

Preparation and properties of porous calcium phosphate

Syed Nuzul Fadzli Syed Adam¹, Ahmad Fauzi Mohd Noor

¹*School of Materials Engineering, Universiti Malaysia Perlis (UniMAP),
02600 Arau, Perlis.*

²*School of Material and Mineral Resources Engineering (USM) 14300 Nibong Tebal,
Penang, Malaysia.*

ABSTRACT

In this study, preparation of porous calcium phosphate was involved the addition of sodium di-hydrogen phosphate, NaH_2PO_4 and di-sodium hydrogen phosphate, Na_2HPO_4 into the raw calcium phosphate powder. The sodium hydrogen phosphates salt was act as the porosity agent for the bio-ceramic samples preparation. This method using sodium phosphates salt produced samples with 20-70% porosities. After sintering the sample above 700°C with 4 hours soaking time, results showed that open-pores structure in the range of 1 to $400\mu\text{m}$ in size were obtained. The pores structure and sizes were depending on the percent addition of the additive and the level of sintering temperature. The compressive strength of porous samples was approximately ranging between 14.38 to 103.42 MPa.

Keywords: *Porous material, porous ceramic, bio-ceramic, biomaterial, calcium phosphate, porosity agent, sintering aid.*

INTRODUCTION

Ceramics are becoming increasingly useful to the medical world. Surgeons are using bio-ceramic materials for repair and replacement of human hips, knees, and other body parts. When used in the human body as implants or even as coatings to metal replacements, ceramic materials can stimulate bone growth, promote tissue formation and provide protection from the immune system [1]. The presence of pores throughout the material gives it the potential for vascularity to develop and for bone to penetrate. A minimum pore size of 100 to $150\mu\text{m}$ has been found to be necessary for in-growth of fully healthy bone, though good interconnectivity of the pores is also an important requirement [3]

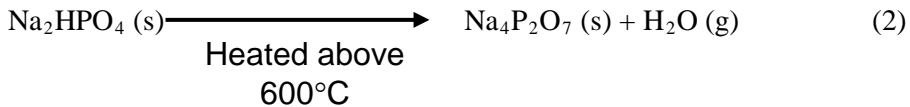
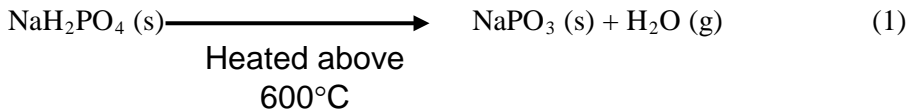
EXPERIMENT METHODOLOGY

The porous specimen preparing process consists of mixing, drying, compacting, and sintering stages. The calcium phosphate powders were first mixed with 5% and 10% of Sodium Dihydrogen Phosphate, NaH_2PO_4 and Disodium Hydrogen Phosphate, Na_2HPO_4 in a ball milling for 30 minutes. The weight ratios of calcium phosphate powders to the amount of calcium phosphate were calculated to obtain defined porosities of approximately 20-70% in the sintered compact. Then the mixtures were uniaxially pressed at 200MPa into spherical shape with 20mm in diameter. Finally, the samples prepared were sintered between 700, 900 and 1100 degrees with $10^\circ\text{C}/\text{min}$ of heating rate in muffle furnace for 4 hours. The pore morphology and microstructure of samples were examined under Scanning Electron Microscope (SEM). The compression test of the specimens was conducted using Instron testing machine meanwhile density and porosity analysis were carried out using porosimeter measurement.

RESULTS AND DISCUSSION

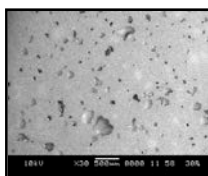
Effect of Phosphates Salt

The addition of sodium phosphates salt and was act as the porosity agent to the calcium phosphate samples. Basically, both of Sodium Hydrogen Phosphate produced water vapors and bubbles when heated to the temperature above 600°C as shown in equation 1 and 2. The water vapors were responsible of creating open pore structures in calcium phosphate sample. The typical formulas are shown below:

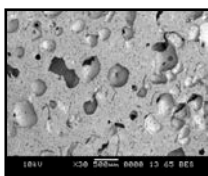


Formation of pores in the calcium phosphate samples by the NaH_2PO_4 were attributed to the evolution of water vapor upon heating. Meanwhile the Na_2HPO_4 was used as the sintering aid. On heating, Na_2HPO_4 produces $\text{Na}_4\text{P}_2\text{O}_7$ (Tetrasodium pyrophosphate), which is more effective for sintering due to its simple chemical nature. On the other hand, NaH_2PO_4 produces $(\text{NaPO}_3)_n$ which is polymeric and is weak sintering aid but a good bonding agent.

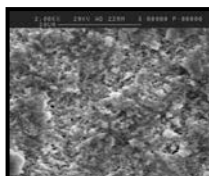
Porous microstructure observation



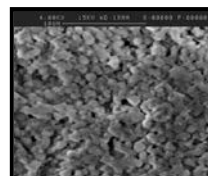
1(a) Image 30x



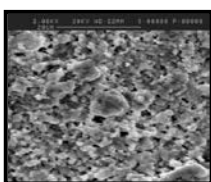
1(b) Image 30x



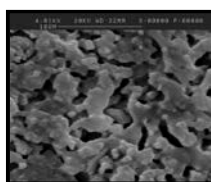
2(a) Image 2000x



2(b) Image 4000x



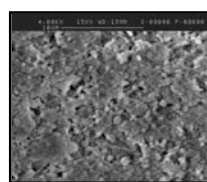
3(a) Image 2000x



3(b) Image 4000x



4(a) Image 4000x



4(b) Image 4000x

Figure 1(a)-(b): microstructure image of sample with 10% and 20% phosphate salt respectively after sintering at 700°C

Figure 2(a)-(b) and 3(a)-(b): microstructure image of sample with 10% and 20% phosphate salt respectively after sintering at 900°C

Figure 4(a)-(b): microstructure image of sample with 10% and 20% phosphate salt respectively after sintering at 1100°C

Figure 1(a) and (b) shows the surface image of porous calcium phosphate sample which is added with 10% and 20% NaH_2PO_4 respectively after sintering at 700°C. The sample with 20% NaH_2PO_4 showed better open pore formation and larger pore size compared to the sample with only 10% addition of the salt. This is due to more formation of water vapors often the sintering process and furthermore creating more pore structures. The size of pore was determined to be in the range of 10 to 100 μm , and in some instances pores of 100 to 400 μm were also observed.

Image of porous calcium phosphate sample with 10% and 20% NaH_2PO_4 fired at 900°C are shown in figure 2(a)-(b) and figure 3(a)-(b) respectively. The figures show the pores are very fine and many in numbers. Interestingly, the pores are also interconnected, particularly when 10 and 20% of the sodium hydrogen phosphate is used. It can also be observed that using 20% NaH_2PO_4 produce better pore shapes and sizes, and being more interconnected. Better formation of pores by the 20% NaH_2PO_4 must be attributed to the evolution of more water vapor upon heating. The open pores created in this sample were only visible at much higher

magnification; from 2000x. The size of pore was determined to be in the range of only 1 to 5µm.

The surface image of sample with 10% and 20% NaH₂PO₄ fired at 1100°C is showed in figure 4 (a) and (b) respectively. This sample showed very fine pores and visibly became dense structure compared to the previous sample which is sintered at 700° and 900°C. The pores images are not clearly visible even under 4000x magnification. This is due to the very high sintering temperature. It also shows that, by increasing the sample sintering temperature while at the same time remained the content of sodium hydrogen phosphate at 10 and 20%, the pore sizes were become smaller and the open cell structure was getting closely dense. The high sintering temperatures tends to densify the sample and reduced the pores size and eliminated any void in the sample by packing the calcium phosphate particles closely together often the sintering stage.

Density and porosity measurement

The table 1 below shows the reading values of bulk density and percent of apparent porosity for six different samples according to the amount of sodium hydrogen phosphate added and sintering temperature applied. These density and porosity values were related to the sintering temperatures and can be summarized in figure 5 and 6. Bulk density of the samples is the density of calcium phosphate powder plus the pores entrapped. Figure 5 shows the bulk density of each sample at different sintering temperature. It shows that as the sintering temperature increased, the bulk densities of samples were also increased.

Table 1. The results for sample density and porosity

Sample	Bulk density gm/cm ³	Apparent porosity (%)
10% NaH ₂ PO ₄ fired at 700°C	1.25	68.54
20% NaH ₂ PO ₄ fired at 700°C	1.22	69.44
10% NaH ₂ PO ₄ fired at 900°C	1.55	50.75
20% NaH ₂ PO ₄ fired at 900°C	1.50	54.45
10% NaH ₂ PO ₄ fired at 1100°C	1.83	20.86
20% NaH ₂ PO ₄ fired at 1100°C	1.77	23.04

This is because, with higher sintering temperature, the porosity level decreased and the body becomes less porous. Meanwhile the percent of apparent porosities were slightly reduced as the sintering temperature increased as shown in figure 6. This is clearly related to the increasing in sample density when sintering temperature increased. Typically, when bulk density increases, the porosities would decrease. Apparent porosity is refers to the percent of open pores obtained in the samples. The apparent porosity is related to bulk density.

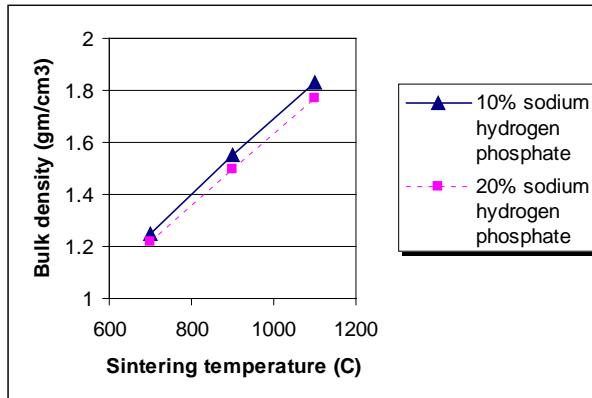


Figure 5. Bulk density vs sintering temperature

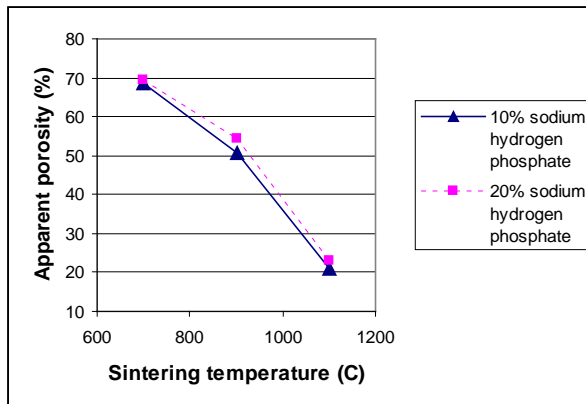


Figure 6. Apparent porosity vs sintering temperature

Evaluation of compressive strength

The Figure 7 shows that the compressive strength of porous calcium phosphate specimen is ranging between 14.38 to 103.42 MPa. It is depending directly on the percent of porosity in the sintered compacts. Samples with higher sintering temperature shows increasing in compressive strength. Samples with higher percent of porosity would have many empty space and defects in their structure, which would not withstand load. This would leads to the decreasing of the sample strength. Normal compressive strength for porous calcium phosphate is approximately ranging from 10 to 80MPa [2].

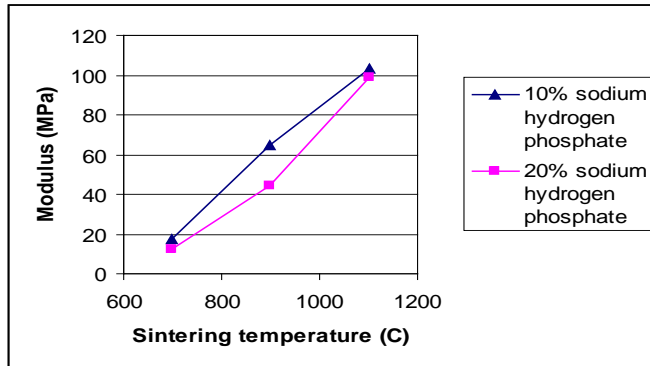


Figure 7. Modulus strength vs sintering temperature

CONCLUSION

Sodium Hydrogen Phosphate (NaH_2PO_4 and Na_2HPO_4) were acted as pores foaming agent and as well as sintering aid in producing porous bio-ceramic sample. Interconnected pores and almost 70% porosity was obtained by addition of 5% and 10% NaH_2PO_4 and Na_2HPO_4 in the HA sample and fired above 700°C . The pores sizes were in the range of 1 to $400\mu\text{m}$ in size, depending on the percent of sodium hydrogen phosphate additions and the level of sintering temperature. By increased the percent of sodium hydrogen phosphate content in sample, the percent porosity of sample was increased meanwhile the sample's bulk density and compression strength were reduced.

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- [2] Lucas-Girot, A., Langlois, P., Sanglebouf, J.C., Ouammou, A., Rouxel, T. and Gaude, J., (2002). A synthetic Aragonite-based bioceramic: influence of process parameters on porosity and compressive strength, *Biomaterials*, 23, 503-510. Kingdom.