Effects of Sintering Temperature Over 1,300°C on the Physical and Compositional Properties of Porous Hydroxyapatite Foam

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Porous hydroxyapatite (HAP) foam permits three-dimensional (3D) structure with fully interconnecting pores as well as excellent tissue response and good osteoconductivity. It is therefore thought to be a good candidate as scaffold material for bone regeneration and as a synthetic bone substitute material. To fabricate better porous HAP foam, improved physical and structural properties as well as higher osteoconductivity are desired. In the present study, the effects of sintering temperature on the physical and compositional properties of porous HAP foam were evaluated by employing high sintering temperature starting at 1,300°C up to 1,550°C. The mechanical strength of porous HAP foam increased with sintering temperature to reach the maximum value at 1,525°C, then decreased slightly when sintering temperature was further increased to 1,550°C. Alpha tricalcium phosphate (α-TCP) was formed, and thus the porous HAP foam became biphasic calcium phosphate. Biphasic calcium phosphate consisting of both α-TCP and HAP had been reported to show higher osteoconductivity than HAP alone. We therefore recommend 1,500-1,550°C as the sintering temperature for porous HAP foam since this condition provided the most desirable physical properties with biphasic calcium phosphate composition.

Key words: Porous hydroxyapatite, Scaffold, Synthetic bone substitute

INTRODUCTION

In the development of scaffold materials for bone tissue regeneration and biomaterials for bone substitution, several stringent requirements exist. Of which, the key requirements are a three-dimensional fully interconnecting porous structure with large porosity, which must be accompanied with excellent tissue response and good osteoconductivity. Porous hydroxyapatite (HAP: Ca_{10}(PO_4)_{6}(OH)_2) foam is a good candidate since it has interconnecting pores similar to the cancellous bone. In addition, the excellent tissue response and good osteoconductive property of HAP have already been well established based on long-term clinical application. Various methods are available for the fabrication of porous HAP foam including burn out method using flammable particles, foaming method, and preparation using polyurethane foams (i.e., ceramic foam method). Among these, only the ceramic foam method is known to produce a three-dimensional fully interconnecting porous structure similar to cancellous bone. Porous HAP foam is prepared by using polyurethane foam as a template to pattern the three-dimensional fully interconnecting porous structure. The polyurethane foam template is immersed into the HAP powder slurry to allow coating of the slurry on all its surfaces. Then, the coated polyurethane foam template is dried and heated to high temperature to burn it out and to sinter the HAP slurry. Although the mechanical strength of porous HAP foam is higher when compared with other porous HAP that have the same porosity, its mechanical strength becomes lower with increase in porosity. It was reported that pure HAP ceramics yielded higher compressive strength when sintered up to 1,200°C from 800°C. Although no explanation was given in their report why they limited the sintering temperature to 1,200°C, the temperature could be the highest temperature for the furnace they employed in their study. If that were the case, the mechanical strength of porous HAP foam may be increased with further increase in sintering temperature. Furthermore, it should be noted that porous HAP foam is useful for bone tissue regeneration since it shows good osteoconductivity. Therefore, porous HAP foam will become more useful if its osteoconductive properties are further improved. It has been reported that biphasic calcium phosphate containing HAP and beta tricalcium phosphate (β-TCP: Ca_3(PO_4)_2) as well as HAP and alpha tricalcium phosphate (α-TCP: Ca_3(PO_4)_2) showed better osteoconductivity than pure HAP alone. One method to prepare biphasic calcium phosphate is to employ high sintering temperature. Given these conditions, porous HAP foam with high mechanical strength and high osteoconductivity may be fabricated by employing high sintering temperature.

The objective of this study, therefore, was to evaluate the feasibility of fabricating porous HAP foam with desirable physical and compositional properties — and which contained additional calcium phosphate phase — by employing relatively high sintering temperature.
temperature from 1,300°C to 1,550°C.

MATERIALS AND METHODS

Fabrication of HAP foam

We used the so-called foam method or ceramic foam method to fabricate the HAP foam. Several polyurethane foam blocks (HR-20D, Bridgestone, Tokyo, Japan) (40 × 30 × 15 mm) with an average pore size of approximately 1 mm in diameter were used as templates. HAP powder obtained commercially (HAP-200, Taihei Chemicals, Osaka, Japan) was calcined at 800°C for an hour in a furnace (SBV-1515D, Motoyama, Osaka, Japan), then mixed with distilled water to prepare the HAP slurry (10 g HAP powder in 20 ml distilled water). No surfactants were used to simplify the system even though they are known to be effective.

The polyurethane foam blocks were impregnated with the slurry and then squeezed to remove the excess HAP slurry. Compressed air was also used to further remove excess HAP slurry inside the polyurethane foam’s frame. This would prevent the pores from being occupied by the HAP slurry. After the impregnated foam blocks were dried for a minimum of 24 hours at room temperature, they were sintered in a programmable electric furnace. Specimens were heated at 1°C/min until 400°C to burn out the polyurethane foam without collapsing the HAP slurry. Then, the heating rate was increased to 5°C/min. The foams were kept at the prescribed temperatures from 1,300°C to 1,550°C for five hours and cooled inside the furnace.

Although the use of surfactants is known to be effective in increasing the mechanical properties of the foam, we employed no surfactants to focus only on the effect of sintering temperature.

Linear shrinkage and porosity of HAP foam

Linear shrinkage was determined by comparing the original size of the polyurethane foam template with that of the porous HAP foam obtained after sintering. In short, the length, width, and height of the porous HAP foam were divided by the corresponding values of polyurethane foam. The averaged values of linear shrinkage in length, width, and height were used as the linear shrinkage measurement and expressed in percentage. Porosity of HAP foam was calculated based on the weight and volume of the HAP foam.

Mechanical strength measurement

Mechanical strength of porous HAP foam was evaluated in terms of compressive strength (CS). This was because the foam was porous, and conventional methods of mechanical characterization such as tensile, biaxial and impact testing were inapplicable to the porous material.

The porous HAP foam was cut by a rotary blade (GC Micromotor, LM-1, Tokyo, Japan) to obtain a square shape with dimensions of 2 × 2 × 1.5 cm. A flat 5-mm thick acrylic plate was placed on top of the HAP foam parallel to the floor, and the HAP foam was crushed vertically by steel plate with a flat and smooth surface at a cross-head speed of 1 mm/min using a universal testing machine (ISS5000, Shimadzu, Kyoto, Japan). The CS values used were average of at least four specimens. The bars in Fig. 7 denote standard deviation.

Powder X-ray diffraction (XRD)

Composition of the HAP foam was evaluated by means of powder X-ray diffraction (XRD). The HAP foam was ground into fine powder and supplied for the XRD analysis. XRD patterns of the vacuum-dried samples were recorded with a vertically mounted diffractometer system (RINT 2500V, Rigaku, Tokyo, Japan) using Ni filtered CuKα generated at 40 kV and 100 mA. Specimens were scanned from 3 to 60° 2θ (where θ is the Bragg angle) in continuous mode, and references for HAP and α-TCP identification were made to JCPDS cards 9-0432 and 9-0348 respectively. Amount of α-TCP formed in the HAP foam samples sintered from 1,450°C to 1,550°C was calculated from an integrated area ratio of the most intense peaks for HAP (31.7°) and α-TCP (30.7°) using MDI JADE 5.0 Software (Materials Data Inc., Livermore, Ca., USA).

Scanning electron microscopy (SEM)

Morphology of the HAP foam was observed using scanning electron microscopy (SEM) (JSM 5400LV, JEOL Co. Ltd., Tokyo, Japan) under an accelerating voltage of 15 kV after being coated with gold. For observation of the cross-sections of sintered porous HAP block and polyurethane foam, they were embedded in epoxy resin and cut vertically using a low-speed diamond saw (Maruto Instruments Co. Ltd., Japan).

Statistics

For statistical analysis, one-way factorial ANOVA and Fisher’s PLSD method as a post-hoc test were performed using the Stat View 4.02 software (Abacus Concepts Inc., Berkeley, California) at a significance level of 5%.
RESULTS

As shown in Figs. 1 and 2, the porous HAP foam obtained after the sintering process showed basically the same morphology except for the size. The porous HAP foam kept its three-dimensional fully interconnecting porous structure, but shrunk during the sintering process. As a result, the porous HAP foam was smaller in size compared to the polyurethane foam template.

Fig. 3 shows the typical SEM images of the porous HAP foam’s surface structure sintered at 1,300°C to 1,550°C. Coalescence of the porous HAP particles was confirmed regardless of the sintering temperature. On the other hand, larger grains were observed on porous HAP foams obtained at higher sintering temperature. It should be noted that micro pores were observed at the intergranular regions. Less amount of micro pores were found on porous HAP foams sintered at higher temperature.

Fig. 4 shows the typical SEM images of the porous HAP foam’s frame in cross-sectional view after sintering at 1,300°C, 1,400°C, and 1,500°C. The SEM image of polyurethane foam’s cross-section is also shown for comparison. As shown in the figure, the frame of porous HAP foam had a hollow structure—and this was previously occupied by the polyurethane foam structure that slowly burned out at the early stages of sintering process.

Fig. 5 shows the linear shrinkage of porous HAP foam as a function of sintering temperature. Shrinkage was relatively constant at about 30% when the sintering temperature was 1,475°C or lower, and then increased with the sintering temperature.

Fig. 6 summarizes the porosity of porous HAP foam as a function of the sintering temperature. Porosity of the porous HAP foam decreased with the sintering temperature. It should be noted that the porosity of porous HAP foam was extremely high. Porosity was approximately 90% even when sintered at 1,550°C.

Fig. 7 summarizes the compressive strength of porous HAP foam as a function of sintering temperature. Compressive strength of the porous HAP foam was relatively constant when the sintering temperature was 1,450°C or lower. It increased with sintering temperature to reach maximum value at 1,525°C, then decreased with further increase in sintering temperature.
Fig. 3 Typical SEM images of the surface of HAP foam sintered at: (a) 1,300°C; (b) 1,400°C; (c) 1,500°C; and (d) 1,550°C.

Fig. 4 Typical SEM image of the cross-section of: (a) polyurethane foam used as a template of HAP foam preparation; (b) HAP foam sintered at 1,300°C; (c) HAP foam sintered at 1,400°C; and (d) HAP foam sintered at 1,500°C.
temperature. This result also showed that a large difference existed between the compressive strength of HAP foam sintered at lower temperature and those sintered at high temperature.

Fig. 8 summarizes the XRD patterns of porous HAP foam sintered at 1,450-1,550°C. XRD patterns of (a) HAP powder used for the preparation of porous HAP foam and (g) α-tricalcium phosphate (α-TCP) were also shown for comparison. When porous HAP foam was sintered at (b) 1,450°C or lower (data not shown), no phases were detected except for HAP.
In contrast, α-TCP was found besides HAP when sintered at 1,475°C or higher — whereby the amount of α-TCP increased with the sintering temperature. Fig. 9 shows the change in the amount of α-TCP formed with temperature. The amount of α-TCP in HAP foam increased almost linearly with sintering temperature above 1,475°C.

DISCUSSION

Results obtained in the present study demonstrated clearly that porous HAP foam that contained α-TCP — biphasic calcium phosphate foam — with good physical properties can be prepared by sintering at 1,500–1,550°C. Porous HAP foam was prepared by sintering HAP powder slurry that was coated on the surface of polyurethane foam template. Therefore, higher sintering temperature was required to complete the sintering process because no compaction process was available as with the ordinary ceramic products. Higher sintering temperature then resulted in larger grain size, as shown in Fig. 3. Although it is known that larger grain size decreases mechanical strength$^{27,28}$, the porous HAP foam with larger grain size showed higher mechanical strength. This may be explained by the less micro pores in the frame of HAP foam sintered at higher temperature. On this note, it can be said that completion of the sintering process and less micro pores in the frame of porous HAP foam are more important than regulating the grain size with respect to mechanical strength. As shown in Fig. 4, porous HAP had small pores in the frame and large pores at the center of its frame. The former small pores were the result of spaces between the HAP particles, and the latter large pores were a result of the burnout of the polyurethane foam used initially as the template of porous HAP foam. Although the large pore also decreased as the sintering temperature increased, the porous HAP foam kept the hollow space previously occupied by the polyurethane foam template — which is a disadvantage with respect to its mechanical strength. However, the hollow space may be useful if the porous HAP foam is to be used as a scaffold for bone regeneration or as artificial bone filler. If one expects the porous HAP foam to be replaced with bone, osteoclasts have to resorb the porous HAP foam. Hence, osteoclasts need to resorb a less amount of HAP if porous HAP foam has hollow space. Moreover, it should be noted that this hollow space may be ideal for drug delivery system$^{29,30}$. Drugs that would enhance formation of new bone would be released gradually from porous HAP foam if such drug can be loaded in the hollow space.

The mechanical strength of porous HAP foam increased with sintering temperature between 1,450°C and 1,500°C, and there were no statistical differences above 1,500°C. In contrast, the porosity of porous HAP foam continued to decrease even at 1,550°C, as shown in Fig. 6. Fig. 10 may be useful to understand the relationship between the mechanical strength of porous HAP foam and porosity. As shown in Fig. 10, the mechanical strength of porous HAP foams in terms of compressive strength increased as porosity decreased. However, the compressive strength did not seem to change even when the porosity of HAP foam decreased to 92% or lower. This meant that the mechanical strength of porous HAP foam was governed not only by the porosity of the frame but also by other factors. Indeed, it has been reported that the mechanical strength of porous foam type structure is governed by the mechanical strength of the frame, as shown in Equation (2)$^{31}$:

$$\sigma_f = C \sigma_{fs} (1-P)^{3/2}$$

(2)

where $\sigma_f$ is the mechanical strength of the porous foam type structure, C the proportional constant, $\sigma_{fs}$ the mechanical strength of the frame of the porous foam, and P the porosity.

This equation emphasizes the strength of the foam’s frame only, and not the whole foam itself. Frame strength, $\sigma_{fs}$, was calculated from $\sigma_f$ and P of the HAP foam obtained at various sintering temperatures by using Equation (2). Fig. 11 shows a change in $\sigma_{fs}$ with the sintering temperature, where frame strength was normalized by the strength at 1,300°C. It is clearly demonstrated that frame strength increased with sintering temperature to reach the maximum value at 1,500°C, then decreased as the sintering temperature was further increased. This decrease in frame strength may be attributed to the formation of α-TCP. As shown in Figs. 8 and 9, α-
TCP was formed when sintered at 1,475°C or higher and the amount of α-TCP increased with sintering temperature. Formation of α-TCP in porous HAP foam is desirable since we aimed for the preparation of biphasic calcium phosphate foam. However, α-TCP formation was a drawback with respect to the mechanical strength of porous HAP foam. Fortunately, porous HAP foam containing α-TCP or biphasic calcium phosphate could be fabricated with a minimal compromise on its mechanical strength.

In conclusion, porous HAP foam that contained α-TCP with desirable physical and compositional properties was fabricated by sintering at 1,500-1,550°C. Investigation including an in vitro cell biocompatibility screening and histopathological studies are now in progress based on the results obtained in this initial study.

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REFERENCES

5) Thalgott JS, Giuffre JM, Fritts K, Timlin M, Klezl Z. Instrumented postolateral lumbar fusion using coralline hydroxyapatite with or without demineralized bone matrix, as an adjunct to autologous bone. Spine J 2001; 1(2): 131-137.