Chapter 018

Effect of Dispersant on Protein Foaming-consolidation Porous Alumina Containing Hydrothermal Derived Hydroxyapatite Nanopowder

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Abstract. Present paper reports the effect of dispersant loading on physical properties of porous alumina-hydroxyapatite (HA) composite bodies fabricated using protein foaming-consolidation method. 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. 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 1400°C for 2 h. The porous alumina-HA composites with pore size in the range of 50-500 µm and densities of 2.23 – 2.83 g cm^{-3} were obtained. Porosity of bodies decreased from 43.9 to 28.6% when dispersant amount increased from 0 to 7.0 g. The compressive strength of sintered bodies was found in the range of 20.3 to 104.8 MPa showing depends on porosity.

Introduction

Orthopaedic implants become an important thing in the biomedical implant market due to all of the problems arise in the medicine today. It is expected to increase 15-18% annually which will lead to market duplication [1]. Metals, polymers and ceramics are the candidate materials for application of bone graft [2]. Calcium phosphate is used in implantation because it can initiate a rapid biological response and able to improve the adhesion between bone and implant. Calcium phosphate also will provide scaffold for bone growth. It has been widely used as an alternative to these biological grafts in various types of bone surgery. Because of its good biocompability, bioactivity and osteoconductivity, calcium phosphate gets more attention to be applied as bone graft. The main constituent of bones from calcium phosphate is hydroxyapatite, ($Ca_{10}(PO_4)_6(OH)_2$) [1]. However, due to its poor mechanical properties, HA ceramics cannot be used for heavy loading application, but most commonly used in bone graft substitution and coating on metallic implants.

Porous HA exhibits strong bonding to the bone where the pores provide a mechanical interlock leading to a firm fixation of the material. However, too many or too large pores will reduce the strength of implant significantly. That is why, HA can only be used for small bone defects. Porous volume and interconnection between pores and size will affect the characteristics of development bioceramics [3]. To improve the mechanical strength while maintaining the bioactivity of the scaffold, porous alumina-hydroxyapatite have been shown to have higher strength than the HA porous implant. It will exhibit implant that enables positive

biological or chemical material connections [4]. 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 [5].

In this paper, we report the effect of dispersant on porous alumina-HA composites fabricated using protein foaming-consolidation method.

Methodology

The green body sample was prepared by dispersing 10 g alumina (Sigma-Aldrich, USA) and 8 g 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. Dispersant amount was adjusted in the range of 0.0 – 7.0 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 1400°C for 2 h.

Foaming capacity was measured based on increasing volume of slurry as a function of drying time. The rheological behaviour of slurries was determined using a Rheometer (Thermo-Haake, VT 550 model). 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

Fig. 1 shows the viscosity of slurries at various dispersant agents loading after it was stirred at 150 rpm for 3 hours. It can be seen that the viscosity value of all slurries decreased as the shear rates increased. A viscosity of as high as 50.07 Pa.s was observed for the slurry with 1 g dispersant agent but it decreased significantly to 13.28 Pa.s when 5 g dispersant agent was added. The viscosity value of all slurries decreased as the shear rates increased. However, it can be seen that even though the viscosity of slurries with 1 g dispersant agent is decreasing as the shear rate increased, it is still too high to be used in moulding. The viscosity value of slurry with 7 g dispersant agent at high shear rate (600 s^{-1}) was in the range of 1.8 – 2.0 Pa.s and it is suitable for casting process.

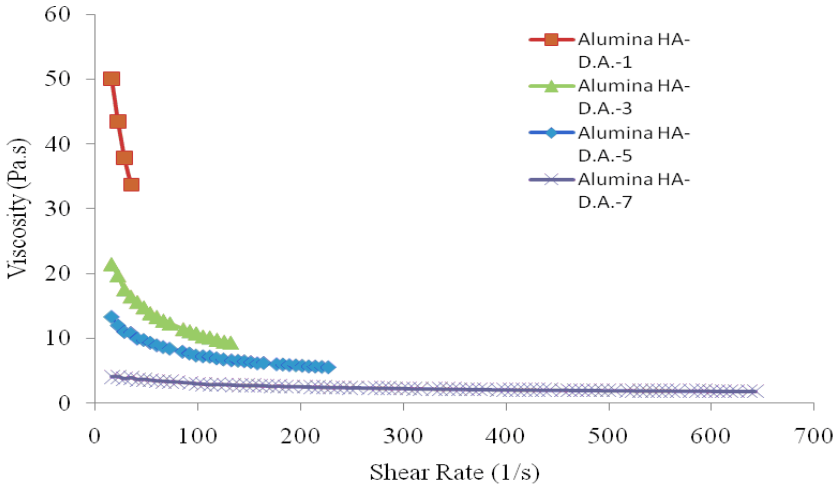

Fig. 1 The viscosity of slurries at various dispersat loadings.

Fig. 2 shows the effect of dispersant agent loaded on volume increase of slurry at temperature of 180ºC. Generally, foaming of slurry took place in three stages: pre-heating, foaming and stabilizing. In the first stage, the structural properties of protein were induced by heating which leads to change its functional properties without increasing slurry volume. Foaming stage with strongly increased until reaches a maximum value. The foaming capacity increased as the amount of dispersant agent loading in slurry increased. The volume increased in the range of 1.8 to 2.2 v/v. This is due to the dispersant molecule that will decrease the viscosity of slurry as shows in Fig. 1 and accelerate transfer proteins from interior of the slurry towards the newly created surface which then decreasing the surface tensions and increasing the foaming capacity.

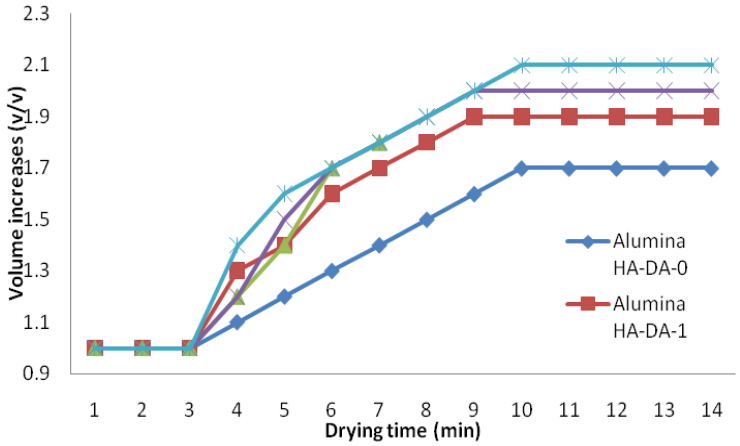

Fig. 2 Foaming capacity of slurry during drying process.

In a period of drying time, the surface tension minimal value, hence the foaming capacity keeps steady and stable. This stability is related to the decrease of foam volume with time. It is found out that the green body dried would be collapse if it is dried less than 9 minutes. This is because the green body is still in the foaming process which is not yet stable (foaming stage) unless the drying time is more than 9 minutes (stabilizing stage) as Fig. 2 shows.

The results for shrinkage, relative density and porosity for porous alumina-HA composite at sintering temperature of 1400ºC are shown in Table 1. It shows that the body without dispersant loading gives the lowest shrinkage of 78.8% and the highest shrinkage of 89.9% for body of 7 g dispersant.

Table 1. The effect of dispersant loading on the physical properties

Sample no.	Dispersant loading (g)	Shrinkage (vol.%)	Density (g/cm^3)	Porosity (%)	Compressive strength (MPa)
1	0.0	78.8	2.23	43.9	20.3
2	1.0	85.9	2.35	40.8	45.5
3	3.0	87.9	2.62	33.8	48.4
4	5.0	87.2	2.79	29.6	65.9
5	7.0	89.9	2.83	28.6	104.8

By referring to Table 1, the dispersant loading is proportional to the apparent density. As the amount of dispersant loading increase, the apparent density also will increase which then directly affected to the value of relative density. In contrast to relative density, the value of porosity decreases when the dispersant loading increases. The porosity calculated from the dimension measured was varied from 28.6% up to 43.9%.

When dispersant loading increase from 0 g to 7 g, the compressive strength obtained increased from 20.3 MPa to 104.8 MPa. This result indicates that the addition of dispersant agent imparts of increasing in density thus will give value of compressive strength. Moreover, the value of compressive strength is related to the porosity of the bodies. When the sample has low porosity, it will give high compressive strength. The compressive strength of bodies is inversely proportional to its porosity. The microstructures of each body under SEM in Fig. 5 show that the pores sizes become smaller with adding dispersant loading. That is why the mechanical strength become higher as more dispersant is loading into the bodies.

Fig. 4 shows the XRD peaks of sintered alumina-HA composite bodies at different dispersant loadings. It shows that after sintering process, the composition of the porous alumina-HA become similar. Different amount of dispersant agent 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 dispersant agent 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 dispersant agent at the beginning. The three strongest peaks obtained were at 43.0381, 34.8353 and 25.2366 2θ for all samples.

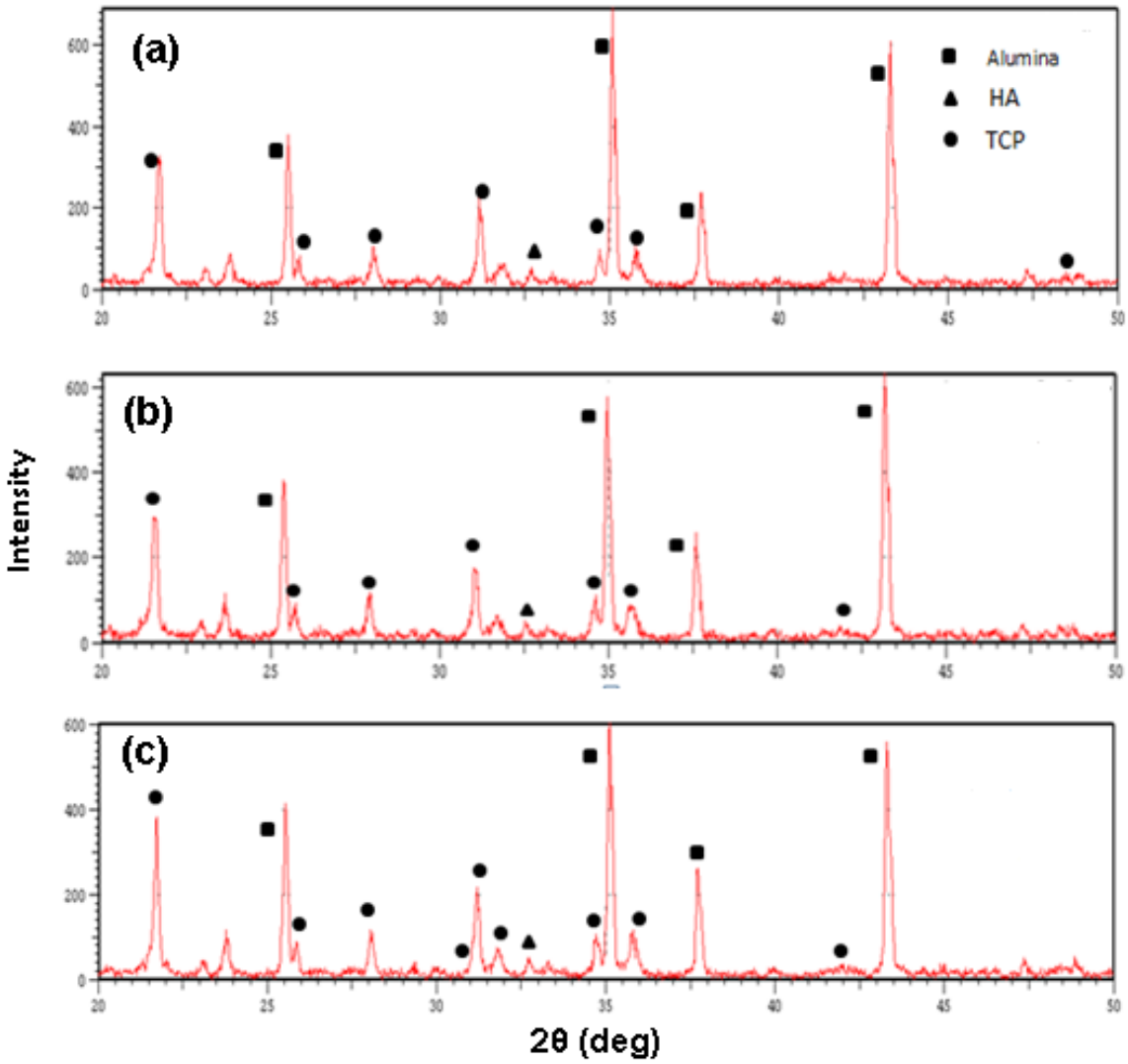

Fig. 4 XRD patterns of sintered body prepared using (a) 0, (b) 3 and (c) 7 g dispersant agents

The SEM micrograph of sintered porous alumina-HA samples are shown in the Fig. 5. The pores were spherical in shape with pore size in the range of 50 – 600 µm. As dispersant loading increase, the pore sizes of sintered body decrease thus provide a good density and strength of the body. The addition of yolk and starch in the slurry were used to provide porosity since they can be act as pores generation and good consolidator or binders. As the dispersant loading increase from 1 g to 7 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.

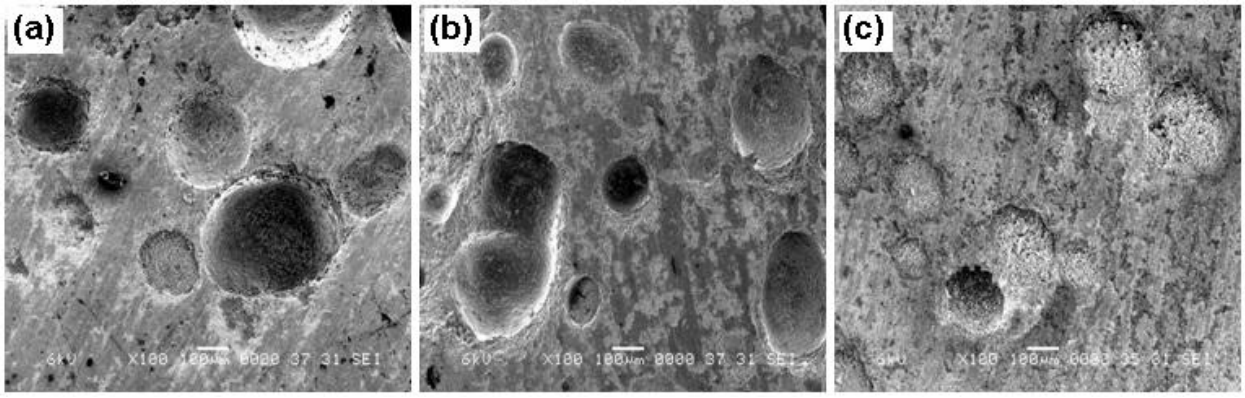

Fig. 5 SEM image of sintered body containing (a) 1, (b) 3 and (c) 7 g dispersant loading.

Fig. 5 also shows that there are varieties of pore size in the bodies. 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.

Summary

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 dispersant in the slurry. The shrinkage and density of bodies increased from 78.8 to 89.9 vol.% and 2.23 to 2.83 g cm^{-3}, respectively when the dispersant amount from 0.0 to 7.0 g. The compressive strength obtained by this method was 20.3 MPa-104.8 MPa with porosity between 28.6-43.9% and the pore size in the range of 50-600 μm.

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