INFLUENCE OF STRUCTURAL ANISOTROPY ON COMPRESSIVE FRACTURE PROPERTIES OF HYDROSTATIC-PRESSURE-EXTRUSION-MOLDED HAP/PLLA COMPOSITE

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Summary

In this study, compression tests were carried out for neat poly-L-lactic acid (PLLA) and hydroxyapatite (HAp)/PLLA composite prepared by the hydrostatic-pressure-extrusion-molding. The influence of hydrolytic absorption on the compressive deformation and fracture properties was evaluated by immersion into the pseudo bio-environment. The effects of microstructural anisotropy and hydrolytic absorption on their compressive properties were discussed from the viewpoint of mesoscopic structures. The results are summarized as follows. (1) It is suggested that the compressive properties of 90° HAp/PLLA specimen were mainly governed by the properties of PLLA matrix. (2) It is suggested that the difference in the effect of HAp on the compressive elastic modulus between 0° and 90° specimens was owing to the highly oriented HAps induced by the hydrostatic-pressure-extrusion-molding. (3) It is suggested that the main damage mechanism was the tensile fracture between highly oriented PLLA molecular chains by the Poisson's effect in neat PLLA and HAp/PLLA composite. In addition, the interfacial debonding between HAps and PLLA matrix initiated the shear fracture of PLLA matrix in HAp/PLLA composite. (4) Since the main compressive fracture mechanism was not dependent on the loading direction, the anisotropy in compressive properties was lower than that in tensile properties for neat PLLA and HAp/PLLA composite. (5) Compressive properties were gradually degraded by hydrolysis of amorphous phase of PLLA. (6) It is possibly suggested that the water molecules diffused in free volume of PLLA matrix and accumulated locally at the initially debonded interface, resulting in selective hydrolysis of PLLA matrix in the vicinity of interface. (7) It is suggested that HAps played a role as the fracture resistance, resulting in the slower degradation rate in HAp/PLLA composite compared with in neat PLLA.

1 Introduction

Biocompatible composites of hydroxyapatite (HAp) particles and poly-L-lactic acid (PLLA) are one of the most promising candidates as the scaffold materials in the bone regeneration technology. This is mainly owing to the bone-conductivity of HAp and the biodegradability of PLLA. However, the poor fracture properties [1] are one of the factors limiting their practical application. Here, the hydrostatic-pressure-extrusion-molding [2, 3] is focused on as a strong candidate for fabricating method, which can improve the fracture properties of HAp/PLLA composites. In this method, PLLA billets are extruded from dies using medium with high pressure. The high orientation of PLLA molecular chains improves the fracture properties of HAp/PLLA composites. Considering the real loading conditions in the biological environment, it is necessary to clarify the effects of the structural anisotropy and the biological environment on the fracture properties of HAp/PLLA composites prepared by the hydrostatic-pressure-extrusion-molding.

In the present study, compression tests were carried out for the hydrostatic-pressure-extrusion-molded HAp/PLLA composite. The compression is the most important loading mode for the bone-substitute materials. Here, the effects of molecular- and micro-structural anisotropies and hydrolytic absorption on the compressive deformation and fracture properties were evaluated by immersion into the pseudo bio-environment. The change in the fracture mechanism by hydrolytic absorption was discussed from the microstructural viewpoint.

2 Materials and Method

The HAp short fibers (Ube Material Industries, ϕ: less than 1 [μm], aspect ratio: about 10) were used as fillers. The PLLA (BMG Inc., initial molecular weight: about 2.4 x 10^5) was used as matrix. The rods (extrusion ratio: 4) of neat PLLA and HAp/PLLA composite were prepared using the hydrostatic-pressure-extrusion-molding [2, 3]. The volume fraction of HAp was about 15 [%] in HAp/PLLA composite.

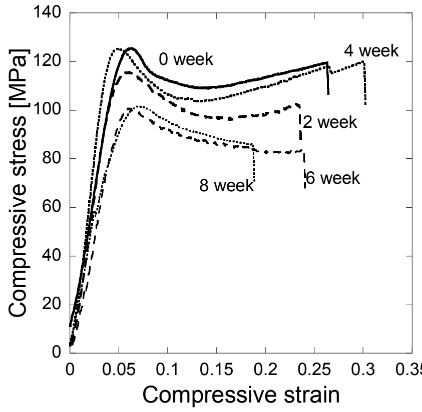
The molecular weight of PLLA after preparation was 1.7 x 10^5 and 1.3 x 10^5 for neat PLLA and HAp/PLLA composite, respectively. The crystallinity of PLLA after preparation was 48 [%] and 57 [%] for neat PLLA and HAp/PLLA composite, respectively. The molecular structure in the hydrostatic-pressure-extrusion-molded rods was highly oriented to the extrusion direction. Thus, it is suggested that the hydrostatic-pressure-extrusion-molded rods have the see-island structure of the microscopic crystals consisted of highly oriented PLLA molecular chains and amorphous phase between them. The HAps, which have higher elastic modulus than PLLA matrix, were almost uniaxially oriented in the extrusion direction without agglomeration. In addition, many interfacial defects initially existed between HAps and PLLA matrix.

The size of specimens was 3.5 [mm] (width) x 3.5 [mm] (thickness) x 4 [mm] (height). Here, the compression direction was parallel (0° specimen) and perpendicular (90° specimen) to the extrusion direction. These specimens were immersed into phosphate buffered saline (PBS) as the pseudo biological environment. During immersion, temperature and pH of PBS was kept as 37 [°C] and 7.4, respectively. Compression tests were carried out using a servohydraulic testing machine (Shimadzu, Servopulser EHF-EB5kN-10LAL) with a load cell of 5 [kN] in capacity. The crosshead speed was 1.2 [mm/min]. After tests, fracture surfaces were observed using a field emission scanning electron microscope (FE-SEM) (Hitachi, Ltd., S-4500).

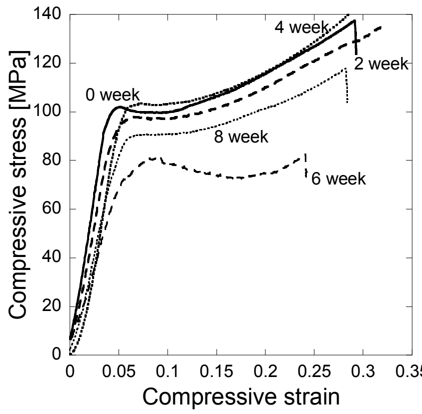
3 Results and Discussion

3.1 Compressive Elastic Modulus

Typical stress-strain curves obtained from compression tests were shown in Figs. 1 and 2. These stress-strain curves indicated the specific characteristic of thermoplastics and the gradual degradation in compressive properties for all specimens.

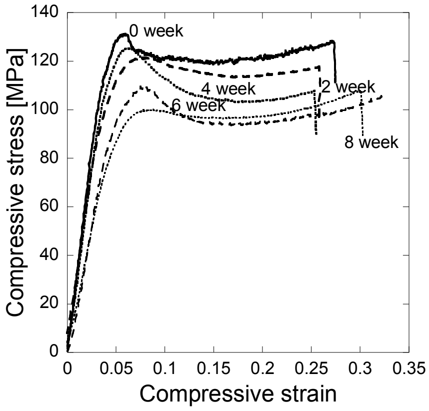


(a) 0° specimen

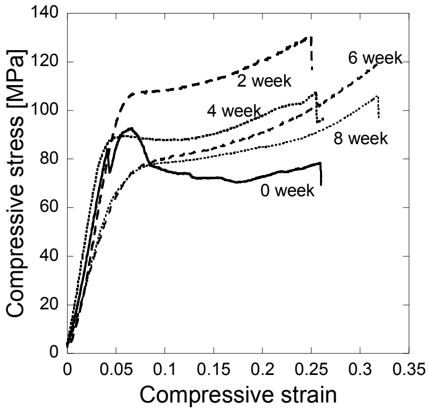


(b) 90° specimen

Fig. 1. Stress-strain curves of neat PLLA.

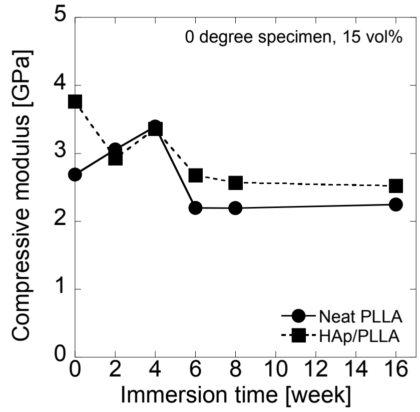


(a) 0° specimen

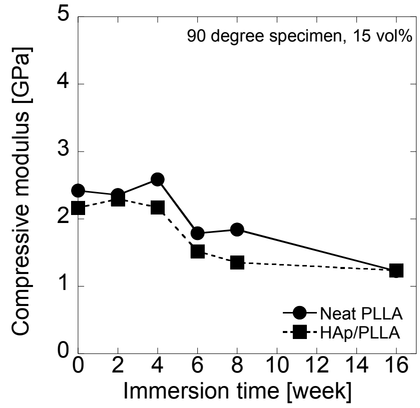


(b) 90° specimen

Fig. 2. Stress-strain curves of HAp/PLLA composite.



(a) 0° specimen



(b) 90° specimen

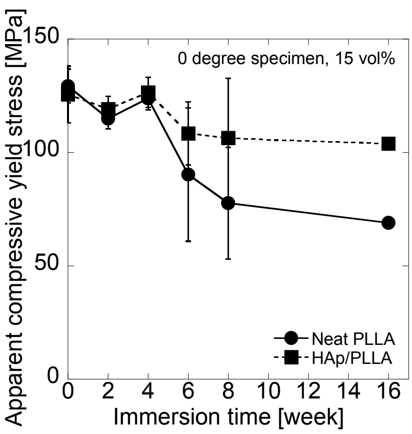
Fig. 3. Change in compressive elastic modulus.

The change in the compressive elastic modulus by immersion into PBS was plotted in Fig. 3. In 0° specimens without immersion into PBS, the compressive elastic modulus of HAp/PLLA composite was about 40 [%] higher than that of neat PLLA. During hydrolysis process, the effect of HAp on the compressive elastic modulus was almost constant in neat PLLA. After 8-week immersion into PBS, the compressive elastic modulus of HAp/PLLA composite was about 20 [%] higher than that of neat PLLA. On the other hand, in 90° specimens, the compressive elastic modulus of HAp/PLLA composite was almost equivalent to that of neat PLLA during hydrolysis process. It is suggested that the compressive elastic modulus of 90° HAp/PLLA specimen was mainly governed by the property of PLLA matrix. In addition, it is suggested that the difference in the effect of HAp on the compressive elastic modulus between 0° and 90° specimens was owing to highly oriented HAps induced by hydrostatic-pressure-extrusion-molding.

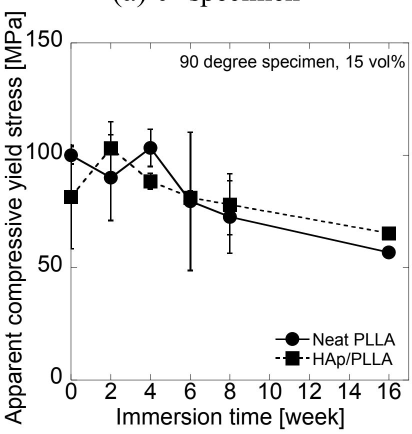
Then, the anisotropy in the compressive elastic modulus will be discussed below. In neat PLLA without immersion into PBS, the compressive elastic modulus of 0° specimen was about 10 [%] higher than that of 90° specimen. During hydrolysis process, the anisotropy in the compressive elastic modulus was almost constant in neat PLLA. After 8-week immersion into PBS, the compressive elastic modulus of 0° specimen was about 20 [%] higher than that of 90° specimen in neat PLLA. It is suggested that this anisotropy in the compressive elastic modulus in the hydrostatic-pressure-extrusion-molded neat PLLA was owing to the highly oriented molecular structure. However, the anisotropy in the compressive elastic modulus was quite lower than that in the tensile elastic modulus [4] for the hydrostatic-pressure-extrusion-molded neat PLLA. On the other hand, the anisotropy in the compressive elastic modulus in HAp/PLLA composite was higher than that in neat PLLA. The compressive elastic modulus of 0° HAp/PLLA specimen was about 70 [%] and 90 [%] higher than that of 90° HAp/PLLA specimen without immersion and after 8-week immersion, respectively. It is suggested that this higher anisotropy in the compressive elastic modulus for HAp/PLLA composite compared with neat PLLA was owing to the highly oriented HAps. However, it was still lower than that in the tensile elastic modulus [4] for HAp/PLLA composite prepared by the hydrostatic-pressure-extrusion-molding.

3.2 Apparent Compressive Yield Stress

The change in the apparent compressive yield stress by immersion into PBS was plotted in Fig. 4. The apparent compressive yield stresses were also gradually degraded by immersion for all specimens.



(a) 0° specimen



(b) 90° specimen

Fig. 4. Change in apparent compressive yield stress.

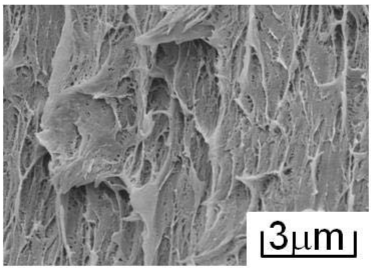
In the early stage of hydrolysis, the effect of HAp on the apparent compressive yield stresses was quite small both for 0° and 90° specimens. It is suggested that the apparent compressive yield stress of HAp/PLLA composite was also mainly governed by the property of PLLA matrix in the early stage of hydrolysis. After 6-week immersion, the effect of HAp on the apparent compressive yield stresses was still small for 90° specimen. On the other hand, the degradation rate of neat PLLA was higher than that of HAp/PLLA composite in 0° specimen. Thus, the degradation tendency in the apparent compressive yield stress for 0° specimen was different between neat PLLA and HAp/PLLA composite.

Then, the anisotropy in the apparent compressive yield stress will be discussed below. In neat PLLA without immersion into PBS, the apparent compressive yield stress of 0° specimen was about 30 [%] higher than that of 90° specimen. During hydrolysis process, the anisotropy in the apparent compressive yield stress was gradually decreased in neat PLLA. After 8-week immersion into PBS, the apparent compressive yield stress of 0° specimen was about 7 [%] higher than that of 90° specimen in neat PLLA. In HAp/PLLA composite without immersion into PBS, the apparent compressive yield stress of 0° specimen was about 50 [%] higher than that of 90° specimen. During hydrolysis process, the anisotropy in the apparent compressive yield stress was also gradually decreased in HAp/PLLA composite. After 8-week immersion into PBS, the apparent compressive yield stress of 0° specimen was about 30 [%] higher than that of 90° specimen in HAp/PLLA composite. We reported that the tensile strength of 90° specimen was about 18 [%] and 28 [%] of that of 0° specimen for neat PLLA and HAp/PLLA composite, respectively [4]. Thus, the effect of microstructural anisotropy was different between the compressive and tensile fracture properties.

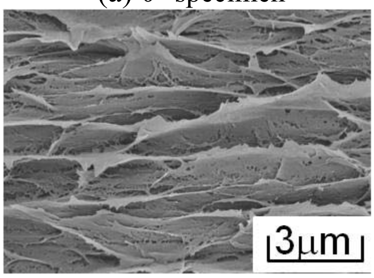
3.3 Damage Morphology and Fracture Surface

The main characteristic of damage morphologies commonly observed for all specimens was the cracks perpendicular to the loading direction. It is suggested that the main damage mechanism was the tensile fracture between highly oriented PLLA molecular chains by the Poisson's effect. In addition, the cracks were also observed in 45° direction to the loading direction in HAp/PLLA composites. It is suggested that the interfacial debonding between HAps and PLLA matrix initiated the shear fracture of PLLA matrix in HAp/PLLA composite.

Figs. 5 and 6 indicate the typical fracture surfaces without immersion into PBS. Here, the vertical direction is the loading direction. For 0° and 90° specimens of neat PLLA, the evidence of plastic deformation was observed along the extrusion direction. Since PLLA crystals, highly oriented to the extrusion direction, have high strength, it is considered that cracks initiated at the intermediate amorphous phase between oriented PLLA crystals. For 0° and 90° specimens of HAp/PLLA composite, the evidence of plastic deformation was also observed along the extrusion direction, similarly to neat PLLA. In addition, PLLA matrix in the vicinity of debonded HAps showed large plastic deformation. This suggests that the interfacial debonding caused by weak bonding between HAps and PLLA matrix led the large shear deformation of PLLA matrix in the vicinity of debonded HAps. As mentioned in the previous section, the typical damage morphology was tensile fracture perpendicular to the loading direction by Poisson's effect for all specimens. Thus, the fracture surface of 90° specimen was similar to that of 0° specimen, for both neat PLLA and HAp/PLLA composite. This means that the compressive fracture mechanism was not dependent on the loading direction. Therefore, it is suggested that the effect of the microstructural anisotropy on the apparent compressive yield stress was lower than that on the tensile strength.

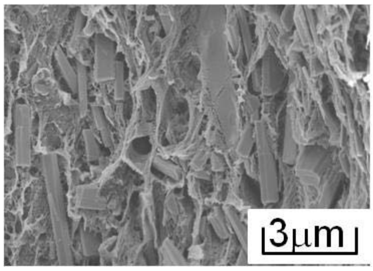


(a) 0° specimen

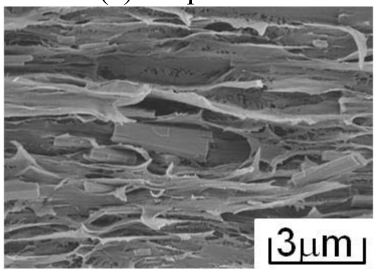


(b) 90° specimen

Fig. 5. Typical fracture surface of neat PLLA without immersion into PBS.



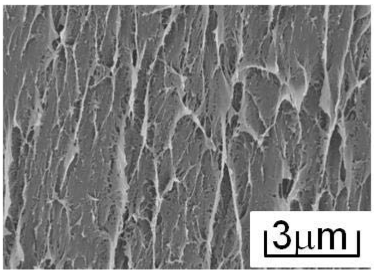
(a) 0° specimen



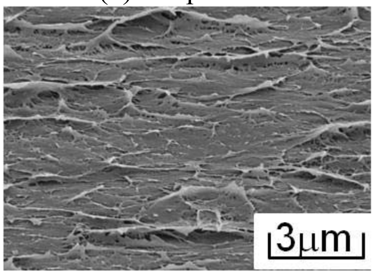
(b) 90° specimen

Fig. 6. Typical fracture surface of HAp/PLLA composite without immersion into PBS.

Then, the fracture surfaces of specimens after immersion into PBS will be discussed below. Figs. 7 and 8 indicate the typical fracture surfaces after 6-week immersion into PBS. Here, the vertical direction is the loading direction. For 0° and 90° specimens of neat PLLA, the size of the evidence of plastic deformation was decreased by immersion into PBS. In crystalline PLLAs, it is known that amorphous phase between crystallized phases are selectively hydrolyzed. Thus, it is suggested that the selective hydrolysis of amorphous phase induced the damage initiation and propagation in the amorphous phase before large plastic deformation was introduced, in degraded neat PLLA. For 0° and 90° specimens of HAp/PLLA composite, the size of the evidence of plastic deformation was decreased by immersion into PBS, similarly to neat PLLA. In addition, the trace of the completely debonded HAps was evident in the specimens after immersion into PBS. It is possibly suggested that the water molecules diffused in free volume of PLLA matrix and accumulated locally at the initially debonded interface, resulting in selective hydrolysis of PLLA matrix in the vicinity of interface. However, the PLLA matrix in the vicinity of debonded HAps still showed plastic deformation. It is suggested that HAps played a role as the fracture resistance, resulting in the slower degradation rate in HAp/PLLA compared with in neat PLLA.

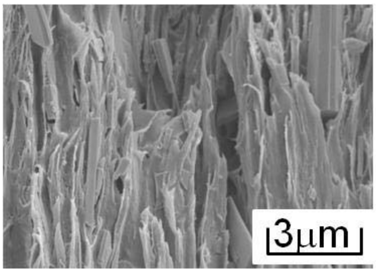


(a) 0° specimen

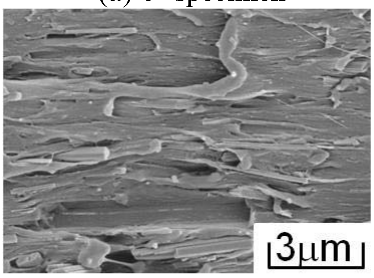


(b) 90° specimen

Fig. 7. Typical fracture surface of neat PLLA after 6-week immersion into PBS.



(a) 0° specimen



(b) 90° specimen

Fig. 8. Typical fracture surface of HAp/PLLA composite after 6-week immersion into PBS.

4 Conclusion

(1) It is suggested that the compressive properties of 90° HAp/PLLA specimen were mainly governed by the properties of PLLA matrix.

(2) It is suggested that the difference in the effect of HAp on the compressive elastic modulus between 0° and 90° specimens was owing to the highly oriented HAps induced by the hydrostatic-pressure-extrusion-molding.

(3) It is suggested that the main damage mechanism was the tensile fracture between highly oriented PLLA molecular chains by the Poisson's effect in neat PLLA and HAp/PLLA composite. In addition, the interfacial debonding between HAps and PLLA matrix initiated the shear fracture of PLLA matrix in HAp/PLLA composite.

(4) Since the main compressive fracture mechanism was not dependent on the loading direction, the anisotropy in compressive properties was lower than that in tensile properties for neat PLLA and HAp/PLLA composite.

(5) Compressive properties were gradually degraded by hydrolysis of amorphous phase of PLLA.

(6) It is possibly suggested that the water molecules diffused in free volume of PLLA matrix and accumulated locally at the initially debonded interface, resulting in selective hydrolysis of PLLA matrix in the vicinity of interface.

(7) It is suggested that HAps played a role as the fracture resistance, resulting in the slower degradation rate in HAp/PLLA composite compared with in neat PLLA.

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