

# Improvement of Microstructure and Fractured Property of Poly(L-lactic acid) and Poly(butylene succinate-co-e-caprolactone) Blend Compatibilized with Lysine Triisocyanate

V. Vilay\*, M. Mariatti, Z. Ahmad, K. Pasomsouk, M. Todo

**Abstract**—Blends of poly(L-lactic acid) (PLLA) and poly(butylene succinate-co-e-caprolactone) (PBSC) with and without addition of lysine triisocyanate (LTI) were prepared by using a conventional melt-mixer. The effect of LTI on the microstructures and fractured property of the blends was characterized by Fourier transform infrared (FT-IR) analysis and field emission scanning electron microscopy (FE-SEM). J-integral at crack initiation,  $J_{in}$ , and the total fracture energy,  $J_f$ , were measured as mode I fracture properties to assess the effect of LTI addition on these properties. Fracture morphologies were also examined by FE-SEM to characterize the effect of structural change due to LTI addition on the fracture micromechanism. It was found that LTI addition dramatically improves the compatibility between PLLA and PBSC and results in the improvement of the fractured energy,  $J_f$  of ACI value was about 17 times larger than that of neat PLLA. FE-SEM also showed that the reduction of the phase-separation increases local ductile deformation in the crack-tip region.

**Keywords:** Polymer blend, Biodegradability, Compatibility, Fracture property, Phase-separation

## 1 Introduction

Biodegradable polylactic acid (PLA) is perhaps the most important polyester in biomedical applications due to its many favorable characteristics, such as high strength, degradability, and biocompatibility [1]-[4]. Poly(L-lactic acid) (PLLA) is a semi-crystalline polymer with a glass transition temperature ( $T_g$ ) of 60°C and melting temperature of 175°C. Recently, PLLA has been used for automobiles, electric appliances, food packages and medical devices. Previous works on fracture properties and behavior of PLLA reported that PLLA exhibits brittle fracture behavior [5]-[8],

therefore, it is needed to improve the fracture properties in order to expand its applicability. Blending of ductile polymer with base brittle polymer is known to be an effective way to improve the impact resistance and fracture toughness of the base polymer. For example, blending of PLLA with ductile polymers such as poly( $\epsilon$ -caprolactone) (PCL) [5], [6], [9], [10], poly(butylene succinate) (PBS) [11], [12], poly(butylene succinate-co-L-lactate) (PBSL) [7], [10], [11], [13], has been tried to improve the fracture properties of PLLA, and it was found that the PLLA blends possesses better properties than neat PLLA [5]-[13]. It was also observed that the PLLA blends are immiscible each other and create phase separation.

In this study, therefore, lysine triisocyanate (LTI) was used as an additive for PLLA/PBSC blends to improve their immiscibility. Fourier transform infra-red (FT-IR) analyses and scanning electron microscopy of cryo-fractured surfaces were performed to characterize the microstructural modification generated in the blend due to LTI addition. Mode I fracture test was also carried out to assess the change appeared in the mechanical properties. These macroscopic properties were then correlated with the microscopic structural modification.

## 2 Materials and experimental

### 2.1 Materials and specimens

PLLA pellets ( $M_w=1.45 \times 10^5$ ) and PBSC pellets ( $M_w=1.7 \times 10^5$ ) were supplied by Toyota Motor Co., Ltd. and Daicel Chemical Industries, Ltd., respectively. These pellets were held into a desiccator to keep them dry and prevent from degradation due to hydrolysis by moisture. High viscous solution of LTI was supplied by Kyowa Co., Ltd. Blends of PLLA and PBSC was fixed at 50/50 wt%, and 2 phr of LTI was added into the blends. The blends were prepared by melt-mixing in a conventional melt-mixer at 190 °C and a rotor speed of 50 rpm for 20 min. The mixtures were then compression molded at 30 MPa for 190 °C, and then followed by cooling process using a water cooling system to produce sheets of 140x140x2 mm<sup>3</sup>. Sheets of neat PLLA were also fabricated through the same molding process. Single-edge-notch-bend (SENB) specimens for mode I fracture test was then prepared from these sheets. The dimensions of testing samples was approximately 50mm x

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10mm x 2mm. PLLA/PBSC and PLLA/PBSC/LTI with 50 wt% PBSC are denoted thereafter as AC and ACI, respectively.

## 2.2 Measurements

The Fourier Transform Infra-red (FT-IR) measurement was carried out using Perkin Elmer Spectrum One spectrometer with resolution of  $2\text{ cm}^{-1}$  for 4 scans over wave number range of  $400\text{--}4000\text{ cm}^{-1}$ . The film samples were obtained by casting polymer resolution on the KRS-5 disk.

The mode I fracture tests of the SENB specimens were performed at  $1\text{ mm/min}$  of loading-rate 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 (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  $\eta$  the geometrical correction factor,  $\eta=2$  for the standard SENB specimen.

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

The average mode I fracture energy,  $J_f$ , is defined by the following formula (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 energy per unit area of fracture surface. At least five specimens were tested to obtain the average and standard deviation (SD).

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

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 minutes and then observed by FE-SEM. Fracture surfaces of SENB specimens were also observed by FE-SEM to characterize the fracture mechanism and the effect of LTI addition on the fracture behavior compared to PLLA/PBSC blend and neat PLLA and PBSC.

## 3 Results and discussions

### 3.1 FT-IR Results

Fig. 1 shows the FT-IR spectra of PLLA, PBSC, LTI, AC and ACI. It is seen that PLLA, PBSC and the blends exhibited very similar spectra patterns with the C=O peak at about  $1700\text{ cm}^{-1}$ . However, the C=O peak of PBSC (Fig. 1-a.iv) was much higher than that of PLLA (Fig. 1-a.i). It is therefore understood that the higher C=O peak of AC (Fig. 1-a.ii) than PLLA was a result of PBSC blending. It is clearly seen that the C=O peak of ACI (Fig. 1-a.iii) became lower than that of AC, suggesting that the mobility of PLLA and PBSC molecules reduced due to LTI addition. On the other hand, the spectrum of LTI (Fig. 1-b) was obviously characterized by the existence of the large NCO peak around  $2200\text{ cm}^{-1}$ . It is noted that there was no apparent peak of NCO in the

spectra of ACI, indicating that NCO groups acted as compatibilizer by attributing secondary process between the two polymers PLLA and PBSC. This secondary process is polar interaction and hydrophobic process. For comparison the spectra of AC and ACI (refer to Figure 2-a.ii & iii).

Based on FTIR analysis, the peak responding to C=O group appeared higher peak intensity for the sample without the addition LTI. This refers to the difference in bonding motion between that of PLLA and PBSC. However, after addition of LTI, these peaks shift lower, which indicate an identical bond motion in carbonyl group between the two copolymers. This can be attributed to the effect of the LTI, which formed good polar interaction between both PLLA and PBSC. This interaction induces the mobilities of the respective carbonyl bonds as unit entity. This is in agreement with the previous works which showed changes in peak shift and intensity as the results interchange of interaction due to the secondary process [14], [15].

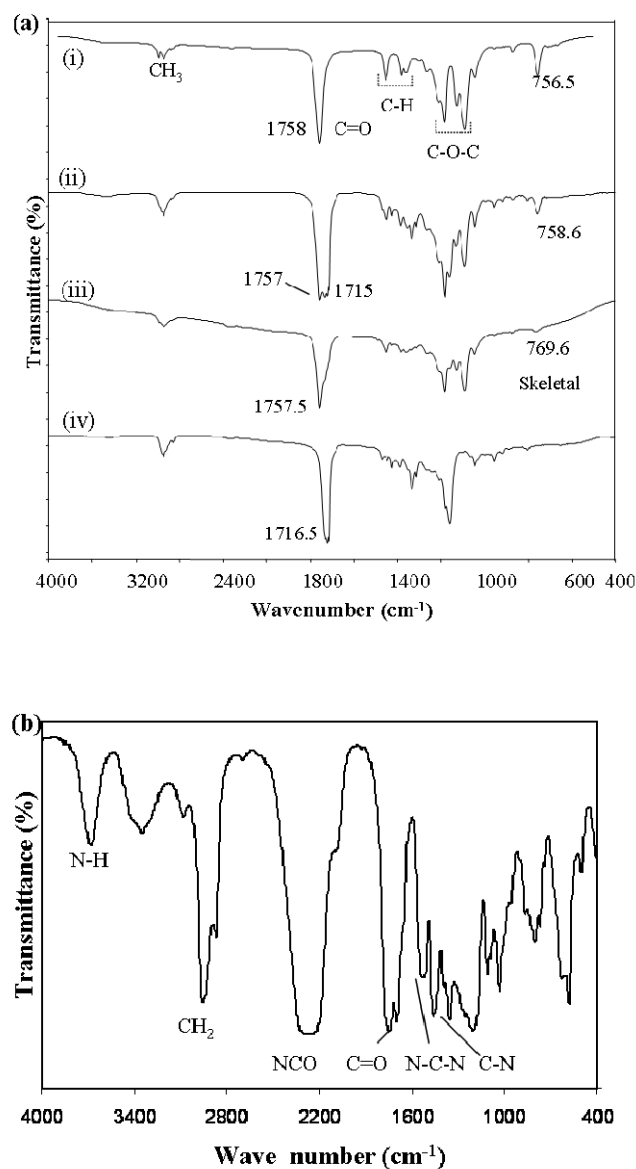


Fig. 1 FT-IR spectra of (a)-(i) PLLA, (ii) AC<sub>20</sub>, (iii) ACI<sub>20</sub>, (iv) PBSC, and (b) LTI.

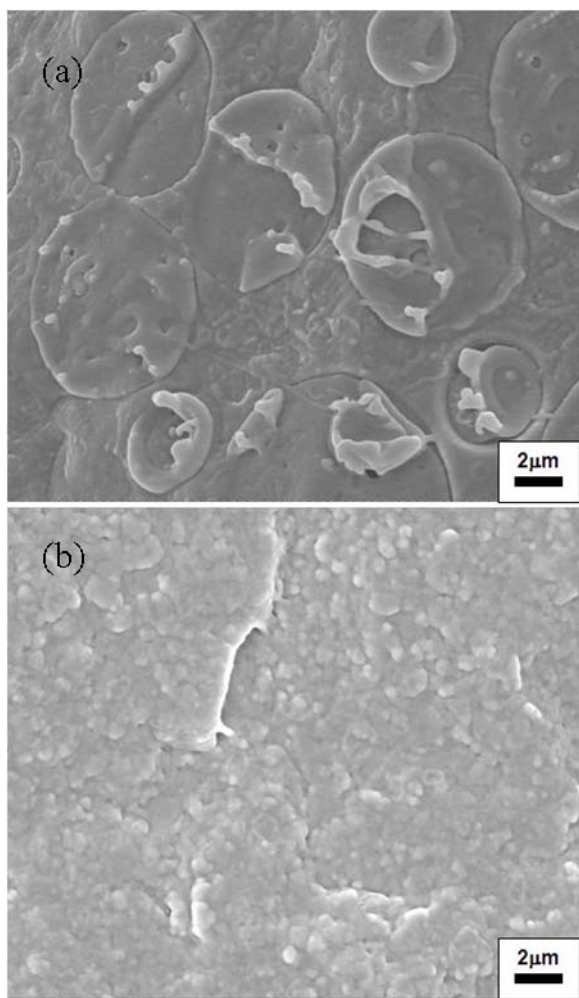


Fig. 3 FE-SEM micrographs fractured surfaces under liquid nitrogen of (a) AC and (b) ACI.

### 3.2 Morphology

FE-SEM micrographs of the cryo-fractured surfaces are shown in Fig.2. Evolution of spherulitic morphology appeared on all of PLLA/PBSC blends. The large spherical structures constructed the secondary phase and therefore corresponded to PBSC spherulites. This kind of morphological result agrees with immiscible polymer blends that generally create macro-phase separation of the two components due to difference of solubility parameter [16]. Such phase separation usually affects the physical and mechanical properties of the blend [17]. On the contrary, for PLLA/PBSC blends with LTI, apparent circular structures of PBSC could not be observed on the surfaces. This is due to improvement of miscibility between PLLA and PBSC. Such microstructural improvement is understood to be caused by the polar interaction and hydrogen bond as discussed based on the FT-IR results in Section 3.1.

### 3.3 Mode I fracture property

Typical load-displacement curves obtained from the mode I fracture tests are shown in Fig.3. In general, the maximum load almost coincides with the onset of crack growth in the tip of notch introduced. It is therefore understood that the much higher maximum load of ACI indicated dramatic improvement of resistibility to crack initiation. The slope of the load-displacement curve after the maximum load usually

corresponds to the rate of crack growth. Therefore, the much gentler slopes of the blends indicated slower crack growth than the rapid growth in PLLA characterized by a steep slope.

Effects of LTI addition on the initial fracture energy,  $J_{in}$ , and the averaged fractured energy,  $J_f$ , are shown in Fig. 4. It is seen that  $J_{in}$  of PLLA/PBSC blends were slightly higher than that of neat PLLA; on the contrary,  $J_{in}$  of ACI is larger than AC, and  $J_{in}$  of PBSC shown largest value corresponding to the ductility polymer.  $J_f$  values of AC blends were higher than that of PLLA. On the other hand,  $J_f$  of ACI effectively improved and  $J_f$  of ACI value was about 17 times larger than that of neat PLLA. These experimental results clearly exhibited that LTI addition effectively improved the mode I fracture properties such as  $J_{in}$  and  $J_f$  of PLLA/PBSC polymer blends.

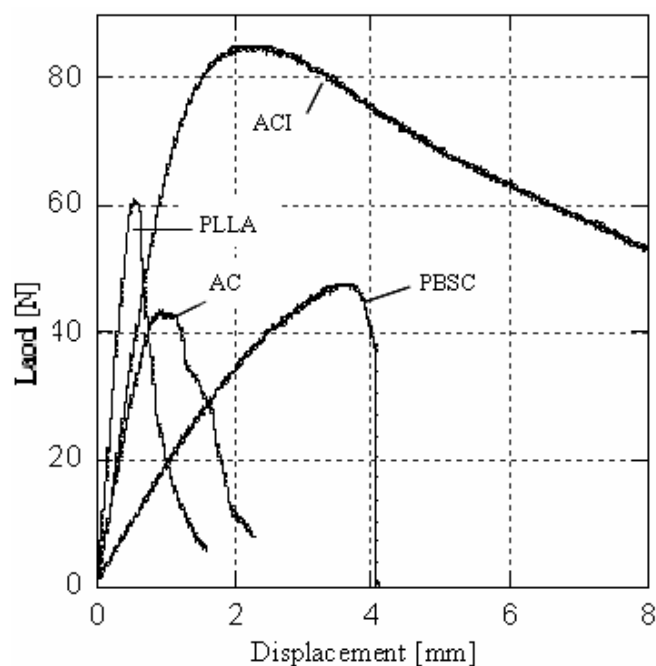


Fig. 3 Load-displacement curves of neat PLLA, PBSC and the blends.

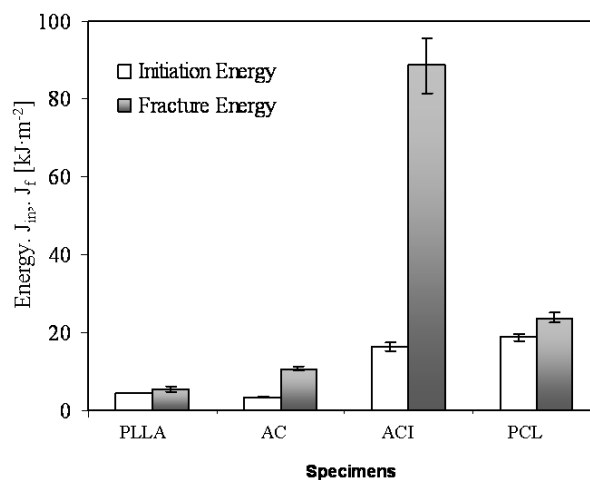


Fig. 4 Effect of LTI addition on the fracture energy values

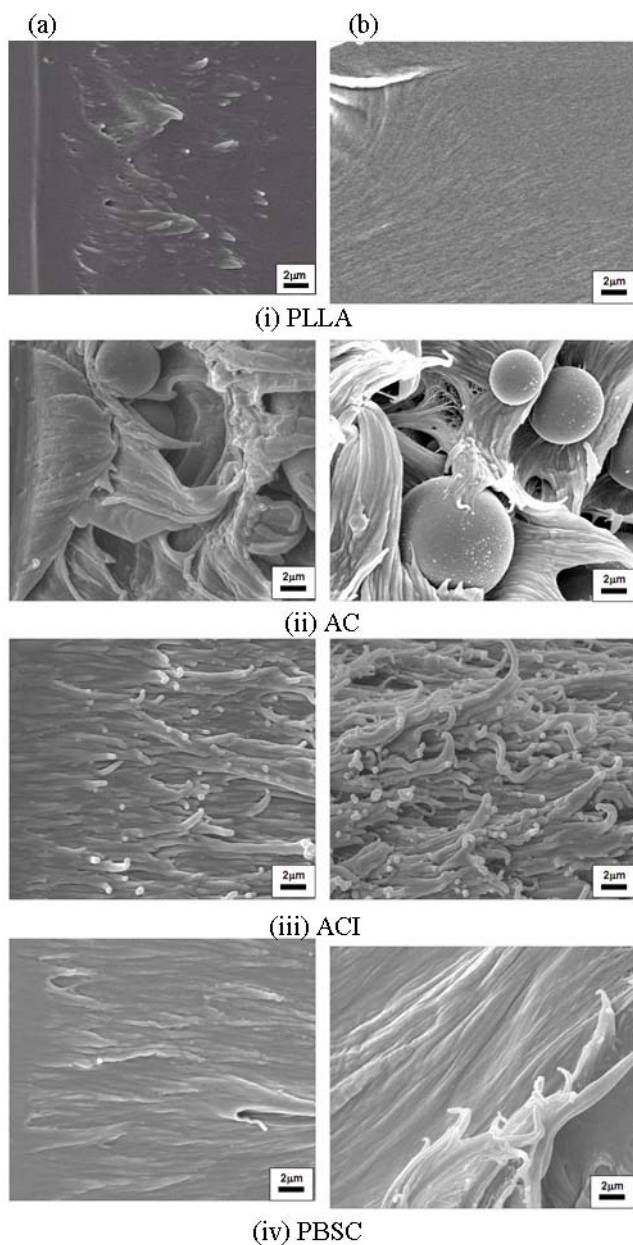


Fig. 5 FE-SEM micrographs of mode I fractured surfaces of (a) crack initiation and (b) propagation regions.

The FE-SEM micrographs of the mode I fracture surfaces in the crack initiation and crack propagation regions are shown in Fig. 5. It is apparent that the fracture surfaces of PLLA are flat and smooth corresponding to the lower dissipated energy during crack initiating to propagate as shown in Fig. 5 (i), whereas the PBSC shows ductile deformation behavior with soft elongated fibril structures (Fig. 5 (iv)). On the other hand, the AC specimen exhibits very rough surfaces and two-phase morphology characterized by the existence of many voids and growth of fibril structures and they can be seen clearly in Fig. 5 (ii). They are naturally understood that these voids were created by removal of the PBSC spherulites. They are noted that the voids were created due to debonding at the interfaces between the spherulites and the matrix under a low stress level because of the lower interfacial strength than the strength of the base polymer. It is easily understood that the voids cause localized stress concentration in the surrounding matrix and therefore, accelerates both fracture surfaces in the

notch-tip regions. However, when copolymer was added to the mixture of PLLA and PBSC, the fracture surfaces turn to dense fibril structures (Fig. 5 (iii)), as a result, improved the immiscibility of the polymers and therefore the fracture energy values are larger than those of the AC and neat PLLA and PBSC.

#### 4 Conclusion

Effect of LTI addition on a polymer blend of PLLA and PBSC results significant improvement in mode I fracture properties of the blends. On the fracture surfaces of PLLA/PBSC blends, many voids were observed, on the contrary, for PLLA/PBSC/LTI blends, void formation was suppressed due to increase of entanglement of PLLA and PBSC molecules caused by chemical reaction. This kind of morphology change due to LTI addition resulted in the dramatic improvement of the fractured energies. FE-SEM observation also showed that for PLLA/PBSC blends with LTI, apparent circular structures of PBSC, that were spherulites, could not be observed on the cryo-fractured surfaces. This corresponded to the improvement of immiscibility between PLLA and PBSC due to LTI addition. FT-IR results suggested that the NCO groups of LTI were acted as compatibilizer by attributing secondary process between the two copolymers PLLA and PBSC. It is thus suggested that LTI worked as a compatibilizer connecting between PLLA and PBSC molecules.

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