Chapter 023

Porous alumina-hydroxyapatite composites via protein foaming-consolidation method: Effect of HA loading on physical properties

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Abstract. The porous alumina-hydroxyapatite (HA) composite bodies with good interconnectivity were successfully prepared via protein foaming-consolidation method. The egg yolk was used as a pore creating agent. Alumina and HA powders were mixed with yolk, starch and darvan 821 A 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 1,550°C for 2 h. The porous alumina-HA composites with pore size in the range of 50-500 µm with good interconnectivity were obtained. The densities and porosity were in the range of 2.15 – 2.48 g cm^{-3} and 36.7 – 45.8%, respectively. The increasing HA-to-alumina mass ratio in slurries from 0.4 to 0.6 w/w increased compressive strength of sintered bodies from 2.9 to 24.2 MPa. XRD pattern result shows presence of tricalcium phosphate (TCP) phase in the sintered bodies.

Introduction

Ceramic materials based on alumina are widely used in the manufacture of medical implants. Today, alumina ceramics as specified by ISO 6474 are generally approved as biomaterials for use in total joint replacement because of inertness, excellent biocompatibility and high wear resistance [1,2]. However, replacement surgery is still associated with complications. For example, in total hip replacements, loosening of the acetablar or femoral components and wear debris remain problem. The problem of loosening is attributed to bioactivity of the material at the bone prosthesis interface, and the problem of wear debris attributed to the articulating surface of the joint prosthesis [3].

Although the mechanical properties of hydroxyapatite (HA) as an implant material are not as good as those of alumina (Al), it has been reported that HA bonds to bone owing to its bioactive property. Therefore, to solve the problem of the border between alumina and bone, we developed HA coated porous alumina ceramics (HA/Al). HA/Al have high mechanical strength as well as bioactive properties [3].

Many investigators have reported HA coating on various implants, and it is known that HA coating stimulates bone formation. Youn et al. (2003) fabricated alumina porous bodies using the polyurethane sponge and the hydroxyapatite were coated onto the porous alumina substrates. This techniques resulted porous bodies with 90-75% porosity and compressive strength of up to 6 MPa [4]. Saki et al. (2009) have developed composite ceramic bioscaffold of hydroxyapatite-alumina and silicon carbide by using an organic template which is commercial polyurethane sponge with an open interconnected microporosity. It has good properties which exhibit better biodegradability, light in weight and can support osteoblast attachment and growth as well [5].

Recently, we have developed protein foaming-consolidation method to produce porous alumina ceramics [6]. Here we report porous alumina-HA composite fabricated through this method and the effect of HA loading is investigated.

Methodology

The slurries were prepared by dispersing alumina (Sigma-Aldrich, USA) and HA (Sigma-Aldrich) powders with starch (FFM berhad, Malaysia) and yolk (freshly isolated from chicken egg (LTK berhad, Malaysia) as well as dispersant (R.T. Vanderbilt, USA) in a beaker glass. The amount of dispersant added was restricted to a level to maintain the slurry flowable for casting. 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 1550°C for 2 h.

Table 1. Composition of slurries studied.

Sample no.	Alumina (g)	HA (g)	Starch (g)	Yolk (g)
R1	10	4	1.0	24
R2	10	4	4.0	24
R3	10	5	4.0	24
R4	10	6	4.0	24

*Dispersant = 1.03-5.43 g

The density of sintered samples was measured using densitometer (Alfa Mirage, MD300S model). 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

Porous alumina-HA composite body has been fabricated using protein foaming-consolidation method [6]. In order to obtain the desire result of high compressive strength, high density as well as suitable porosity, slurry with optimum amount of alumina, HA, yolk and dispersant agent should be obtained. This means that the concentration of the slurry must not be too high; or otherwise it will result in difficulty in moulding process. But if the concentration of the slurry is too low, the number of alumina-HA particles will be less and it will affect the apparent density, compressive strength and crystallinity of the prepared sample (too fragile and may fracture). Moreover stirring time of alumina-HA slurry also affect the slurry due to the fact that longer stirring time will yield in higher apparent density and higher compressive strength. The stirring time of the slurry was set for 3 hours for all samples. The stirring time was not set be more than 3 hours because it will make the slurry become too viscous thus will affect during moulding process. Moreover, starch was added in the slurry in order to get good shape of porous body.

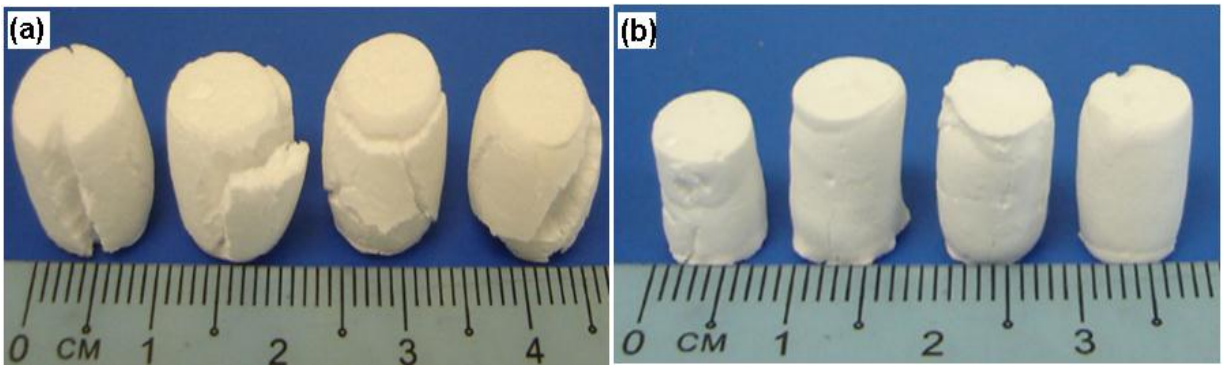

Fig. 1 Sintered porous alumina-HA composite bodies (a) without and (b) with adding starch.

Fig. 1a shows that before adding starch into the slurry, the porous body after sintering process was not good in shape and crack appeared. But after adding the starch (Fig. 1b), the porous body after sintering process was good in shape and no crack appeared. Thus the starch was being added to the slurry in order to get good shape of porous alumina-HA composite body.

Table 2. The effect of slurry compositions on the physical properties

Sample no.	HA (g)	Starch (g)	Shrinkage (vol.%)	Density (g/cm^3)	Porosity (%)	Compressive Strength (MPa)	Young's Modulus (MPa)
R1	4.0	1.0	68.8	2.48	37.5	0.2	324.2
R2	4.0	4.0	76.7	2.39	36.7	2.9	241.8
R3	5.0	4.0	76.5	2.15	45.8	4.2	730.0
R4	6.0	4.0	89.3	2.31	41.8	24.2	838.8

The result for shrinkage, apparent density, relative density and porosity for sample R1 to R4 is shown in Table 2. The volume shrinkage of sintered sample increased from 76.7 % to 89.3% as the amount of HA powder increase from 4 to 6 g. The shrinkage of the sintered body occurred as the yolks were removed and the particles, which were initially packed loosely, approached and contacted. The effect of starch addition on density and porosity can be seen where at sample R1 the apparent density of the sample is 2.48 g/cm^3 where the porosity obtained is 37.5%. Whereas when starch is increase to 4 g at sample R2, the apparent density obtained is 2.39 g/cm^3 and its porosity is 36.7% which is much higher than sample R1. This is because the starch is act as pore generation in this porous sample. From the result obtained, sample 5 with highest amount of HA addition which is 5 gram result in higher apparent density which is 2.15 g/cm^3 and also result in lower percentage of porosity which is 45.8%. As the amount of HA powder increased from 5 to 8 gram, the apparent density increased and the porosity decreased from 2.15 g/cm^3 to 2.31 g/cm^3 and from 45.8% to 41.8% respectively. From this result it is shown that as HA powder increase, the porosity of the sintered sample decreased.

When starch is increased from 1 to 4 gram at sample R2, the compressive strength obtained is 2.86 which it is higher than sample R1 with compressive strength only 0.2 MPa. This indicates that the addition of starch imparts of increasing of compressive strength as well as provides high porosity of the porous sample. In addition, sample 4 which contain 4 gram amount of HA powder posses the highest compressive strength which is 24.2 MPa, compared to sample R2 where the compressive strength obtained is 2.9 MPa. As HA increased from 4 to 6 gram, compressive strength of the sintered sample also increased. As compressive

strength increased, the Young's modulus also increases from 241.8 MPa to 838.8 MPa. It is means sample R4 tends to resist external force or pressure applied before fracture better than sample R1, R2 and R3.

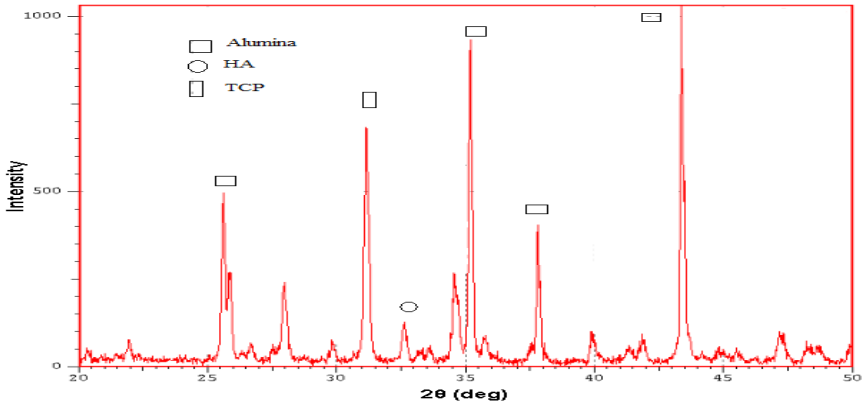

Fig. 2 XRD pattern of sintered body of sample R4.

Fig. 2 shows the XRD peaks for sintered sample containing 6 g HA loading (sample R4). The alumina, HA and TCP phases were detected in the sample. Sintering of HA is complicated by the fact that HA is hydrated phase that decomposes to anhydrous calcium phosphates such as TCP at ~1200 – 1450˚C. Decomposition results from dehydroxylation beyond a critical point. For temperatures below the critical point (1300˚C), the HA crystal structure is retained despite dehydroxylation, and then the HA rehydrates on cooling. If the critical point is exceeded, complete and irreversible dehydroxylation occurs, resulting in collapse of the HA structure and decomposition. After the critical point α-TCP and β-TCP are often formed [7,8].

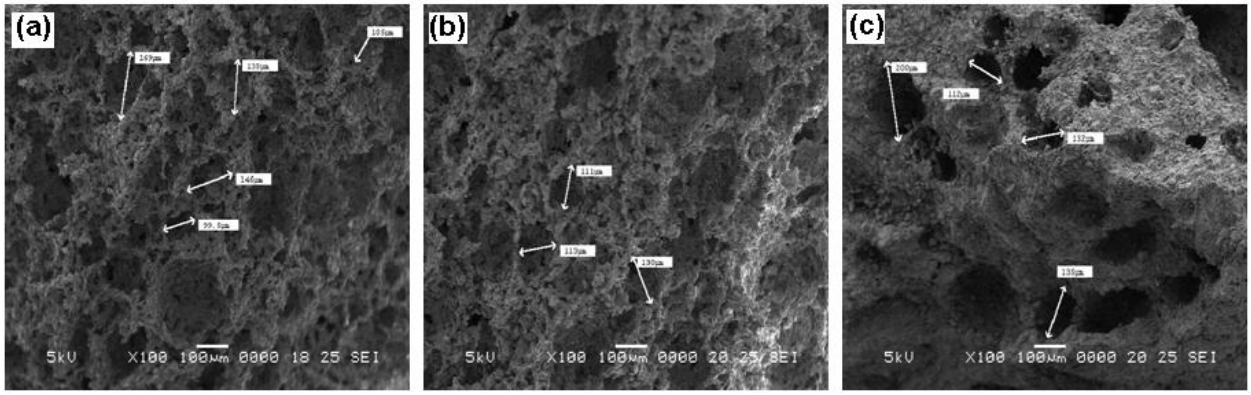

Fig. 3 SEM image of (a) R1 (b) R3 and (b) R4 sintered samples.

The SEM micrograph of sintered porous alumina-HA samples are shown in the Fig. 3. The starch addition into the initial slurry resulted in lower porosity and smaller pore size as Fig. 3b shows. It can be explained that the addition of starch in the slurry increase viscosity, thus foaming capacity of the slurry

decrease and reducing the pore size. On the other hand, slurry without less starch content has low viscosity and bigger pore size would be generated eventually (Fig. 3a).

The increasing HA loading provided bigger pores and thicker struts (Fig. 3c). The pores have interconnectivity with average pore size ranging from 30-200 μm. In contrast, the smaller pore sizes were observed at lower HA loading (Fig. 3b).The morphology of the porous body contain very large sizes of porosity thus give low in density and low mechanical properties. As the HA loading increase from 4 g to 6 g, the pores become denser and thicker pore wall and this shows that it is important factors that improve the mechanical properties of the porous sample. Since the higher density usually leads to higher mechanical strength, a balance between porosity and density for a porous body must be achieved for specific application. Other than that, an interconnected open pore structure is also needed for a material to allow biomolecular and degrade substances to freely flow into and out the material.

In the figure above, it can be seen that there are variety of pore size. The large pores are due to the foaming consolidation while the small pores are the effect of starch. There are starch particles inside the green body before it is sintered. During the sintering process, the starch will be burned out at temperature of 600ºC which the leads to the formation of small pores inside the sintered bodies.

Conclusions

Porous alumina-hydroxyapatite composite was successfully fabricated by using protein foaming consolidation method. The physical properties of the porous sample can be controlled by manipulating the HA-to-alumina mass ratio in the slurry. The addition of starch into slurry resulted in bigger pore size and avoided the porous bodies from cracks. The shrinkage bodies increased from 76.7 to 89.3 vol.% when the HA-to-alumina mass ratio from 0.4 to 0.6 w/w. The compressive strength obtained by this method was 0.2 MPa - 24.2 MPa with porosity between 37.5 – 45.8% and also have open, interconnected porous structure with pore size of 95-300 μm. The TCP phase was detected in porous body after sintered at 1550ºC.

Acknowledgements

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