Chapter 020

Investigation of the Effect of Starch Addition on Protein Foaming-Consolidation Porous Alumina Containing Hydroxyapatite Nanopowder

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Abstract. The object of this study was to produce porous alumina-hydroxyapatite (HA) composite bodies via protein foaming-consolidation method. 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 temperature of 1400°C for 2 h. The starch addition was selected as the variable factor. The density of porous bodies increased from 2.40 to 2.81 g cm^{-3} when starch amount increased from 1.0 to 3.0 g. The compressive strength was found 18.0 MPa at 38.3% porosity and it increased to 102.3 at 29.1% porosity. The pores of 50-600 µm size illustrating the rough enough internal surfaces, were obtained for potential use in hard tissue engineering.

Introduction

Hydroxyapatite (HA) with the chemical formula $Ca_{10}(PO_4)_6(OH)_2$ has been widely used extensively in medicine and dentistry for implant fabrication because of its biocompability with human bone and teeth [1]. Porous hydroxyapatite exhibit strong bonding to the bone where the pores provide a mechanical interlock leading to affirm fixation of the material. Bone tissue can growth well into the pores, increasing the strength of the HA implant. The minimum pore size required to enable ingrowth of the surrounding bone together with blood supply is about 100- 150 micron meter while for colonization of osteoblast in the pores, fibrovascular ingrowh and the deposition of new bone the pore size should be 200- 500 micron meter [2]. Porous HA cannot be heavy loaded because it usually possesses very low strength and toughness as its porosity increase. Compression strength of porous human bones vary between 2-12 MPa for cancellous bone and between 100-230 MPa for cortical bone while porous HA only have mechanical strength as low as 1.3-16 MPa [3].

On the other hand, porous alumina is relatively strong and tough, but has problem of biological inertness to bone tissue [4]. Therefore, it is interesting to manufacture alumina-hydroxyapatite composite of porous shape.

In a previous study, porous alumina ceramics were fabricated by a protein foaming-consolidation method and the control in slurry composition and drying processes resulted in the porosity of 40 – 71% [5]. In this paper, porous alumina-HA porous bodies were fabricated using this method and the effect of starch addition is investigated.

Methodology

The porous alumina-HA porous bodies were prepared through protein foaming-consolidation method. The slurry was composed of 10 g alumina powder (Sigma-Aldrich, USA), 8 g HA powder (Sigma-Aldrich, USA), starch (FFM berhad, Malaysia) and 24 g yolk (LTK berhad, Malaysia) in a beaker glass. Amount of starch added into slurry was 1, 2 and 3 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 and 1400˚C for 2 h.

An 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 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. The crystallinity of samples was analyzed by XRD (Shimadzu Diffractometer, XRD-6000 model). The macrostructures of bodies were examined using SEM (JEOL, 5600 model).

Results and discussion

The variation of slurry viscosity as a function of starch amount with respect to shear rate is shown in Fig. 1. It can be seen that the viscosity value of all slurries decreased as the shear rates increased. A viscosity of as high as 61.8 Pa.s was observed for the slurry with 3 g starch agent but it decreased significantly to 22.68 Pa.s when 3 g starch was added. The viscosity value of slurry with 1 g starch agent at high shear rate (47.35 s^{-1}) was in the range of 10.6 – 11.2 Pa.s and it is easily flow for casting process. On the other hand the slurries with 3 g dispersant agent cannot naturally flow into the moulding which then gives some layers to the body when it is moulded.

The measured flow curves for fresh slurries were fitted with Power law model, $\eta = k\,\gamma^{n-1}$ where η is the viscosity of the slurry, γ is the applied shear rate, *k* ad n are the consistency factor and non-Newtonian index [6]. The n value that closed to 1.0 indicate the behaviour closer to Newtonian while the n value that closed to 0.0 indicate the behaviour closer to non-Newtonian behaviour. From the *n* value in Table 1 and graph plotted in Fig. 1, it shows that the slurry changed the behaviour from Newtonian to non-Newtonian as the starch content increased. It is because, as the starch loading increase, the *n* value is decreasing. Highly shear thinning slurries with a strong inter-particle network show a rapid decrease in viscosity with an increase in shear rate, corresponding to a lower value on non-Newtonian index, *n*. The relation between shear stress and shear rate is different. Constant coefficient of viscosity cannot be defined. The viscosity change when the slurries stirred, shaken or otherwise agitated. The slurries with weak or no inter-particle network become closer to the Newtonian behaviour with *n* values approaching 1.0 [7].

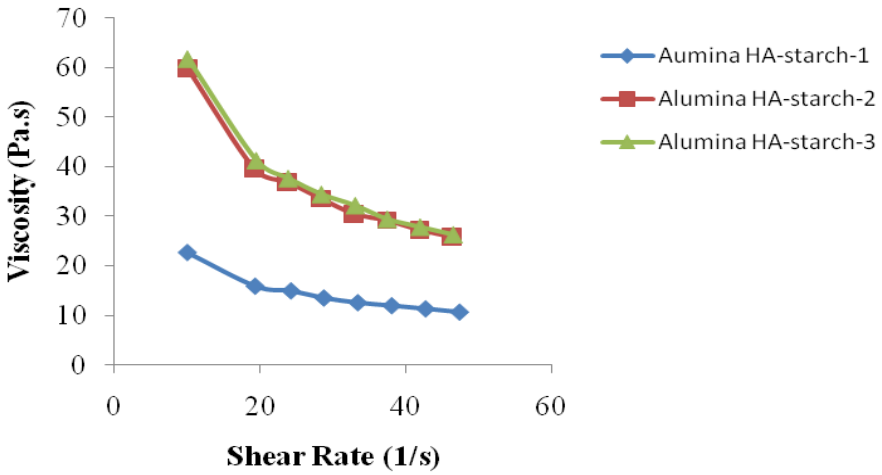

Fig. 1 Viscosity of slurries at various amount of starch loading.

Table 1 The parameters *n* ad *k* of slurry

Starch loading (g)	*k*	*n*
1	67.538	0.5222
2	204.139	0.4591
3	217.5655	0.4491

The dimension of the green body was measured before and after sintering, there is a reduction in their size. After the sintering process, the diameter and height of the body is smaller than before sintering. It can be shown in Fig. 2a and b:

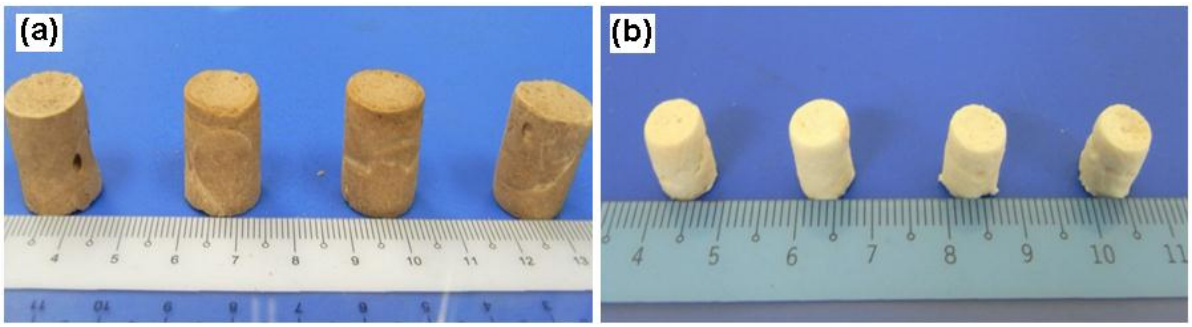

Fig. 2 Porous alumina-HA (a) before and (b) after sintering process.

Table 2. The effect of starch loading on the physical properties

Starch amount (w/w)	Shrinkage (vol.%)	Density (g/cm^3)	Porosity (%)	Compressive strength (MPa)
1.0	86.7	2.81	29.1	102.3
2.0	86.9	2.65	33.0	64.3
3.0	83.4	2.40	38.3	18.0

Measurement of shrinkage, density, porosity and compressive strength of all the samples are presented in Table 2. The samples show high shrinkage after sintering with value of more than 80%. They are not

much different in the shrinkage as the amount of starch added is different. It shows that as the amount of starch added increases, the average shrinkage is decrease a little bit. The starch loading is inversely proportional to the apparent density. As the amount of starch composition added is increase, the apparent density will decrease. In contrast to others, the porosity will increase when the starch loading increase. The porosity calculated from the dimension measured was vary from 29.1% up to 38.3%.

The compressive strength of porous alumina-HA bodies reduced from 102.3 MPa to 18.0 MPa when starch loading increased from 1 g to 3 g. This result indicates that the addition of starch imparts of decreasing in density thus will give lower value of compressive strength. It is due to bodies that have high density is lower in porosity which means they contain less pores which the lead to high in mechanical strength.

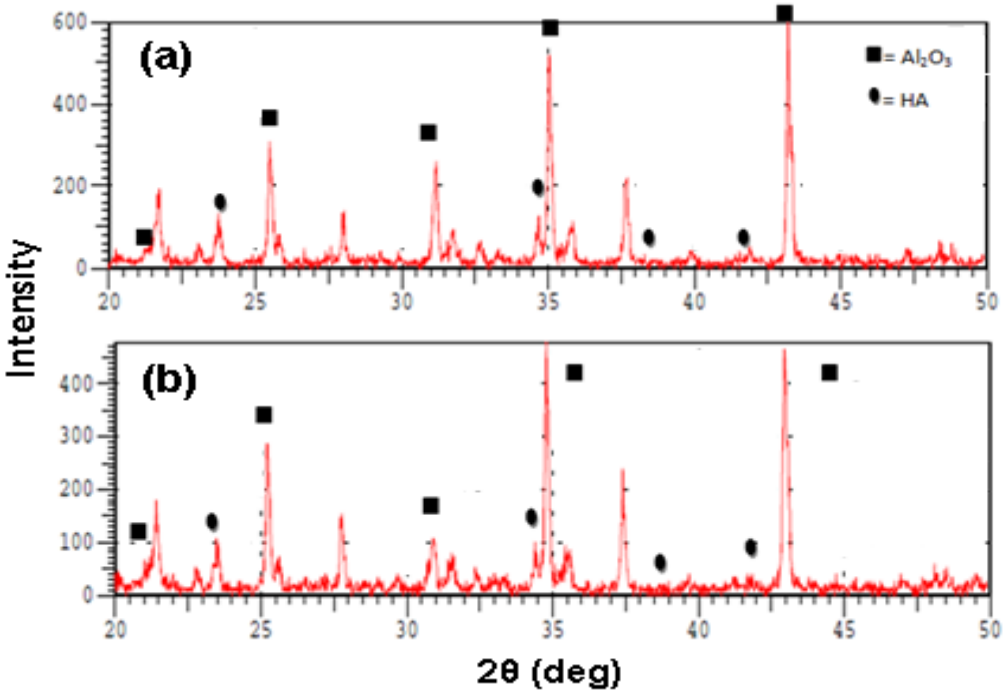

Fig. 3 XRD patterns of sintered bodies prepared using (a) 1 and (b) 2 g starch amounts.

Fig. 3 shows XRD patterns of sintered bodies prepared from slurry containing 1 g and 2 g starch loadings. It has shown that all different starch composition, the peaks produced are the same. Alumina and HA phases were identified in the two patterns and the three strongest peaks obtained were at 43.0381, 34.8353 and 25.2366 2θ for all samples. After sintering process, the composition of the porous alumina-HA become similar. Different amount of starch will not give any effect to the final sample of porous alumina-HA. It is because, when the sample is heated up to 600°C in sintering process, all of the yolk and starch were completely burned out from the samples for creating agent. That is the reason why, they give same composition in the final product even though they are different in starch composition at the beginning.

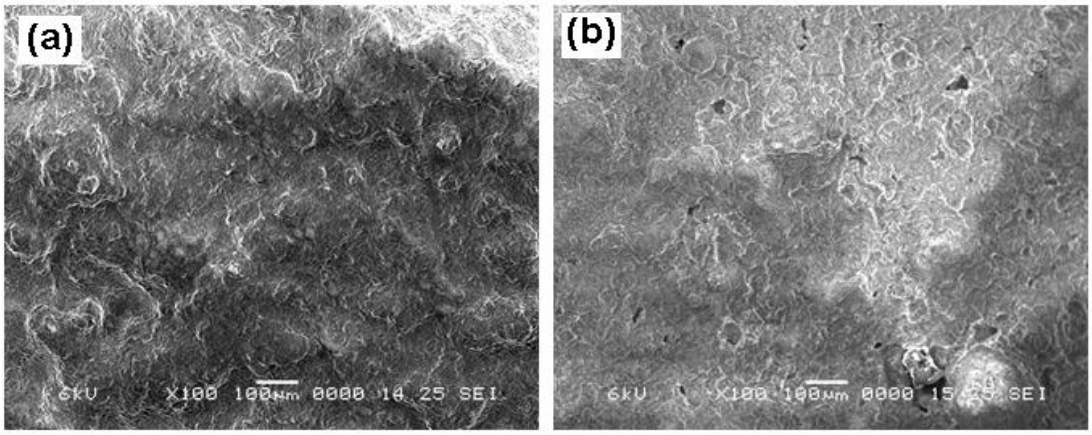

Fig. 4 SEM images of sintered bodies containing (a) 2 and (b) 3 g starch loading

Fig. 4 shows the surface morphology of the porous alumina-HA containing 2 g and 3 g starch loadings. The purpose of the SEM analysis is to see the pore size of the samples and also the interconnection between one pore to another. The shape of the samples also can be observed by using this test. However, the pore size in this sample cannot be observed very clearly because the amount of HA is too much so that, it cover the surface of alumina. That is the reason why, the microstructure look likes the dense structure, not a pores one. Therefore, the amount of alumina used need to be added more so that, the pore size can be observed.

Conclusion

The effect of starch loading on the physical and mechanical properties of porous alumina-HA prepared by protein foaming consolidation method was investigated. The density of bodies decreased from 2.81 to 2.40 g cm^{-3}, when the starch loading increased 1.0 to 3.0 w/w. The compressive strength obtained by this method was 102.3 MPa-18.0 MPa with porosity between 29.1-38.3%. Alumina and HA phases were identified in the sintered samples and the three strongest peaks obtained were at 43.0381, 34.8353 and 25.2366 2θ. The phases of porous alumina-HA composite remain unchanged after high temperature sintering.

Acknowledgements

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