Chapter 021

The influence of hydroxyapatite loading on protein foaming-consolidation porous alumina sintered at 1300°C

Ahmad Fadli[1, 2] and Iis Sopyan[1]
[1, 2.] Department of Manufacturing and Materials Engineering,
Faculty of Engineering – International Islamic University Malaysia
[2.] Department of Chemical Engineering, Faculty of Engineering – Riau University
✉ : fadliunri@yahoo.com; sopyan@iium.edu.my /

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Abstract. Aim of this work is to investigate the effect of hydroxyapatite (HA) on physical properties of porous alumina bodies fabricated through protein foaming-consolidation method using egg yolk as a pore creating agent. Hydrothermal derived HA powder was used as bioactive ceramic. Alumina and HA powders were mixed with yolk, starch and darvan 821 A at an adjusted mass ratio to make slurry. HA-to-alumina mass ratio were in the range of 0.0 to 0.8 w/w. 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 1,300°C for 2 h. The porous alumina-HA composites with pore size in the range of 50-500 µm and densities of 2.7 – 2.9 g cm^{-3} were obtained. Porosity of bodies decreased from 35.9 to 31.7% when HA-to-alumina mass ratio increased from 0.0 to 0.8 w/w. Compressive strength of sintered body was 0.8 MPa at 35.9% porosity and 2.9 MPa at 31.7% porosity. XRD pattern results show intensity of tricalcium phosphate (TCP) phase in bodies increased with HA loadings.

Introduction

Calcium phosphate ceramics have received much attention as potential bone graft substitute because of their biocompatibility, bioactivity and osteoconduction characteristics. The most widely used calcium phosphate-based bioceramics in bone replacement is hydroxyapatite (HA, $Ca_{10}(PO_4)_6(OH)_2$) [1]. HA also has excellent biocompatibility with hard tissues and high osteoconductivity and bioactivity despite its low degradation rate, mechanical strength and osteoconductive potential [2]. Porous HA exhibits strong bonding to the bone because the porosity and bioactivity allows the in-growth of bone tissue to achieve full integration with the living bones. Thus porous HA have been applied in many applications such as for cell loading, drug releasing agents, chromatography analysis and most extensively, for hard tissue scaffolds [3]. Porous HA has low mechanical properties, therefore normally porous HA implants cannot be heavy loaded and are used to fill only small bone defects. This is due to larger pores, strength of the implant decreases significantly [4]. The porous HA are usually very brittle and prone to fracture upon sudden impact, particularly during the healing stage. Therefore, it is desirable to develop scaffold implant materials with both reliable mechanical properties and porous structures, similar or superior to natural bones [5]. To improve the mechanical strength while maintaining the bioactivity of the scaffold, porous alumina-HA have been shown to have higher strength than the HA porous implant and exhibited a similar bioactivity and osteoconductivity property to the HA porous implant [4].

In this report, we report the effect of hydroxyapatite loading on the physical and mechanical properties of porous alumina prepared through protein foaming-consolidation method sintered at 1300ºC.

Methodology

The slurries were prepared by dispersing 10 g alumina (Sigma-Aldrich, USA) and hydrothermal derived HA powders with 3 g starch (FFM berhad, Malaysia) and 24 g yolk (freshly isolated from chicken egg (LTK berhad, Malaysia) as well as dispersant (R.T. Vanderbilt, USA) in a beaker glass. HA loading added into the slurry was 0, 2, 4, 6 and 8 g. The slurries were then mechanically stirred with rate of 150 rpm for 3 h at room temperature. Then the slurries were cast in cylindrical shape mould which has 10.75 mm in diameter and 15.10 mm in height. Subsequently, the slurries were dried in an air oven (Memmerts, 100-800 model) with temperature 180°C for 1 hour. In order to easy mould removal, castor oil was used as lubricant. The dried samples then were burned in a furnace (Protherm, PLF 160/5 model) at a rate of 10°C/min up to 600°C for 1 h for removal of the creating agent and then at rate of 2°C/min up to 1300°C for 2 h.

Electronic densitometer (Alfa Mirage, MD300S model) was used to measure the density of sintered samples. The theoretical density of fully densified alumina, 3.98 g cm^{-3} and HA, 3.14 g cm^{-3} was used as reference to calculate the total volume fraction of porosity. The crystallinity of samples was analyzed by XRD (Shimadzu Diffractometer, XRD-6000 model). The macrostructures of bodies were examined using SEM (JEOL, 5600 model). The mechanical strength of the specimens (typically 15 mm height and 10 mm diameter) was measured using a universal testing machine (Lloyd, LR10K plus model) by diametrical compression at a loading rate of 2.5 mm min^{-1}. Five specimens were used to determine the average maximum compressive strength.

Results and discussion

Protein foaming-consolidation technique has been employed for the first time to fabricate porous alumina [6]. It was found that physical properties of the porous alumina bodies obtained can be controled 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 contrrol processing condition could be provide considerably low density porous bodies and floatable on water [6].

The result of measurements for shrinkage, relative density and porosity of porous alumina-HA composite after sintered at 1300ºC is described in Table 1.

Table 1. The effect of slurry compositions on the physical properties

Sample no.	HA-to-alumina mass ratio (w/w)	Shrinkage (vol.%)	Density (g/cm^3)	Porosity (%)
1	0.0	58.8	2.55	35.9
2	0.2	61.0	2.64	33.4
3	0.4	66.7	2.65	33.1
4	0.6	67.6	2.66	32.9
5	0.8	70.5	2.71	31.7

When the HA-to-alumina mass ratio increased from 0.0 to 0.8 w/w, the shrinkage increased from 63.5 to 78.4 vol.% The melting point of HA is 1650°C and at approximately 1350°C, HA starts to decompose into highly degradable α-TCP [6]. When the composite was sintered at 1300°C, the TCP particles melted and resulted in smaller pore sizes and denser walls. Thus, the shrinkage and density increased. The density of

sintered sample was found in the range of 2.55 to 2.71 g cm^{-3}. The shrinkage occurred as the yolk and starch particles were removed, thus the shrinkage became intensive with the increasing sintering temperature.

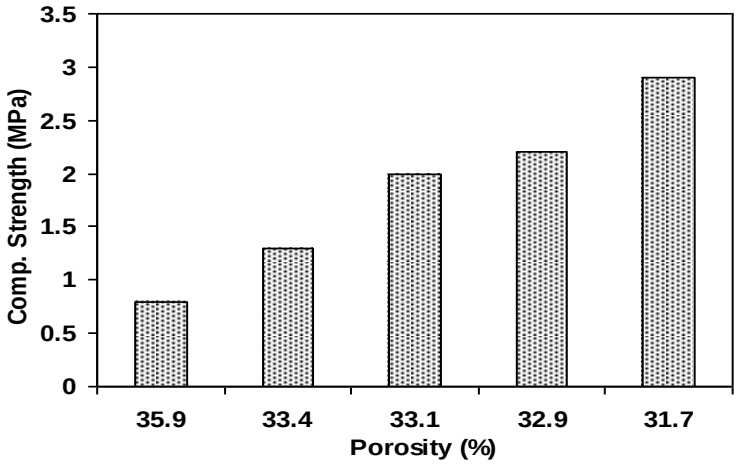

Fig. 2 Compressive strength of sintered samples as function of porosity.

The porosity decreased from 32.7 to 27.6% when the HA-to-alumina mass ratio increased from 0.0 to 0.8 w/w. The compressive strength of porous materials is strongly affected by the strength of the materials wall (struts) and the surface defects of the strut. Porosity is also considered to have a significant impact on compressive strength. The compressive strength remarkably increased from 0.8 to 2.9 MPa with the decreasing porosity from 35.9 to 31.7%. Besides the nanostructures HA powder can improve the sinterability due to higher surface energy and improves mechanical properties [7].

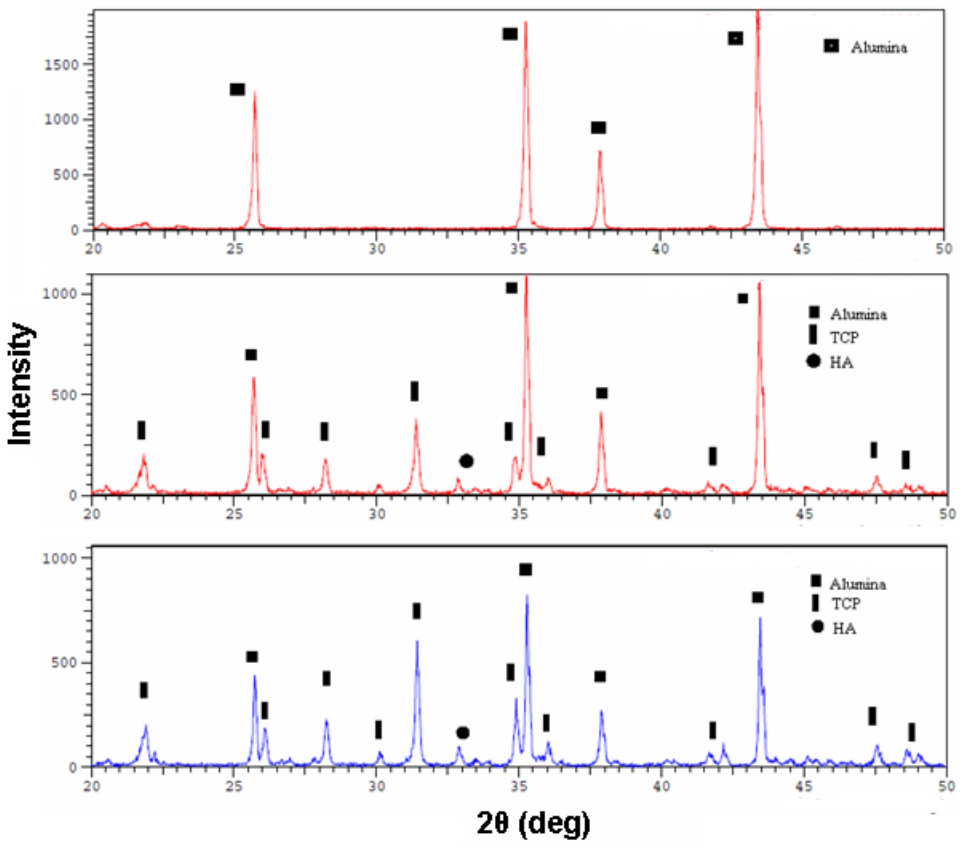

Fig. 2 XRD patterns of sample containing HA-to-alumina ratio of (a) 0, (b) 0.4 and (c) 0.8 w/w.

Fig. 2 shows the result of XRD peaks of porous alumina-HA composites prepared using slurry containing HA-to-alumina mass ratio of 0.0, 0.4 and 0.8 w/w. Sample without any HA loading shown that the alumina peak obtained at 43.4770, 35.2798, 25.7011 and 37.9037 2θ with intensity of 1051, 917, 544 and 361 cps respectively. As HA loading increase at 4 g, the strongest peak of alumina was obtained at 25.6888, 35.2679, 37.8879 and 43.4627 2θ at intensity of 255, 549, 194 and 550 cps respectively. The highest TCP peak was occurred at 31.3969 2θ at intensity of 169 cps. While HA peak was marked at 32.8733 2θ at small intensity of 36 cps. As HA loading increase at 8 g, the strongest peak of alumina was obtained at 25.7361, 35.3117, 37.9273 and 43.5085 2θ at intensity of 203, 397, 129 and 355 cps respectively. The highest TCP peak was occurred at 31.4407 2θ at intensity of 261 cps. While HA peak was marked at 32.9139 2θ at small intensity of 42 cps.

At sintering temperature above 1350°C, HA becomes unstable and forms decomposed phases such as α-TCP and β-TCP, tetracalcium phosphate and calcium oxide [8]. It is well known that the solubility of TCP is much higher than that of HA. Moreover there is a small difference among the three patterns observed and no additional phase was identified. This indicates that the sintering process does not change the composition of the porous composite. When HA-to-alumina mass ratio increased from 0.2 to 0.8 w/w, the peaks of HA and TCP become more crystalline but in a small amount of intensity due to HA as the minor composition in this porous composite.

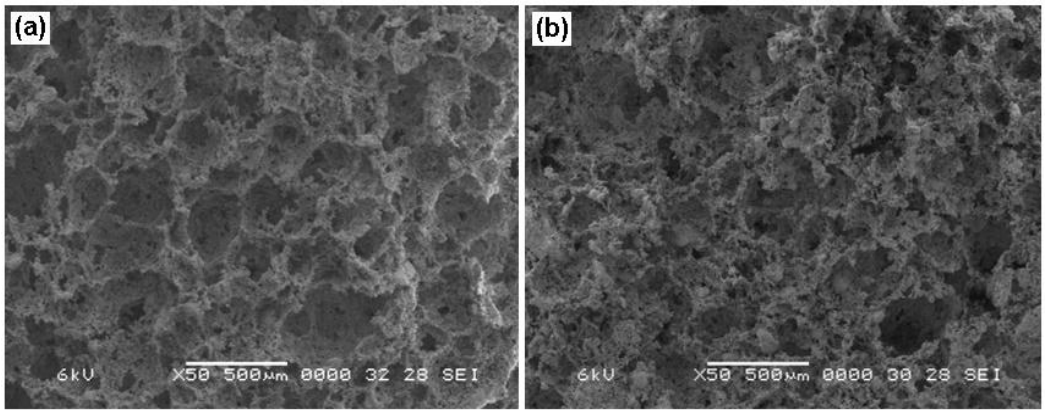

Fig. 3 SEM image of bodies with HA-to-alumina mass ratio of (a) 0.0 and (b) 0.8 w/w.

The SEM micrograph of sintered porous alumina-HA samples are shown in Fig. 3. The bodies have pore size in the range of 50 - 500 μm and completely interconnected. The pore sizes decreased when HA-to-alumina mass ratio increased thus provide a good density and strength of the porous body. The pore size of pure alumina body (sample 1) was largest thus give low in density and low mechanical properties. As the HA-to-alumina mass ratio increased from 0.0 (sample 1) to 0.8 w/w (sample 5), the pores become less interconnected with more dense and thicker pore wall and it is important factors that improve the mechanical properties of the porous sample [9].

Conclusion

The effect of HA loading on the physical properties of protein foaming-consolidation porous alumina has reported. The physical properties of the porous sample can be controlled by manipulating the HA-to-alumina mass ratio in the initial slurry. The shrinkage and density of bodies increased from 58.8 to 70.5 vol.% and 2.55 to 2.71 g cm^{-3}, respectively when the HA-to-alumina mass ratio from 0.0 to 0.8 w/w. The compressive strength obtained by this method was 0.8 MPa - 2.9 MPa with porosity between 35.9 – 31.7% and also have open, interconnected porous structure with pore size of 95-300 μm. XRD results shows that the cystallinity of TCP phase increased with the increasing HA loading.

Acknowledgements

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