Effect of LTI Blending on Fracture Properties of PLA/PCL Polymer Blend*

Mitsugu TODO**, Tetsuo TAKAYAMA***, Hideto TSUJI**** and Kazuo ARAKAWA**

**Research Institute for Applied Mechanics, Kyushu University,
6-1 Kasuga-koen, Kasuga, Fukuoka 816-8580, Japan
E-mail: todo@riam.kyushu-u.ac.jp

***Interdisciplinary Graduate School of Engineering Science, Kyushu University,
6-1 Kasuga-koen, Kasuga, Fukuoka 816-8580, Japan

****Faculty of Engineering, Toyohashi University of Technology,
Tenpaku-cho, Toyohashi, Aichi 441-8580, Japan

Abstract
Lysine triisocyanate (LTI) was used to blends of poly(lactide) (PLA) with poly(\(\varepsilon\)-caprolactone) (PCL) to improve the immiscibility of the two different kinds of biodegradable polymers. Fracture properties such as the J-integral at initiation, \(J_{\text{in}}\), and the total fracture energy, \(J_{\text{f}}\), of PLA/PCL and PLA/PCL/LTI were evaluated, and compared the results to assess the effectiveness of LTI additive on improvement of the fracture properties. Fracture surfaces were also examined using a scanning electron microscope (SEM) to characterize fracture mechanism. The results of the SEM observation exhibited that the size of PCL spherulites became smaller by adding LTI, and therefore void formation was inhibited, resulting in improvement of the fracture properties.

Key words: Polymer Blend, Biodegradable Polymer, Fracture Energy, Crystallization

1. Introduction
Much attention has recently been paid to poly(lactide) (PLA), a biodegradable polymer, due to high strength and stiffness equivalent to commercial polymers, and has been utilized in variety of industrial fields such as medical devices, automobiles and electric appliances. It has been known that PLA is brittle in nature [1-5], and therefore, improvement of its fracture properties has been considered by blending a ductile biodegradable polymer such as poly(\(\varepsilon\)-caprolactone) (PCL) [4, 9-11]. PLA/PCL blend successfully exhibited higher fracture properties than neat PLA; however, immiscibility of PLA and PCL prevents the blend from further improvement of the fracture properties. Just recently, it has been shown that an additive such as lysine triisocyanate (LTI) can improve the immiscibility [10]; however, effects of such modification on the fracture properties and mechanisms of PLA/PCL blends have not been clarified yet.

In the present study, PLA/PCL blends with addition of LTI were fabricated, and the fracture properties were evaluated to assess the effect of improvement of the immiscibility on the fracture properties. Scanning electron microscopy (SEM) of the mode I fracture surfaces was also performed to characterize the fracture micro-mechanisms and then the microscopic mechanisms were correlated with the macroscopic fracture properties.

2. Experimental
2.1 Material and specimen
PLA (Lacty#9030, Shimazu Co. Ltd.) and PCL (CelgreenH7, Daicel Chemical Industry) pellets were used to fabricate PLA/PCL blends. The weight average molecular weights of the pellets were $1.58 \times 10^5$ and $7 \times 10^4$ g/mol, the glass transition temperatures 62.2 ºC and -60 ºC, and the melting points 166.6 ºC and 60 ºC, respectively. The weight fractions of PCL were chosen to be 5, 10, 15 and 20 wt%. These PLA/PCL blends fabricated are thereafter denoted as L/C5, L/C10, L/C15 and L/C20, respectively. PLA/PCL blends with addition of 0.5 wt% LTI (Kyowa Co., Ltd.) were also fabricated, and denoted as L/C5L, L/C10L, L/C15L and L/C20L, respectively. PLA and PCL pellets and LTI were dry-blended at first, then melt-mixed under a condition of 180 ºC, 50 rpm and 20 min. The mixtures were hot-pressed at 180 ºC and 30 MPa to fabricate plates of 140x140x2 mm$^3$.

Single-edge-notch-bend (SENB) specimens were prepared from these plates. The geometry of the SENB specimens is shown in Fig.1. Initial cracks were introduced into the specimens using flesh razor blades. Some of the specimens were also freeze-fractured using liquid nitrogen, and the cryo-fracture surfaces were observed by a scanning electron microscope to analyze the microstructures.

2.2 Mode I fracture test

Fracture testing of the SENB specimens was performed using a servohydraulic testing machine under displacement control mode. The loading-rate was chosen to be 1mm/min. Load-point displacement was assumed to be equivalent to the displacement of the crosshead, and the load and displacement at the load-point were recorded using a digital recorder. Critical energy, $U_m$, corresponding to the initiation of crack growth was determined from the load-displacement curves, and as a critical energy release rate, $J_m$, at crack initiation was determined by

$$J_m = \frac{\eta U_m}{B(W-a)}$$

(1)

where $B$, $W$ and $a$ are the thickness, width and initial crack length of the SENB specimens, respectively. For the standard SENB specimen, the geometrical factor $\eta$ is equal to 2. The critical point corresponding to the onset of crack growth can be found as the point at which the stiffness of specimen, $dP/d\delta$, suddenly decreases as shown in Fig.2.

Fracture energy, $J_f$, was also defined as the energy per unit fracture surface dissipated during complete fracture of a specimen such that

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

(2)

where $U_f$ is the energy corresponding to the area under load-displacement curve up to the point of complete fracture of the specimen.

SEM of fracture surfaces was also performed to characterize the fracture mechanisms of the different types of PLA/PCL blends prepared in the present study.

![Fig. 1  Geometry of SENB specimen (unit:mm)](image)
3. Results and Discussion

3.1 Microstructure

SEM micrographs of the freeze fracture surfaces are shown in Fig. 3. PCL spherulites are uniformly distributed, and their sizes increase as PCL content increases. It is noted that the size of the PCL spherulites in the blends with LTI is much smaller than that in the blends without LTI. This clearly shows that LTI works as an additive in PLA/PCL blends to improve the immiscibility of the two components by decreasing the surface tension of PCL similar to the effect of surface active agent [8].

Fig. 2 Definition of critical point corresponding to crack initiation

Fig. 3 FE-SEM micrographs of microstructures of PLA/PCL blends
3.2 Fracture properties

Load-displacement curves obtained from the mode I fracture tests are shown in Fig. 4. The maximum loads of L/C10 and L/C15 are almost equivalent to that of PLA and the decreasing behavior of load after the maximum load is much gentler, suggesting that more ductile crack growth takes place in these blends than in the neat PLA. The maximum load values tend to increase with LTI addition, and ductility of crack growth also increases. It is noted that the maximum load of L/C10L is greater than that of the neat PLA.

The results of $J_{in}$ and $J_f$ are shown in Figs. 5 and 6, respectively. $J_{in}$ of the PLA/PCL blends are almost equivalent to that of PLA, while $J_{in}$ of the PLA/PCL/LTI blends are larger than that of PLA except L/C5L. $J_{in}$ of PLA/PCL/LTI is maximized with 10wt% PCL, and

![Fig. 3](image1)

Fig. 3  (continued)

![Fig. 4](image2)

Fig. 4  Load-displacement curves of PLA/PCL blends

![Fig. 5](image3)

Fig. 5  Critical J-integral, $J_{in}$

![Fig. 6](image4)

Fig. 6  Fracture energy, $J_f$
the value is 1.8 times greater than that of PLA. $J_f$ of PLA/PCL tends to increase with increase of PCL content up to 15wt%. $J_f$ of the PLA/PCL/LTI blends also exhibits similar tendency with much greater improvement. $J_f$ of L/C20L is 5.7 and 3.6 times greater than those of PLA and L/C20, respectively. These results show that LTI addition can improve the resistances to both the initiation and propagation of crack growth, and these improvements of the fracture properties appear to be closely related to the change of microstructure shown in Fig.3.

3.3 Fracture surface morphology

SEM micrographs of fracture surfaces in notch-tip regions are shown in Fig.7. Fracture surfaces of the PLA/PCL blends are much rougher than that of the neat PLA, and contain many voids. These voids are thought to be created by removal of PCL spherulites under high stress concentration in the crack-tip regions. It is noted that some of the spherulites were elongated and became fibrils as shown in Fig.8. Although PCL blending results in the increase of ductility, PCL forms spherulites which easily create voids due to debonding at the interfaces between the spherulites and the surrounding matrix. These voids result in local stress concentrations that could drive crack initiation. Thus, the increase of ductility tends to rise $J_{in}$, on the other hand, the creation of voids lowers $J_{in}$; as a result, $J_{in}$ of the PLA/PCL blends became almost equivalent to that of the neat PLA.

For the PLA/PCL/LTI blends, creation of these voids suppresses because of the decrease of the spherulite formation as a result of the improvement of the immiscibility. This

![SEM micrographs of fracture surfaces in notch-tip regions](image)

Fig. 7  SEM micrographs of fracture surfaces in notch-tip regions
suppression of voiding results in the reduction of local stress concentration; as a result, $J_{\mu}$ becomes greater than that of PLA.

SEM micrographs of crack propagation regions are shown in Fig.9. For the PLA/PCL blends without LTI addition, many voids, fracture of PCL spherulites and ductile failure of PLA/PCL matrix are observed. Since strain-rate in the crack-tip region during crack propagation is known to be much higher than during crack initiation process, the spherulites fracture before they elongate and become fibrils as shown in Fig.8. It is thought that due to the energy dissipation by these damage formations, $J_f$ of the blend becomes greater than that of the neat PLA exhibiting smooth brittle fracture surface as shown in Fig.9(a). On the other hand, for the PLA/PCL/LTI blends, the number of voids decreases and ductile fracture is observed. This is considered to be due to decrease of the size of the PCL spherulites by LTI.
addition, and suppression of the debonding between the spherulites and the matrix. Furthermore, the ductility of the fracture surface dramatically increases above 15wt% of PCL, corresponding to the rapid increase of $J_f$ shown in Fig.6. Thus, LTI addition tends to relax local stress concentrations in the crack-tip region owing to decrease of void formations, and larger plastic deformation is generated in the crack-tip region as PCL content increases; as a result, $J_f$ of PLA/PCL/LTI becomes much larger than PLA and PLA/PCL.

4. Conclusions

Ductile poly($\varepsilon$-caprolactone) (PCL) was blended to brittle poly(lactide) (PLA) to improve the fracture properties of PLA, and further, LTI was added to the PLA/PCL blend to improve the immiscibility of the two polymers. $J$-integral at crack initiation, $J_{in}$, as the nonlinear critical energy release rate and the fracture energy per unit surface area, $J_f$, were evaluated as the fracture properties. Scanning electron microscopies of the microstructures and fracture surfaces were performed to characterize the fracture micromechanisms. The results were obtained as follows:

1. $J_{in}$ and $J_f$ were improved by 1.8 and 5.7 times, respectively, at the highest level due to the addition of LTI.
2. The size of PCL spherulites decreased due to LTI addition, clearly indicating that LTI works to improve the immiscibility in the system of PLA/PCL blends.
3. It was observed from SEM that many voids were formed on the fracture surfaces in the PLA/PCL blends, while these voids decreased in the PLA/PCL/LTI blends and ductile deformation was observed on the fracture surfaces.
4. The primary mechanisms of improvement of the fracture properties due to LTI addition were thought to be the relaxation of stress concentration in crack-tip region owing to subdivision of PCL spherulites, and increase of ductile deformation of PLA/PCL fibrils.

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References

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