CAS No. 138009-59-3) was purchased from PARATHAI. Stannous (II) Octoate ($\text{Sn}(\text{Oct})_2$) as a catalyst (CAS No. 301-10-0) was purchased from Sigma aldrich.

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.

4.3.2 Preparation of ENR-g-PLA copolymer

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 4.3.1.

Table 4.1 The mixtures of ENR-g-PLA copolymerization in Brabender mixer

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

The crudes of copolymer were extracted by Soxhlet extractor to find the amount of copolymer. The solvents that used to extract copolymer were chloroform and toluene at 180 °C for 3 hours. After that, the resulting yield was dried in vacuum oven at 80 °C.

The functional group of ENR-g-PLA copolymer was characterized by using Nicolet Nexus 670 FT-IR spectrometer and the molecular weight of copolymer was determined by using gel permeation chromatography (GPC).

4.3.3 Characterizations

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

The amounts of copolymers 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 was calculated as shown in Eq.4.1

$$\text{The amount of copolymer (\%)} = \frac{W_{\text{insoluble (g)}}}{W_{\text{crude (g)}}} \times 100\% \quad (\text{Eq. 4.1})$$

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 of 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.

4.4 RESULTS AND DISCUSSION

4.4.1 Chemical analysis

The functional group of the copolymer that occurred is confirmed by Fourier Transform Infrared Spectroscopy (FT-IR). FTIR spectra of LA, ENR and ENR-g-PLA synthesized are shown in Figures 4.1. There is a strong peak at 1740 cm^{-1} in the spectra of both LA and ENR-g-PLA, assign to carbonyl (C=O) in branch of copolymer. At the wave number 894 cm^{-1} and 1655 cm^{-1} are attributed to C=C bending and C=C stretching in $\text{R}_2\text{C}=\text{CHR}$ which is one of the functional groups of ENR. The two transmission peaks at 1190 cm^{-1} and 1090 cm^{-1} are the symmetric C-O-C stretching of ester group [1].

There are two other peaks at 1130 cm^{-1} and 1370 cm^{-1} , attributed to C- CH_3 stretching and C-H bending in CH_3 group. Moreover, the peak around 3400 cm^{-1} indicated the presence of the reactive functional group (-OH) [5] used as the reactive sites for graft copolymerization of PLA to ENR. Figure 4.2 shows the mechanism of the preparation of ENR-g-PLA copolymer.

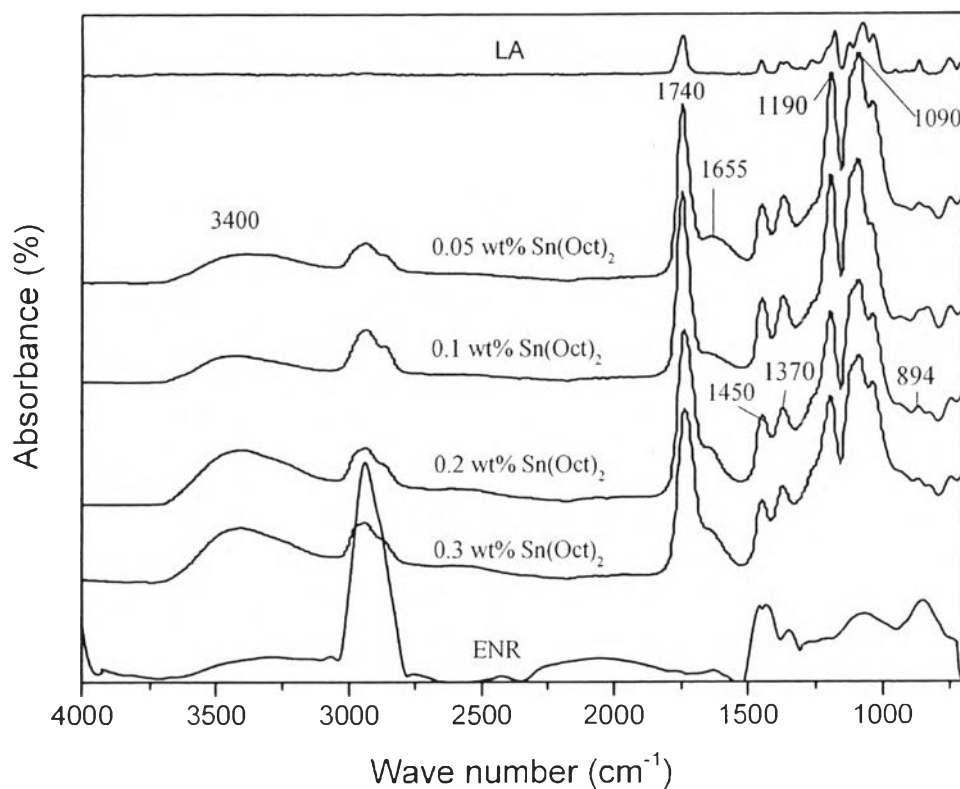


Figure 4.1. FTIR spectra of LA, ENR and ENR-g-PLA synthesized with different catalyst concentration at 160 °C.

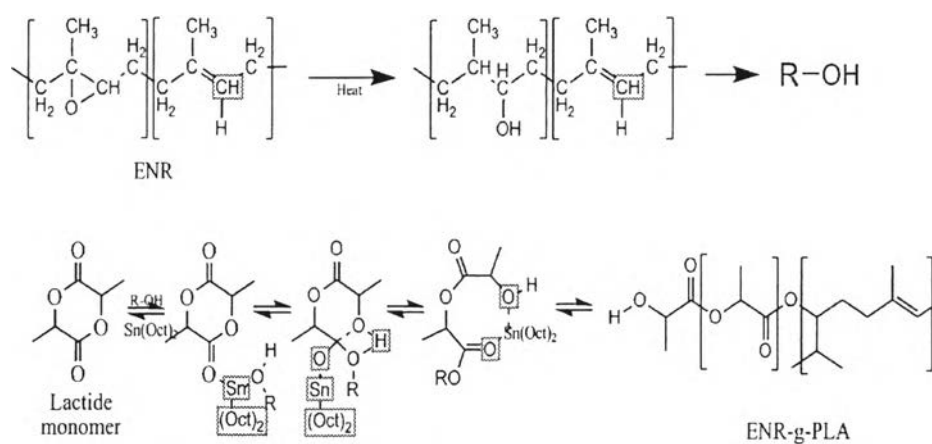


Figure 4.4.2. Mechanism of the preparation of ENR-g-PLA.

4.4.2 The amount of copolymer

The copolymer between ENR and PLA (ENR-g-PLA) is extracted by toluene and chloroform in Soxhlet extractor. The amounts of ENR-g-PLA copolymer at different temperature and various catalyst concentrations are presented in Figure 4.3. The values of percent yield of copolymer are shown in Table 4.2. The amounts of ENR-g-PLA copolymers decrease as the temperature of mixing increase because an catalyst is more active. An active catalyst can react with monomer very fast resulting in the chain scission, so the amounts of copolymers are decreased. The optimum temperature that polymerized copolymer is 160 °C. Moreover, the increasing of catalyst causes the high generated copolymer. The maximum of the amount of copolymer are obtained at 0.2 wt% of a catalyst concentration. After the amount of catalyst over 0.2 wt%, the chain scission is occurred leading to the decreasing of the copolymer amount [1].

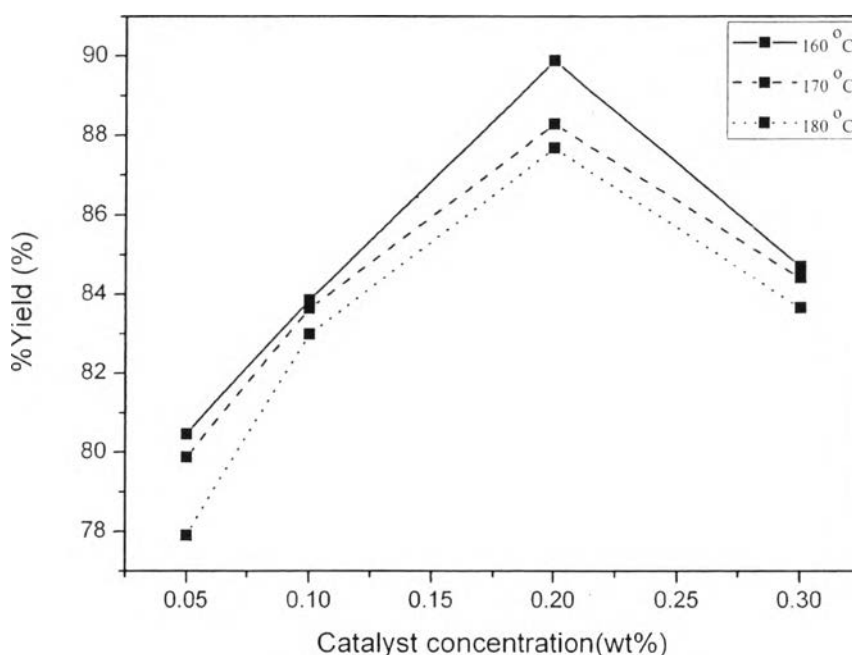


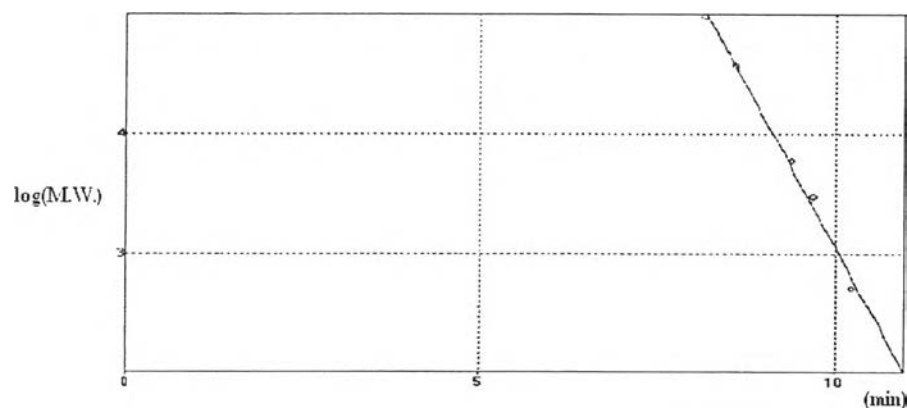
Figure 4.3. The amounts of LA/ENR copolymer at different temperature and various catalyst concentrations.

Table 4.2 The values of percent yield of copolymer

| Temperature of mixing (°C) | Catalyst concentration (wt%) | The amount of copolymer (%) |
|----------------------------|------------------------------|-----------------------------|
| 160 | 0.05 | 80.46 |
| | 0.1 | 83.85 |
| | 0.2 | 89.88 |
| | 0.3 | 80.7 |
| 170 | 0.05 | 79.86 |
| | 0.1 | 83.64 |
| | 0.2 | 88.29 |
| | 0.3 | 84.41 |
| 180 | 0.05 | 77.90 |
| | 0.1 | 82.98 |
| | 0.2 | 87.68 |
| | 0.3 | 81.65 |

4.4.3 Molecular weight measurement

The molecular weight (MW) and molecular weight distribution (MWD) of copolymers were measured by using the gel permeation chromatography (GPC). Figure 4.5 to 4.7 present the molecular weight and molecular weight distribution of copolymers that were calculated in reference of polystyrene calibration curve: $\log M = -0.853t + 13.001$.

**Figure 4.4.** Polystyrene calibration cuve.

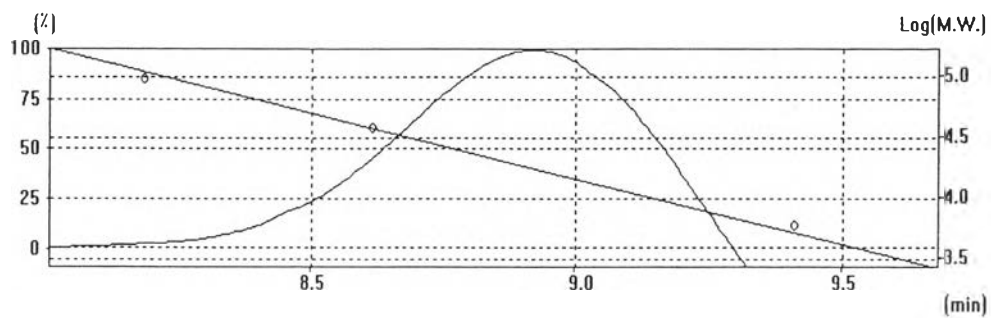


Figure 4.5. The calculation of M_w with polystyrene reference.

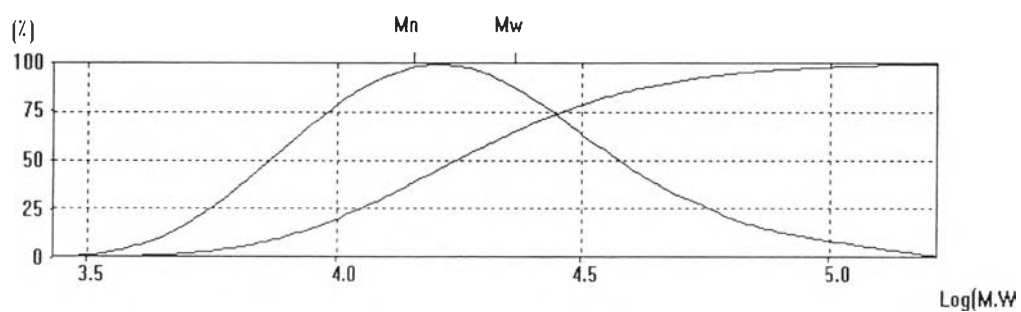


Figure 4.6. The calculation of M_n and M_w .

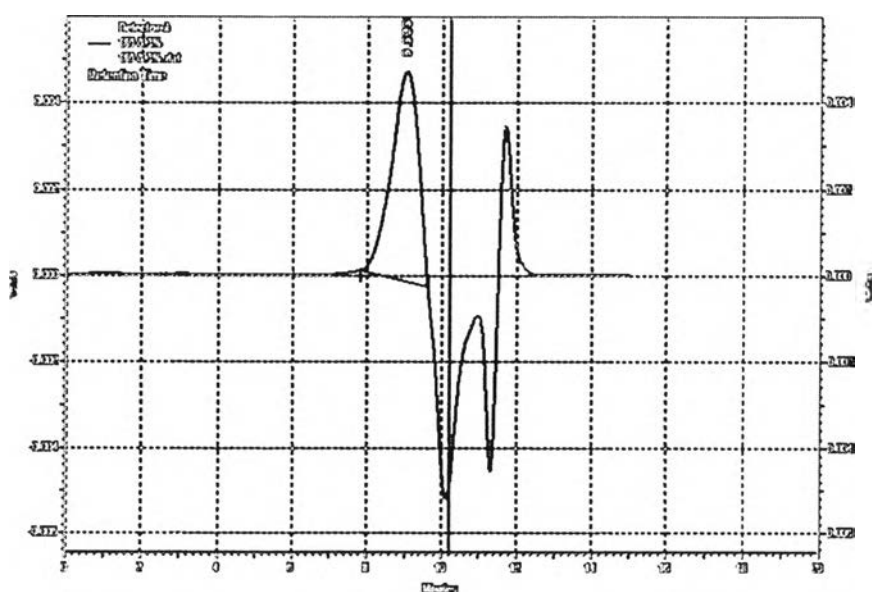


Figure 4.7. GPC curve of ENR-g-PLA extracted with 50/50 wt% LA/ENR content, at 180 °C and 0.3 wt% $\text{Sn}(\text{Oct})_2$.

The molecular weight (MW) and molecular weight distribution (MWD) of ENR-g-PLA copolymer were analyzed by GPC. MW and MWD are shown in Table 4.3 Molecular weight parameters of ENR-g-PLA copolymers synthesized with different catalyst concentration at 160 °C is shown in Figure 4. 8 to Figure 4. 10. Increasing catalyst concentration results in the increase of weight average molecular weight (Mw). The optimized catalyst concentration is 0.2 wt%. The amount of catalyst over 0.2 wt% results in the decrease of Mw because chain scission is occurred in system [5]. In addition, the temperature of mixing affects Mw. The increase of temperature results in the decrease of MW due to the chain scission. Thus, the temperature of mixing at 160 °C gives the highest Mw [1].

Table 4.3 MW and MWD of ENR-g-PLA with different temperature and various catalyst concentrations

| Temperature of mixing (°C) | Catalyst content (wt%) | Mw (g/mol) | Mn (g/mol) | MWD |
|----------------------------|------------------------|------------|------------|-----|
| 160 | 0.05 | 18776 | 11226 | 1.7 |
| | 0.1 | 26754 | 13781 | 1.9 |
| | 0.2 | 27816 | 13459 | 2.1 |
| | 0.3 | 21984 | 10917 | 2.0 |
| 170 | 0.05 | 18290 | 13526 | 1.4 |
| | 0.1 | 25478 | 12170 | 2.1 |
| | 0.2 | 26781 | 11206 | 2.4 |
| | 0.3 | 24255 | 10596 | 2.3 |
| 180 | 0.05 | 19827 | 13860 | 1.4 |
| | 0.1 | 21059 | 14104 | 1.5 |
| | 0.2 | 22374 | 14008 | 1.6 |
| | 0.3 | 20370 | 13273 | 1.5 |

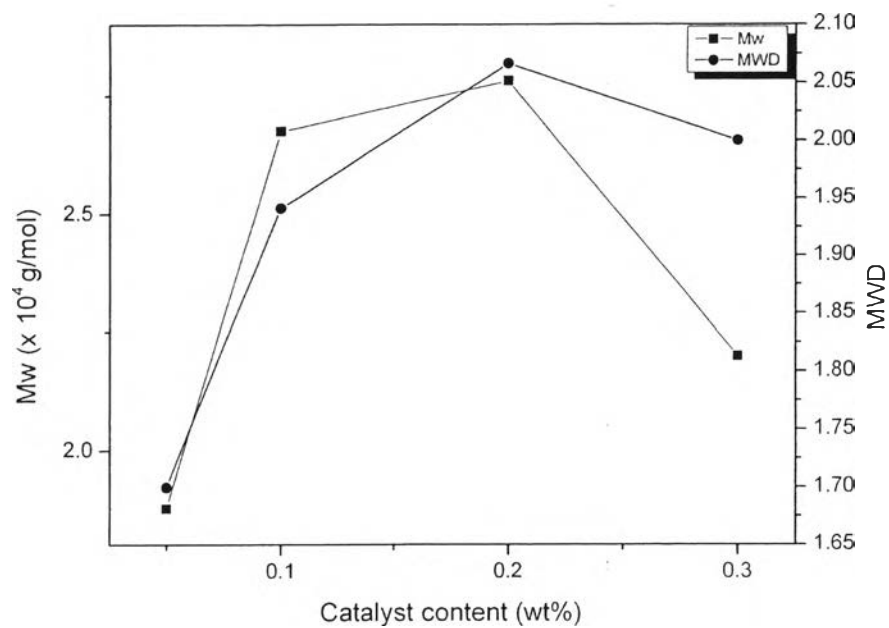


Figure 4.8. Molecular weight parameter of copolymer at 160 °C.

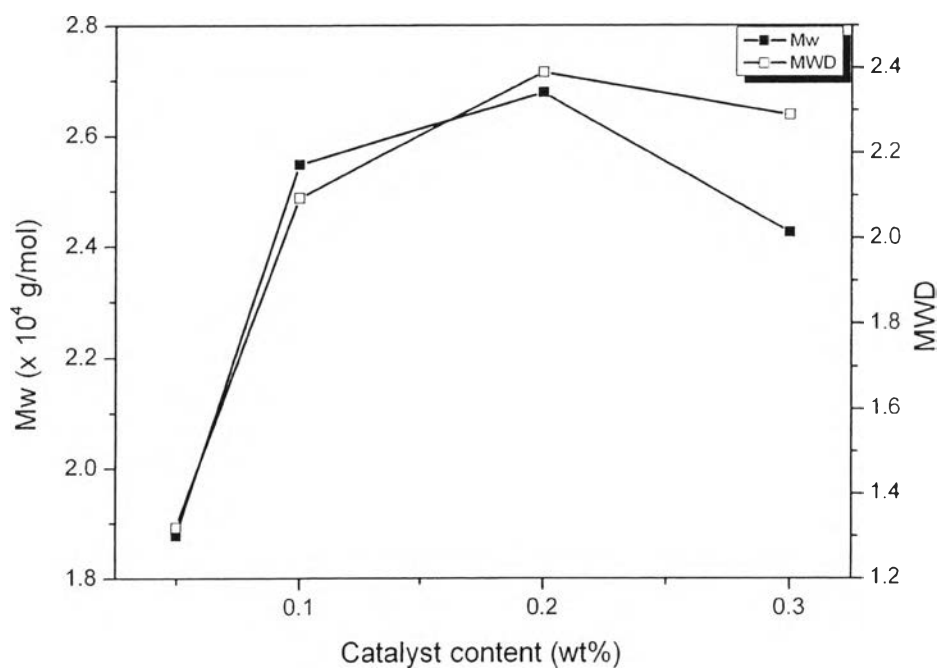


Figure 4.9. Molecular weight parameter of copolymer at 170 °C.

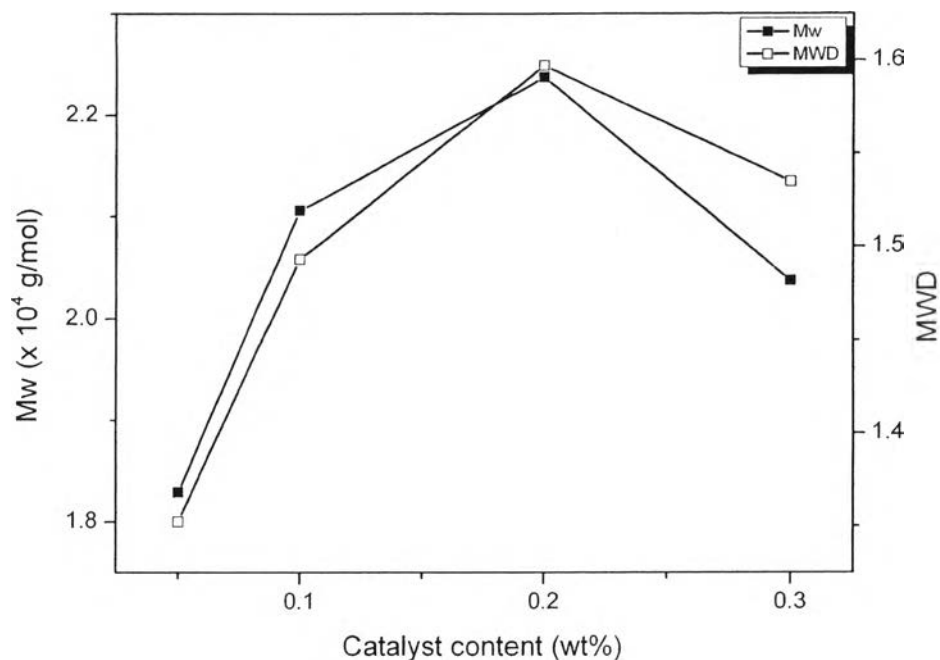


Figure 4.10. Molecular weight parameter of copolymer at 180 °C.

4.5 Conclusion

ENR-g-PLA copolymers are successfully prepared by ring-opening graft copolymerization of lactide monomer on ENR using stannous octoate as a catalyst. This can be confirmed by the FTIR absorption spectrum at 1740 cm^{-1} (C=O group), 1655 cm^{-1} (C=C stretching), and 3400 cm^{-1} (-OH group) corresponding to ENR-g-PLA structure. The highest yield of copolymer and Mw are 89.88% and 27,816 g/mol. The temperature of mixing and catalyst content are the important parameters that affect the yield of copolymer, Mw, and MWD. The optimum temperature of mixing and the catalyst concentration are $160\text{ }^{\circ}\text{C}$ and 0.2 wt% Sn(Oct)₂ respectively.

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4.7 Reference

1. Hyon,S.H., Jamshidi,K. and Ikada,Y. (1997). Synthesis of polylactides with different molecular weights. Biomaterials , 22 (18), 1503-1508.
2. Anderson, K.S. et al. (2008). Toughening Polylactide. Polymer Reviews , 1 (48), 85-108.
3. Gross, R.A. and Kalra, B. (2002). Biodegradable Polymers for the Environment. Science (297), 803-807.
4. Kricheldorf, H. (2001). Syntheses and application of polylactides. Chemosphere (43), 49-54.
5. Nooeaid, P., M.S. Thesis, Chulalongkorn University, 2008.
6. Gelling, I. (1991). Epoxidised Natural Rubber. Journal of Natural Rubber Research , 3 (6), 184-205.
7. Nakason, C., Tobprakhon, A., Kaesaman A. (2005). Thermoplastic Vulcanizates Based on Poly(methyl methacrylate)/Epoxidized Natural Rubber Blends:Mechanical, Thermal, and Morphological Properties. Wiley InterScience , 1251-1261.
8. Yew G.H. et al. (2005). Water absorption and enzymatic degradation of poly(lactic acid)/rice starch composites. Polymer Degradation and Stability (90), 488-500.