Effect of poly(ethylene oxide) on the properties of poly(lactic acid)-based blends

R. Khanteesa\textsuperscript{1}, P. Threepponmatkul\textsuperscript{1,}\textsuperscript{*} and A. Sittattrakul\textsuperscript{1}

\textsuperscript{1}Department of Materials Science and Engineering, Faculty of Engineering and Industrial Technology, Silpakorn University, Nakhon Pathom, 73000, Thailand

*Corresponding author: poonsubt@yahoo.com

Abstract. Poly(lactic acid) (PLA) was blended with poly(ethylene oxide) (PEO) with four different molecular weights of 1×10\textsuperscript{5}, 2×10\textsuperscript{5}, 3×10\textsuperscript{5}, and 4×10\textsuperscript{5} g/mol to improve the flexibility of PLA. The blends were compounded in an internal mixer at 190 °C with 50 rpm for 15 minutes and using a hot press to mold rectangular sample sheets. The mechanical properties of PLA blends were analyzed to prove the ductility. Additionally, phase morphologies of blends were investigated by using tensile fracture surface. The addition of PEO into PLA matrix leads to slight increase in tensile strength, while the elongation at break was decreased by increasing the molecular weight of PEO. However, the elongation at break of PLA/PEO blends was higher than the one of neat PLA. In other words, PEO enhanced the flexibility of PLA blends, according to scanning electron microscope images. In brief, PLA-based blends greatly increased in ductility.

1. Introduction

Currently, biopolymers have been considered as a substitute for traditional petroleum-based polymers. Poly(lactic acid) (PLA) is biodegradable aliphatic polyester that is derived from renewable resources such as corn, cassava, potato and sugarcane. PLA has a wide range of applications such as in properties such as high mechanical strength, high modulus, biodegradability, biocompatibility, bioabsorbability, transparency, low toxicity and easy process ability [1]. However, PLA have been limited for applications due to poor thermal stability and low impact strength [2].

The toughness of PLA can be improved by blending with other polymers, such as poly(butylene succinate) (PBS) [3], poly(ethylene glycal) (PEG) [4], and poly(ethylene oxide) (PEO) [5]. PEG and PEO have a similar chemical structure and they are biodegradability, biocompatibility, and nontoxicity. It will be called PEO when the molecular weight was over 100,000 g/mol. Meanwhile, the incorporation of PEG can still maintain biodegradability, biocompatibility and low toxicity of PLA [6].

Recently, many studies on properties of PLA-based blends. Jacobsen et al. [7] investigated the effect of different plasticizers (i.e., glucose monoesters, PEG [M\textsubscript{w} = 1500 g/mol], and partial fatty acid esters) on the mechanical properties of PLA. They found that the best amount of the three plasticizers was 10 % wt. The incorporation of PEG to PLA caused the greatest reductions in glass transition temperature (T\textsubscript{g}), tensile modulus and strength, whereas the largest increments in elongation at break (up to 180%) and impact strength. Feng-Jiao Li et al. [8] plasticized PLA using PEG with different molecular weights (6,000, 10,000, and 20,000 g/mol) and different contents (0-20 % wt). They reported that the tensile modulus and strength increased, while tensile stress at break and strain at break decreased when increasing the molecular weight of PEG. Zhang et al. [6] blended PLA and PEG with five different
molecular weights (200–20,000 g/mol) and various content of PEG-10,000 ranged from 0 to 20 %wt and reported the increases in both V-notched Izod and Charpy impact strengths of PLA/PEG-10,000 blends were 206.10% and 137.25%, respectively. Meanwhile, the crystallinity of PLA/PEG-10,000 blends increased from 3.95% to 43.42%. For 10 %wt PEG content, the crystallization and impact properties of PLA/PEG blends mainly depended upon PEG molecular weight. The introduction of PEG reduced the intermolecular force and enhanced the mobility of PLA chains, thus improving the crystallization capacity and flexibility of PLA. Yoojun et al. [9] have investigated the mechanical and thermal properties of PLA films blended with PEO (M_w = 100,000 g/mol). The blend films exhibited a elongation at break was increased by 4 times at 5 %wt PEO loading, while the tensile strength was decreased by 17%. In addition, the glass transition temperature (T_g), melting temperature (T_m), and cold crystallization temperature (T_c) decreased with adding 5 %wt PEO.

Furthermore, the high molecular weight of PEO is an important factor that affects on properties of polymer blends. However, there have been very few researches. Therefore, the major objective of this research is to study the effects of high molecular weight of PEO on the mechanical properties and morphologies of PLA/PEO blends.

2. Experimental

Materials

PLA (4043D, M_w = 190,000 g/mol) was purchased from NatureWorks. Density, melt flow index, glass transition temperature (T_g), and melting temperature (T_m) were 1.24 g/cm³, 6 g/10 min, 60 °C, and 160 °C, respectively. PEOs were purchased from Sigma Aldrich. Molecular weight (M_w) and melting temperature (T_m) were 10^5 - 4x10^5 g/mol and 65 °C, respectively.

Melt blends and sample preparation

The blends were carried out in internal mixer (Brabender Mixer Docking Station W50EHT series) at 190 °C with a capacity of 50 g and rotor speed of 50 rpm for 15 minutes. The sample sheets were obtained using a hot press at 190 °C into rectangular sample sheets. The thickness of each sheet was in range of 300-350 microns. The specimens were then kept in plastic bags before testing. The composition of PLA blends were shown in Table 1.

Table 1 Compositions of PLA-based blends with PEO

| Sample     | Molecular weight (M_w) of PEO (g/mol) | Composition (%wt) |
|------------|--------------------------------------|-------------------|
|            |                                      | PLA  | PEO  |
| Neat PLA   | -                                    | 100  | 0    |
| PLA_1PEO   | 100,000                              | 90   | 10   |
| PLA_2PEO   | 200,000                              | 90   | 10   |
| PLA_3PEO   | 300,000                              | 90   | 10   |
| PLA_4PEO   | 400,000                              | 90   | 10   |

Characterizations

Mechanical properties of the blends were performed by Universal Testing Machine according to ASTM D882 (Instron 5969, USA). A 5 kN load cell was used. The crosshead speed was 12.5 mm/min. The morphology of the tensile fractured surface of specimens was investigated using a Scanning Electron Microscope (SEM) (Hitachi TM3030, Japan). The samples were sputtered coated with Pd/Au.
3. Results and discussion

3.1. Mechanical properties

Figure 1. Effect of PEO molecular weight on tensile properties (a) Tensile strength, (b) Young’s Modulus and (c) Elongation at break of PLA/PEO (90/10) blends

Figure 1 presents the mechanical properties of neat PLA compared with PLA blended with different molecular weight of PEO. Tensile strength is an importance parameter to characterize the largest stress limit of materials under tensile load. Tensile strength of neat PLA was 37.16 MPa. Similar mechanical values of neat PLA have been reported previously, i.e., tensile strength of neat PLA was from 36 to 52 MPa [5, 10]. The tensile strength of PLA/PEO blends gradually increases with an increase in molecular weight of PEO. The increase of intermolecular forces, surface energy and molecular chain entanglement were caused by the increment of the molecular weight of PEO during this study. This could reduce the slippage of PLA molecular chains under tensile loading which resulted in an increase of tensile strength. The addition of PEO into the PLA matrix reduced the tensile modulus of the blends in comparison with neat PLA. This is due to the interactions between plasticizer and polymers which weaken the polymeric intermolecular interactions and therefore improved the rearrangement between polymer chains under external force, and flexibility to the PLA. The elongation at break of PLA/PEO blends was improved compared with the one of neat PLA. However, the elongation at break of PLA blended with lower molecular weight PEO was higher than the one with higher molecular weight PEO. This illustrated that lower molecular weight PEO can more efficiently improve the ductility of PLA. Generally, the miscibility of PEG with other polymers deteriorated with an increase in PEG molecular weight [6].
3.2. Fracture surface morphology analysis

![Figure 2](image)

**Figure 2.** Scanning electron micrographs of tensile fracture surfaces of (a) Neat PLA, (b) PLA/1PEO, (c) PLA/2PEO, (d) PLA/3PEO, and (e) PLA/4PEO blends containing 10 %wt PEO content.

SEM was utilized to investigate the morphologies of the tensile fractured surface of PLA blended with four different molecular weight PEO. From Figure 2, neat PLA (Fig. 2a) shows a smoother surface than PLA/PEO blends (Fig. 2b-2e). When the molecular weight of PEO was increased, the fracture surface of PLA/PEG blend becomes rougher because of the increment of entanglement between higher molecular weight PEG and PLA molecular chains [6].

4. Conclusion

To improve the ductility of PLA and reduce brittleness, PLA was blended with four different molecular weight PEO at a constant concentration of 10 %wt. The PLA/PEO blends were prepared using an internal mixer and then hot press into specimens. The properties of the blends were characterized by
Tensile testing and SEM. The ductility of PLA was significantly increased when PEO was added into PLA matrix. The tensile modulus of PLA blends film declined but the tensile strength increased by addition of higher molecular weight of PEO. In this study, the elongation at break of PLA/PEO blends increased when compared with neat PLA, but decreased with increasing molecular weight of PEO. SEM images reveal that when the molecular weight of PEO was increased, the fracture surface of the PLA/PEO blends becomes rougher. Besides, PEO enhanced the flexibility of PLA blends.

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