Optimization of poly(L-lactide)-polybutylene adipate terephthalate diblock copolymer by ring opening polymerization

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Abstract. Polylactide (PLA) is a brittle biodegradable polymer: co-bonding of a higher flexibility polymer such as polybutylene adipate terephthalate (PBAT) into the PLA chains has been shown to make it more flexible. We studied the optimum conditions for synthesizing poly(L-lactide)-polybutylene adipate terephthalate diblock copolymer (PLLA-b-PBAT), with ratios by weight of L-lactide:PBAT from 100:0.3 to 100:1. Incubation times of polymerization were varied from 4 to 8 hours at 160°C. Nuclear magnetic resonance (NMR) spectra were used to verify the structure of synthesized polymers. Differential scanning calorimetry thermograms showed melting temperatures of diblock copolymers at around 161-168°C - characteristic of PLA. The optimum conditions for PLLA-b-PBAT synthesis by ring opening polymerization were 100:0.3 ratio and eight hour incubation leading to 95% yield, a high degree of crystallinity (71%) and the highest molecular weight (34,000g/mol, measured by gel permeation chromatography).

1. Introduction
Nowadays, there is considerable interest in polylactide (PLA) from industrial, medical and research fields because it has many advantages such as biodegradability, easy processing, nontoxicity and biocompatibility[1]. There is special interest in one of its optical isomers, poly(L-lactide)(PLLA)[2]. However, brittleness, poor thermal stability and low crystallization rate present significant disadvantages of PLA [3]. Blending PLA with other more flexible biodegradable polymers such as poly(butylenes adipate terephthalate)(PBAT) would result in higher elongation at break of PLA [4]. Although PBAT and PLA have a similar carbonyl groups on their backbone chains, low interfacial adhesion and macro-phase separation between them lead to immiscibility. Studies have reported that the addition of more than 5% of PBAT into PLA could cause phase separation [5]. In order to reduce that problem, this study tried to co-bond between PLLA and PBAT to form a single chain of diblock copolymer via bulk ring opening polymerization from L-lactide. The reactions were optimized by varied ratios of L-lactide:PBAT and incubation time when the temperature was constant at 160°C.
2. Experimental

2.1 Materials

98% L-lactide (LL) was donated by Purac (Thailand) Ltd. For ring opening polymerization, a stannous octoate (Sn(Oct)₂) used as catalyst was supplied by Sigma Aldrich and PBAT (ecoflex®; Mₙ ~ 100,000 g/mol) acted as self macro-initiator and was obtained from BASF corporation. Solvents, including toluene, methanol, tetrahydrofuran (THF) and chloroform, were obtained from RCI Lab scan.

2.2 Synthesis of poly(L-lactide)-polybutylene adipate terephthalate diblock copolymers

Poly(L-lactide)-polybutylene adipate terephthalate diblock copolymers (PLLA-b-PBAT) were prepared via bulk ring opening polymerization of L-lactide. Before using, LL was dried in a vacuum oven at 45°C for 12 h. The ring opening polymerization proceeded in nitrogen atmosphere at 160°C. It initiated by PBAT that have a hydroxyl group on chain-end. PBAT would act as maro-initiator by itself and reacted with LL under insertion-coordination mechanism [6]. The ratios by weight of LL:PBAT were 100:0.3 100:0.6 and 100:1. Sn(Oct)₂ 0.1mol% was used as a catalyst in the reaction. The reaction times was 4 and 8 h. After incubation, the product was dissolved in chloroform and removed to purify by precipitation in methanol. The precipitate was filtered under vacuum. Finally, PLLA-b-PBAT was dried in a vacuum oven at 50°C for 24 h. The synthesis scheme of the PLLA-b-PBAT by ring opening polymerization is shown in Figure 1.

![Figure 1. Synthesis of PLLA-b-PBAT by ring opening polymerization](image)

2.3 Measurements and characterization

2.3.1 Yield percent. The yield percent of product obtained from the reactions was calculated by equation (1)

\[
\text{Yield percent (\%) = } \frac{W_{DB}}{W_{LL} + W_{PBAT}} \times 100
\]

Where \(W_{DB}\) is weight of dried PLLA-b-PBAT, \(W_{LL}\) is weight of L-lactide and \(W_{PBAT}\) is weight of PBAT before incubation in the reaction.

2.3.2 Gel permeation chromatography (GPC). The Mᵣ, Mₑ and PDI of PLLA-b-PBATs were measured by GPC. GPC columns were packed with Styragel HR5E 7.8 × 300 mm columns. A Waters 2414 refractive index (RI) detector was used. The GPC columns were eluted using THF at a flow rate of 1.0 mL/min at 40°C and monodispersed polystyrenes were used for calibration.

2.3.3 Differential scanning calorimetry (DSC). Thermal properties of the samples were analyzed by DSC (Perkin-Elmer, model DSC 4000). Approximately 5 mg of samples were placed in aluminium pans and subjected to two heating scans from -10 to 200°C at 10°C/min. The melting temperature (Tₘ) and apparent melting enthalpy (ΔHₘ) were determined from the second heating scan. The degree of crystallinity \(\chi_c(\%)\) was estimated from the first heating cycle using

\[
\chi_c(\%) = \frac{\Delta H_m}{\Delta H_m^0} \times 100
\]

where \(\Delta H_m\) is the heat of fusion of PLA and \(\Delta H_m^0\) is theoretical melting enthalpy of perfect PLA crystal(93 J/g) [7]
2.3.4 Proton Nuclear Magnetic Resonance (\(^1\)H-NMR). To verify the chemical structure of PLLA-b-PBAT, a Bruker Advanced DPX 300 MHz \(^1\)H-NMR spectrometer was used. CDCl\(_3\) was used as a solvent at ambient temperature and tetramethyl silane was used as internal chemical shift standard.

3. Results and Discussion

3.1 Percent yield and molecular weight
Yield percent and molecular weight of PLLA-b-PBATs are presented in Table 1. It is remarkable that when the incubation time was increased from 4 to 8 h, the yield percent of PLLA-b-PBATs increased around 10%. The higher yield percent indicated a more complete reaction. Using an 8h incubation time, we found that different ratios of LL:PBAT influenced M\(_w\) and M\(_n\) of the synthesized polymers. Highest molecular weight of PLLA-b-PBAT (M\(_w\) = 34,000 g/mol and M\(_n\) = 22,000 g/mol) was obtained when the LL:PBAT was 100:0.3. These results indicate that the most efficient condition for ring opening polymerization was 8h incubation time and LL:PBAT was 100:0.3.

3.2 Chemical structure
The NMR spectra of PLLA, PBAT and PLLA-b-PBAT are shown in Figure 2. The signals at 5.16 (peak a) and 1.56 (peak b) correspond to the methine proton (-OCH) and methyl proton (-OCH\(_3\)) in the PLLA unit [8-10]. The PBAT segment has two polymer proton; chain A and B (see structure in Figure 2). At 2.34 ppm (peak c) assigned to outer CH\(_2\) groups in adipic acid. 4.11-4.17 ppm (peak e) was the outer CH\(_2\) groups in 1,4-butanediol unit in chain A. At 4.34-4.41 ppm (peak f) assigned to the outer CH\(_2\) groups of 1,4-butanediol unit and 8.11 ppm (peak g) meant to CH in benzene ring of chain B. Further, the signal found at 3.67-3.75 ppm (peak d), assigned to the CH\(_2\) groups of the 1,4-butanediol adjacent to the terminal –OH group of chain A in PBAT[5]. However, it entirely disappeared in spectrum of PLLA-b-PBAT. This clearly demonstrated that the hydroxyl group of PBAT initiated the L-lactide in the ring opening polymerization.

![Figure 2 NMR spectra of PLLA, PBAT and PLLA-b-PBAT](image)

3.3 Thermal properties
The thermal properties of the samples were analyzed by DSC. DSC thermogram and the data are shown in Figure 3 and Table 1, respectively. The melting peak of all PLLA-b-PBAT samples occurred at around 161-168°C that is the characteristic of PLA [11]. It is obvious that when using LL:PBAT at 100:0.3 and incubated for 8 h, the degree of crystallinity of PLLA showed a high value (70.89%). These results correlate with the NMR spectrum and confirm that the synthesized polymer were actually possessed PLA structure.
Figure 3. DSC thermogram of L-lactide, PBAT and PLLA-b-PBATs with different condition and LL:PBAT ratio

Table 1. Yield percent, molecular weight and DSC data of PLLA-b-PBATs

| Samples  | Temp. (°C) | Time (hour) | $M_n$ (g/mol) | $M_w$ (g/mol) | PDI | Yield percent | $\Delta H_{m}$ (J/g) | $T_m$ (°C) | $\chi_c$ (%) |
|----------|-----------|-------------|---------------|---------------|-----|---------------|-----------------|------------|-------------|
| 100:0.3  |           |             | 7,600         | 6,400         | 1.19 | 83            | 74.01           | 162.90     | 79.58       |
| 100:0.6  |           | 4           | 17,900        | 9,300         | 1.92 | 87            | 64.55           | 162.00     | 69.41       |
| 100:1.0  |           | 8           | 16,800        | 11,000        | 1.52 | 82            | 41.91           | 161.65     | 44.09       |
| 100:0.3  | 160       |             | 34,000        | 22,000        | 1.56 | 95            | 65.93           | 168.61     | 70.89       |
| 100:0.6  | 8         |             | 31,500        | 18,600        | 1.69 | 96            | 36.42           | 167.47     | 60.67       |
| 100:1.0  | 8         |             | 26,700        | 13,200        | 2.03 | 93            | 65.86           | 167.38     | 70.82       |
| PBAT     | -         | -           | -             | -             | -   | -             | -              | -          | -           |
| LL       | -         | -           | -             | -             | -   | -             | -              | -          | -           |

4. Conclusions

The PLLA-b-PBAT was successfully synthesized via bulk ring opening polymerization of L-lactide and PBAT acting as macro-initiator. The optimum condition found from this study was using ratio of LL:PBAT at 100:3 and incubating the reaction for 8 h. This conclusion is inferred from the highest of yield percent (95%) and molecular weight ($M_w$ = 34,000 g/mol). The NMR and DSC results could mutually verify the structure of PLLA-b-PBAT. Future work of this study will be mechanical properties and heat resistance of PLA triblock copolymer.

5. References

[1] Yang B, Raza S, Li S, and Deng J 2017 Polymer 127 214-9.
[2] Lopes M S and Jardini A L 2014 Chem. Eng. Trans.
[3] Jing Z, Shi X, Zhang G, Li J, Li J, Zhou L, and Zhang H 2016 Polymer 92 210-21.
[4] Freitas A L P d L, Tonini Filho L R, Calvão P S, and de Souza A M C 2017 Polym. Test. 62 189-95.
[5] Ding Y, Lu B, Wang P, Wang G, and Ji J 2018 Polym. Degrad. Stab. 147 41-8.
[6] Ryner M, Stridsberg K, Albertsson A-C, von Schenck H, and Svensson M 2001 Macromolecules 34 3877-81.
[7] Xiao H, Lu W, and Yeh J T 2009 J. Appl. Polymer. Sci. 113 112-21.
[8] Kaitian X, Kozluca A, DENKBAŞ E B, and PIŞKİN E 1996 Turk. J. Chem. 20 43-53.
[9] Supthanyakul R, Kaabbuathong N, and Chirachanchai S 2017 Polym. Degrad. Stab. 142 160-8.
[10] Ba C, Yang J, Hao Q, Liu X, and Cao A 2003 Biomacromolecules 4 1827-34.
[11] Jing Z, Shi X, Zhang G, Li J, Li J, Zhou L, and Zhang H 2016 Polymer 92 210-21.

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