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LETTER

Improvement of fracture energy of HA/PLLA biocomposite material due to press processing

Mitsugu Todo · Takeru Kagawa

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Introduction

Much attention has recently been paid to poly (L-lactic acid) (PLLA) as a biomaterial, mainly owing to its bioabsorbability and biocompatibility. For example, PLLA has widely been used for bone fixation devices in orthopedic and oral surgeries. Recently, different types of hydroxyapatite (HA) filled PLLA composite materials have been developed to improve the bioactivity of such orthopedic implants, and their structures and mechanical properties were investigated [1–9]. Todo et al. recently reported that HA addition dramatically reduced the mode I fracture property of the neat PLLA mainly because of the weak interfacial bonding between PLLA and HA particles [8, 9]. On the other hand, drawing process is known to be an effective way to improve the fracture properties such as strength and fracture toughness of thermoplastics and just recently, unidirectional drawing was applied to PLLA and dramatic improvement of mode I fracture property was reported [10]. It is also known that conventional press-process is an easy way to obtain two-dimensional drawing effect; however, few attempts have been made to study the effectiveness of this technique for PLLA and HA/PLLA.

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

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

In this study, PLLA and HA/PLLA composite plates were intentionally processed by press-process method using a hot press at a temperature close to the glass transition temperature of PLLA. Mode I fracture energy was then evaluated for the pressed and the control (non-processed) specimens. Fracture surface morphology was also characterized using a field emission scanning electron microscope (FE-SEM) to investigate the relationship between the microstructure and the fracture property.

PLLA pellet (Toyota Motor Co.) and HA particles (Sangi Co., Ltd) were used to fabricate HA/PLLA composites. The average molecular weight of the PLLA pellets is $M_w = 2.2 \times 10^5$ gmol^{-1}, the glass transition temperature $T_g = 66$ °C and the melting point $T_m = 177$ °C. The average particle size of the HA particles is about 5 μm. They were mixed at 185 °C and a rotor speed of 50 rpm for 20 min in a conventional batch type mixing machine. The weight fraction of the HA particles was fixed at 10 wt%. The compound was then pressed for 30 min under the condition of 185 °C and 30 MPa using a hot press to fabricate HA/PLLA plates of 140 × 140 × 5 mm^3. Square plates of 30 × 30 × 5 mm^3 were then cut out from these plates and then hot-pressed at 60 °C so that the thickness was reduced to about 2 mm. This kind of compression process is considered to be similar to two-axis drawing process which creates stretched and aligned molecules. Pressed PLLA plates were also fabricated using the same procedure. Unpressed PLLA and HA/PLLA samples of 2-mm thick were fabricated for comparison and called 'control' thereafter. Single-edge-notch-bending (SENB) specimens were fabricated from these pressed and unpressed plates for mode I fracture testing.

Mode I fracture tests of the SENB specimens were performed at a loading-rate of 1 mm/min by a servohydraulic testing machine. The J-integral at critical point, J_C, was then evaluated as the mode I fracture energy using the following formula:

$$J_C = \frac{\eta U_C}{B(W-a)} \quad (1)$$

where U_C is the critical energy corresponding to the maximum load. B, W, and a are the specimen thickness, width and initial crack length, respectively, and η the geometrical correction factor, which is equal to 2 for the geometry of standard SENB specimen. Fracture surfaces created under mode I loading condition were also observed by a field emission scanning electron microscope (FE-SEM) to characterize the effect of press-process on the fracture micromechanism of PLLA and HA/PLLA.

The results of the mode I fracture energy, J_C, are shown in Fig. 1. It is clearly seen that for both PLLA and HA/PLLA, J_C values are dramatically improved due to press processing. In the present study, J_C values of PLLA and HA/PLLA were increased by 250 and 375%, respectively. FE-SEM micrographs of fracture surfaces of PLLA are shown in Fig. 2. The control PLLA showed very flat and smooth surface, indicating a typical brittle fracture pattern with low fracture energy as shown in Fig. 1. On the contrary, the press-processed PLLA exhibited very rough surface with formation of crevasse structures running in the direction of crack growth. This specimen was press-processed in the direction perpendicular to the crack-growth direction; therefore, a layered structure could be formed and the interlayer failure is thought to create such crevasse-like damages. Some additional energy is dissipated in the formation process of the crevasses, resulting in the improvement of J_C.

FE-SEM micrographs of fracture surfaces of HA/PLLA are shown in Fig. 3. The control HA/PLLA showed flat and

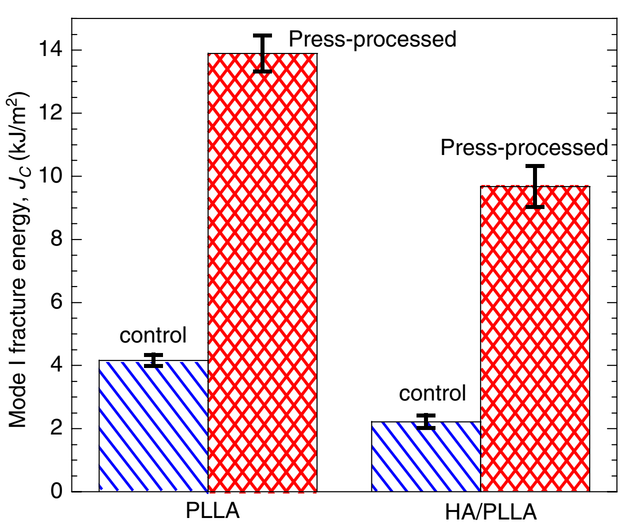

Fig. 1 Mode I fracture energy, J_C

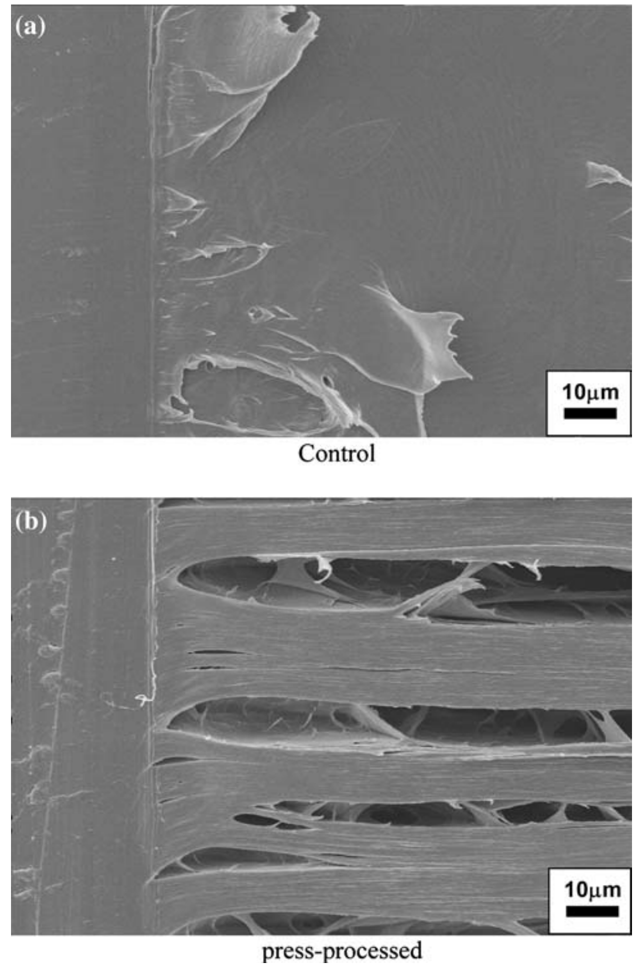

Fig. 2 FE-SEM micrographs of fracture surfaces of PLLA. (**a**) control (**b**) press-processed

little rough surface, indicating low fracture energy as shown in Fig. 1. The fracture surface of the press-processed HA/PLLA was similar to that of the press-processed PLLA shown in Fig. 2(b). Crevasse-like structures were also created on this surface, indicating greater energy dissipation in the pressed than in the control. FE-SEM micrographs of HA/PLLA interfaces are shown in Fig. 4. On the fracture surface of the control HA/PLLA, interfacial debonding was observed. On the other hand, the press-processed HA/PLLA exhibited strong adhesion between the HA particle and the PLLA matrix. It is thus presumed that press process dramatically improved HA/PLLA interfacial strength. This kind of structural improvement is thought to effectively contribute to the improvement of the mode I fracture energy.

In summary, effects of the press-process on the mode I fracture behavior of PLLA and HA/PLLA were investigated. It was shown that for both PLLA and HA/PLLA, the mode I fracture energy could dramatically be improved by press processing. It was also shown that the press process

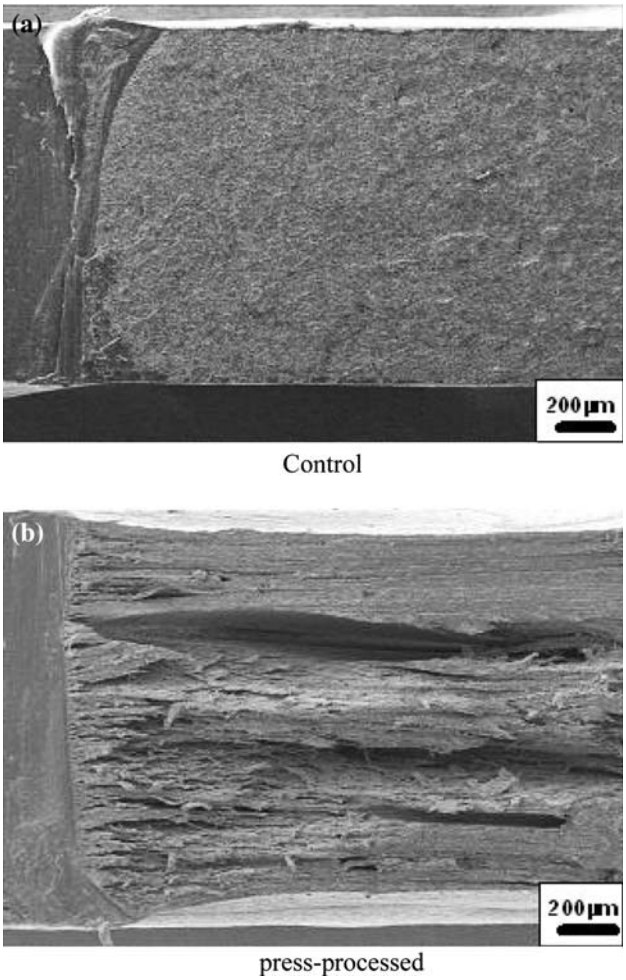

Fig. 3 FE-SEM micrographs of fracture surfaces of HA/PLLA. (**a**) control (**b**) press-processed

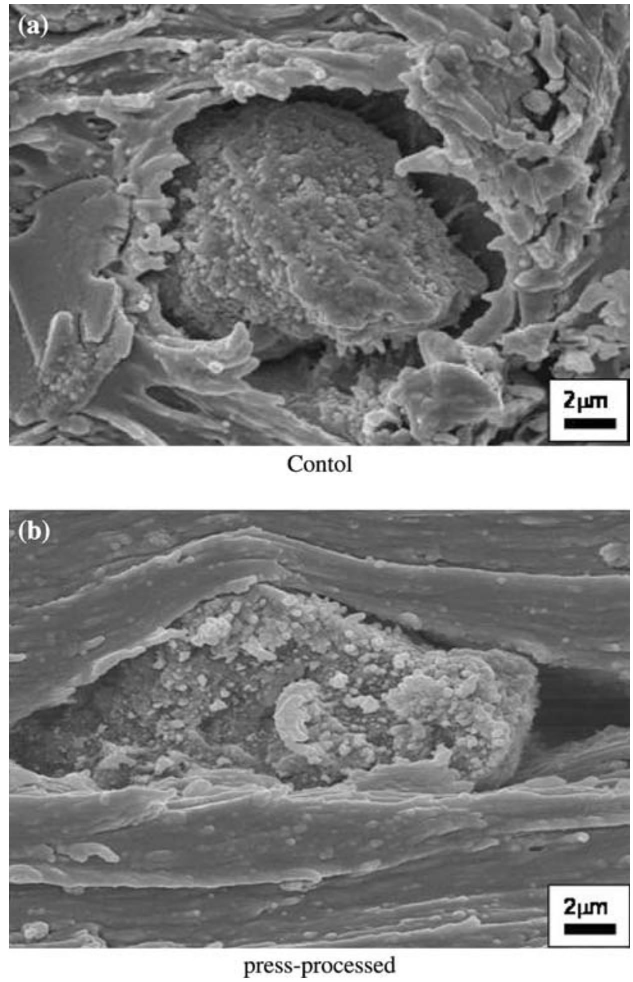

Fig. 4 FE-SEM micrographs of HA/PLLA interfaces. (**a**) control (**b**) press-processed

created layered structure aligned in the direction perpendicular to the pressing direction. This kind of layered structure resulted in crevasse-like failure mode during mode I crack growth and as a result, fracture energy was enlarged. Furthermore, in HA/PLLA, interfacial strength at the HA/PLLA interfaces was effectively improved due to press processing, contributing to the improvement of the fracture energy.

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