Preparation and Characterization of Cross-linked Poly(lactic acid)/Poly(butylene succinate) Blends

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Abstract. Bio-based blends were prepared via solution blending and thermal cross-linking of poly(lactic acid) (PLA) and poly(butylene succinate) (PBS) using dicumyl peroxide (DCP) as a cross-linking agent. The thermal stability, flexural properties, and fracture toughness of PLA/PBS blends were investigated. The thermal stability of the blends increased with the addition of PBS and further improved by the cross-linking. The flexural properties of the blends decreased with the addition of PBS and increased after the cross-linking. The impact strength of the blend cross-linked with 0.10 wt% DCP increased to 4.25 kJ/m², which increased by 32% compared to that of pristine PLA.

1. Introduction
Poly(lactic acid) (PLA) is a completely biodegradable material synthesized from lactic acid. Due to its biodegradability, PLA can be eventually decomposed into water and carbon dioxide and re-participate in the natural ecological cycle. PLA has excellent properties such as high melting point, hardness, high transparency, and biocompatibility, which is widely used in food packing, electronic, medical products, and engineering applications [1–3]. As a sustainable bio-based material, PLA is expected to partially or completely replace the traditional petroleum-based materials, but its shortcoming of poor toughness lead to its limitations in some application fields. Therefore, on the basis of preserving the biodegradability of PLA and overcoming the poor toughness of PLA, the development of high-performance PLA materials meeting the market demand has become one of the key topics in the future research [4–6].

To improve the toughness of PLA, several methods such as plasticization, copolymerization, incorporation of nanofillers, cross-linking, and blending with flexible polymers have been widely explored. Among them, the blending PLA with other polymers is the most practical and economic route for toughening the materials. Poly(butylene succinate) (PBS), as a flexible linear polymer, with a high melting point and good mechanical properties is biodegradable and often used for toughening modification of polymers including PLA [7–10]. Chemical or physical cross-linking is another way to improve the thermal and fracture toughness of PLA [11–13].

In this study, bio-based PLA/PBS blends were prepared by solution blending and thermal cross-linking using dicumyl peroxide (DCP) as a cross-linking agent. The effect of DCP content on the
thermal stability, flexural properties, and fracture toughness of PLA/PBS blends was investigated using thermogravimetric analysis (TGA), thermal mechanical analysis (TMA), a universal testing machine, and Izod impact tester.

2. Experimental

2.1 Materials
PLA pellets (4032D, density of 1.25 g/cm$^3$, weight average molecular weight of 207,000) were supplied from NatureWorks. PBS (density of 1.26 g/cm$^3$, melting point of 114 °C) was purchased from Dongguan Zangmutou Dansheng Plastic Raw Material Management Department. DCP (analytical pure) was provided from Sinopharmaceutical Chemical Reagent Co., LTD. Dichloromethane (CH$_2$Cl$_2$, analytical pure) was supplied from Tianjin Bohua Chemical Reagent Co., LTD.

2.2 Sample preparation
Weight fraction of PLA/PBS was 90/10. The desired amounts of PLA, PBS, and DCP were mixed in CH$_2$Cl$_2$. The CH$_2$Cl$_2$ in the mixture was removed at 60 °C under a reduced pressure. The mixture was injected into a mold and cross-linked at 130 °C for 0.5 h. The mixture was compression-molded at 180 °C under a pressure of 4 MPa.

2.3 Characterization and measurements

2.3.1 Thermal stability. The thermal stability of PLA/PBS blends was measured using TGA (TA Q50) in the range of 30−600 °C at a heating rate of 10 °C/min under a nitrogen atmosphere. The glass transition temperature of the blends was measured using TMA (TA Q400) at a heating rate of 5 °C/min under a nitrogen atmosphere.

2.3.2 Flexural properties. The flexural properties of the blends was tested according to ASTM D790-86 using a universal testing machine (WDW 3010). The sample size was 5 × 10 × 100 mm$^3$ and the cross-head speed was 2.0 mm/min. The flexural strength and elastic modulus were obtained from the average of five experimental values.

2.3.3 Critical stress intensity factor ($K_{IC}$). The $K_{IC}$ tests were performed according to ASTM E399 using a three-point bending test on a universal testing machine (WDW 3010). The sample size was 5 × 10 × 50 mm$^3$ and the cross-head speed was 10 mm/min. The $K_{IC}$ value was obtained from the average of five experimental values.

2.3.4 Impact strength. Impact strength of the blends was measured using Izod impact tester (TP04G-AS1) according to GB/T 1843-2008 standard. The impact pendulum energy was 5.5 J. The impact strength was obtained from the average of five experimental values.

3. Results and discussion

3.1 Thermal stability
The thermal stability of PLA/PBS blends was measured using TGA, and the TGA thermograms of the blends are shown in Figure 1. The thermal stability factors, including the decomposition temperature for a weight loss of 5% ($T_{5\%}$) and the char at 500 °C, were determined from the TGA thermograms [14,15]. The $T_{5\%}$ value of the blend increased from 305.9 °C to 309 °C with the addition of PBS. The $T_{5\%}$ value of the blend cross-linked with 0.1 wt% DCP increased from 309 to 311 °C compared to that of PLA/PBS blend. This result indicates that cross-linking structure improve the thermal stability of PLA [16−18]. The char value at 500 °C of the blend increased from 0.6% to 2.1% with the addition of PBS and decreased slightly to 1.9% after the cross-linking.
Figure 2 shows the TMA results of PLA/PBS blends. The glass transition temperature was determined from the TMA curves. The glass transition temperature of PLA decreased from 59.7 to 58°C with the addition of PBS and increased to 59.3°C after the cross-linking.

3.2 Flexural properties
The flexural properties of PLA/PBS blends were characterized based on flexural strength and flexural modulus. The flexural strength and flexural modulus values were calculated using the following equations [19]:

\[
\sigma_f = \frac{3PL}{2bd^2}
\]

\[
E_b = \frac{L^3 \Delta P}{4bd^4 \Delta m}
\]

where \(P\) is the applied load, \(L\) is the span length, \(b\) is the specimen width, \(d\) is the specimen thickness, \(\Delta P\) is the change in force in the linear portion of the load-deflection curve, and \(\Delta m\) is the corresponding change in deflection.

Figure 3 shows the flexural strength of PLA/PBS blends as a function of DCP content. The flexural strength of PLA/PBS blend decreased significantly with the addition of PBS, which was due to high flexibility of PBS. The flexural strength of cross-linked PLA/PBS blends increased with increasing DCP content up to 0.05 wt% and then decreased. These results demonstrate that the cross-linking reaction between the PLA and PBS induced by DCP does not affect the flexural strength of PLA/PBS blends [4,20].

Figure 4 shows the flexural modulus of PLA/PBS blends as a function of DCP content. The flexural modulus of the blend decreased with the addition of PBS, which was due to the increased flexibility of the blends. The flexural modulus of the cross-linked blends increased gradually with increasing DCP content. This was due to that the cross-linking reaction enhances the interface adhesion between the PLA and PBS, which improve the flexural modulus of PLA/PBS blends [21].
3.3 Fracture toughness

The Fracture toughness was determined by measurements of $K_{IC}$ and impact strength. The $K_{IC}$ value was calculated using the following equation [22]:

$$K_{IC} = \frac{PBW^{1/2}Y}{2}$$

where $P$ is the rupture force, $B$ is the specimen thickness, $W$ is the specimen width, and $Y$ is the geometrical factor.

Figure 5 shows the $K_{IC}$ value of PLA/PBS blends as a function of DCP content. The $K_{IC}$ value of the blend increased with the addition of PBS compared to that of pristine PLA, which was due to high flexibility of PBS. When PLA/PBS blends were cross-linked by DCP, the impact strength of the blends increased with increasing DCP content up to 0.025 wt% and then decreased.

Figure 6 shows the impact strength of PLA/PBS blends as a function of DCP content. The impact strength of the blend increased slightly with the addition of PBS compared to that of pristine PLA. When PLA/PBS blends were cross-linked by DCP, the impact strength of the blends increased significantly with increasing DCP content. When the DCP content was 0.10 wt%, the impact strength of PLA/PBS blend increased to 4.25 kJ/m$^2$, which increased by 32% compared to that of pristine PLA. During peroxide-initiated cross-linking reaction, PLA and PBS coupled together into PLA–PBS copolymer, which acts as a compatibilizer. This copolymer is usually located at the interface of the PLA matrix and PBS dispersed phase and improved compatibility between the PLA and PBS, leading to improved interface adhesion of PLA/PBS blends [23–25].
4. Conclusions

Bio-based PLA/PBS blends were prepared via solution blending and thermal cross-linking. The thermal stability, flexural properties, and fracture toughness of PLA/PBS blends with various DCP amount were investigated. The thermal stability of PLA increased with the addition of PBS and further improved by the thermal cross-linking. The flexural strength of PLA decreased with the addition of PBS and increased with increasing DCP content up to 0.05 wt%. The flexural modulus of PLA decreased with the addition of PBS and increased gradually with increasing DCP content. The impact strength of PLA increased slightly with the addition of PBS and increased significantly after the cross-linking.

References
[1] F.L. Jin, R.R. Hu, S.J. Park, Compos. Part B 164, 287 (2019).
[2] A.L. Hou, J.P. Qu, Polymers 11, 771 (2019).
[3] M.K. Lila, K. Shukla, U.K. Komal, I. Singh, Compos. Part B 156, 121 (2019).
[4] F.L. Jin, H. Zhang, S.S. Yao, S.J. Park, Macromol. Res. 26, 211 (2018).
[5] N. Wu, J. Yu, W. Lang, X. Ma, Y. Yang, Polymers 11, 1129 (2019).
[6] J. Andrzejewski, M. Szostak, M. Barczewski, P. Łuczak, Compos. Part B 163, 655 (2019).
[7] S. Liu, G. Wu, X. Chen, X. Zhang, J. Yu, M. Liu, Y. Zhang, P. Wang, Polymers 11, 1015 (2019).
[8] J. Li, W.J. Peng, Z.J. Fu, X.H. Tang, H. Wu, S. Guo, M. Wang, Compos. Part B 171, 204 (2019).
[9] C. Vasile, E. Stoleru, R.N. Darie-Nița, R.P. Dumitriu, D. Pamfil, L. Tarțau, Polymers 11, 941 (2019).
[10] A. Djukić-Vuković, D. Mladenović, I. Ivanović, J. Pejin, L. Mojović, Renew. Sust. Energ. Rev. 108, 238 (2019).
[11] M. Shayan, H. Azizi, I. Ghasemi, M. Karrabi, Carbohydr. Polym. 124, 237 (2015).
[12] M. Tesfaye, R. Patwa, P. Dhar, V. Katiyar, ACS Omega 2, 7071 (2017).
[13] Z. Ren, H. Li, X. Sun, S. Yan, Y. Yang, Ind. Eng. Chem. Res. 51, 7273 (2012).
[14] F.L. Jin, Q.Q. Pang, T.Y. Zhang, S.J. Park, J. Ind. Eng. Chem. 32, 77 (2015).
[15] W. Jiang, F.L. Jin, S.J. Park, J. Ind. Eng. Chem. 27, 40 (2015).
[16] X. Zhao, T. Wu, S. Peng, P. Fang, J. Wuhan Univ. Technol.-Mater. Sci. Ed. 33, 1239 (2018).
[17] L. Wei, A.G. McDonald, J. Appl. Polym. Sci. 132, 41724 (2015).
[18] X. Ai, D. Wang, X. Li, H. Pan, J. Kong, H. Yang, H. Zhang, Li. Dong, Polym. Bull. 76, 575 (2019).
[19] H. Jin, B. Yang, F.L. Jin, S.J. Park, J. Ind. Eng. Chem. 25, 9 (2015).
[20] W. Du, H. Shao, Z. He, C. Tang, Y. Liu, T. Shen, Y. Zhu, W.g Lau, D. Hui, J. Agric. Food Chem. 63, 10604 (2015).
[21] S.S. Yao, Q.Q. Pang, R. Song, F.L. Jin, S.J. Park, Macromol. Res. 24, 961 (2016).
[22] W. Dong, F.L. Jin, S.J. Park, J. Ind. Eng. Chem. 20, 1220 (2014).
[23] C. Deetuan, C. Samthong, P. Pratumpol, A. Somwangthanaroj, Iran Polym. J. 26, 615 (2017).
[24] K.M. Choi, S.W. Lim, M.C. Choi, Y.M. Kim, D.H. Han, C.S. Ha, Polym. Bull. 71, 3305 (2014).
[25] J. Chen, T.Y. Zhang, F.L. Jin, S.J. Park, Adv. Mater. Sci. Eng. In press (2019).