



EFFECT OF PRESS PROCESS ON THE FRACTURE BEHAVIOR OF HA/PLLA BIOCOMPOSITE MATERIAL

Takeru Kagawa*, Mitsugu Todo**, Yasuharu Takenoshita***, Akira Myoui****

*Graduate School, Kyushu University

**Research Institute for Applied Mechanics, Kyushu University

***Faculty of Dental Science, Kyushu University

****Faculty of Medicine, Osaka University

Keywords: *Hydroxyapatite, Poly(L-lactic acid), Biomaterial, Composite material
Mode I fracture property, Toughening mechanism*

Abstract

Press process was performed in order to toughen HA/PLLA bio-composite material. Mode I fracture properties and bending mechanical properties of forged and unforged HA/PLLA were then evaluated to assess the effect of press process on these properties. FE-SEM was also used to characterize the toughening mechanism due to press. Testing results showed that the bending strength and modulus slightly increased due to press; on the other hand, the bending absorbed energy and the mode I fracture property dramatically improved. FE-SEM observation of the fracture surfaces showed that ductile deformation and fracture of PLLA fibrils were enhanced and in addition, interfacial cohesion strength was improved. These microstructural modifications appear to result in the toughness improvement.

1 Introduction

Poly (L-lactic acid) (PLLA), a bioabsorbable plastics, has been paid to much attention as a biomaterial for bone fixation devices in orthopedic and oral surgeries. Recently, Hydroxyapatite (HA) particles filled PLLA composite materials have been developed to improve the bioactivity of PLLA implants [1,2]. Todo et al. recently reported that HA addition dramatically reduced the mode I fracture property of the neat PLLA mainly because of the low interfacial bonding between PLLA matrix and HA particles [3].

Deformation process is known to be an effective way to improve the fracture properties such as strength and fracture toughness of thermoplastics.

However, few attempts have been made to understand the effect of deformation process on the fracture behavior of HA/PLLA composite materials.

In this research, HA/PLLA samples were intentionally processed by press process method, one of the typical deformation processes, using a hot press at a temperature close to the glass transition temperature of PLLA. Fracture properties were then evaluated for the pressed and the control (non-processed) samples. Fracture surfaces were also observed using a field emission scanning electron microscope (FE-SEM) to characterize the relationship between the microstructural change due to press process and the fracture properties.

2 Experimental

2.1 Material and specimen

PLLA pellet and HA particles (Sangi Co., Ltd) were used to fabricate HA/PLLA composites. The weight-average molecular weight of the PLLA pellets is $M_w=2.2 \times 10^5 \text{ gmol}^{-1}$, the glass transition temperature $T_g=66 \text{ }^\circ\text{C}$ and the melting point $T_m=177 \text{ }^\circ\text{C}$. The average particle size of the HA particles is about $5 \mu\text{m}$. They were mixed at $185 \text{ }^\circ\text{C}$ and a rotor speed of 50 rpm for 20 min in a conventional 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 $185 \text{ }^\circ\text{C}$ and 30 MPa using a hot press to fabricate HA/PLLA plates of $140 \times 140 \times 5 \text{ mm}^3$. Beam specimens of $30 \times 30 \times 5 \text{ mm}^3$ were then cut out from these plates. These beam specimens were hot-pressed at $60 \text{ }^\circ\text{C}$ such 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. PLLA and HA/PLLA plates of 2 mm thick were fabricated for comparison. Beam specimens of $50 \times 10 \times 2 \text{ mm}^3$ for bend testing were then processed from these pressed and control plates. Single-edge-notch-bend (SENB) specimens were also fabricated from the beam specimens by introducing notches of 5 mm in the middle sections.

2.2 Crystallinity measurement

Crystallinity values of PLLA and HA/PLLA specimens fabricated were determined by DSC analysis using DSC-60 (Shimadzu Co., Ltd) equipped with a TA-60WS thermal analysis system. The apparatus was calibrated with an indium standard in nitrogen atmosphere. Samples of about 3 mg were placed in aluminum cells, and heated from 40 to 200 °C at a rate of 10 °C/min in nitrogen atmosphere. Crystallinity, x_c , of PLLA was then evaluated using the following formula[4]:

$$x_c = 100 \times (\Delta H_m + \Delta H_c) / 135 \quad (1)$$

and x_c of PLLA in HA/PLLA was also evaluated using the following formula:

$$x_c = 100 \times 0.9 \times (\Delta H_m + \Delta H_c) / 135 \quad (2)$$

where ΔH_m and ΔH_c are the enthalpies of melting and crystallization of PLLA, and 135 (J/g of polymer) is the enthalpy of fusion of PLLA [4].

2.3 Three-point bending tests

Three-point bending tests of the bend specimens were performed using a servohydraulic testing machine at a loading-rate of 10 mm/min. The load-displacement relations were recorded using a digital recorder, and the bending absorbed energy, U_{ab} , was then evaluated from the area under the load-displacement curve for each of the specimens. The bending strength was also examined using the following formula:

$$\sigma_f = 3P_{max}L/2WB^2 \quad (3)$$

where P_{max} is the maximum load of the load-displacement curves. B, W and L are the specimen thickness, width and span length. The bending elastic modulus, E , were evaluated using the following formula:

$$E = L^3 S / 4WB^3 \quad (4)$$

where S is the slope of the load-displacement curve at initial stage.

2.4 Mode I fracture testing

Mode I fracture tests of SENB specimens were performed at a loading-rate of 1 mm/min by a servohydraulic testing machine. The J -integral at maximum load, J_{max} , was then evaluated using the following formula:

$$J_{max} = \eta U_{max} / B(W-a) \quad (5)$$

where U_{max} is the critical energy at 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 standard SENB specimen.

2.5 Observation of fracture morphology

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.

3 Results and Discussion

3.1 Crystallinity

Crystallinity values of the four samples fabricated are shown in Fig.1. For PLLA, there is no difference between the pressed and the control samples. It is noted that the crystallinity of HA/PLLA was larger than that of PLLA, suggesting that HA particles worked as nucleuses for crystallization of PLLA. For HA/PLLA, the pressed sample exhibited slightly higher crystallinity than the control sample.

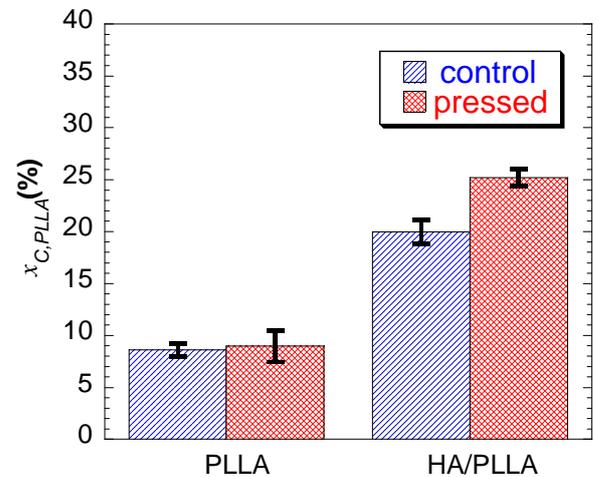


Fig.1 Crystallinity

3.2 Mechanical properties

Bending mechanical properties were shown in Fig.2. For PLLA, there was no effect of press process on the bending strength and modulus. On the other hand, for HA/PLLA, the pressed sample exhibited higher modulus and strength than the control sample. Bending absorbed energy was dramatically improved for both PLLA and HA/PLLA. Especially, U_{ab} of the pressed HA/PLLA was about 9 times larger than that of the control HA/PLLA.

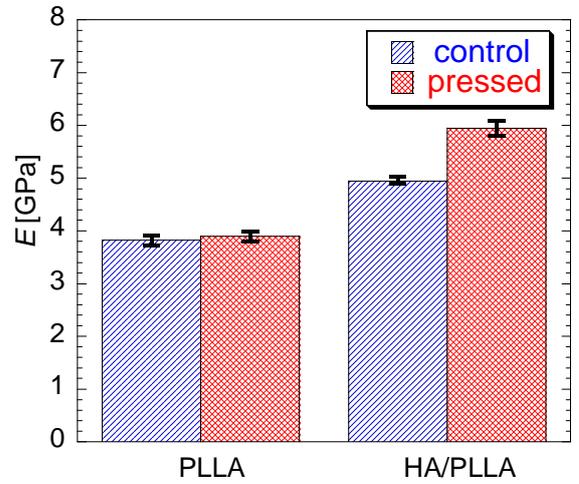
Results of J_{max} evaluation are shown in Fig.3. For both PLLA and HA/PLLA, J_{max} values were dramatically improved due to press process. J_{max} values of PLLA and HA/PLLA were increased by 250% and 375%, respectively.

It is thus noted that press process was effectively improved all the four mechanical properties of HA/PLLA, especially, the fracture properties, bending absorbed energy and J_{max} , exhibited dramatic improvement. For neat PLLA, only fracture properties were improved by press process.

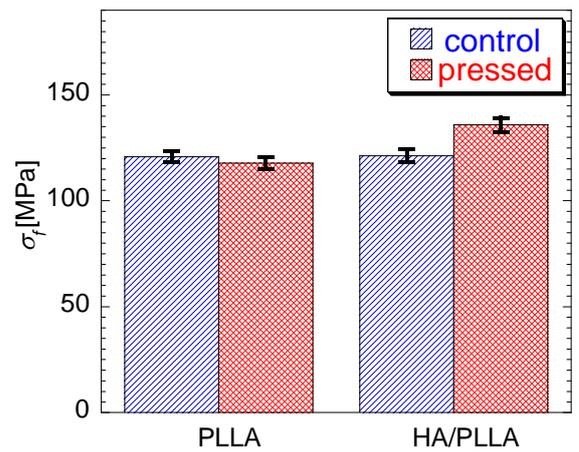
3.3 Fracture surface morphology

FE-SEM micrographs of fracture surfaces of PLLA and HA/PLLA specimens are shown in Figs.4 and 5, respectively. The control PLLA (Fig.4(a)) showed very flat and smooth surface, indicating a typical brittle fracture pattern with low fracture energy as shown in Fig.3. On the contrary, the pressed PLLA (Fig.4(b)) 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 was dissipated in the formation process of the crevasses, resulting in the improvement of J_{max} .

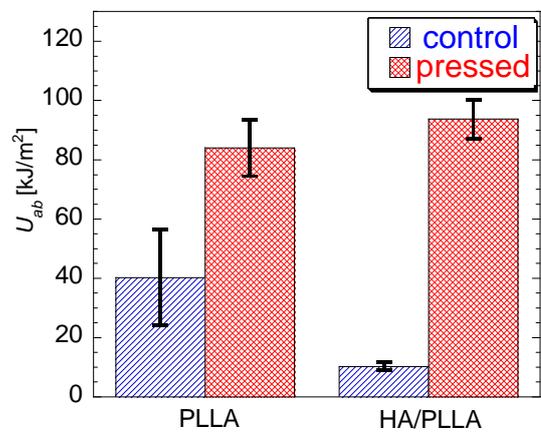
The control HA/PLLA specimen (Fig.5(a)) showed flat and little rough surface, indicating low fracture energy as shown in Fig.3. The surface of the pressed HA/PLLA (Fig.5(b)) was similar to that of the pressed PLLA shown in Fig.4(b). Crevasse-like structures were also created on this surface, indicating greater energy dissipation in the pressed HA/PLLA than in the control HA/PLLA.



(a) Modulus



(b) Strength



(c) Absorbed energy

Fig. 2 Bending mechanical properties

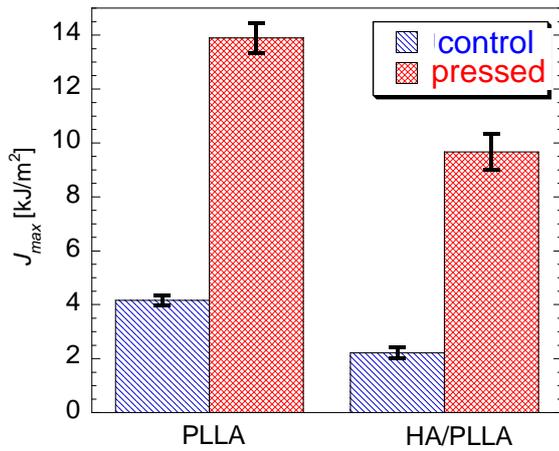
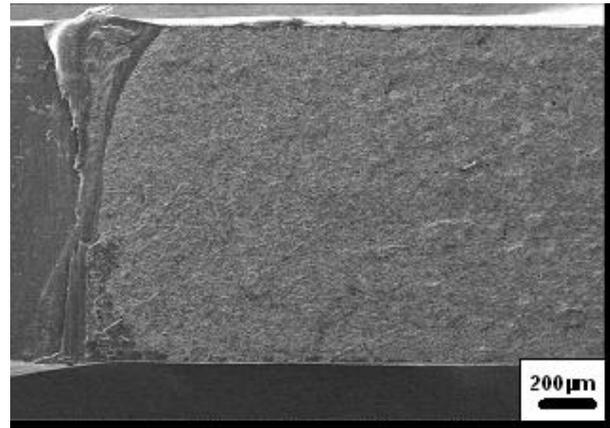
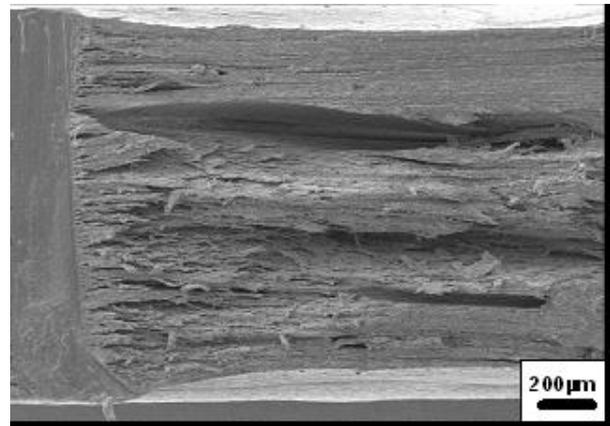


Fig. 3 The J -integral at maximum load

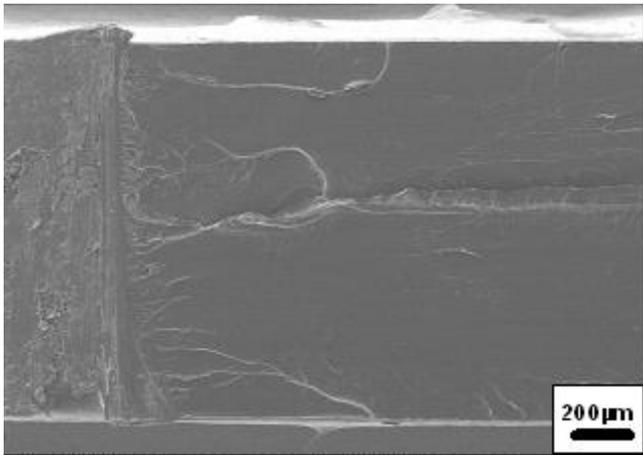


(a) Control HA/PLLA

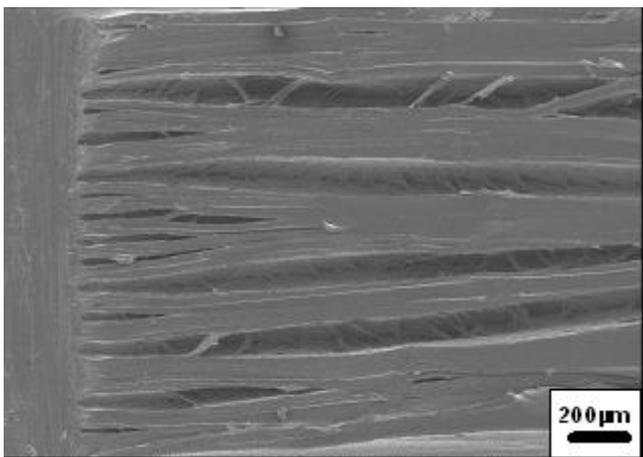


(b) Pressed HA/PLLA

Fig.5 FE-SEM micrographs of fracture surfaces of HA/PLLA samples



(a) Control PLLA



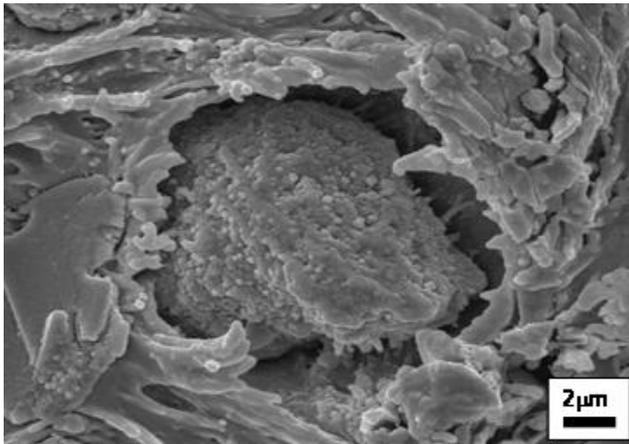
(b) Pressed PLLA

Fig.4 FE-SEM micrographs of fracture surfaces of PLLA samples

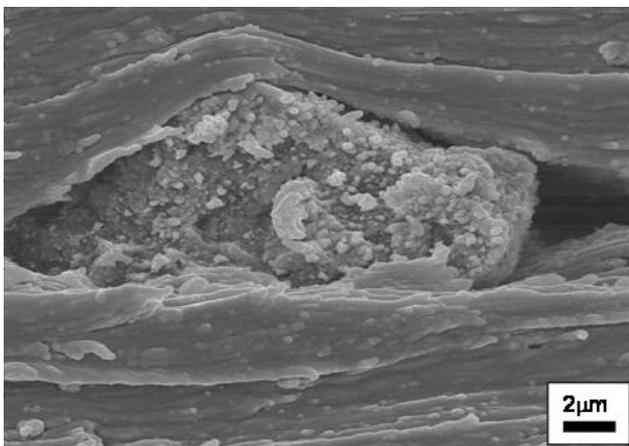
FE-SEM micrographs of HA/PLLA interfaces are shown in Fig.6. On the surface of the control HA/PLLA, interfacial debonding was observed. On the other hand, the pressed HA/PLLA exhibited strong adhesion between the HA particle and the PLLA matrix. It is thus presumed that press process dramatically improved HA/PLLA interfacial strength. This kind of structural improvement is considered to effectively contribute to the improvement of the fracture properties.

4 Conclusions

Effects of press process on the mechanical properties and fracture micromechanism of PLLA and HA/PLLA biocomposites were investigated in this study. The results obtained are as follows:



(a) Control HA/PLLA



(b) Pressed HA/PLLA

Fig.6 FE-SEM micrographs of HA/PLLA interfaces

(1) Bending modulus and strength of HA/PLLA were slightly improved by press process; on the other hand, PLLA did not show such improvement.

(2) For both PLLA and HA/PLLA, their fracture properties such as bending absorbed energy and the mode I fracture property, J_{max} , were dramatically improved by press process.

(3) Press process 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 dramatically improved due to press process, contributing to the improvement of the fracture properties.

References

- [1] Shikinami Y., Okuno M. “Bioresorbable devices made of forged composites of hydroxyapatite(HA) particles and poly-L-Lactide(PLLA) : Part I basic characteristics” *Biomaterials*, Vol.20,pp.859-877,1999.
- [2] Shikinami Y., Okuno M. “Bioresorbable devices made of forged composites of hydroxyapatite(HA) particles and poly-L-Lactide(PLLA):Part II :practical properties of miniscrews and miniplates”*Biomaterials*, Vol.22,pp.3197-3211,2001.
- [3] Todo M., Park SD. Arakawa K, Takenoshita Y. “Relationship between microstructure and fracture behavior of bioabsorbable HA/PLLA composites”.*Composites: Part A*, Vol.37, No.12, pp.2221-2225,2006.
- [4] Tsuji H, Ikarashi K, Fukuda N. “Poly(L-lactide): XII. Formation, growth, and morphology of crystalline residues as extended-chain crystallites through hydrolysis of poly(L-lactide) films in phosphate-buffered solution”. *Polymer Degradation and Stability*, Vol. 84, pp. 515-523, 2004