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LETTER

Effects of lysine triisocyanate on the mode I fracture behavior of polymer blend of poly (L-lactic acid) and poly (butylene succinate-co-L-lactate)

Vilay Vannaladsaysy · Mitsugu Todo ·
Tetsuo Takayama · Mariatti Jaafar ·
Zulkifli Ahmad · Korakanh Pasomsouk

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Poly(L-lactic acid) (PLLA), a typical biodegradable polymer made from bioresources, has extensively been used in many industrial fields such as automotive, electrical, and medical industries. Fracture properties of PLLA are generally better than those of brittle polymers such as PMMA and polystyrene, however, much lower than engineering polymers with high toughness. For example, the mode I energy release rate of PLLA was reported to be about 4 kJ/m^2 [1], that is, actually much lower than typical engineering polymers such as polyethylene (20 kJ/m^2) and HIPS (16 kJ/m^2) [2]. Different types of PLLA-based polymer blends have been developed to overcome such low fracture property, and their physical and chemical properties have been tried to be characterized [3–13]. These polymer blends are fabricated by blending PLLA with ductile biodegradable polymers such as poly(ε-caprolactone) (PCL), poly(butylene succinate) (PBS), and poly(butylene succinate-co-L-lactate) (PBSL) in order to keep its biodegradability. Although the fracture property of PLLA is effectively improved by such polymer blending, in general, phase separation caused by the immiscibility between PLLA and the blending partner tends to prevent further improvement of the fracture property [1]. Just recently, it was found that addition of lysine triisocyanate (LTI) can dramatically improve the immiscibility in PLLA/PCL and PLLA/PBS blend systems and as a result, their mechanical properties are effectively improved [13–16]. However, the effect of LTI on PLLA/PBSL has not been clarified yet.

In the present study, pelletized PLLA (Lacty#5000, Toyota Motor Co., Ltd) and PBSL (GS Pla® AZ-type, Mitsubishi Chemical Co., Ltd) were blended using a conventional melt-mixer at 190 °C and a rotor speed of 50 rpm for 20 min. The blend ratio of PBSL was fixed at 20 wt%. The weight average molecular weight values of PLLA and PBSL were $M_w = 1.45 \times 10^5$ and $M_w = 1.47 \times 10^5$, respectively. High viscous LTI liquid (Kyowa Co., Ltd) was also added during blending process. The content of LTI was chosen to be 2 wt%. The mixtures were then molded at 30 MPa and 190 °C using a hot press, and then followed by cooling process to produce sheets of 140 × 140 × 2 mm^3. Sheets of neat PLLA were also fabricated by the same molding process. The single-edge-notch-bend (SENB) specimens were then prepared from these sheets for mode I fracture testing. The mode I fracture tests of the SENB specimens were performed at a loading-rate of 1 mm/min using a servohydraulic testing machine. The J-integral at crack initiation, J_{in}, was evaluated as the mode I critical energy release rate using the following formula:

$$J_{in} = \frac{\eta U_{in}}{B(W - a)} \qquad (1)$$

where U_{in} is the critical energy at crack initiation that was defined as the point where the stiffness of the specimen starts to rapidly decrease. B and W are the specimen thickness and width, respectively, a is the initial crack length, and η the geometrical correction factor; $\eta = 2$ for the standard SENB specimen. The average mode I fracture energy, J_f, is defined by the following formula:

V. Vannaladsaysy · M. Todo (✉) · T. Takayama
Research Institute for Applied Mechanics, Kyushu University,
6-1 Kasuga-koen, Kasuga, Fukuoka 816-8580, Japan
e-mail: todo@riam.kyushu-u.ac.jp

V. Vannaladsaysy · M. Jaafar · Z. Ahmad
School of Materials and Mineral Resources Engineering,
Universiti Sains Malaysia, 14300 Nibong Tebal, Pulau Pinang,
Malaysia

K. Pasomsouk
Department of Mechanical Engineering, Faculty of Engineering,
National University of Laos, P.O. Box 3166, Vientiane, Laos

$$J_f = \frac{U_f}{B(W-a)} \qquad (2)$$

where U_f is the total fracture energy that is dissipated by the complete fracture of the specimen. Thus, J_f, is recognized as the average fracture energy per unit area of fracture surface. At least five specimens were tested to obtain the average and standard deviation. The microstructures of the blends were investigated by using a high-resolution field emission scanning electron microscope (FE-SEM). Cryo-fracture surfaces were obtained by immersing the specimens in liquid nitrogen for about 30 min and then observed by FE-SEM. Fracture surfaces of the SENB specimens were also observed by FE-SEM to characterize the fracture micro-mechanism.

FE-SEM micrographs of the cryo-fractured surfaces of PLLA/PBSL and PLLA/PBSL/LTI are shown in Fig. 1. On the surface of PLLA/PBSL, it is observed that PBSL-rich phases are dispersed as circular structures. On the contrary, on the surface of PLLA/PBSL/LTI, the interface between the PLLA- and PBSL-rich phases is not clear, indicating that the compatibility between the two phases is improved due to LTI addition. It is considered that the hydroxyl groups at the ends of PLLA and PBSL molecules are chemically reacted with the isocyanate groups during melt processing, resulting in the improvement of compatibility [14]. Typical load–displacement curves obtained from the mode I fracture tests are shown in Fig. 2. It is clearly seen that PLLA/PBSL/LTI exhibits higher maximum load than

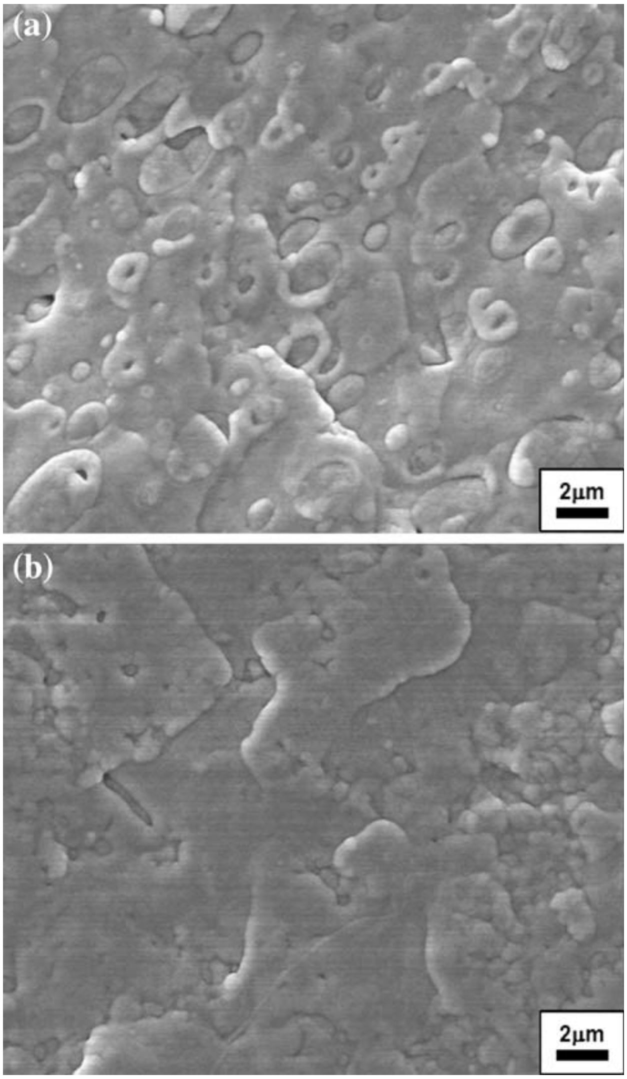

Fig. 1 FE-SEM micrographs of cryo-fractured surfaces. **a** PLLA/PBSL and **b** PLLA/PBSL/LTI

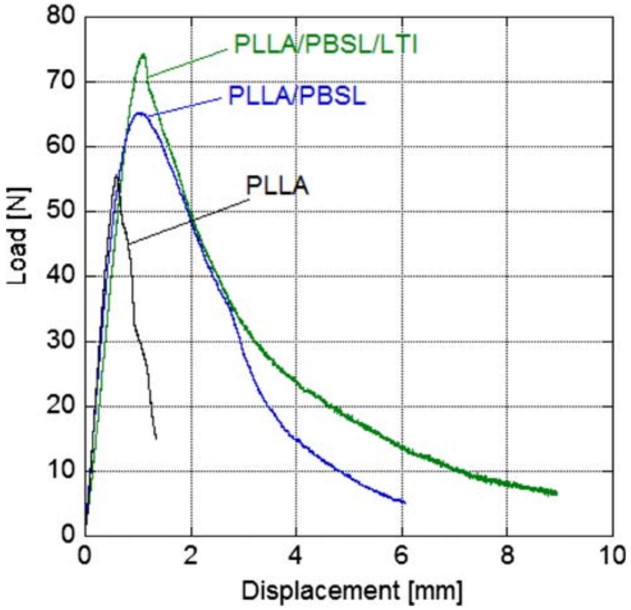

Fig. 2 Typical load–displacement curves

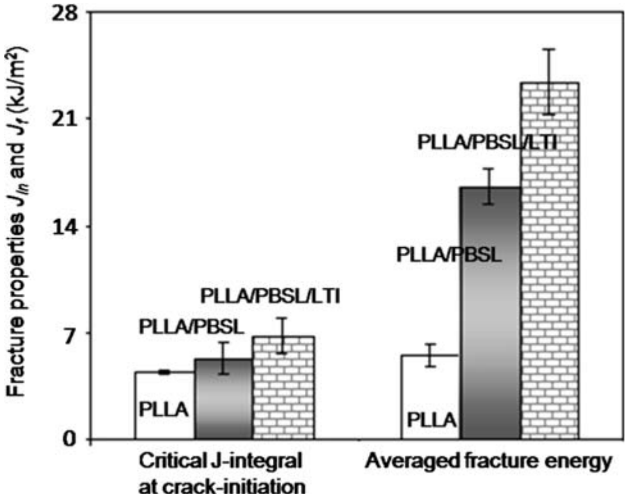

Fig. 3 Critical *J*-integral at crack initiation J_{in} and average of fracture energy J_f

PLLA/PBSL and neat PLLA. Sudden drop of the load appeared in PLLA suggests that the crack propagates in a brittle manner. On the contrary, in the blend systems, the slope of the load–displacement curves after the peak of load becomes gentle, indicating that the crack growth behavior turns to relatively ductile manner with slow crack propagation. Effects of LTI addition on J_{in} and J_{f} are shown in Fig. 3. It is seen that both J_{in} and J_{f} of PLLA/PBSL/LTI are larger than those of PLLA/PBSL and neat PLLA. Improvement of J_{f} is more significant than J_{in}. Fracture surfaces of PLLA, PLLA/PBSL, and PLLA/PBSL/LTI are shown in Fig. 4. It is apparent that PLLA shows smooth surface corresponding to brittle fracture, on the other hand, both polymer blends exhibit plastic deformation behavior indicated by elongated fibril structures. The fracture surface of PLLA/PBSL is characterized by many voids and much rougher than that of PLLA/PBSL/LTI. These voids are thought to be created by removal of PBSL spherulite under high stress concentration in the crack-tip region. Existence of these voids results in enhancement of local stress concentration that could accelerate crack initiation and propagation. On the other hand, such voids are hardly seen on the surface of PLLA/PBSL/LTI, suggesting that the molecules of PLLA and PBSL are well entangled and a firm structure is constructed. This kind of improved molecular structure results in the improved J_{in} and J_{f} as shown in Fig. 2.

In summary, the mode I fracture properties, J_{in} and J_{f}, of PLLA/PBSL polymer blend are found to be dramatically improved by LTI addition. Incorporation of LTI into PLLA/PBSL effectively improves the immiscibility between PLLA and PBSL, resulting in the suppression of

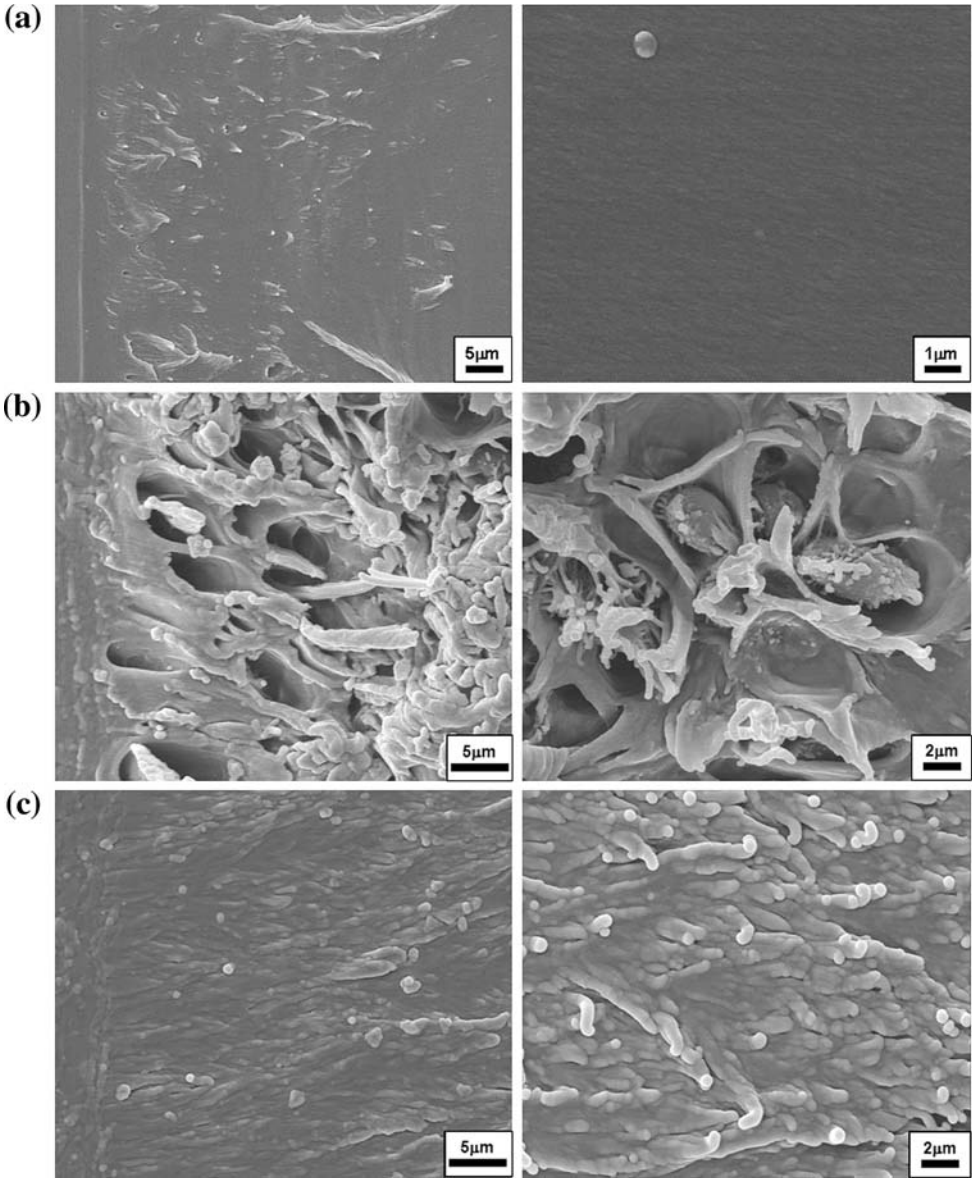

Fig. 4 FE-SEM micrographs of mode I fracture surfaces (the left is the crack initiation region and the right is the crack propagation region). **a** PLLA, **b** PLLA/PBSL, and **c** PLLA/PBSL/LTI

spherulite formation of PBSL and the formation of firm structure consisting of entanglements of PLLA and PBSL molecules and therefore higher energy dissipation during the initiation and propagation of crack growth.

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References

1. Todo M, Park SD, Takayama T, Arakawa K (2007) Eng Fract Mech 74:1872
2. Kinloch AJ, Young RJ (1983) Fracture behaviour of polymers. Applied Science Publishers, New York
3. Domb AJ (1993) J Polym Sci A 31:1973
4. Hiljanen-Vainio M, Varpomaa P, Seppälä J, Törmälä P (1996) Macromol Chem Phys 197:1503
5. Wang L, Ma W, Gross RA, McCarthy SP (1998) Polym Degrad Stab 59:161
6. Tsuji H, Mizuno A, Ilada Y (1998) J Appl Polym Sci 70:2259
7. Yuan Y, Ruckenstein E (1998) Polym Bull 40:485
8. Dell'Erba R, Groeninckx G, Maglio G, Malinconico M, Migliozzi A (2001) Polymer 42:7831
9. Cao X, Mohamed A, Gordon SH, Willett JL, Sessa DJ (2003) Thermochim Acta 406:115
10. Anderson KS, Lim SH, Hillmyer MA (2003) J Appl Polym Sci 89:3757
11. Shibata M, Teramoto N, Inoue Y (2007) Polymer 48:2768
12. Shibata M, Inoue Y, Miyoshi M (2006) Polymer 47:3557
13. Harada M, Ohya T, Iida K, Hayashi H, Hirano K, Fukuda H (2007) J Appl Polym Sci 106:1813
14. Harada M, Iida K, Okamoto K, Hayashi H, Hirano K (2008) Polym Eng Sci 48:1359
15. Takayama T, Todo M (2006) J Mater Sci 41:4989. doi:10.1007/s10853-006-0137-1
16. Takayama T, Todo M, Tsuji H, Arakawa K (2006) J Mater Sci 41:6501. doi:10.1007/s10853-006-0611-9