1 Introduction

Bioactive ceramics attracts attentions as materials of the bone implant, because of their high biocompatibility. Among them, hydroxyapatite \((Ca_{10}(PO_4)_6(OH)_2):HA\) has bone-bonding ability through the bonelike apatite layer which is formed on its surface in body environment. On the other hand, \(\beta\)-tricalcium phosphate \((Ca_3(PO_4)_2:\beta-TCP)\) has a high bioreasorbability in body environment. In previous investigation, mechanical properties of HA and \(\beta\)-TCP were reported [1-3]. Ability of apatite formation was also reported [4]. It seems that HA/\(\beta\)-TCP composites could have good functions of both HA and \(\beta\)-TCP. In HA/\(\beta\)-TCP composites, the ratio between HA and \(\beta\)-TCP is a very important parameter to determine the rate of apatite formation and bioreasorbability in body environment. As a study example about HA/\(\beta\)-TCP composites, mechanical properties of HA/\(\beta\)-TCP composites which were prepared by partial decomposition from HA into \(\beta\)-TCP during sintering were investigated. Raynaud et al. showed that HA/\(\beta\)-TCP composites with \(\beta\)-TCP content of 10wt% had the highest strength [5], whereas Shiota et al. showed that those with \(\beta\)-TCP content of 30wt% had the highest strength [6]. In this method, however, it is difficult to control the ratio of the partial decomposition from HA into \(\beta\)-TCP. On the other hand, the ratio of HA/\(\beta\)-TCP is easier to control by sintering of HA and \(\beta\)-TCP powder mixture. However, little study about HA/\(\beta\)-TCP composites prepared by powder has been investigated in terms of its mechanical properties and bioactivity in body environment, because it is difficult to obtain dense composites by sintering of different kind of powder. Therefore, the effect of sintering additive of MgO was investigated [7] for a HA/\(\beta\)-TCP composite with weight ratio of 50/50. Considering a possibility of HA/\(\beta\)-TCP for a tailor-made treatment considering a location and degree of a disease, it is important to clarify effects of HA/\(\beta\)-TCP ratio on mechanical properties and bone-formation ability of HA/\(\beta\)-TCP.

This study attempts to evaluate mechanical properties and bioactivity of HA/\(\beta\)-TCP composites which are prepared by sintering of HA and \(\beta\)-TCP mixed powder. To improve mechanical properties of HA/\(\beta\)-TCP composites, the effect of additive of SiO\(_2\) and MgO were also investigated.

2 Experimental Procedures

2.1 Preparation of Specimen

Measured amount of HA powder (Taihei Chemical Industrial Co. Ltd., Japan, HAP-200) and \(\beta\)-TCP powder (Taihei Chemical Industrial Co. Ltd., Japan, \(\beta\)-TCP-100) were dispersed in ethanol with \(\beta\)-TCP content of 0, 10, 20 and 30wt%. After stirring for 24h, ethanol was evaporated from slurry to obtained HA/\(\beta\)-TCP powder mixture. The resultant powder was then uniaxially pressed in a die at 98.8 MPa. The green compact was sintered in a furnace. The sintering employed a holding time of 5h at 1250 \(^\circ\)C with heating rate of 10\(^\circ\)C/min and cooling in the furnace for 5h to the room temperature. The sintering compact was grinded, polished and cut into rectangular specimens of 18mm \(\times\)2.0mm \(\times\)1.5 mm. The tensile surfaces in bending test as mentioned below were polished. Finally, the corners of specimen were chamfered by an emery paper.

In order to investigate the effect of additive, 1wt% of SiO\(_2\) powder or MgO powder (Wako Pure Chemical Industries Co. Ltd., Japan) was added in ethanol when HA/\(\beta\)-TCP was stirred, only for \(\beta\)-TCP content of 30wt%.

2.2 Microstructural characterization

Relative density was measured by Archimedes method. It was calculated from the following equations,

\[
\rho_r = \frac{W_1}{W_1 - W_2} \times \rho_b, \quad \rho_s = \frac{\rho_b}{\rho_2} \times 100
\]
where $\rho_b$ is the bulk density, $W_1$ the dry weight, $W_2$ weight in water, $W_3$ the water-saturated weight, $\rho_1$ the density of water, $\rho_r$ the relative density, $\rho_2$ the theoretical density of powder.

Average grain size of the sample was measured as following steps. First, thermal etching was applied by using a furnace. The program was employed a holding time of 1h at 1150 °C with heating rate of 50 °C /min and furnace cooling to the room temperature. Then, average grain size was measured by line intercept method using the picture observed by scanning electron microscopy (SEM) (Fig. 1). Average grain size was calculated from the following equations,

$$A = \frac{d_1d_2}{n_1n_2M^2}$$

$$d = \sqrt[4]{\frac{4A}{\pi}}$$  

where $A$ is average grain area, $d_1$ the horizontal line length, $d_2$ the vertical line length, $M$ the magnification of picture, $n_1$ the number of horizontal grain, $n_2$ the number of vertical grain, $d$ the average grain size.

2.3 Mechanical Properties

Four-point bending tests were performed with a cross-head speed of 0.1mm/min. The upper span was 5mm, the lower span was 15mm. Bending strength was calculated from the following equation,

$$\sigma_B = \frac{3Fl}{bh^2}$$  

where $\sigma_B$ is the bending strength, $F$ the maximum applied load, $l$ the upper span, $h$ the thickness, $b$ the width.

2.4 Bioactivity

Simulated Body Fluid (SBF) was proposed by Kokubo to evaluate the bioactivity in vitro [8]. SBF was prepared by dissolving the reagent-grade chemicals into distilled water and buffered with Tris and HCl to pH 7.4 at 37 °C. The ion concentrations of SBF used in this study was compared with the human blood plasma in Table. 1. It is nearly equal to those in human blood plasma. The specimens were soaked in SBF at 37 °C up to 4weeks. After soaking, bending strength was measured and the surface of specimens was examined by scanning electron microscopy (SEM) to confirm the bonelike apatite formation.

<table>
<thead>
<tr>
<th>Ion</th>
<th>SBF [mM/l]</th>
<th>Blood Plasma [mM/l]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na⁺</td>
<td>142</td>
<td>142</td>
</tr>
<tr>
<td>K⁺</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>Ca²⁺</td>
<td>2.5</td>
<td>2.5</td>
</tr>
<tr>
<td>Mg²⁺</td>
<td>1.5</td>
<td>1.5</td>
</tr>
<tr>
<td>Cl⁻</td>
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<td>104</td>
</tr>
<tr>
<td>HCO₃⁻</td>
<td>4.2</td>
<td>27</td>
</tr>
<tr>
<td>HPO₄⁻₂</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>SO₄²⁻</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>Tris(Hydroxymethyl)</td>
<td>100</td>
<td>***</td>
</tr>
</tbody>
</table>

3 Results and Discussion

Fig. 2 shows relative density of HA/β-TCP composites. Relative density of HA/β-TCP composites decreased with increasing β-TCP content. It is suggested that porosity increased with β-TCP content. Particularly in case of 30 wt%, the relative density decreased significantly. This result suggests the poor sinterability of HA/β-TCP powder mixture.

![Fig. 2 Relative density of HA/β-TCP composites.](image)

Fig. 3 shows SEM photographs of grain size of HA/β-TCP composites. Fig. 4 shows grain size of
HA/β-TCP composites calculated by equation (2) using SEM photographs. Grain size of HA/β-TCP composites increased with β-TCP addition. SEM photographs in Fig. 3 show that samples of containing β-TCP had bimodal structure of grain distribution: larger grains and smaller grains. That is, abnormal grain growth occurred. It is speculated that β-TCP accelerated the grain growth in HA/β-TCP composites.

![SEM photographs of the grain size of HA/β-TCP.](image)

**Fig. 3** SEM photographs of the grain size of HA/β-TCP.

![Grain size of HA/β-TCP composites.](image)

**Fig. 4** Grain size of HA/β-TCP composites.

Fig. 5 shows bending strength of HA/β-TCP composites. It is found that bending strength of HA/β-TCP composites decreased by ~20% comparing with pure HA. This is because that HA/β-TCP composites have more lower relative density, that is, higher porosity, than pure HA. This is also because HA/β-TCP composites have larger grain size than pure HA.

![Bending strength of HA/β-TCP composites.](image)

**Fig. 5** Bending strength of HA/β-TCP composites.

Fig. 6 shows SEM photographs of the fracture surface of HA/β-TCP composites. In each sample, it is found that transgranular fracture occurred. It can be seen from SEM photograph of fracture surface of 30wt% that neck formation was not progressed well. This result indicates that composites of 30wt% did not sinter enough.

![SEM photographs of the fracture surface of HA/β-TCP.](image)

**Fig. 6** SEM photographs of the fracture surface of HA/β-TCP.

Fig. 7 and Fig. 8 show SEM photographs of the surface of HA/β-TCP composites after 1 and 3 weeks soaking in SBF, respectively. It can be seen from Fig. 7 that pure HA formed apatite layer on its surface after 1 week soaking, and a composite (10wt%) did not form apatite layer but formed small crystals of apatite on its surface after 1 week soaking. Composites (20wt%, 30wt%) did not form apatite after 1 week soaking. It also can be seen from Fig. 8
that all composites (0, 10, 20, 30wt%) formed apatite on their surface after 3 weeks soaking. This result indicates that the rate of apatite formation for composites decrease comparing with pure HA, and that the rate of apatite formation decreases as content percentage of β-TCP increased.

![Fig. 7 SEM photographs of the surface of HA/β-TCP after 1 week soaking.](image)

![Fig. 8 SEM photographs of the surface of HA/β-TCP after 3 week soaking.](image)

Bending strength of HA/β-TCP composites measured after soaking in SBF, as shown in Fig. 9. The bending strength of pure HA (0wt%) decreased rapidly with soaking, however the strength of composites (10 and 20wt%) did not decrease after soaking. This is because of the high dissolution reaction and apatite formation of the surface of pure HA (0wt%), as shown in Fig. 7(a). Although the low dissolution reaction of the surface was observed for 30wt% composites, as shown in Fig. 7(d), the bending strength of the composite decreased after soaking. This is attributed to the high porosity due to the low relative density, as shown in Fig. 2. As a result, SBF diffused into the composite and the dissolution occurred inside of the composite. Thus, it could be stated that the difference in surface reactivity and porosity affect the strength of composites in body environment significantly.

![Fig. 9 Bending strength of HA/β-TCP composites on each soaking condition.](image)

As described above, it is suggested that the composites (30wt%) did not sinter enough. To improve the sinterability, composite (30wt%) was doped by addition of silica (SiO₂) and magnesia (MgO). Fig. 10 shows relative density of HA/β-TCP /SiO₂ and MgO composites. It is found that relative density of HA/β-TCP /SiO₂ decreased compared with HA/β-TCP, whereas those of HA/β-TCP /MgO increased. This result indicates that the addition of SiO₂ did not act as a sintering additive, whereas that the addition of MgO accelerate densification. Fig. 11 shows SEM photographs of the grain size of HA/β-TCP /SiO₂ or MgO composites. Fig. 12 shows grain size of HA/β-TCP /SiO₂ or MgO composites calculated by equation (2) using SEM photographs. It is found that grain size of HA/β-TCP /SiO₂ decreased in comparison to HA/β-TCP. From Fig. 11 (a), it is also apparent that neck formation did not progress in HA/β-TCP /SiO₂. This result means that HA/β-TCP /SiO₂ didn’t sinter enough. On the other hand, grain size of HA/β-TCP
/MgO did not change in comparison to HA/β-TCP. As shown in Fig. 11 (b), it is found that the abnormal grain growth of HA/β-TCP was inhibited by addition of MgO. Thus, it is speculated that addition of MgO had an effect on inhibiting of grain coarsening.

Fig. 10 Relative density of HA/β-TCP/SiO₂ or MgO.

Fig. 11 SEM photographs of the grain size of HA/β-TCP/SiO₂ or MgO.

Fig. 12 Grain size of HA/β-TCP/SiO₂ or MgO.

Fig. 13 Bending strength of HA/β-TCP/SiO₂ or MgO.

Fig. 14 SEM photographs of the fracture surface of HA/β-TCP/SiO₂ or MgO.

It is speculated that the difference in effectiveness as an additive is the different kind of chemical bonding of chemical compounds. The chemical bonding of SiO₂ is covalent binding, whereas, that of MgO is ion binding. The covalent binding is comparatively strong, whereas the ion binding is comparatively weak. In case of ion binding, the binding is easy to be separated due to its weak chemical binding, therefore atoms are easy to react into HA/β-TCP in sintering. These results led to high densification of HA/β-TCP/MgO. It was reported that Mg of HA/β-TCP/MgO incorporates preferentially into β-TCP phase of HA/β-TCP, therefore, densification occurs in sintering [8]. It is suggested that the reaction that Mg atom of MgO displaced Ca atom of β-TCP occurred in sintering. It is also speculated that Mg was easy to displace Ca, because both Ca and Mg were atoms of second row of periodic table, and had similar characteristic.
Fig. 15 shows SEM photographs of the surface of HA/β-TCP /SiO$_2$ or MgO composites after 4 weeks soaking is SBF. In comparison to HA/β-TCP (30wt%), it is found that the ability of apatite formation of HA/β-TCP /SiO$_2$ or MgO decrease.

![SEM photographs of HA/β-TCP, SiO$_2$, and MgO composites](image)

(a)HA/β-TCP          (b)+SiO$_2$          (c)+MgO

Fig. 15 SEM photographs of the surface of HA/β-TCP/SiO$_2$ or MgO after 4 weeks soaking.

Bending strength of HA/β-TCP /SiO$_2$ and MgO composites were measured after soaking in SBF, as shown in Fig. 16. Bending strength of HA/β-TCP /SiO$_2$ decreased after soaking. This is because of the high porosity due to the low relative density of HA/β-TCP /SiO$_2$. As a result, SBF diffused into the composite and the dissolution occurred inside of the composite. On the other hand, bending strength of HA/β-TCP/MgO did not decrease after soaking, because of its low reactivity of the surface.

![Bending strength graph](image)

Fig. 16 Bending strength of HA/β-TCP/SiO$_2$ or MgO on each soaking condition.

4 Conclusions

In this study, mechanical properties and bioactivity of HA/β-TCP composites which were prepared with sintering of HA and β-TCP powder mixture were investigated. The effect of additive of SiO$_2$ and MgO was also investigated. As content of β-TCP increased, relative density decreased and grain size increased. Bending strength of composites also decreased by ~20% due to β-TCP addition because of lower relative density and larger grain.

The ability of apatite formation in SBF decreased with increasing β-TCP content. It is indicated that the change in bending strength after soaking related to its surface reaction in SBF and its porosity.

Because a composite (30wt%) had low sinterability, SiO$_2$ and MgO were added as sintering agents. As a result, it is found that MgO addition improved sinterability, however, SiO$_2$ did not. These results were attributed to high reactivity of MgO.

References