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# Bending and Compressive Properties of Crystallized TCP/PLLA Composites

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**Abstract**

$\beta$-Tricalcium phosphate ($\beta$-TCP) particles reinforced bioresorbable plastics poly-L-lactide (PLLA) composites were prepared by injection molding. The nominal weight ratio of $\beta$-TCP was selected as 5, 10 and 15%. In order to clarify effects of the PLLA crystallinity on the mechanical properties, the specimens were heat treated isothermally. Results of differential scanning calorimetry indicated that the PLLA crystallinity increased with increasing heat treatment temperature. Bending and compressive tests were conducted on the specimen with different $\beta$-TCP contents and crystallinities. The results show that the bending and compressive moduli increased with increasing $\beta$-TCP contents and crystallinity. On the other hand, bending strength decreased with increasing $\beta$-TCP contents. Maximum bending strength was obtained at the heat treatment of 70°C for 24 h, whereas compressive 0.2% proof strength increased with increasing heat treatment temperature. This difference is attributed to the difference in the microscopic damages.


**Keywords**

Bioresorbable composite, poly-L-lactide, $\beta$-tricalcium phosphate

## 1. Introduction

Metallic bone fixations have a necessity to be removed from a body after a complete recovery to avoid inflammatory reactions surrounding tissues and/or osteoporosis due to stress shielding. For this reason, bioresorbable plastic fixation devises made of poly-L-lactide (PLLA) have been developed and used clinically in order to improve the QOL (quality of life) of patients. Commercially-available bioresorbable fixation devises made of PLLA, however, have lower stiffness and are limited to low-loaded location. Furthermore, the bioresorption period of PLLA is very long (over a year). Thus, in order to improve the mechanical properties and biocompatibility, PLLA composites with high modulus bioactive ceramics have been

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developed. Two types of bioactive ceramics have been used. One is hydroxyapatite (HA) [1–9] and the other is bioresorbable ceramics based on $\beta$-tricalcium phosphate ($\beta$-TCP) [2, 7, 10–12]. In the present study, we selected a $\beta$-TCP with good bioresorption property as a reinforcement. Most of the previous studies evaluated macroscopic modulus and strength of the composites experimentally. On the other hand, it is also important to clarify the effects of the microstructures and microfracture process on the macroscopic mechanical behavior. Considering the actual usage, mechanical behavior under bending and compressive loading is especially important.

The purposes of the present study are to characterize bending and compressive properties of $\beta$-TCP/PLLA composites experimentally. The $\beta$-TCP/PLLA composites with different $\beta$-TCP contents were injection molded and heat treated to clarify the effects of matrix crystallinity on the mechanical properties of $\beta$-TCP/PLLA composites. In terms of the practical use of this kind of materials, bending and compressive tests were conducted. The fracture processes were also characterized by scanning electron microscopy.



## 2. Experimental Methods

### 2.1. Materials

Fabrication process of the composites was similar to [12]. Poly-L-lactide, Lacty® #5000 (Shimadzu Co. Ltd., Japan) and $\beta$-tricalcium phosphate, $\beta$-TCP (Taihei Chemical Industrial Co. Ltd., Japan) were used as the matrix and the filler materials, respectively. The diameter of $\beta$-TCP particle is less than 2.0 μm with spherical shape. Specific surface area is 50–60 $m^2/g$. The PLLA pellets and $\beta$-TCP powder were mixed in a polyethylene bottle in dry condition. The $\beta$-TCP/PLLA mix proportions were 10/190, 20/180, and 30/170 in weight. The mixture was used for injection molding. Specimen size was 100 mm × 10 mm × 4 mm. The injection molding condition is listed in Table 1. After molding, some residual $\beta$-TCP powder was observed in the bottle. So the actual weight fractions, $W_{fa}$ of $\beta$-TCP particles contained in the composites were calculated by the following equation:

$$W_{fa} = \frac{W_f - W_r}{W_m + W_f - W_r} \times 100, \tag{1}$$

**Table 1.**
Condition of injection molding

| | |
|---|---|
| Mold clamping force (kN) | 69 |
| Injection pressure (MPa) | 114 |
| Fusion temperature (°C) | 200 |
| Mold temperature (°C) | 50 |
| Cooling time (°C) | 30 |

where $W_f$ is the initial weight of $\beta$-TCP particles, $W_r$ is the residual $\beta$-TCP weight in the polyethylene bottle used for mixing of $\beta$-TCP powder and the PLLA pellets, and $W_m$ is weight of PLLA pellets. In the present methods, the mix proportions of $\beta$-TCP in composites of 10/190, 20/180, and 30/170 corresponded to the weight fractions of approximately 5.0, 9.5 and 13.9%, respectively.

In order to investigate the effects of the crystallinity of PLLA on the mechanical behavior of $\beta$-TCP/PLLA composites, some specimens were isothermally crystallized with hot press system without loading. The heat treatment conditions for crystallization were 70°C for 24 h and 130°C for 3 h, which correspond to the conditions of the maximum strength and maximum crystallinity for the monolithic PLLA [13].



### 2.2. Crystallinity Measurements

The crystallinity of the specimen was measured with a differential scanning calorimeter (DSC-60, Shimadzu Co. Ltd., Japan). The samples used were cut into about 3 mg portions from the specimens. Heating rate was 10°C/min. Considering the $\beta$-TCP contents, the crystallinity, $X_c$, was calculated from the nominal fusion enthalpy of composite, $\Delta H_{composite}$ ($= \Delta H_m + \Delta H_c$, are the nominal enthalpy of crystallization and fusion, respectively) as:

$$X_c = \frac{\Delta H_{composite}}{\Delta H_{PLLA,100\%}} \times \frac{1}{1 - W_{fa}} \times 100\ (\%), \tag{2}$$

where $\Delta H_{PLLA,100\%}$ is the enthalpy of fusion of PLLA crystals having infinite crystal thickness, as 135 (J/g) [14].

### 2.3. Bending and Compressive Tests

We conducted 4-point bending tests to evaluate the bending properties of the $\beta$-TCP/PLLA composites. For the bending tests, the specimens as injection molded were used. A strain gauge was glued onto the compressive surface of the specimen. The outer and inner span length of the 4-point bending tests were 66 and 22 mm (JIS K7171), respectively. The tests were conducted with a lower capacity universal testing machine (LSC-05/30, JT Toshi Co., Japan) at a cross-head speed of 1 mm/min under room temperature.

For the compressive tests, the injection molded specimens were cut into the geometry of $10 \times 10 \times 4$ mm$^3$ using a micro cutting machine (Maruto Co., Japan). Strain gauges were glued on both surfaces of the specimen to monitor the strain during tests. The compressive tests were conducted with a universal testing machine (AG-10kNE, Shimadzu Co. Ltd., Japan) instrumented with a support jig at a cross-head speed of 1 mm/min under room temperature.

Six specimens were tested for each tests condition. The fracture surfaces of the specimens were observed using a scanning electron microscope (S2500CX, Hitachi Co., Japan) to clarify the fracture process.

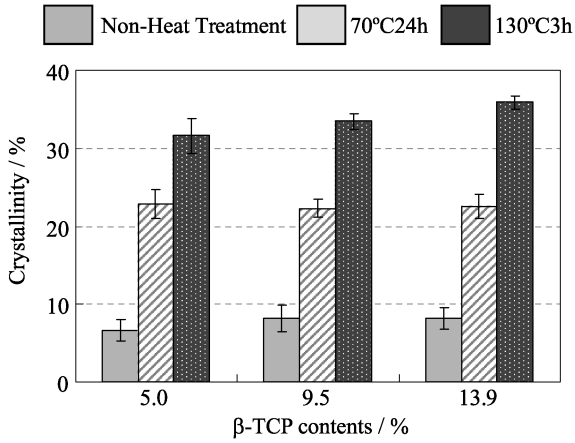


**Figure 1.** Crystallinity of PLLA in composites.

## 3. Experimental Results and Discussion

### *3.1. Crystallinity*

Figure 1 shows the crystallinity of the $\beta$-TCP/PLLA composites with and without heat treatment. The crystallinity increased with heat treatments. Before tests, the crystallinity was expected to increase with increasing $\beta$-TCP contents because of the larger heat capacity and higher thermal conductivity of $\beta$-TCP. However, the crystallinities are almost the same values for each specimen. This is due to the low fraction of the $\beta$-TCP in the present composites.

### *3.2. Bending Tests*

Figure 2 shows the bending stress–strain curves. Fracture strain decreased with increasing $\beta$-TCP contents. The heat treatment at 70°C for 24 h increased the fracture strain compared with non-heat treatment. On the other hand, the heat treatment at 130°C for 3 h decreased the fracture strain. These results are due to the release of the residual stress and the embrittlement with crystallization, respectively [12].

Figures 3 and 4 show bending Young's modulus and the bending strength. Young's modulus increased with increasing $\beta$-TCP contents and crystallinity of PLLA. The bending strength degradation with increasing $\beta$-TCP contents is due to the stress concentration around the $\beta$-TCP particles. In the specimens heat treated at 70°C for 24 h and 130°C for 3 h, Young's modulus also increased and bending strength decreased with increasing $\beta$-TCP contents.

Considering the effect of the crystallinity due to heat treatment, Young's modulus increased with increasing crystallinity. On the other hand, tensile strength reached its maximum values with about 23% of crystallinity of PLLA, which corresponded with a heat treatment of 70°C for 24 h. This is due to the release of the residual stress induced during the injection molding process.

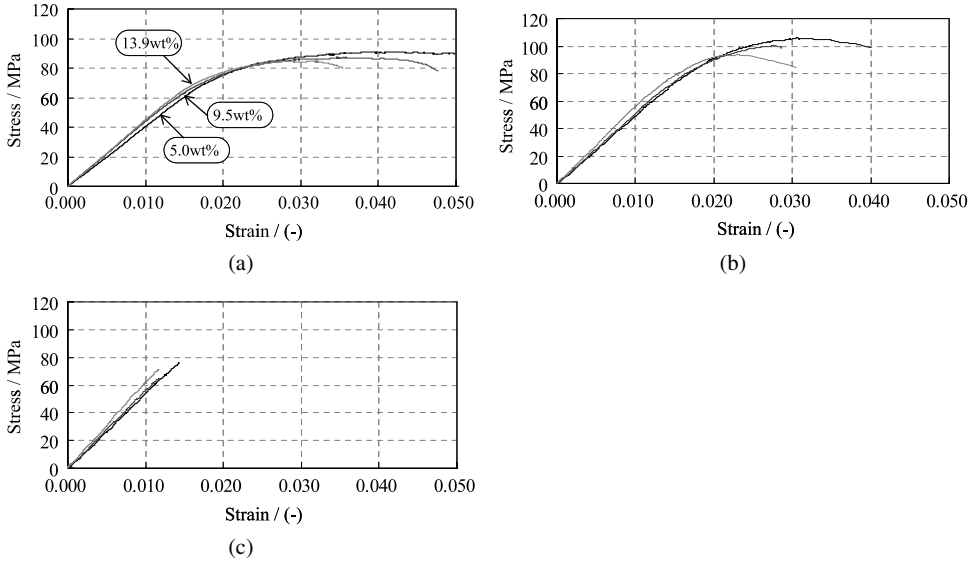


**Figure 2.** Bending stress–strain curve of $\beta$-TCP/PLLA composites. (a) Non-annealing, (b) 70°C-24 h and (c) 130°C-3 h.

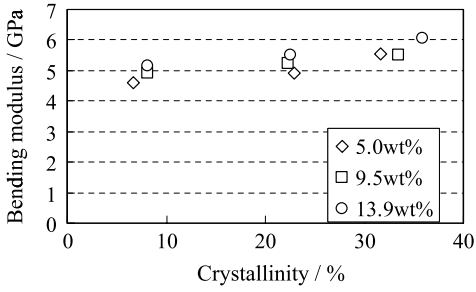


**Figure 3.** Bending Young's modulus of $\beta$-TCP/PLLA composites.

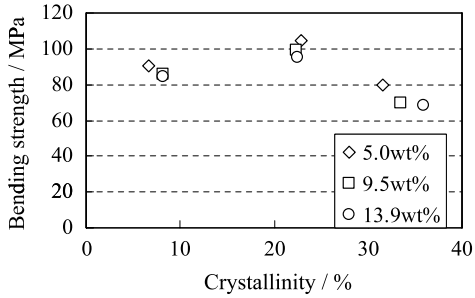


**Figure 4.** Bending strength of $\beta$-TCP/PLLA composites.

For the 13.9 wt% specimen, bending Young's modulus was improved by 32% with about 35% of crystallinity of PLLA, which corresponded with a heat treatment at 130°C for 3 h. Considering the actual usage, the bone fixation devices are subjected to bending and compressive loading. For this reason, the bending properties are important factors to consider in the materials for bone fixation devices. Bending strength and Young's modulus of the human cortical bone were reported as 96–196 MPa and ∼16.8 GPa, respectively. In the present study, we can obtain the materials with the same strength and 1/3 modulus compared with the human bone.

Figure 5 shows the fracture surface after bending tests. The fracture surface was divided into two types: ductile fracture (Fig. 5(d)) and brittle fracture (Fig. 5(e)). At the ductile fracture surface, fibril-like structures were observed around the debondings at the $\beta$-TCP/PLLA interface. This corresponded to the crazing. Futhermore, the debondings at the $\beta$-TCP/PLLA interface grew into the void shapes. On the other hand, no voids were observed at the brittle fracture surface. These differences in the fracture surface morphologies are attributed to crack growth rate [12]. In the fracture surfaces of the bending tests, a ductile fracture surface was observed in the tensile side of the specimen (upper side of Fig. 5(a–c)). For the case of bending, the specimen is loaded in tensile and compressive simultaneously. Since the voids were formed by tensile loading, the voids formed at the tensile side.

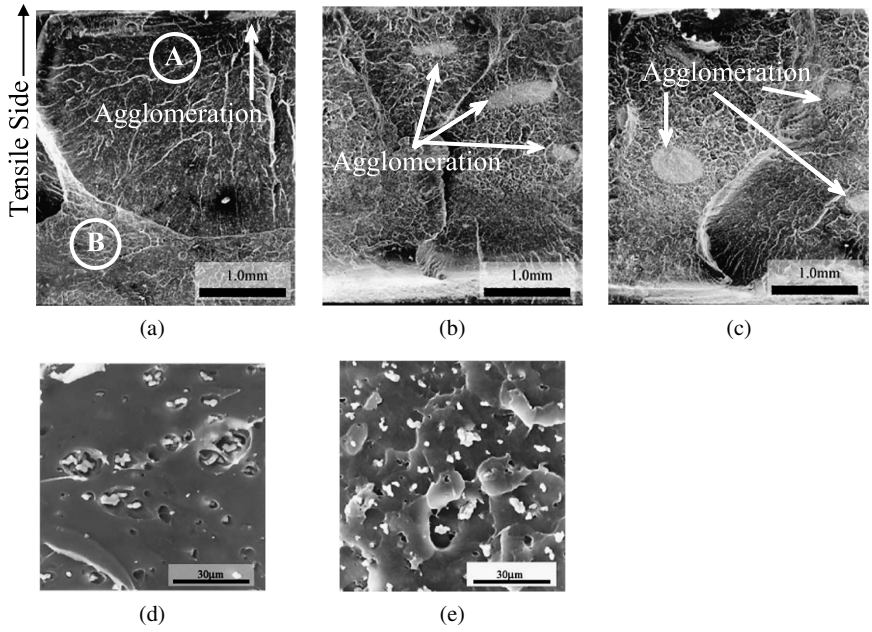


**Figure 5.** Fracture surface of the $\beta$-TCP/PLLA composites without heat treatment after bending tests. (a) 5.0 wt%, (b) 9.5 wt%, (c) 13.9 wt%, (d) enlargement of A and (e) enlargement of B.

### 3.3. Compressive Tests

Figures 6, 7 and 8 show the compressive stress–strain curves, compressive Young's modulus and the 0.2% proof strength. In the compressive tests, all specimens deformed in the barrel shape and squashed perfectly. From the results of the specimen with heat treatment at 130°C for 3 h, strain hardening was observed. Compressive Young's modulus increased with increasing $\beta$-TCP contents and with heat treatments, similar to the results of the bending tests. Moreover, compressive Young's modulus is almost the same with bending Young's modulus in the specimen with and without a heat treatment. For the 13.9 wt% specimen, compressive Young's modulus was improved by 36% with about 35% of crystallinity of PLLA, which corresponded with a heat treatment at 130°C for 3 h.



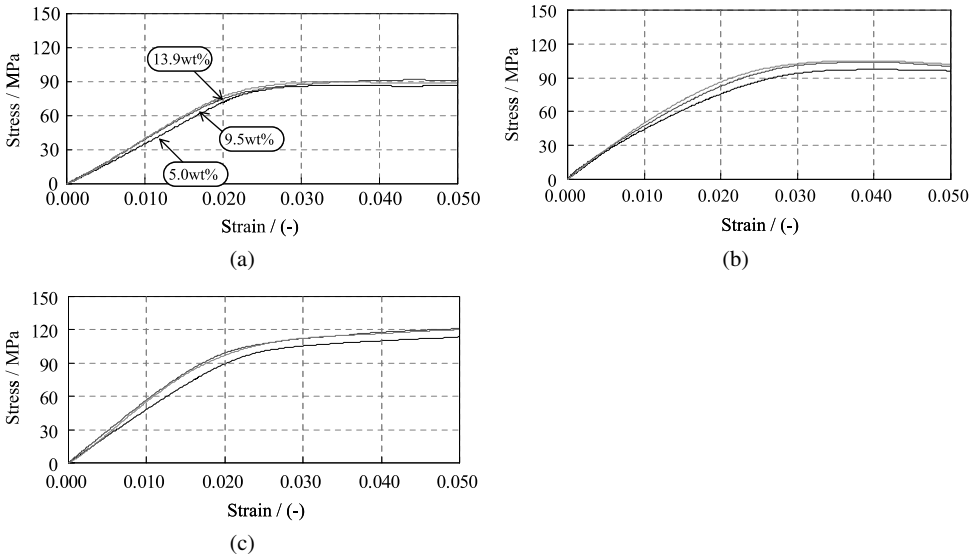


**Figure 6.** Compressive stress–strain curve of $\beta$-TCP/PLLA composites. (a) Non-annealing, (b) 70°C-24 h and (c) 130°C-3 h.

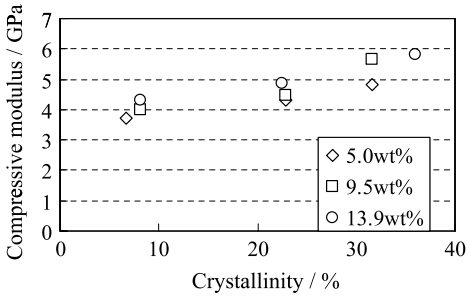


**Figure 7.** Compressive Young's modulus of $\beta$-TCP/PLLA composites.

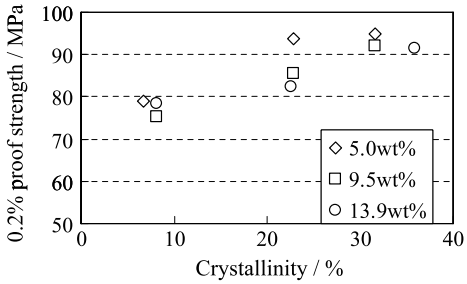


**Figure 8.** Compressive 0.2% proof strength of $\beta$-TCP/PLLA composites.



The effect of $\beta$-TCP contents on the 0.2% proof strength is very little. This is due to the little stress concentration effect around the $\beta$-TCP particles. Unlike the bending, 0.2% proof strength increased with heat treatments. This result indicates that the residual stress induced during injection molding is less effective Debondings do not open and do not affect the macroscopic mechanical behavior in the case of the compressive loading. That is, increasing modulus and crystallinity which suppressed non-linearity in stress–strain behavior are more effective on the 0.2% proof strength.

## 4. Conclusion

In order to evaluate the effect of crystallinity on the mechanical properties of $\beta$-TCP/PLLA composites, the composites were fabricated by injection molding and were crystallized. Bending and compressive tests were performed and fracture surfaces were observed. Young's modulus increased with $\beta$-TCP contents in both bending and compressive tests. Maximum bending strength was achieved with heat treatment at 70°C for 24 h, whereas compressive 0.2% proof strength increased with heat treatments. These were attributed to the release of residual stress and improvement in modulus with crystallization. The bending fracture surfaces were divided into two types, namely, a ductile region and a brittle region. Ductile and brittle regions were observed in the tensile and compressive sides, respectively. In the ductile region, fibril-like structures corresponding to crazing and debondings between $\beta$-TCP particles and the PLLA matrix that grew into a void shape were observed. The ductile region was observed in the tensile side. These results suggest that consideration of the type of loading is very important for material design of bone fixations.

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