Role of Sn-based and Ti-based catalysts on melt copolymerization of PLA-Polyols

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Abstract. Aiming at improving the ductility of PLA, two polyols: polyethylene glycol (PEG), and polypropylene glycol (PPG) were introduced individually to the PLA structure as a soft component. Copolymerization of PLA and polyols was performed in a melt-mixer via transesterification in the presence of a catalyst. $^1$H-NMR and GPC results revealed that PLA-PEG and PLA-PPG copolymers with different molecular weights were successfully formed. The copolymer formation and characteristics depended strongly on the structure of polyol and type of catalyst. Titanium butoxide (TBT) was found to be a more effective catalyst than dibutyltin dilaurate (DBTL). The effects of catalyst content and reaction time on the characteristics of the copolymers are also reported.

1. Introduction
Interest in polylactic acid (PLA)-based material has grown continuously in various industries. Copolymerization of PLA with soft segment could turn a brittle PLA into a ductile product. A traditional method for producing PLA copolymer is ring-opening copolymerization of lactide monomer with soft components as polyethylene glycol (PEG), polypropylene glycol (PPG), polycaprolactone (PCL), etc. [1-3]. The reaction is commonly performed under reduced pressure for 4 - 8 h and a large amount of solvent is required in the process [1, 5]. In this study, melt-copolymerization of PLA polymer with two types of polyols: PEG and PPG, was carried out via transesterification reaction in a melt-mixer in the absence of solvent. The effects of catalyst types (i.e. titanium butoxide (TBT) and dibutyltin dilaurate (DBTL)), content, and time of reaction on the characteristics of the copolymers are reported.

2. Experimental

2.1. Materials
PLA 2003D was from NatureWorks LLC. PEG (Mw ~ 4000 g/mol) was from Ajax Finechem Pty Ltd. PPG (Mw ~ 2000 g/mol) was from Acros Organics. TBT and DBTL catalysts were from Sigma-Aldrich.

2.2. Melt copolymerization of PLA and polyols in a mixer
PLA-PEG and PLA-PPG copolymers were prepared via melt-transesterification method in a Haake internal mixer at 170°C. The detail of this method has been reported elsewhere [4]. The contents of PEG and PPG were kept constant at 20 w/w%. TBT and DBTL catalysts were used with various amounts of 0, 0.5, 0.75 and 1.5 phr. The reaction time was varied at 5, 10, 20 and 30 min.
2.3. Characterizations
Chemical structure of the obtained PLA-PEG and PLA-PPG copolymers was investigated using $^1$H-NMR spectroscopy (Bruker 500 MHz, USA). Molecular weights of the copolymers were evaluated by Gel permeation chromatography (GPC) (Waters 1515, USA) using polystyrene as a standard. Mechanical properties of the copolymers were characterized by Instron 5566 tensile testing machine.

3. Results and discussion

3.1. Chemical structure of PLA-PEG and PLA-PPG copolymer
Figures 1a and 1b demonstrate the chemical structures of PLA-PEG and PLA-PPG copolymers, as characterized by $^1$H-NMR. Methyl protons (-CH$_3$, a) and methine protons (-CH, b) of the PLA unit are clearly seen at $\delta$ of 1.60 ppm and 5.20 ppm, respectively. The PEG unit exhibits a characteristic signal of methylene protons (-CH$_2$, c) at $\delta$ of 3.60 ppm [1, 4] whereas the PPG unit shows a signal of methyl protons (-CH$_3$, d), methylene protons (-CH$_2$, e) and methine protons (-CH, f) at $\delta$ of 1.14, 3.55 and 3.40 ppm, respectively [2]. The signal at $\delta$ of 4.20 - 4.30 ppm belonging to methylene protons (-CH$_2$, g) of PEG that attached to the PLA unit, and the signal at $\delta$ of 4.15 ppm belonging to methylene protons (-CH$_2$, h) of PPG that attached to the PLA unit confirm that PLA-PEG and PLA-PPG copolymers are successfully prepared by a melt-transesterification approach.

![Figure 1](image_url) $^1$H-NMR spectra of a.) PLA-PEG copolymer and b.) PLA-PPG copolymer.

3.2. Effect of catalyst type, content, and reaction time
Figure 2 shows the GPC curves of the copolymers prepared by using different catalysts. Individual peaks of the PLA and PEG component are clearly seen in the sample prepared without adding catalyst (PLA/PEG blend) (Figure 2a), indicating that no copolymer is formed under this condition. In the presence of catalyst, copolymerization between PLA and PEG segments occurs as evidenced by a single-modal curve centered at a higher molecular weight region than that of PEG. Compared between Sn-based and Ti-based catalyst, the results of Figure 2a show that TBT is more effective than DBTL in catalyzing the copolymerization of PLA and PEG. In the case of PLA-PPG system, both catalysts exhibit similar effects and two separate peaks corresponding to the individual species are still observed even after a longer period of reaction (Figure 2c). The bi-modal peaks of PLA-PPG are observed in the sample
prepared by using a higher loading of TBT catalyst (Figure 2d). The difficulties of copolymer formation in the PLA-PPG system is mainly due to the immiscibility between the molten PLA and PPG components. Additionally, the reactivity of the hydroxyl-end groups of PPG is rather different to that of the PEG since the PPG structure consists of reactive primary hydroxyl group on the one side and secondary hydroxyl-end group which is less effective, on the other side. The iH-NMR signal at δ of 4.35 ppm (-CH, i) of figure 1b is corresponding to the attached secondary hydroxyl protons of PPG.

Figure 2 Effect of TBT and DBTL catalysts, reaction time, and content of catalyst on the GPC chromatograms of various copolymers (a, b) PLA-PEG, and (c, d) PLA-PPG system.

Figure 3 Evolution of molecular weights of PLA-PEG and PLA-PPG copolymer as affected by type and (a) content of catalyst, and (b) reaction time.

The effects of catalyst type, content, and reaction time on the molecular weight of PLA copolymers are shown in Figure 3. Comparing to the starting PLA (~ 1.7 x 10^5 g/mol), all copolymers prepared exhibit lower molecular weights. Type of catalyst plays a strong role in determining the molecular weight of the copolymers whereas catalyst content and reaction time in the studied range show minor effects on
the molecular weight of the copolymer. In this work, the PLA-PEG copolymers obtained have molecular weight in a range of 5.0 x 10^4 – 1.1 x 10^5 g/mol when TBT was used as a catalyst and 3.3 x 10^4 – 2.6 x 10^4 g/mol in case of using DBTL catalyst. The molecular weight of PLA-PPG copolymers is in a range of 7.8 x 10^4 – 5.5 x 10^4 g/mol for the system with DBTL catalyst.

3.3. Mechanical properties

Figure 4 shows the tensile stress-strain curves of PLA and its copolymers. In order to obtain the materials with good mechanical performance, chain extender was added with the objective of linking the short-chain copolymers formed via melt-transesterification to form into the long-chain copolymers. From Figure 4, the PLA sample exhibits a high tensile strength of 64 MPa with a very low elongation at break of ~ 5%. As expected, the PLA copolymers with a soft component in the structure show much higher ductility than the PLA. The PLA-PEG copolymers prepared in this study have a strength of 25 MPa with a high elongation of 600%. The properties of the copolymers vary depending on the type of soft segment, type of catalyst, and also reaction conditions.

![Figure 4: Stress-strain curves of PLA, PLA-PEG, and PLA-PPG copolymers](image)

4. Conclusions

The PLA-PEG and PLA-PPG copolymers were prepared using a transesterification reaction in melt state in the presence of either TBT or DBTL catalyst. The effects of catalyst type, content, and reaction time on the characteristics of the copolymers have been investigated. 1H-NMR results confirmed the formation of these copolymers. The copolymers with different structures and molecular weights could be prepared by controlling the type of polyol used as a soft component, the type and content of catalyst, as well as the time of reaction. The long-chain copolymers obtained in this study exhibited a remarkable high elongation and their tensile properties are comparable to those of the petroleum-based polyolefins.

5. References

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