# Characterization Porous HA/$SiO_2$ Composite Prepared Using Natural Space Holder

**Amir Arifin, Gunawan, M. Wahyudi Amin, Alim Mardhi, Ganang Trycahyono, and Firmansyah Burlian**

**Abstract** Hydroxyapatite based on bovine bone has been developed in addition to medical needs, adsorbents, catalysts, and other engineering applications. The use of hydroxyapatite-based catalysts in the industry is still very high, one of which is solid catalysts. This study aims to develop a solid porous catalyst from a HA/$SiO_2$ composite. The porous composite was prepared with $SiO_2$ as much as 25% of the total weight fraction and utilized sweet potato powder heated at a temperature of 150 °C as a space holder. The manufacturing process begins by mixing hydroxyapatite powder (200 μm), $SiO_2$ powder (200 μm), and purple sweet potato powder (200 μm), then mixing it using a ball mill with a rotating speed of 225 rpm for 1 h. The mixture was then put into the molding and compacted with a pressure of 69.805 MPa. The green body was then sintered at 1100 and 1200 °C and held for 3 h. Apparent density measurements were carried out using the Archimedes method, and the highest density was 1.4983 g/$cm^3$ with a porosity of 50.34% in the 30% space holder specimen. The XRD test shows that the dominant phases are hydroxyapatite (HA), β-TCP, and $SiO_2$. The compressive strength test showed the highest average compressive strength of 33,073 MPa in the 30% space holder specimen. The SEM observations showed pores formed in the samples with varying sizes ranging from 4.510 to 67.32 μm and showed interconnecting porous.

**Keywords** Porous · Hydroxyapatite · Space holder · Powder metallurgy

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## 1 Introduction

The development of science in the health sector has developed very rapidly, including efforts to improve the body to develop in line with the increasing number of accidents. Efforts to repair the body include using biomaterials that are non-toxic, can work following the compatibility of the recipient body (biocompatible), and can quickly form direct bonds with bones (bioactive) [1].

Calcium hydroxyapatite, $Ca_{10}(PO_4)_6(OH)_2$, commonly referred to as HA, is a synthetic biomaterial similar to the biology of HA, which is a structural component of human bones and teeth. HA widely used for various bone and dental implants due to its excellent biocompatibility and bioactivity. It binds firmly to the bone and supports the Osseointegration of the bone-implant, which is necessary to minimize damage to the surrounding tissue. BCP ceramics, consisting of a mixture of hydroxyapatite and beta-calcium phosphate (β-TCP, $Ca_3(PO_4)_2$) are considered useful in promoting bone formation at the implant site. The bioceramic properties of BCPs can be attributed to the fact that they consist of the more stable HA stage and the highly soluble TCP [2].

Bovine bone heated at 600–1000 °C shows the formation of pure hydroxyapatite and the crystallinity of HA increases with an increase in heating temperature. At a temperature of 1100–1200 °C, it is found that a small portion of B-TCP shows the partial decomposition of hydroxyapatite however, the calcination process at temperatures below 1000 °C is preferred [3].

The application of porous hydroxyapatite in the non-medical field is packaging media, catalysts, gas sensors, and column chromatography [4]. Hydroxyapatite serves as the main catalyst for the preparation of ribose from formalin and glyceraldehyde [5]. The utilization of biowaste as a resource of catalyst for biofuel production increased in the recent report due to its low cost and sustainability [6].

Researchers have developed various methods to make porous hydroxyapatite, one of which is by using a space holder. At the sintering process, a porous structure (sponge) will be formed in the hydroxyapatite composite caused by the burnt space holder during the sintering process [7]. Recently, several types of natural space holders have been developed as alternative space holders, which are abundant, cheap, and easy to process [8, 9]. However, the resulting porous hydroxyapatite still shows low mechanical strength. In this study, the porous HA/$SiO_2$ composite material used a purple sweet potato space holder then characterized its properties.

## 2 Materials and Method

The first thing that is done from this research process is to prepare all the tools and materials regarding the system related to the materials to be processed, hydroxyapatite (HA) extracted from bovine femur bones obtained from the local waste restaurant. Hydroxyapatite is produced using a calcination process as previous research [10].

The raw material for reinforced in the form of $SiO_2$ was obtained from glass waste that crushed using grinding, then continued using mortar, and then sieved into a powder measuring 200 μm. The space holder's raw material, i.e., sweet potato, is collected from the local market and then processed independently. Refer to the TGA result; the space holder was sieved into a 200 μm powder and then heated in an oven at a temperature of 150 °C for 1 h.

The preparation of porous HA/$SiO_2$ composites was carried out by mixing hydroxyapatite powder, reinforced powder, and space holder powder using a ball mill for 1 h at a speed of 225 rpm. The composition reinforced $SiO_2$ with 25% of the total weight fraction that then added space holder with variation 20 and 30% of the weight. The powder that has been mixed is then weighed as much as 10 g and put into the molding. The pressing process is then carried out using a compacting device by applying a pressure of 69.805 MPa for 10 min. Furthermore, in the sintering process, the molded specimen is put into an electric furnace heating rate of 10 °C/min. Then at a temperature of 600 °C, it is held for 1 h to give enough time for the space holder to burn completely. Heating then continued with a higher temperature with sintering temperature variations of 1100 and 1200 °C, with holding time for 3 h.

To determine the mechanical, physical and chemical properties of porous HA/$SiO_2$ composite some characterization process has been performed including Thermo Gravimetric Analyzer (TGA) on TA Instruments TGA Q500, X-Ray Diffraction (XRD) testing on Rigaku MiniFlex 600, Scanning Electron Microscopy (SEM) on Inspect S50 testing by FEI company. Composite density is determined based on Archimedes' theory. The compressive test is carried out on a porous cylindrical specimen; the testing was carried out using a Universal Hydraulic Testing Machine.

## 3 Results and Discussion

Porosity of samples at various space holder (SH) percentages as depicted in Fig. 1 can be seen that the porosity shows the average percentage value of porous HA/$SiO_2$ composites with 20% of SH at 1100 °C of 42.01% smaller than at 1200 °C of 44.61%. Meanwhile, HA/$SiO_2$ composites with 30% of SH at 1100 °C has an average porosity value of 41.24% at 1200 °C temperature of 44.50%. The results show an increasing porosity trend when sintered up to 1200 °C.

The results obtained in this study are in good agreement with previous studies [11], where the average porosity increases with increasing sintering temperature. The

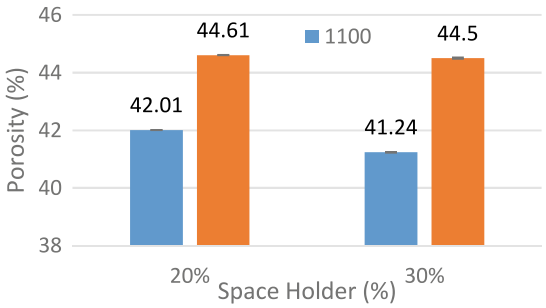


**Fig. 1** Porosity of 75% HA/25% $SiO_2$ composites at 1100 and 1200 °C with various space holder (SH) content

increase in porosity was due to an increase in the lost mass of $SiO_2$. Based on TGA analysis, when heating at 1200 °C, it loses more weight than 1100 °C. So, because at a temperature of 1200 °C, more $SiO_2$ mass lost will increase the sample's porosity.

The XRD test for the bovine bone powder that has been calcined at a temperature of 900 °C can be seen in Fig. 2. From the resulting graph, the XRD test graph after calcination at 900 °C has peaks that are almost the same as the ICDD 09-432 standard for hydroxyapatite. It shows 5 highest peaks at the angle of 2θ equal to 32.13, 26.27, 49.82, 47.07, and 40.18°. The $SiO_2$ XRD test obtained in Fig. 3 has graphical results similar to those of the reference $SiO_2$ graph [12].

XRD test results of porous HA/$SiO_2$ composites figured in Fig. 4. For this graph, the peaks that appear are hydroxyapatite, β-TCP, and silica. The one that dominates the peaks in the 1100 °C temperature specimen is hydroxyapatite, which has 14 peaks, then β-TCP with six peaks then silica has a peak number of 2 peaks. The hydroxyapatite peak is marked (HA), while the β-TCP peak is marked with β, and

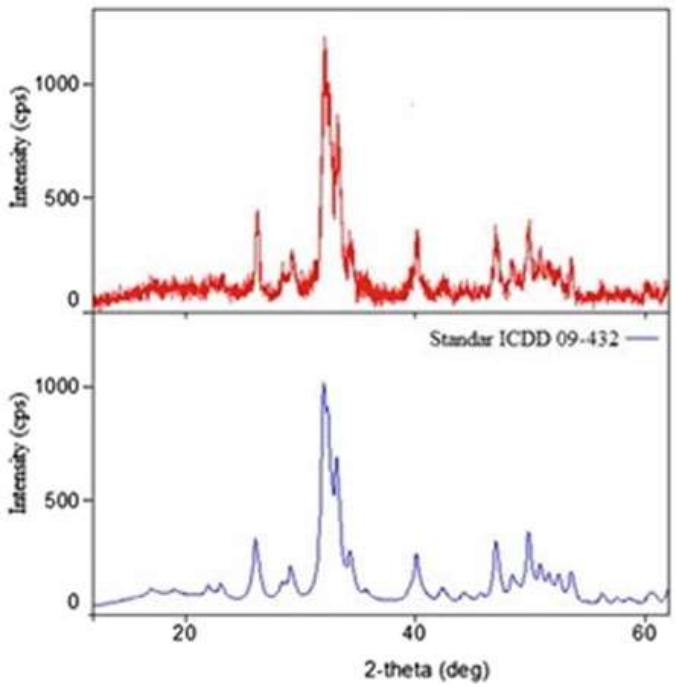


**Fig. 2** XRD of Calcined bovine bone at 900 °C

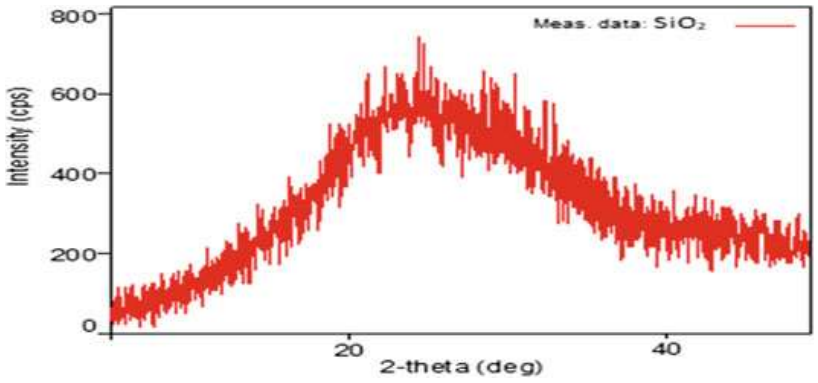


**Fig. 3** The spectrum of $SiO_2$ powder XRD results

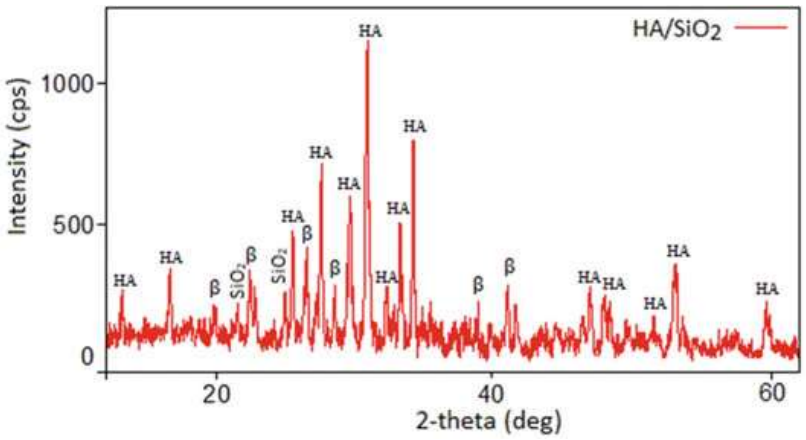


**Fig. 4** The spectrum XRD results for porous 75% HA/25% $SiO_2$ sintered at 1100 °C

the silica peak is marked with $SiO_2$. The HA has been decomposed to β-TCP at a sintering temperature of 1100 °C.

Figure 5 shows XRD test results of porous HA/$SiO_2$ composites that have been sintered at a sintering temperature of 1200 °C. It can be seen that the peaks that appear are hydroxyapatite, β-TCP, and silica. The peaks in this temperature specimen, the dominant peak, are still the same at 1100 °C, namely the hydroxyapatite peak with 14 peaks, while for the β-TCP peak, it has a peak of 7 peaks, and then for silica, it has two peaks. The more HA has been decomposed to β-TCP at sintering temperature of 1200 °C than at lower temperatures.

The test (TGA) of the Thermo Gravimetric Analyzer is useful for determining the speed of change in weight to the temperature function of sweet potato powder from room temperature to 600 °C. It can be seen that at the initial temperature (Fig. 6), 49.78 °C, the weight of sweet potato powder is still 100%. The weight reduction of sweet potato powder began to be seen at a temperature of 200.2 °C with a weight of 94.88% until the final temperature is 586 °C; the weight of sweet potato weights 0.99%. The weight reduction does not reach 0% because at a temperature of 600 °C,

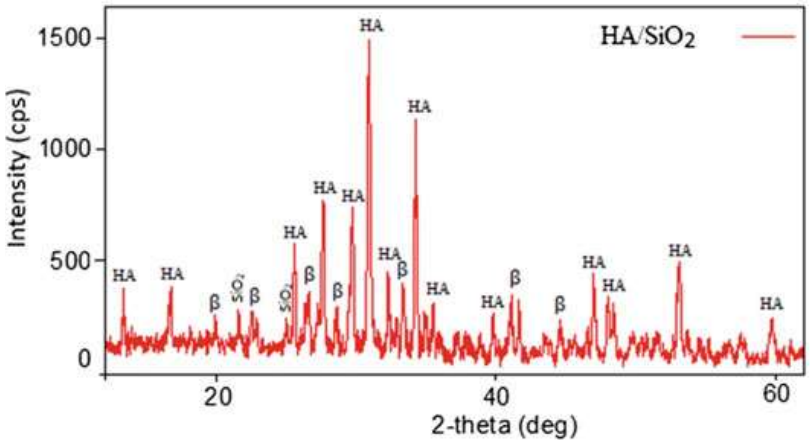


**Fig. 5** The spectrum of XRD results for 75% HA / 25% $SiO_2$ composites with 20% SH sintered at 1200 °C

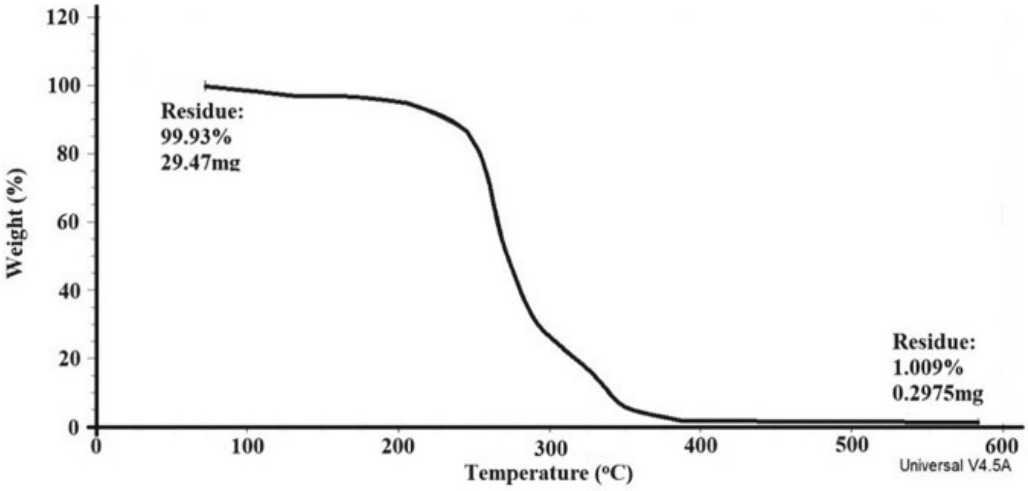


**Fig. 6** TGA of sweet potato

the sweet potato powder remains in the form of ash. During the sintering process, the sweet potato powder will become a pore agent on the specimens.

The results of the compressive strength test at Fig. 7 can be seen that it has a graphical form of an increase in the average compressive strength. The porous $HA/SiO_2$ composite of 20% SH at a temperature of 1100 °C having an average compressive strength of 7735 MPa. However, for a temperature of 1200 °C it has an average compressive strength of 28.008 MPa. The same trend also can be found at $HA/SiO_2$ composite of 30% SH which has an average compressive strength of 33,073 MPa at the temperature of 1200 °C.

The compressive strength increases with increasing sintering temperature because the composite materials diffuse to one another. In this study, each temperature's average strength is much greater than in previous studies [8] because the composite has reinforced silica and modified on SH processing.

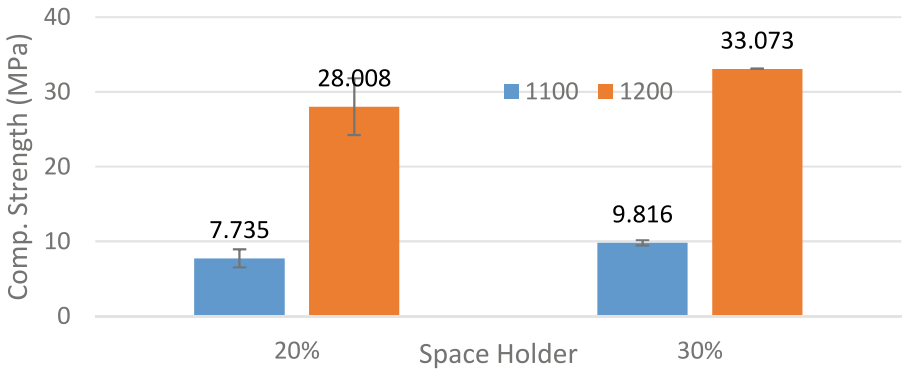


**Fig. 7** Compressive strength test for composite 75%HA/25% $SiO_2$ porous at various sweet potato space holder percentages

During the sintering process, the composite undergoes a more significant decomposition process that the resulting value of porosity is smaller and causes the compressive value to increase as the porosity value decreases in the composite. The decreasing porosity value is due to the variety of space holder powder treatment used in this study. The heat treatment was carried out at a temperature of 150 °C for one hour, while the previous research only reached the powder stage. In previous studies [8], where the same SH is used, the maximum compressive strength at a temperature of 1200 °C was 4.41 MPa. There is a possibility that this might happen because water vapor has been lost when heating at 150 °C; there is no excessive evaporation, which encourages the bonding of particles during sintering, which can reduce the strength of the bonds between particles.

In the observations using SEM, the porous HA/$SiO_2$ composite at two different magnifications can be seen in Fig. 8. The composite has seen the shape and size of the pores, and the pores appear due to the loss of space holder used in the composite.

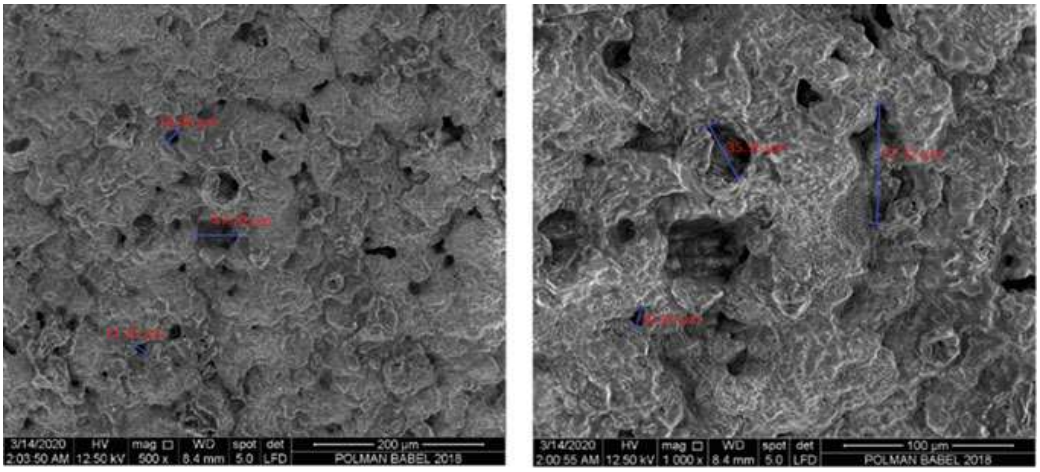

**Fig. 8** SEM observations of composites 75% HA/25% $SiO_2$ with 20% SH 1200 °C at 2 different magnification

It can be seen that the shape and size of the micropores have variations ranging from 10.35 to 67.32 μm. It also can be seen clearly that some pores are interconnected.

## 4 Conclusion

Porous composite HA/$SiO_2$ successfully fabricated using sweet potato starch as a space holder. The porosity shows an increasing porosity trend when sintered up to 1200 °C, due to at a temperature of 1200 °C, more $SiO_2$ mass lost increase. The XRD testing of HA/$SiO_2$ composites at temperatures of 1100 and 1200 °C depicts 3 phases, namely hydroxyapatite, β-TCP, and silica. The dominant phase is the hydroxyapatite phase, followed by the β-TCP phase and the silica phase. The compressive strength test was found that the HA/$SiO_2$ porous at the temperature of 1200 °C has an average compressive strength of 33,073 MPa. The Scanning electron microscopy (SEM) clearly shows pore in micro size and interconnected porosity.

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