Abstract

Biodegradable PLLA was toughened by blending with four different ductile bio-polymers such as PBS, PCL, PBSL and PBSC using a technique of melt-mixing. Mechanical properties were measured and compared to assess their effectiveness as a blending partner for PLLA. It was found that the bending properties are the best with PBS; on the other hand, the mode I fracture toughness and impact resistance are most improved with PBSC. For PLLA/PBSC, FE-SEM observation showed that the fracture surface exhibited ductile fracture with elongated fibrils, and POM result clearly indicated that the largest damage zone is generated in the vicinity of crack-tip, suggesting the highest energy dissipation in the crack-tip region.

1 Introduction

Poly(L-lactide) (PLLA) is widely known as biodegradable polymer made from starch of corns and potatoes. Recently, PLLA has been used for automobiles, electric appliances, food packages and medical devices. Fracture properties and behavior of PLLA has been investigated, and it was found that PLLA exhibits relatively brittle fracture behavior in nature [1-4], 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 PLLA, for example, blending with poly(ε-caprolactone), another biodegradable polymer, has been tried to improve the fracture properties of PLLA, and it was found that PLLA/PCL blend possesses better properties than neat PLLA [5-8]. It was also found that PLLA and PCL are immiscible each other and create phase separation.

In the present study, four different kind of ductile biodegradable polymers, namely, PCL, poly(butylenes succinate) (PBS), poly(butylene succinate-co-L-lactate) (PBSL) and poly(butylenes succinate-co-ε-caprolactone) (PBSC), were blended with PLLA to improve the mechanical properties such as bending modulus, strength, impact fracture energy and mode I fracture property, and compared the results to assess the suitability as a blending partner of PLLA. Mode I fracture mechanism was also investigated by observing the fracture surfaces using a field emission scanning electron microscope (FE-SEM) and the crack growth behaviors using a polarizing optical microscope (POM). The results of the microscopies were then correlated with the macroscopic mode I fracture property values to understand the microstructural effects on the toughening mechanisms of the polymer blends.

2 Experimental

2.1 Materials and Specimens

PLLA, PBS, PCL, PBSL and PBSC were obtained as pellets from Japanese industries. The fundamental thermal properties and the molecular weight values of the pellets are shown in Table 1. PLLA pellets and each of the four blending partners were melt-mixed by using a conventional melt mixer at 180°C and a rotor speed of 50 rpm for 20 min. The mixtures obtained were then hot-pressed at 180°C and a pressure of 30 MPa for 30 min to fabricate plates of 140x140x2 mm³. Bend specimens and single-edge-notch-bend (SENB) specimens for mode I fracture tests were then processed from those plates. The geometries of the specimens are shown in Fig.1.
2.2 Mechanical Tests

Bending tests and mode I fracture tests were performed using a servo-hydraulic testing machine at a loading-speed of 10mm/min and 1mm/min, respectively. Load-displacement relations were recorded using a digital recorder. Bending modulus was evaluated from the initial slope of the load-displacement curves obtained, and the bending strength was calculated from the maximum peak load. The bending absorbed energy was also evaluated by calculating the area under the load-displacement curve up to a constant displacement of 5 mm. The mode I fracture property $J_{\text{max}}$ was evaluated from the load-displacement curves obtained from the mode I fracture tests using the following formula:

$$J_{\text{max}} = \frac{\eta U_{\text{max}}}{B(W - a)}$$  \hspace{1cm} (1)

Where $B$, $W$ and $a$ are the thickness, width and the initial crack length of the specimen, respectively. Geometrical correction factor $\eta$ is 2 for the standard SENB specimen. The energy $U_{\text{max}}$ was obtained as the energy up to the maximum load point.

Impact perforation tests of PLLA blends were also performed to compare the impact resistance. Schematic of the impact testing system is shown in Fig.2. The circumference of a square plate specimen of 2mm thick was fixed living a circular region of 40mm diameter for impact loading as shown in Fig.2. Impact load was measured using a piezo-electric load cell. Load-displacement relation of the specimen was then evaluated from the load data, and the impact absorbed energy was calculated by integrating the load-displacement curve. Impact speed was chosen to be 2m/s in this test.

2.3 Microscopic studies

Cryo-fractured surfaces of the blends were observed using a field emission scanning electron microscope (FE-SEM) to characterize the microstructures and the phase morphology. Mode I fracture surfaces were also examined using FE-SEM to characterize the fracture micromechanisms under Mode I loading condition.

3 Results and Discussion

3.1 Microstructure

FE-SEM micrographs of the cryo-fractured surfaces are shown in Fig.3. All the blends exhibit phase
separation with spherical domains of the ductile polymer, and PLLA/PBSL shows the smallest size of the spherical PBSL domains. Only PLLA/PCL exhibits interfacial debonding in the surroundings of the PCL domains. It is thus presumed that PBSL has the better miscibility with PLLA than the other polymers.

3.2 Mechanical Properties

Bending properties such as bending modulus, strength and absorbed energy are shown in Fig.4. The modulus and strength tended to be lower than the base polymer PLLA, as a result of blending of ductile phases, and the differences between the blends were small. On the other hand, the absorbed energy values of the blends were much larger than that of PLLA, suggesting the effectiveness of blending on this property. It is noted that PLLA/PBS exhibited the best absorbed energy.

$J_{max}$ values of PLLA and the blends are shown in Fig.5. $J_{max}$ of the blends were higher than that of PLLA, and among the blends, PLLA/PBSC exhibited the highest $J_{max}$ which was about twice of that of PLLA.

Results of the impact absorbed energy are shown in Fig.6. The blends showed better values than PLLA. PLLA/PBSC exhibited the highest value about 5 times higher than PLLA. PLLA/PCL showed the second largest value with large deviation. It is interesting to note that PLLA/PBSC possessed the highest values of $J_{max}$ and the impact absorbed energy. On the contrary, PLLA/PBS exhibited the highest values of the bending strength and the bending absorbed energy.

3.3 Mode I Fracture Surface Morphology

FE-SEM micrographs of the mode I fracture surfaces are shown in Figs.7 and 8. It is obvious that PLLA showed very smooth and flat surface, corresponding to brittle fracture with low dissipated energy (see Fig.7). Elongated fibril structures were observed on the fracture surfaces of the blends. PLLA/PBS showed less fibrils than PLLA/PBSC and PLLA/PBSL. Spherulites of PCL were seen on the fracture surface of PLLA/PCL, and interfacial debonding was also observed on the surface, resulting in the generation of the crater-like structures. PLLA/PBSC and PLLA/PBSL exhibited ductile deformation and fracture. It is difficult to distinguish the difference between PLLA/PBSC and PLLA/PBSL; however, it might be concluded that

Fig.3. FE-SEM micrographs of cryo-fractured Surfaces
Fig. 4. Bending mechanical properties

(a) Modulus

(b) Strength

(c) Absorbed energy

Fig. 5. Mode I fracture property, $J_{max}$

Fig. 6. Impact absorbed energy

Fig. 7 FE-SEM micrograph of fracture surface of PLLA
the elongated fibrils of the ductile phase were more in PLLA/PBSL than in PLLA/PBSC.

### 3.4 Toughening Mechanism

Ductility of the four different kinds of biodegradable polymers blended with PLLA was evaluated on the basis of their thermal properties. It is assumed that lower melting temperature corresponds to more ductility; therefore, referring Table 1, it is understood that the order of ductility is PCL, PBSC, PBSL and PBS. It is interesting to see that from Figs. 4, PBS with the lowest ductility showed the highest bending mechanical properties; on the other hand, from Figs. 5 and 6, PBSC and PCL with higher ductility exhibited better $J_{\text{max}}$ and impact absorbed energy. Although the ductility of PCL is higher than that of PBSC, creation of larger spherulites and interfacial failure at the PCL/PLLA interfaces in PLLA/PCL tended to lower the fracture properties than PLLA/PBSC in which the spherulites are smaller. It is thus presumed that high ductility mainly affects localized deformation such as crack-tip deformation in mode I fracture specimen and impact perforation specimen. On the contrary, global deformation such as bending deformation is affected effectively by ductile polymers such as PBS and PBSL with less ductility.

### 4 Conclusions

Four different kinds of PLLA polymer blends were fabricated, and their mechanical properties were examined to assess the effectiveness of each blending partner. Fracture micromechanisms of those polymer blends were also characterized by using FE-SEM. The conclusions obtained are as follows:

1. PLLA/PBS exhibited the best bending mechanical properties such as modulus, strength and absorbed energy. Ductility of PBS is thought to be lower than the other three ductile polymers; thus, it is presumed that ductile polymer with less ductility is an effective blending partner to improve the bending properties of PLLA.
2. PLLA/PBSC exhibited the best fracture properties such as mode I fracture energy $J_{\text{max}}$ and impact perforation energy. Ductility of PBSC appears to be the highest and therefore, localized ductile deformation in crack-tip region was effectively enhanced.

Fig. 8 FE-SEM micrographs of fracture surfaces of PLLA polymer blends
References


