J Mater Sci (2006) 41:6501–6504
DOI 10.1007/s10853-006-0611-9

LETTER

Effect of LTI content on impact fracture property of PLA/PCL/LTI polymer blends

Tetsuo Takayama · Mitsugu Todo · Hideto Tsuji · Kazuo Arakawa

Received: 16 June 2006 / Accepted: 21 June 2006 / Published online: 16 September 2006

Biodegradable thermoplastic, poly (lactic acid) (PLA), has been used in a variety of industrial fields including automotive, computer, food and electric appliances. PLA has also been utilized as a bioabsorbable material in medical fields such as orthopedics and oral surgery [1, 2]. Fracture properties and behavior of PLA have been characterized, and it was found that multiple-crazes are formed in crack-tip region prior to crack initiation, similarly to the fracture behavior of brittle polymers such as PP and PS [3–7]. Improvement of toughness of such brittle polymers can generally be achieved by blending a ductile secondary phase to the base polymer. Recently, poly(ϵ-caprolacton) (PCL), a ductile biodegradable thermoplastics, has been chosen as a blending partner for PLA [8–14], and the fracture toughness of PLA/PCL blend was found to be effectively greater than that of neat PLA [9]. It was, however, also found that the immiscibility between PLA and PCL causes phase separation, and tends to lower the fracture toughness especially when PCL content increases. Just recently, it was found that such immiscibility can be improved by adding lysine triisocyanate (LTI) as a compatibilizer, and as a result, the fracture toughness is effectively improved due to LTI addition [15, 16].

In the present study, effect of LTI content on the impact fracture toughness of PLA/PCL/LTI blend was investigated. Fracture micromechanism was also studied by observing fracture surfaces using a scanning electron microscope (SEM). The fracture mechanism was then correlated with the macroscopic impact fracture toughness value.

PLA/PCL/LTI blend was fabricated from PLA pellets (Lacty #9030, Shimadzu Co Ltd), PCL pellets (CelgreenH7, Daicel Chemistry Industries Co Ltd) and LTI (Kyowa Co Ltd) by melt-mixing in a conventional melt-mixer at 180 °C and a rotor speed of 50 rpm for 20 min. The mixing ratio of PLA and PCL was fixed at 85:15 in weight fraction, and three different LTI contents were chosen, namely, 1, 1.5 and 2 wt%. Three kinds of blends are denoted thereafter as L/C-1, L/C-1.5 and L/C-2 based on the LTI content. Plates of 2 mm thick were then fabricated from the mixtures using a hot press attached with water-cooling system. The 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 plates for mode I fracture testing.

The J-integral at crack initiation, $J_{\rm in}$, was evaluated as an impact fracture toughness at an impact rate of 1.4 m/s using an instrumented drop weight impact testing system with dynamic displacement measuring apparatus [17, 18]. $J_{\rm in}$ was calculated using the following formula:

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

T. Takayama
Interdisciprinary Graduate School of Engineering Science, Kyushu University, Kasuga, Fukuoka 816-8580, Japan

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

H. Tsuji
Department of Ecological Science, Toyohashi University of Technology, Toyohashi, Aichi 441-8580, Japan

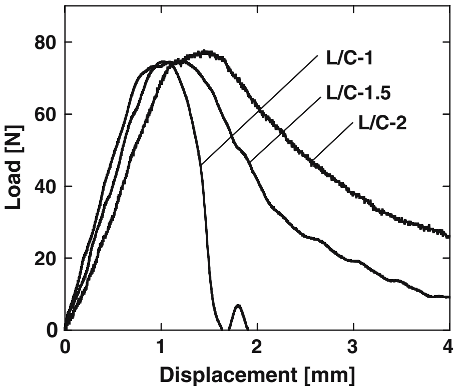


Fig. 1 Load-displacement curves of PLA/PCL/LTI blend

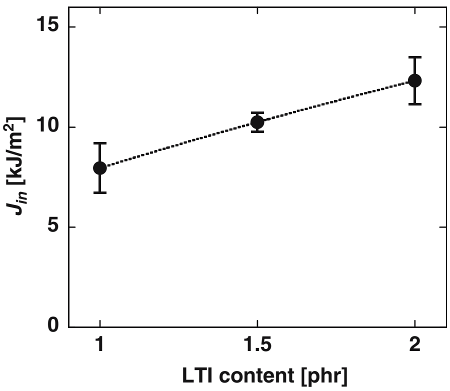
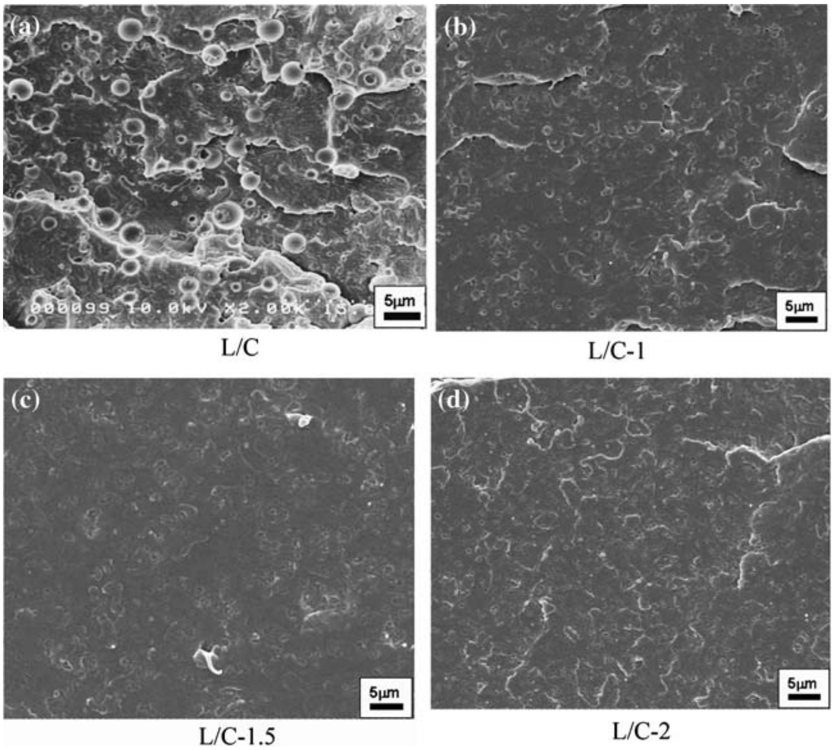


Fig. 2 Dependence of LTI content on J_{in}

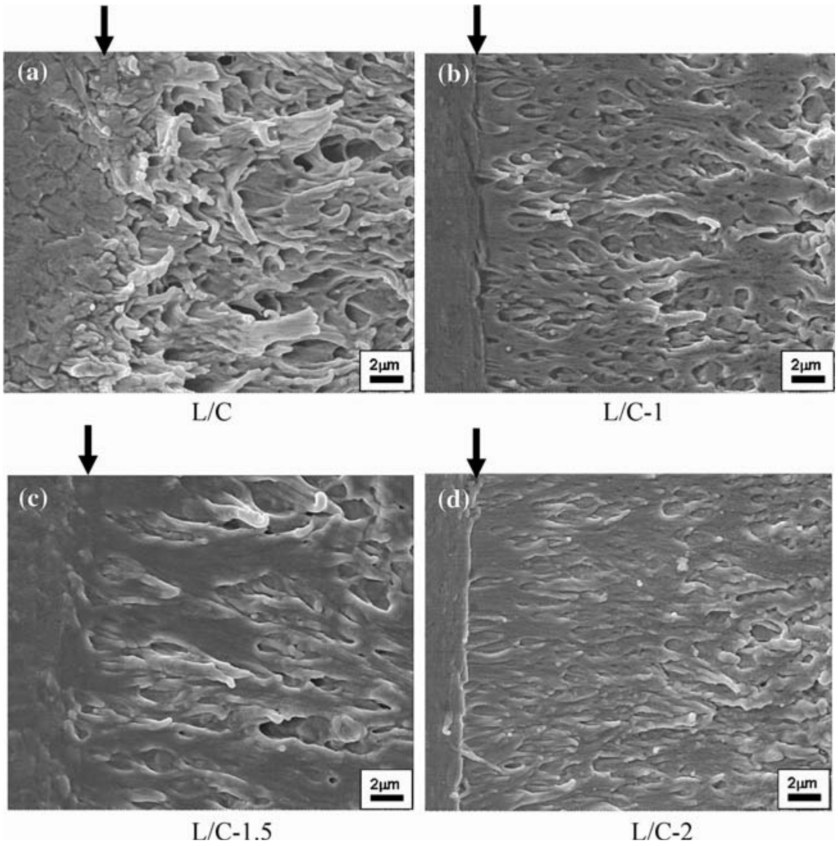
where U_{in} is the critical energy at crack initiation. The critical point for crack initiation was assumed to be detected as a sudden reduction of the specimen stiffness B and W are the specimen thickness and width, respectively, and η the geometrical correction factor, equal to 2 for the standard SENB specimen. The microstructures were characterized by observing the fracture surfaces of cryo-fractured SENB specimens under liquid nitrogen environment using SEM. Fracture surfaces created by the impact fracture tests were also observed by SEM to understand the effect of LTI content on the fracture micromechanism.

Load–Displacement curves obtained from the mode I fracture tests under impact loading are shown in Fig. 1. It is seen that increase of LTI content dramatically affects the load reduction behavior after the load reaches its maximum. This reduction of load normally has a close relationship with crack growth behavior, and slow reduction corresponds to slow crack growth accompanied by ductile deformation in the crack-tip region. The maximum load also increases slightly with increase of LTI content. Effects of LTI content on J_{in} are shown in Fig. 2. It is obviously seen that J_{in} effectively increases with increase of LTI content.

Fig. 3 SEM micrographs of microstructures of PLA/PCL/LTI blend



L/C
L/C-1
L/C-1.5
L/C-2



L/C L/C-1

L/C-1.5 L/C-2

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

SEM micrographs of the cryo-fractured surfaces are shown in Fig. 3. For comparison, PLA/PCL blend without LTI addition is also shown in Fig. 3a. Spherical structures observed in these figures are thought to be distributed PCL phases [9]. It is seen that the size of the spherical PCL dramatically decreases due to LTI addition, and tends to further decrease with increase of LTI content. This kind of size reduction suggests that the immiscibility between PLA and PCL is improved with increasing LTI content. SEM micrographs of fracture surfaces in notch-tip regions are shown in Fig. 4. Ductile deformation is observed in each of the surfaces, and cavities are also observed on the surface of L/C, as a result of removal of spherical PCL phases. The size of the cavities tends to decrease with increase of LTI content as a result of reduction of the size of the spherical PCL phases Weight-average molecular weight, M_w, was measured by GPC analysis, and the dependence of LTI content on M_w is shown in Fig. 5. It is clearly seen that M_w increases with increase of LTI content. LTI is thought to cause crosslinking reaction with hydroxyl lying in the ends of PLA or PCL molecules, and this crosslinking reaction progresses with increasing LTI content, resulting in the increase of M_w. This kind of reaction is also considered to reduce the size of spherical PCL phases. Thus, increase of M_w corresponds to crosslinking formation which is likely to strengthen the structure of the blend, resulting in the increase of J_{in}.

In summary, the effect of LTI content on the impact fracture toughness of PLA/PCL blend was assessed. J_{in} is dramatically improved by increasing LTI content. The weight-average molecular weight increases with increase of LTI content as a result of crosslinking reaction. The phase transformation due to LTI addition tends to strengthen the microstructure and reduce

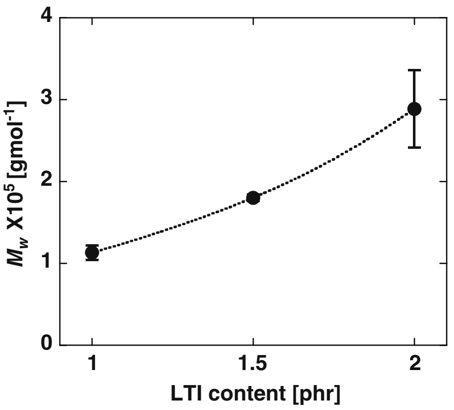


Fig. 5 Dependence of LTI content on M_w

the size of the spherical PCL phases, resulting in increase of energy dissipation at crack initiation and therefore improvement of the impact fracture toughness, J_{in}.

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