

Improvement of impact fracture properties of PLA/PCL polymer blend due to LTI addition

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Recent years, considerable attention has been paid to biodegradable polymers, mainly owing to increasing interest for preservation of environment and substitution of petrochemical polymers. Poly (lactic acid) (PLA), one of typical biodegradable polymers, is being considered for use in a variety of industrial fields including car, computer and electric appliances. PLA is also utilized as a biomaterial in medical fields such as orthopedics and oral surgery [1, 2], due to bioabsorbability and biocompatibility. Fracture properties and fracture behavior of PLA have been studied, and it was found that crazes are formed in crack-tip region prior to crack initiation, that is similar to the fracture behavior of brittle polymers such as PP and PS [3–7]. Improvement of the fracture properties of such brittle polymers can generally be achieved by blending a ductile secondary phase to the base polymer. Poly (ϵ -caprolacton) (PCL), a ductile biodegradable polymer, has been chosen as a blending partner for PLA [8–14], and the fracture properties of PLA/PCL was found to be greater than those of neat PLA [9]. However, it was also found that the immiscibility of PLA and PCL causes phase separation, and tends to lower the fracture properties especially when PCL content increases.

In the present study, lysine triisocyanate (LTI) was used as an additive for PLA/PCL blend to improve such immiscibility. Impact fracture properties of PLA/PCL/LTI

blend was evaluated and compared to those of PLA/PCL blend to assess the effectiveness of LTI addition. Effect of LTI addition on fracture micromechanism was also investigated by observing their fracture surfaces using a scanning electron microscope (SEM).

PLA/PCL and PLA/PCL/LTI blends were fabricated from PLA pellets (Lacty #9030, Shimadzu Co. Ltd), PCL pellets (CelgreenH7, Daicel Chemistry Industries Co.) and LTI (Kyowa Co. Ltd) by melt-mixing in a conventional melt-mixer at 180 °C for 20 min at a rotor speed of 50 rpm. The mixing ratio of PLA and PCL was fixed at 85:15 in weight fraction, and the LTI content was chosen to be 1 wt% in this study. Plates of 2-mm thick were then fabricated from the mixtures using a hot press attached with water-cooling system. These mixtures were melted at 180 °C and pressed at 30 MPa, and then quenched to room temperature using the cooling system. Single-edge-notch-bend (SENB) specimens were prepared from these PLA/PCL and PLA/PCL/LTI plates.

The J -integral at crack initiation, J_{in} , and the average fracture energy, J_f , were evaluated at an impact rate of 1.4 m/s using an instrumented drop weight impact testing system with dynamic displacement measuring apparatus [15, 16]. J_{in} and J_f were calculated using the following formulae:

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

where U_{in} and U_f are the critical energy at crack initiation and the total fracture energy, respectively. Initiation of crack growth was assumed to take place at a critical load where the stiffness of the specimen starts to rapidly decrease. B and W are the specimen thickness and width,

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respectively, and η the geometrical correction factor, which is equal to 2 for the standard SENB specimen. The microstructures of the blends were characterized by observing the fracture surfaces of cryofractured SENB specimens under liquid nitrogen environment using SEM. Fracture surfaces created under impact loading were also observed by SEM to understand the effect of LTI addition on the fracture micromechanism.

Load–displacement curves obtained from the mode I fracture tests are shown in Fig. 1. It is clearly seen that dramatic improvement of mechanical behavior is achieved due to LTI addition. The maximum load increases, and the slope of the load–displacement curve after the load reaches its maximum becomes gentle, indicating crack growth behavior turns to relatively ductile manner. Sudden drop of the load appeared in PLA/PCL suggests that the crack growth behavior is brittle. It is also noted that the initial slope of the curve becomes gentle due to LTI addition, corresponding to the reduction of stiffness of the specimen. This is thought to be related to the change of phase morphology as discussed later. Effects of LTI addition on J_{in} and J_f are shown in Fig. 2. Dramatic improvements are clearly seen on both J_{in} and J_f . Improvement of J_f is greater than J_{in} , corresponding to the drastic change of crack growth behavior from brittle to ductile as shown in Fig. 1.

SEM micrographs of the cryofractured surfaces are shown in Fig. 3. Circular structures observed in PLA/PCL are the spherulites of PCL [9]. Similar structures are still observed in PLA/PCL/LTI; however, their sizes are much smaller than those of PLA/PCL. This size reduction of spherulites suggests that the miscibility of PLA and PCL can be improved by LTI addition. These micrographs also indicate the reduction of crystallinity due to LTI addition; DSC analysis quantitatively showed this behavior such that the crystallinities of PLA and PCL were 11.4% and 60.2%

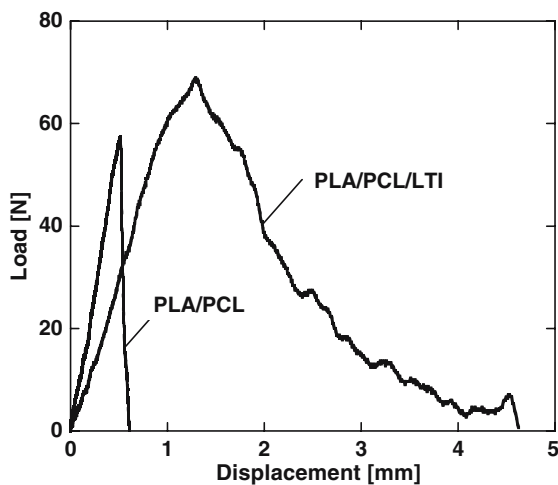


Fig. 1 Load–displacement curves of PLA/PCL and PLA/PCL/LTI blends

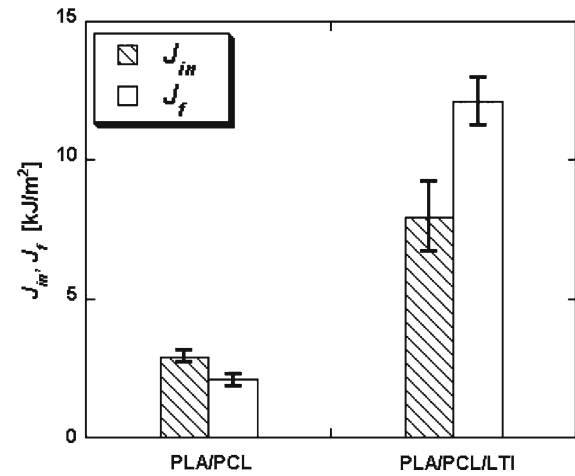
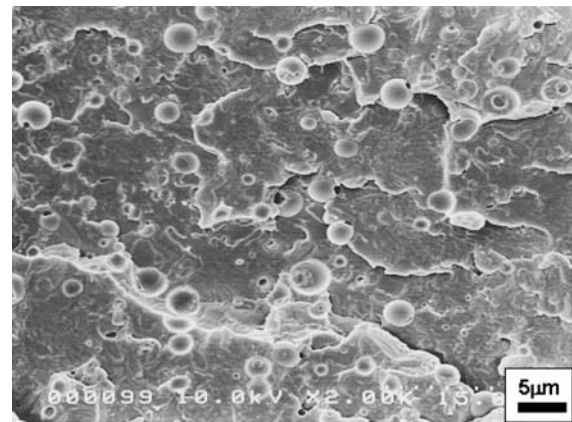
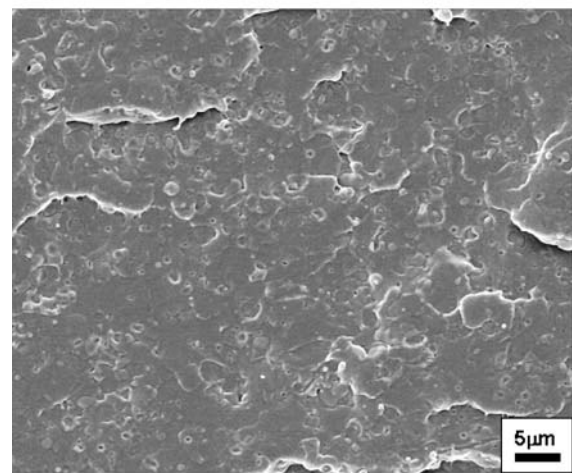


Fig. 2 Effects of LTI addition on J_{in} and J_f



(a) PLA/PCL



(b) PLA/PCL/LTI

Fig. 3 SEM micrographs of microstructures of PLA/PCL and PLA/PCL/LTI blends

for PLA/PCL, and 4.8% and 43.6% for PLA/PCL/LTI. It is thus understood that such reduction of crystallization causes the reduction of stiffness as shown in Fig. 1.

SEM micrographs of fracture surfaces in notch-tip regions are shown in Fig. 4. Elongated fibril structures are observed in both blend systems, and the surface of PLA/PCL is much rougher than PLA/PCL/LTI. It is also observed that this rough surface contains cavities that are the evidence of void formation. It is known that in PLA/PCL blend system, voids are created by interfacial failure between PCL spherulites and surrounding continuous phase under high stress state in crack-tip region [9], and this void formation causes localized stress concentration that accelerates the initiation of crack growth, therefore,

lower the fracture energy. On the other hand, such stress concentration is effectively reduced through the size reduction of PCL spherulites in PLA/PCL/LTI, resulting in the improved J_{in} value. SEM micrographs of crack growth regions are shown in Fig. 5. Smooth surfaces are seen in both blends. The difference of surface morphology between Figs. 4 and 5 is due to the change of rate of crack growth, and the growth rate in the propagation region is faster than in the notch-tip region. Smooth fracture surfaces of PCL spherulites and drawing structures observed in PLA/PCL suggest very fast crack propagation in this region, corresponding to the low J_f value as shown in Fig. 2. On the other hand, the surface morphology of PLA/PCL/LTI is rather similar to the notch-tip region, and this

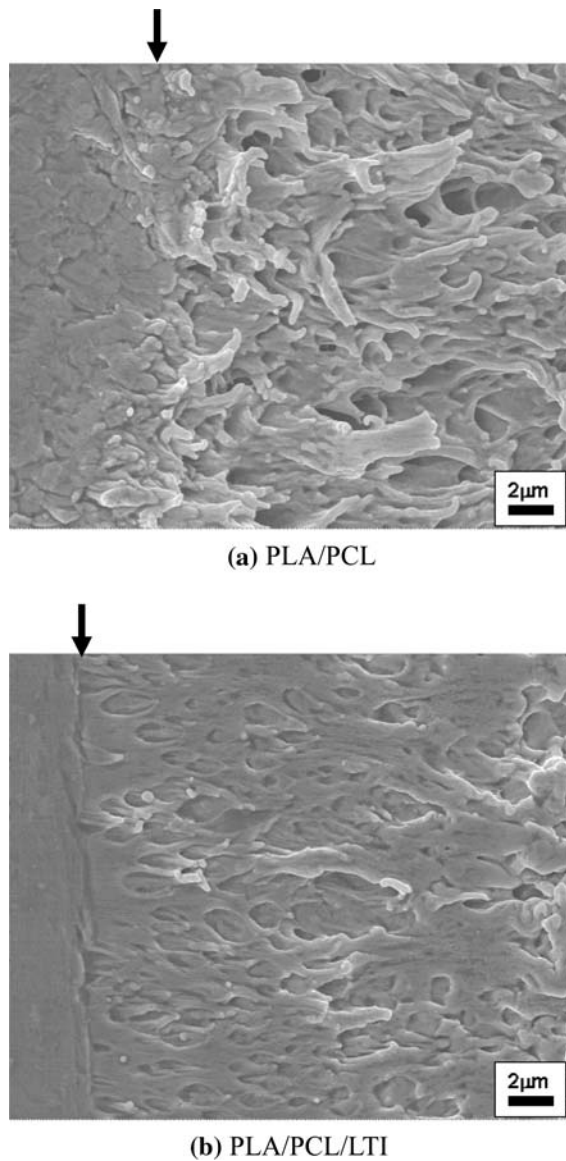


Fig. 4 SEM micrographs of fracture surfaces in notch-tip regions. The arrows indicate notch-tips

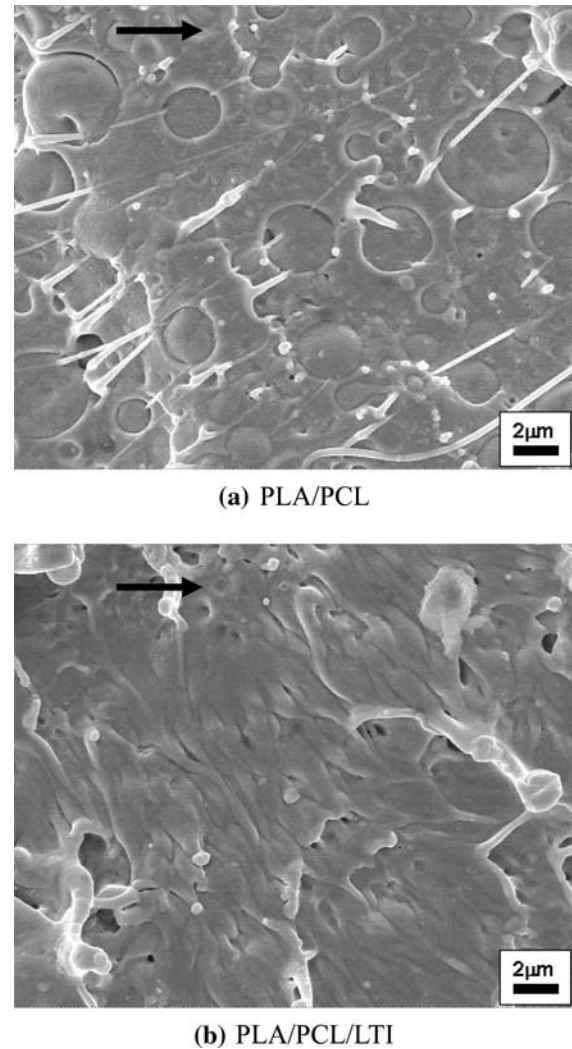


Fig. 5 SEM micrographs of fracture surfaces in crack propagation regions. The arrows indicate the direction of crack propagation

suggests that crack growth is relatively slow in the propagation region, corresponding to the high J_f value.

In summary, the effect of LTI addition on the impact fracture behavior of PLA/PCL blend was assessed on the basis of the fracture properties, J_{in} and J_f , and fracture micromechanism. Both properties are dramatically improved by LTI addition. Immiscibility of PLA and PCL is well improved by LTI addition, resulting in the reduction of size of PCL spherulites. This type of change of phase morphology lowers localized stress concentration caused by interfacial failures, and as a result, more energy is dissipated during the fracture process of well-blended continuous phase in PLA/PCL/LTI. Further study is needed to understand the chemical role of LTI addition to this kind of blend system.

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