Fabrication of porous alumina-hydroxyapatite composites via protein foaming-consolidation method: Effect of sintering temperature

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Abstract

In this study, porous alumina-hydroxyapatite (HA) composite bodies were designed for the use in bone implant via protein foaming-consolidation method and the effect of sintering temperature was investigated. Commercial HA powder was used as a bioactive ceramic. Alumina and HA powders were mixed with yolk at an adjusted mass ratio to make slurry. The slurries were cast into cylindrical shaped molds and then dried for foaming and consolidation process. Subsequently, the dried bodies were burned at 600°C for 1 h, followed by sintering at temperatures of 1200, 1350, 1400 and 1550°C for 2 h, respectively. The results show that the sintered bodies were porous with pore size in the range of 20-250 μm and porosity of 42 – 45 %. Increasing sintering temperature from 1200 to 1550°C improved compressive strength from 1 MPa to 8 MPa. TCP phase was found in sintered bodies.

Keywords: Porous alumina, Hydroxyapatite, Composites, Protein foaming-consolidation.

1 Introduction

Implantation of bone by using bone grafts is known strategies for treatment of large bone defects which all lead to limited degree of structural and functional recovery. However, limited supply, donor site morbidity and risk of transmission of pathological organisms impose major limits to their widespread use (Saki et al, 2009). Bone implants become an important thing in the biomedical implant market due to all of the problems arise in the medicine today. To date, several bone substitutes have been approved for clinical applications using a wide range of scaffold materials. In orthopedic applications, a range of bioactive ceramics such as tricalcium phosphate (TCP), hydroxyapatite (HA), bioglass and glass ceramics have been employed because of their excellent bioactivity and bone bonding ability. However, most of them have relatively poor mechanical strength and they cannot meet the requirements for many applications (Kapoor et al, 2010).

Alumina is used to make implantable orthopaedic devices, is a very well tolerated material with minimum tissue reaction after implantation. It exhibits high mechanical strength and minimum wearing. Therefore, it is frequently used in high load-bearing sites such as hip prostheses and dental implants (Saki et al, 2009). No material with both good mechanical and good biological properties exists. However, keeping in mind that bioactivity is more a surface property and mechanical properties are due to the bulk, it is possible to conceive a functionally graded composite deriving its strength from a strong, bio-inert core (like alumina or zirconia) and its bioactivity from a calcium phosphate coating (Gremillard et al, 2006).

The objective of this work is the production of porous alumina-HA composite through protein foaming-consolidation method for potential use as bone substitute. This approach aims to combine the higher strength of the alumina with the biological advantages of the tri calcium phosphate surface, that is, its bioactivity and octeoconduction properties. The effect of sintering temperature on physical and mechanical properties of porous body is investigated.

2 Experimental

2.1 Materials

A commercial alumina powder (Sigma-Aldrich, USA) with a BET specific surface area of 0.39 m^2/g and an average particle size of 0.25 μm was used as the bioinert ceramic. Commercial HA (Sigma-Aldrich, USA) was used as the bioactive material. Protein used was yolk that freshly isolated from chicken egg (LTK Berhad, Malaysia). Castor oil (Sigma Aldrich, USA) was used as the lubricant for facilitating demolding.

2.2 Preparation of porous alumina-HA composite

Protein foaming-consolidation method was used to fabricate porous alumina bodies as reported elsewhere (Fadli and Sopyan, 2009). The slurries were prepared by mixing the alumina, HA powder with yolk in a beaker glass. The slurries were mechanically stirred (Heidolph, RZR 2052 control model) at 150 rpm for 3 h in ambient environment. Subsequently, the slurries were cast in cylindrical open stainless steel mould with 10.75 mm diameter and 15.10 mm height and dried in an air oven (Memmert, 100-800 model) at 180°C for 1 h. Covering the molds with castor oil made demolding easier and led to better surface qualities. Finally, the dried samples were burned in a furnace (Protherm, PLF 160/5 model) at a rate of 10°C min^{-1} up to 600°C for 1 h for removal of the yolk and then sintered at rate of 2°C min^{-1} up to 1200°C - 1550°C for 2 h. Composition of slurries and sintering temperatures studied are as listed in Table 1.

Table 1 Slurry composition and sintering temperature studied

Slurry	Alumina (g)	HA (g)	Yolk (g)	Sintering temperature (ºC)
S0	24	3.2	24	1200
S1	24	3.2	24	1350
S2	24	3.2	24	1400
S3	24	3.2	24	1550

2.4 Characterization

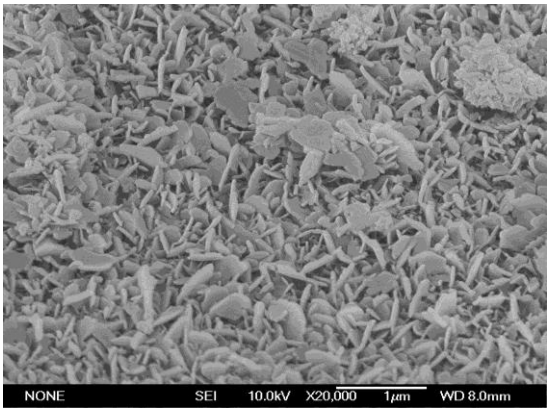
The particle size of powder was measured using a Nanosizer (Malvern, ZEN1600 model). The apparent density of sintered porous composite samples obtained was measured in an electronic densimeter (Alfa Mirage, MD300S model). The theoretical densities of fully densified alumina, 3.98 g cm^{-3}, and hydroxyapatite, 3.14 g cm^{-3}, are used as the references to calculate the total volume fraction of porosity. The crystallinity of the sintered porous samples was analyzed by XRD (Shimadzu, XRD-6000) using Cu Ka radiation at 30 mA, 40 kV. The pore size, interconnection among pores and also the grain structure were examined using FESEM (JEOL, JSM 6700 F model). The mechanical strength of the porous alumina-HA bodies was measured using a universal testing machine (Lloyd, LR10K plus model) by diametrical compression at a loading rate of 2.5 mm min^{-1} on the samples of 8 mm diameter and 10 mm height. Five scaffolds were used to determine the average value of each compressive test.

3 Results and Discussion

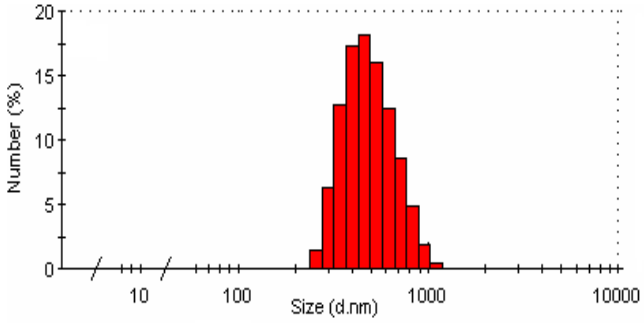
Protein foaming-consolidation method has been employed for the first time to prepare porous alumina (Fadli and Sopyan, 2009). It was found that physical properties of the porous alumina bodies obtained can be controlled by regulating slurry composition and drying process. The alumina bodies after sintering process show good interconnectivity with pore size in the range of 200-1,000 µm. Even proper control processing condition could provide considerably low density porous bodies, such low (< 1 g cm^{-3}) that they are floatable on water (Sopyan and Fadli, 2012). Such properties, combined with high mechanical strength, make the porous alumina potential to be a candidate for floating microcarrier application, especially in a bioreactor cell culture.

3.1 Characterization of HA powder

Powder of commercial HA revealed flat structure in shape and the particles tend to scatter with size in the range of 100-600 nm (Figure 1a). The average particle size of commercial HA powder was found to be of 765 nm as shown in Fig. 1b. The size of particles will effect on stability and flowability of slurries, leading to variation in porosity and mechanical strength of materials.



(a)



(b)

Figure 1. (a) Morphology and (b) Particle size distribution graph of commercial HA powder

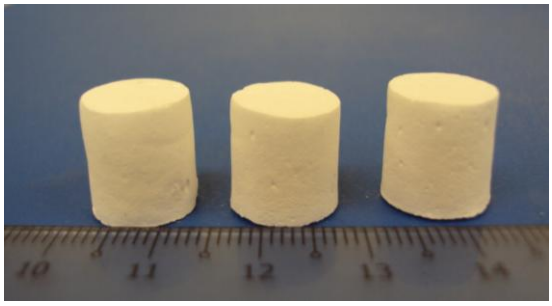


Figure 2. Porous alumina-HA composites with cylindrical shape.

Figure 2 shows a photograph three sintered porous alumina-HA composites with cylindrical shapes. The bodies did not show any cracks during both burn out of pore former and sintering.

3.2 Effect of sintering temperature on physical properties

To investigate effect of sintering temperature on the physical properties of porous alumina-HA, samples S0, S1, S2 and S3 were evaluated. Measurement of shrinkage, density, porosity and compressive strength of all the samples are presented in Table 2.

Table 2 Effect of sintering temperature on shrinkage, density, porosity and compressive strength

Slurry	Shrinkage (Vol.%)	Density (g cm^{-3})	Porosity (%)	Compr. strength (MPa)
S0	24.4	2.3	41.8	0.8
S1	28.6	2.0	48.5	1.8
S2	33.0	2.4	39.0	2.1
S3	43.3	2.2	44.6	7.5

When the sintering temperature increased from 1200 to 1550°C, the shrinkage of porous alumina-HA increased from 24.4 to 43.3%. The shrinkage occurred as the yolks were removed and the particles, which were initially packed loosely, approached and contacted. The removing yolks left holes in the walls. These holes were the source of void that would move from the centre to the outer surface during sintering, at the same time the particles moved towards the internal surface of bodies. These kind of movements led to the shrinkage of bodies. Therefore the shrinkage became intensive with the increasing sintering temperature.

The influence of sintering temperature on the density and porosity is not clear from Table 2. In fact, at a constant slurry composition, sintering temperatures should not have any effect on the density and porosity. The fluctuation of density and porosity due to temperature sintering effect may be caused by the differences of thickness of alumina, HA or TCP phases in the bodies which produced some minor influence of density and porosity. Any clear trend due sintering temperature could not be elucidated from these experimental data.

Table 2 also reveals that the compressive strength of both porous alumina-HA slowly increased when sintering temperature increased from 1200 to 1400°C. The compressive strength of porous alumina-HA in the temperature range was 0.8 – 2.1 MPa. On the other hand, the compressive strength increased faster when sintering temperature increased from 1400 to 1550°C. Owing to a decrease in porosity with the elevating sintering temperature, the compressive strength is supposed to increase with sintering temperature. An increase in sintering temperature led to the higher strength but also reduced the overall porosity. The maximum compressive strength values for porous alumina-HA bodies were 7.5 and 10.6 MPa and achieved at sintering temperature of 1550°C.

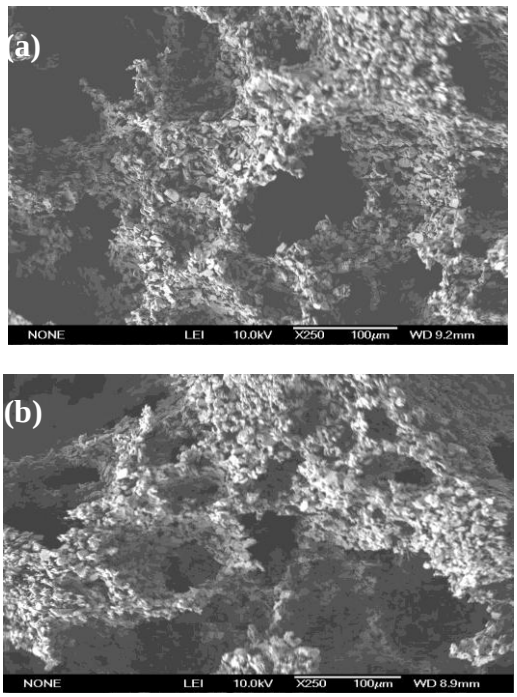


Figure 3. Macro structures of bodies after sintered at (**a**) 1350 and (b) 1550°C

The micro and macrostructure of samples changed obviously with the increasing sintering temperature. Figure 3 shows the surface morphology of the porous alumina-HA samples sintered at 1350 (S1) and 1550°C (S4). Pore size in the sintered bodies was in the range of 20-250 µm. The increased sintering temperature resulted in smaller pore size and denser struts as well as higher interconnectivity of pores (Figure 3b). It is understandable that the shrinkage increased with sintering temperature, thus the pore sizes decreased whereas window size in the pore walls increased.

Figure 4a shows that the particles shape in porous body after 1350°C sintering are irregular. When the sintering temperature increased, the irregular particles enlarged and fused into larger grains. The microstructure of 1550°C sintered sample in Figure 4b shows that HA powder melted and solidly bonded together with alumina particles which led to the enhancement of strength.

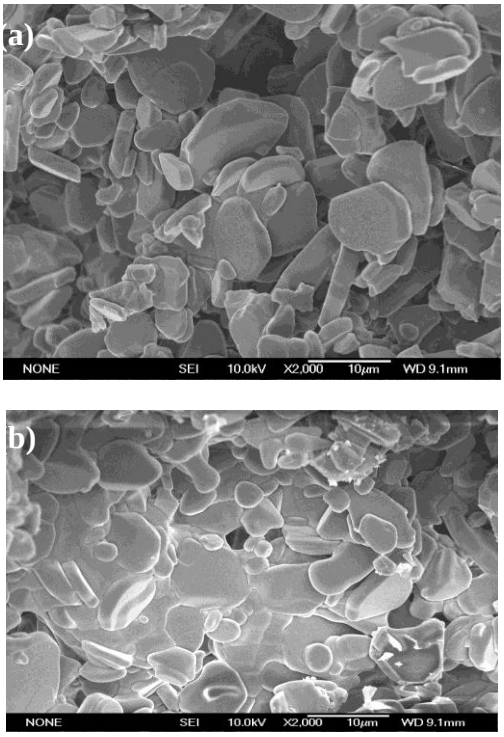


Figure 4. Micro structures of bodies after sintered at (**a**) 1350 and (b) 1550°C.

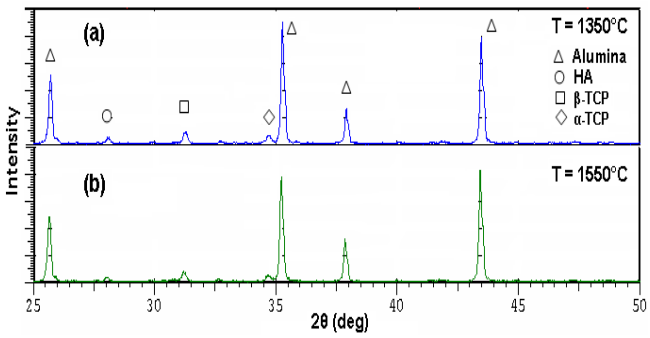


Figure 5. XRD pattern of porous alumina-HA bodies after sintered at (a) 1350 and (b) 1550ºC

Figure 5 shows XRD patterns of porous alumina-HA sintered at 1350°C (S1) and 1550°C (S4). The crystallinity of HA in the porous alumina-HA sintered at 1550° was lower than that sintered at 1350ºC. The increasing HA peak intensity is believed due to instability of HA at sintering temperatures above 1350°C, and forms decomposed phases such as α-TCP and β-TCP (Jun et al, 2003). However, Figure 4 reveals that crystallinity of TCP almost did not alter after the samples sintered at 1350 and 1550ºC. The alumina phase peaks were constant due to the sintering temperature set was still less than melting point of alumina (i.e 2072ºC). Moreover, no additional phase other than alumina, HA and β-TCP identified in the two patterns. This indicates that the sintering process does not alter the composition of the porous composite.

4 Conclusion

Porous alumina-HA composite were successfully manufactured via protein foaming-consolidation technique using egg yolk as the foaming agent. The compressive strength of sintered porous alumina-HA obtained by this method was 1 – 8 MPa, respectively. The sintered porous bodies have open, interconnected porous structure with pore size of 20-250 μm. When the sintering temperatures increased from 1200 to 1550°C, the porous bodies shrunk dramatically leading to the porosity decreasing. The grain size of samples enlarged and fused with the increasing sintering temperature, which lead to the improvement of body strength. XRD results show that crystallinity of porous bodies decreased with the increasing sintering temperatures while the phase of the bodies remains unchanged.

Acknowledgmets

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