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LETTER

Improvement of mechanical properties of Poly (L-lactic acid) by blending of lysine triisocyanate

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Abstract LTI was attempted to modify the microstructure of poly (L-lactic acid) (PLLA) and to improve its mechanical properties in this study. Bending modulus, strength and fracture toughness of PLLA/LTI were evaluated, and compared to those of the base PLLA to assess the effectiveness of LTI blending. Effect of LTI addition on fracture micromechanism was also investigated by observing and comparing the fracture surfaces of PLLA/LTI and PLLA using a field emission scanning electron microscope (FE-SEM). Experimental results showed that the bending properties such as the bending modulus and the strength are effectively improved due to polymerization of PLLA molecules by LTI blending. The fracture toughness value was also improved due to increase of ductile deformation, i.e., energy dissipation in the crack-tip region.

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 has also been utilized for bioabsorbable bone fixation devices [1, 2]. Thus, PLA has widely been used as load carrying materials in many fields, and therefore, its fracture behavior need to be understood to assess the safety of such PLA devices. Our group has tried to characterize the fracture properties of PLA, and it was found that PLA exhibits brittle fracture manner with multiple craze formation in crack-tip region, similar to the fracture behavior of brittle polymers such as PP and PS [3–7]. Improvement of the fracture property 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 to improve the fracture toughness [8–14]. It was, however, also found that the miscibility between PLA and PCL causes phase separation, resulting in preventing the toughness improvement. Just recently, we found that lysine triisocyanate (LTI) can be effectively used to improve the miscibility between PLA and PCL, and as a result, dramatic improvement of the fracture toughness is achieved [15, 16].

In the present study, LTI was attempted to modify the microstructure of poly (L-lactic acid) (PLLA) and to improve its mechanical properties. Bending modulus, strength and fracture toughness of PLLA/LTI were evaluated, and compared to those of the base PLLA to assess the effectiveness of LTI blending. Effect of LTI addition on fracture micromechanism was also investigated by observing and comparing the fracture surfaces of PLLA/LTI and PLLA using a field emission scanning electron microscope (FE-SEM).

PLLA/LTI mixtures were fabricated from PLLA pellets (TOYOTA Co. Ltd) and LTI (Kyowa Co. Ltd) by melt-mixing in a conventional melt-mixer at 190 °C for 20 min at a rotor speed of 50 rpm. LTI content were chosen to be 0.5 and 1 phr. 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 190 °C and pressed at 30 MPa, and then quenched to room temperature using the cooling system. Beam and Single-edge-notch-bend

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(SENB) specimens were prepared from those PLLA/LTI plates to evaluate bending mechanical properties and mode I fracture toughness, respectively. Same types of specimens were also fabricated for neat PLLA directly by hot-pressing the PLLA pellets.

The weight average molecular weights, M_w, and the crystallinities of PLLA and PLLA/LTI were measured using GPC and DSC, respectively. Three-point bending tests of the beam specimens were also performed at 10 mm/min using a servohydraulic testing machine. Bending modulus, E, and bending strength, σ_f, were then calculated from the linear potion of the load-displacement curve and the maximum load, respectively, using the following formulae:

$$E = \frac{L^3}{4bh^3} S \text{ and } \sigma_f = \frac{3PL}{2bh^2} \tag{1}$$

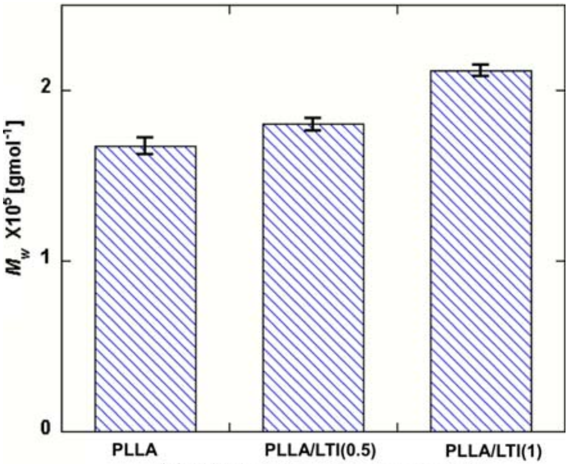
where S is the initial slope of the load-displacement curves. L is the span length. b and h are the width and thickness of the specimen, respectively, and P the maximum load.

Three-point bending tests of the SENB specimens were also conducted at 1 mm/min, and the J-integral value at the maximum load, J_C, was evaluated as a mode I fracture toughness using the following formula:

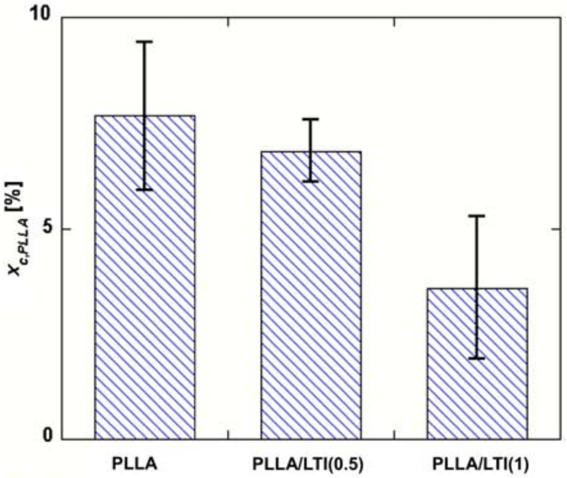
$$J_C = \frac{\eta U_C}{W(B-a)} \tag{2}$$

where U_C is the energy corresponding to the area under the load-displacement curve up to the maximum load. B and W are the thickness and width of the SENB specimen, respectively, and a the initial crack length. η is the geometrical correction factor and equal to 2 for the standard SENB specimen. Fracture surfaces of the SENB specimens were examined using FE-SEM to characterize the fracture mechanism of PLLA/LTI by comparing the fracture surface morphology with that of neat PLLA.

M_w and $x_{c,PLLA}$ are shown in Fig. 1. It is interesting to see that M_w increases with increase of LTI fraction; on the other hand, $x_{c,PLLA}$ decreases with LTI. The increase of M_w suggests polymerization of PLLA molecules. Chemical reaction between hydroxyl group of PLLA and isocyanate group of LTI is thought to cause such polymerization. The decrease of $x_{c,PLLA}$ is therefore considered to be caused by the decrease of mobility of PLLA molecules due to the polymerization. E and σ_f values calculated by Eq. (1) are shown in Fig. 2. E and σ_f effectively increase by LTI addition. It is presumed that the crosslinking reaction of PLLA molecules due to LTI results in those improvements. J_C values obtained from Eq. (2) are shown in Fig. 3. It is clearly seen that J_C is effectively improved by LTI blending. It is thus concluded that LTI uniquely improves both the bending mechanical properties such as the modulus and strength and the mode I fracture toughness. FE-SEM micrographs of the fracture surfaces of PLLA/LTI and PLLA are shown in Fig. 4. PLLA exhibited flat surface corresponding to brittle crack growth behavior. On the other hand, PLLA with LTI showed much rougher and ductile surfaces with formation of elongated fibrils in the crack-tip region, suggesting larger energy dissipation in the crack-tip region, corresponding to the improved J_C values.



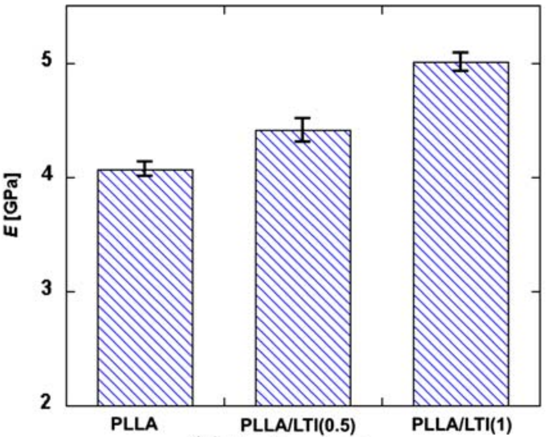
(a) Weight average molecular weight



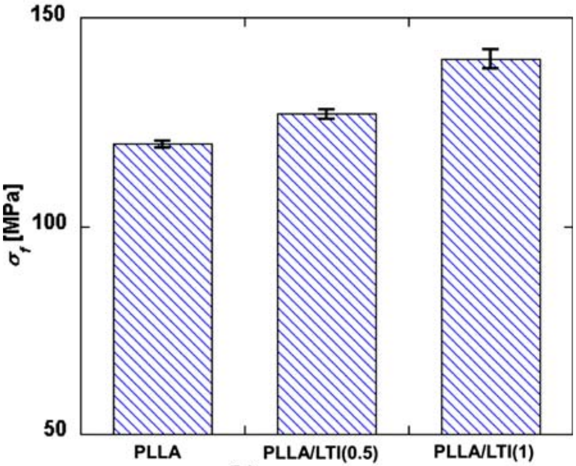
(b) crystallinity

Fig. 1 Effect of LTI on the microstructural properties: (**a**) Weight average molecular weight; (**b**) Crystallinity

In summary, Effect of LTI blending on the bending mechanical properties and the mode I fracture toughness of PLLA was examined. The bending properties such as the bending modulus and the strength are effectively improved due to polymerization of PLLA molecules by LTI blending. The fracture toughness value is also improved due to increase of ductile deformation, i.e., energy dissipation in the crack-tip region.



(a) Bending modulus



(b) Bending strength

Fig. 2 Effect of LTI on the bending mechanical properties: (**a**) Bending modulus; (**b**) Bending strength

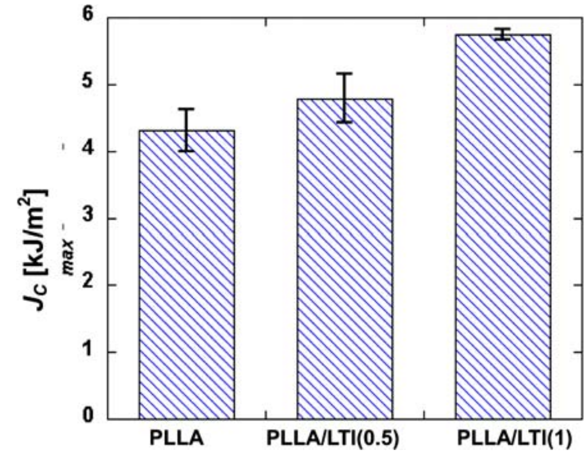
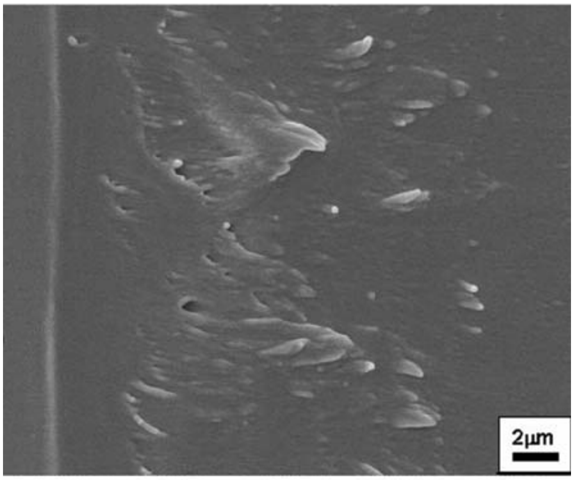
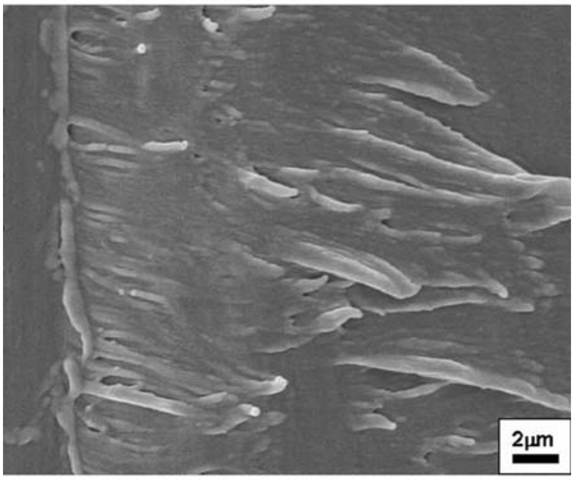


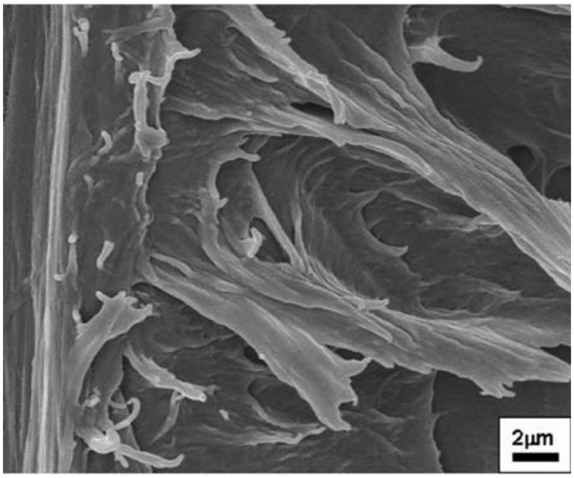
Fig. 3 Effect of LTI on the mode I fracture property, J_C



(a) PLLA



(b) PLLA/LTI(0.5)



(c) PLLA/LTI(1)

Fig. 4 FE-SEM micrographs of fracture surfaces in notch-tip region: (**a**) PLLA; (**b**) PLLA/LTI(0.5); (**c**) PLLA/LTI(1)

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