Experimental and Analytical Characterization of β-Tricalcium Phosphate Particle Reinforced Poly-L-Lactide Composites*

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Bioactive ceramics, β-tricalcium phosphate (β-TCP), particles reinforced bioabsorbable plastics poly-L-lactide (PLLA) composites have been expected to apply for the fracture fixations which have more biocompatibility than monolithic PLLA. In this study, β-TCP/PLLA composites containing three different β-TCP contents (4.8, 9.5, 14.3 wt%) were prepared by injection molding. The results of bending tests show bending strength decreases with increasing β-TCP contents. On the other hand, bending modulus increases with increasing β-TCP contents. After immersion tests in PBS at 37°C up to 8 weeks, the mechanical properties were hardly degraded in all specimens. The results of fracture surface observation by scanning electron microscopy indicated that microscopic damage such as debonding between β-TCP and PLLA initiates at β-TCP agglomeration and grows with increasing loading. Analytical predictions of the relationship between stress and strain based on micromechanics considering the progress of debonding between β-TCP and PLLA were in good agreement with experimental results.

1. Introduction

Metallic bone fixation devices must 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, bioabsorbable plastic fixation devises such as poly-L-lactide (PLLA) have already been in clinical use to reduce patient burdens. Commercially-available bioabsorbable fixation devises made of PLLA, however, have some problems: limitation of application to low-loaded location, a long period of time necessary for complete resorption (over a year) and inflammatory reactions in case of the usage of PLLA with high crystallinity due to needle-like degradation products. Thus, composites consists of high-modulus bioactive ceramics and PLLA with low-crystallinity have been studied to improve mechanical properties and biocompatibility. Two types of bioactive ceramics have been used. One is hydroxyapatite(1)–(10), which is the major component of inorganic compounds in the living body, and the other is bioabsorbable ceramics, β-tricalcium phosphate (β-TCP)(4), (10)–(13). Most of those studies about physical biocompatibility were in vitro experimental evaluations of macroscopic modulus and strength of the composites, whereas the effects of the microstructures and microfracture process on macroscopic mechanical behavior are important for material design. For example, particle volume fraction is one of the main factors on the modulus of particle dispersed composites and the shape of particles affects the microfracture process of the composites. Microfracture processes consists of the debonding between particle/matrix, particle fracture and matrix fracture degrade the loading capacity of the composites. In addition, the mechanical properties necessary for the bone fixation materials are different according to locations and degrees of diseases. That is, the analytical modeling for the prediction of macroscopic mechanical behavior of the composites considering the particle contents and microfracture processes enable an order-made clinical activity according to the location and the degree of diseases.

The purposes of the present study are to characterize β-TCP/PLLA composites experimentally and analytically. The β-TCP/PLLA composites with different β-TCP contents were prepared by injection molding. In vitro mechanical properties of the β-TCP/PLLA composites were...
evaluated, and the fracture processes were characterized by scanning electron microscopy. Stress-strain relationships of the composites were predicted based on micromechanics and damage mechanics.

2. Experimental Methods

2.1 Materials

Poly-L-lactide, Lacty®#5000 (Shimadzu Co., Ltd.) β-tricalcium phosphate, β-TCP (Taihei Chemical Industrial Co., Ltd.) were used as the matrix material and the filler material, respectively. The diameter of β-TCP particle is less than 2.0 µm with spherical shape. Specific surface area is 50 ∼ 60 m²/g. The PLLA pellets and β-TCP powder were mixed in the polyethylene bottle in the dry condition. The β-TCP/PLLA mix proportions were 10/190, 20/180, and 30/170. Rectangular specimens (100 mm × 10 mm × 4 mm) of the β-TCP/PLLA composites were then fabricated from the mixtures by injection molding under the conditions listed in Table 1. The actual weight fractions, \( W_{fa} \) of β-TCP particles contained in the composites were given by the following equation:

\[
W_{fa} = \frac{W_f - W_r}{W_m + W_f - W_r} \times 100, 
\]

where \( W_f \) is the initial weight of β-TCP particles, \( W_r \) is the residual β-TCP weight in the polyethylene bottle used for mixture of β-TCP powder and the PLLA pellets, and \( W_m \) is weight of PLLA pellets. In the present methods, the mix proportions of β-TCP in composites of 10/190, 20/280, and 30/170 corresponded to the weight fractions of approximately 4.8, 9.5, and 14.3%, respectively.

2.2 In vitro degradation and four-point bending tests

The β-TCP/PLLA specimens were immersed in phosphate buffer solution (PBS, Wako Chemical) with pH 7.4 at 37°C. The immersion periods were 2, 4, and 8 weeks. After soaking, specimens were washed with purified water and dried for 24 h at 37°C in incubator. In vitro mechanical behavior was evaluated by four-point bending testing using universal testing machine (AUTOGRAPH, Shimadzu Co., Ltd.). Strain was measured with the strain gauge glued on the compressive side of the specimen. A crosshead speed was 1 mm/min, and lengths of inner span and outer span were 22 mm and 66 mm (JIS K7171), respectively. Specimen geometry is 100 mm in length, 10 mm in width and 4 mm in thickness.

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 |

3. Experimental Results

Figures 1 and 2 show the bending strength and modulus of β-TCP/PLLA composites with 4.8, 9.5, 14.3 wt% β-TCP contents with and without the immersion tests. Dotted line denotes the average values of monolithic PLLA. In the Fig. 1, 95% confidence intervals obtained with Student t-distribution are also shown in Fig. 1. The maximum value of error span for bending modulus is 0.04 GPa. The bending strength of composites decreased with increasing β-TCP contents in all immersion times. The decreases in bending strength are considered to be resulted from stress concentration caused by the existence of higher modulus of particles than matrix. The increases in bending modulus are due to the reinforcing effect of β-TCP particles. Considering the fact that the bending modulus and strength of the cortical bones are ∼16.8 GPa and 96 ∼ 196 MPa(14), the bending strength of the present β-TCP/PLLA composite has almost the same strength with cortical bones.

The bending modulus was independent of the period of up to 8 weeks immersion time and the bending strength slightly increased after 4 weeks soaking, and then decreased. According to Ignatius et al.(13), the degradation behavior of β-TCP/PLLA composites with 10 wt% β-TCP particles, which is similar to that of PLLA-only, indicates that the mechanical properties barely lessen after initial 2 weeks, and remain nearly unchanged up to 26 weeks. In the present composites, the hydrolysis of PLLA can
hardly proceed during 8 weeks immersion for the same reason. The increase in the bending strength up to 4 weeks is due to improvement of fracture toughness caused by water absorption of PLLA. The mechanical properties after 8 weeks immersion showed slight decline as compared with those after 4 weeks. The decrease in strength for the composites containing 4.8 wt% β-TCP particles was about 1%. And 6% decrease in the strength was observed for 9.5 and 14.3 wt%. The hydrolysis proceeded preferentially at the interface between PLLA and β-TCP and it played a role of microscopic defect at the surface of β-TCP/PLLA. The degradation in the strength for larger β-TCP contents is attributed to the existence of larger amount of β-TCP aggregates at the surface.

Figure 3 shows the fracture surfaces observed by scanning electron microscopy. The fracture surfaces had almost the same morphology in all specimens and immersion periods. The area of a fracture surface was able to classified into two different areas as shown in Fig. 3 (d) and (e). Figure 3 (d) shows the area where debondings between β-TCP and PLLA have grown into the void shapes and Fig. 3 (e) shows the area without debonding around particles. Figure 3 (d) and (e) was observed at the tensile side and compressive side, respectively. These differences in the fracture surface morphologies are attributed to crack growth rate. Debondings formed at the β-TCP/PLLA interface where the energy release rate reaches the critical values. When the energy release rate at the matrix in front of the process zone reaches the fracture toughness of PLLA with successive loading, matrix catastrophic failure occurs without β-TCP/PLLA debondings. In addition, β-TCP aggregations with the size more than 200 µm were observed on the fracture surfaces. The number and the size of aggregations tended to increase with β-TCP contents.

No differences presented in the fracture surfaces with the immersion periods up to 8 weeks. That is, the fracture process of β-TCP/PLLA composites in this study was more affected by β-TCP aggregates within composites. The technique to disperse the β-TCP particles without aggregation makes the composites higher strength.

4. Discussion

4.1 Fracture process

From the results mentioned above, the fracture process of the β-TCP/PLLA composites expected are schematically illustrated in Fig. 4. First, the β-TCP/PLLA interfaces debond partially around the β-TCP aggregations (Area a). Then, Area a extends with increasing loading and the β-TCP/PLLA interfaces debond perfectly (Area b) in Area a. The debondings in Area b become the void-like shape with loading. Stress distributed on the matrix region increases with increasing Area b and loading. The crazes initiate in the matrix among the debonded particles and progress slightly because of the larger deformation due to lower load capacity of debonded particles. When the stress at crazing region reaches the strength of craze, fibrils in crazing region break and large energy is released rapidly.
It follows that the energy release rate in matrix surpass the fracture toughness, matrix crack progresses rapidly (Area d) and specimen fails catastrophically. In addition, Area a decreased with increasing $\beta$-TCP contents. The composites with 4.8 wt% $\beta$-TCP contents had a larger debonding area from one aggregation. On the other hand, Area b from several aggregation was observed in the composites with 9.5 and 14.3 wt% $\beta$-TCP contents. Each size of Area b with 9.5 and 14.3 wt% $\beta$-TCP contents is smaller than with 4.8 wt% $\beta$-TCP contents. The distributed small areas act as a larger process zone, which results in the larger energy release rate and decrease in strength with increasing $\beta$-TCP contents.

4.2 Prediction of stress-strain relation

The observations of the fracture surfaces indicated that the debondings between particle and matrix accumulated in the fracture process of $\beta$-TCP/PLLA composites. In this study, the only debondings between particle and matrix are considered and the analysis based on micromechanics and damage mechanics proposed by Wada et al.\(^{15}\) is conducted to predict the stress-strain relationship. The theoretical concept is outlined as follows.

Wada et al. obtained the effective rigidity of 3-phase composite which consists of matrix and two kinds of particles using the theory of reinforced solids containing spherical inclusions developed by Weng\(^{16}\). They also obtained the effective rigidity, $C$, of particle dispersed composites with damaged particles through the applying that of non- and debonded particles. The effective rigidity is given by

$$C = C_0[I + c_1[(1-c_1S_1+A-c_2S_2[S_2+B]-1[S_1+A])^{-1}] + c_2[(1-c_2S_2+B-c_1S_1[S_1+A]-1[S_2+B])^{-1}]$$

where $C_0$ is the rigidity of matrix, $I$ is the 4th-rank unit tensor, $A = [C_1-C_0]^{-1}C_0$, $B = [C_2-C_0]^{-1}C_0$ and $c_1$ and $S_1$ ($= C_1^{-1}$) are the volume fraction and the compliance of $i$th phase, respectively. The effective rigidity of the debonded particles is calculated based on the analysis developed by Chow and Wong\(^{17}\), and expressed as following equation,

$$C' = [M'CM]^{-1}$$

where $C$ is initial rigidity of a material and damage effect tensor, $M'$, is given by below:

$$[M(D)] = \begin{bmatrix}
1 & 0 & 0 & 0 & 0 & 0 \\
0 & 1-D_1 & 0 & 0 & 0 & 0 \\
0 & 0 & 1-D_2 & 0 & 0 & 0 \\
0 & 0 & 0 & 1-D_3 & 0 & 0 \\
0 & 0 & 0 & 0 & \sqrt{(1-D_2)(1-D_3)} & 0 \\
0 & 0 & 0 & 0 & 0 & \sqrt{(1-D_3)(1-D_1)}
\end{bmatrix}$$

where $D_1$, $D_2$, and $D_3$ are the damage variables at their respective principal axes. In the present study, tensile direction (specimen length direction) is denoted as 1 axis, 2 and 3 axes are denoted as width and thickness direction, respectively. The analysis of Wong and Ait-Kadi\(^{18}\) is used as the debonding initiation law, as described below

$$\varepsilon_{11}^i = \frac{12kG_i}{r(dE/dc)}$$

where $G_i$ is the critical energy release rate associated with interfacial fracture, $c$ is a volume fraction, $r$ is the particle radius, $E$ is the Young’s modulus of composites, $k$ is a separated area. The value of $k$ is 1 in case of the whole area debonding.
Table 2 Material properties

|                | Elastic Modulus [GPa] | Poisson's Ratio | Density [g/cm³] |
|----------------|-----------------------|----------------|----------------|
| PLLA          | 4.2                   | 0.45           | 1.34           |
| β-TCP{(4),(2)}| 95                    | 0.22           | 3.07           |

The bending stress-strain relationships of β-TCP/PLLA composites were predicted. In the present study, it is assumed that the distribution of particle size and the critical energy release rate is normally-distributed. Table 2 shows the material properties used in the analysis. The distribution of β-TCP particles size was evaluated by scanning electron microscopy and the mean value and the standard deviation were 1.3 μm and 0.5 μm, respectively. Debonded particles are assumed to have a little load capacity, which results in the damage variables \((D_1 = 0.9, D_2 = D_3 = 0.64)\) in stead of \((D_i = 1)\) without any load capacity. Anisotropic material damage is also took into account. The critical energy release rate associated with β-TCP/PLLA interface debonding was estimated by bending tests of PLLA specimen melt bonded with β-TCP block and was obtained as the mean value of 0.64 J/m² and the standard deviation of 0.38 J/m²\(^{20}\).

Figure 5 shows the experimental results and analytical predictions. The analytical results using the condition above (Analysis 1) were in good agreement with experimental ones during the initial stage without β-TCP/PLLA interfacial debonding. The debonding initiation strain, however, is overestimated. That is, the transition to nonlinear behavior in stress-strain relationship is poorly-estimated. This is because the aggregations of β-TCP particles are not taken into consideration. In order to take into account of the aggregations, we measured the aggregation sizes at the fracture surface by scanning electron microscopy. An aggregation is regarded as a larger size particle. Table 3 shows the result of the measurement. The particles size enlarged with β-TCP contents. This results also indicates that the aggregation tends to occur with increasing β-TCP contents. In this study, the analysis is conducted using the distribution of the aggregated particle size (Table 3). The analytical results (Analysis 2) considering the aggregations show that the initiation of debonding strain is in good agreement with experimental results.

The macroscopic load capacity, however, decreased significantly at the transition point. This is due to the successive debonding initiation at this point. In the present study, the shape of the particles is assumed as a sphere, whereas the particles in the composites are rough shape with markedly uneven. The mechanical anchor effect for such rough shapes results in the larger nominal critical en-

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Table 3 Particle diameter distribution in B-TCP/PLLA composite

| Weight Fraction | Average Diameter [μm] | Standard Deviation [μm] |
|-----------------|-----------------------|-------------------------|
| 4.8             | 2.22                  | 1.55                    |
| 9.5             | 2.44                  | 1.68                    |
| 14.3            | 2.68                  | 1.64                    |
energy release rate associated with debonding. Taking account of the increase in nominal critical energy release rate, curve fittings were conducted. The curves of Analysis 3 in Fig. 5 are the curve fitting results. The energy release rates obtained are shown in Table 4. The average values in Table 4 increased with β-TCP contents. That is, aggregation associated with increasing β-TCP contents results in larger nominal critical energy release rate, because of the rough surface of aggregations. Theoretical and/or experimental methods to obtain the critical energy release rates are necessary to evaluate stress-strain behavior of the β-TCP/PLLA with β-TCP aggregation.

As described above, the elastic behavior before the initiation of the debonding can be estimated with accuracy. Additionally, when the distributions of the particle size and the critical energy release rate associated with debonding between particles and matrix are given, the stress-strain behaviors after the initiation of debondings can be predicted. The present analysis is effective for the material design to develop bone fixation devices.

5. Conclusion

Bioabsorbable ceramics β-TCP particles reinforced bioabsorbable plastics PLLA composites were fabricated to evaluate the effect of particle contents. Bending tests after in vitro immersion were performed and fracture surface were observed. In addition, stress-strain relations were predicted based on the micromechanics and the damage mechanics. Consequently, we obtain the following conclusions.

(1) The bending modulus of β-TCP particles/PLLA composites was clarified to increase with increasing β-TCP contents.

(2) The mechanical properties of the present β-TCP/PLLA composites retained up to 8 weeks in vitro immersion, and the bending strength of composites was within that of cortical bone.

(3) Analysis predictions based on micromechanics and damage mechanics considering the debonding between particle and matrix were in good agreement with experimental results. The effectiveness of the present analysis were confirmed.

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