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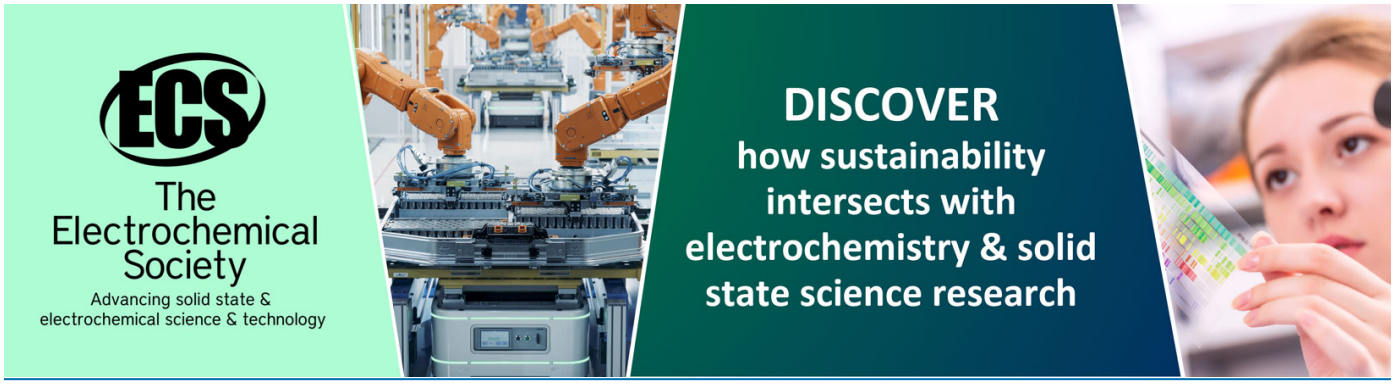

Development and characterization of porous hydroxyapatite-Alumina composite for engineering application

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Abstract. Synthetic hydroxyapatite is a material that has a chemical composition and molecular structure similar to bones and teeth, generally this material is widely used for medical applications including as an implant material. Non-medical applications of porous HA include as catalyst in chemical reaction, packing media for column chromatography, and as probe for gas sensors. The study aims to develop porous material based HA/Al_2O_3 composites. HA/Al_2O_3 composites prepared with three variations of latex space holder weight fractions namely 10%, 20%, and 30% and using the unidirectional compaction method to produce composites. Two step holding process sintering process applied on the green body specimens. Firstly, hold for 60 minutes at temperature of 600^{o}C and secondly 3 hours at final temperature of 1200^{o}C with 5^{o}C/min heating rate. The apparent density test was performed based on the Archimedes' principle. Porosity characteristics of the sample show that density of the composite decreased with increased space holder. Compressive strength results show that the addition of SH weight fraction decreased the compressive strength of porous hydroxyapatite-Al_2O_3 composites. The morphology observation via SEM showed pore formation due to burning of space holder and interconnecting porous formed.

Keywords: porous, hydroxyapatite, alumina; space holder, powder metallurgy

1. Introduction

Hydroxyapatite (HA) synthetic with calcium and phosphor as main composition is having excellent biocompatibility and osteoconductivity properties. Both natural properties of synthetic HA material is main reason of using it as bone grafting material in hard tissue implants in medical applications [1]. Generally porous HA ceramics for non-medical applications used as catalyst in chemical reaction, packing media for column chromatography, and as probe for gas sensors [2]. For catalyst application, in hot water environment about 80^{o}C, HA increased ribose formation [3,4]. It is believed that the effect of spacing of calcium ions on the external surface of HA effectively enhanced chemical reactions.

HA with chemical composition $Ca_{10}(PO_4)_6(OH)_2$ can be produced from synthetic materials and natural resources. HA prepared from natural sources including animal bones, corals, eggshells, etc. [4]. The advantages of syntheses HA from natural sources are simpler and cheaper since no chemicals addition. Several methods to produce porous hydroxyapatite established in literatures [5][6][7]. The aim of many of these methods is the manufacture of porous HA, with controlled percentage of porosity without decreasing its mechanical properties. One of the method is by applying a material as space

holder in powder metallurgy methods to produce porous material that offers flexibility and it is also a cost-effective alternative.

In this case, in the conventional method several parameters must be considered to limitation in controlling the quantity, size, distribution and pore morphology. In addition, in an effort to obtain efficient process in terms of cost factors, reproducibility and flexibility compared to new technologies such as field assisted sintering technology (FAST), ion beam milling, laser sintering, etc. must be considered. In contrast, applying a material as space holder in powder metallurgy methods techniques provide suitable routes for obtaining porous HA structures; these method also have extraordinary advantages including cost-effective and non-toxic methods, without toxic agents that be able to affect porous purpose

Space holder is short-term constituent part mixed to the matrix. The porosity formed from constituent burnt in the sintering process and leave marks. Some types of space holder material have been used including polymethyl methacrylate, NaCl, NH_4HCO_3, corn and tapioca starch [8].

Hydroxyapatite intrinsically owing to low mechanical properties such as compressive strength and bending strength, therefore it is necessary to improve its mechanical properties by reinforcing with Al_2O_3. The main objective of this work is to characterize fabricated porous hydroxyapatite-Al_2O_3 composites with the application of space holder materials (i.e. latex powder) through the powder compaction method.

2. Materials and Method

In the research process Hydroxyapatite (HA) material is derived from cattle bones obtained from waste or residual bovine bones in Palembang. The bones collected are femur bones. The raw material for reinforcement in the form of Al_2O_3 (Alumina) is obtained from the Online Store and the raw material for the space holder in the form of latex powder is obtained by crushing the rubber eraser into powder.

HA prepared by boiling bovine bones to eliminate of fat contained in bones and to clean the remaining meat and muscles for 4 hours.

Bovine then dried to remove the remaining moisture content and reduced the dimensions by using a cutting grinder. r use as hydroxyapatite must be calcined using an electric furnace at a temperature of 600^{o}C for 2 hours and cooled slowly to match room temperature. Furthermore, the calcined bovine bone is mashed by using mortar by pulverizing it. The result of mashed beef bone powder is then sifted to get the desired particle size. Afterward calcination process on electric furnace at 600°C and 3^{o}C/min heating rate for 30 minutes before cooled inside furnace. During calcination process the organic substances decomposed and water evaporated. Furthermore, the calcined bovine bone is mashed by using mortar by pulverizing it.

The result of mashed bone powder is then sieved to get the desired particle size. The production of porous HA/Al_2O_3 composites was carried out by mixing hydroxyapatite powder (200 μm), alumina powder (55 μm) and space holder powder with composition 75%:25% of weight fraction. Subsequently space holder of latex powder (200 μm) added to composite with 10%, 20% and 30% weight fraction variations of total composite weight. The weighed powder was then mixed for 1 hour using a ball mill with a spin speed of 225 rpm using a Groschopp Viersen FRG ball mill.

The mixed powder then is loaded into a die (die) cylindrical samples with length 12 mm and diameter 10 mm for the compacting process with a pressure of 2000 Psi for 10 minutes. After the compacting process is carried out, then the specimen is removed from the mold. The sintering process is carried out in conventional electrical furnace Nabertherm GmbH. For adequate sintering process complete burn of latex powder facilitated via two step holding process (fig. 1). First, hold for 60 minutes at temperature of 600^{o}C and secondly 3 hours at final temperature of 1200^{o}C with 5^{o}C/min heating rate.

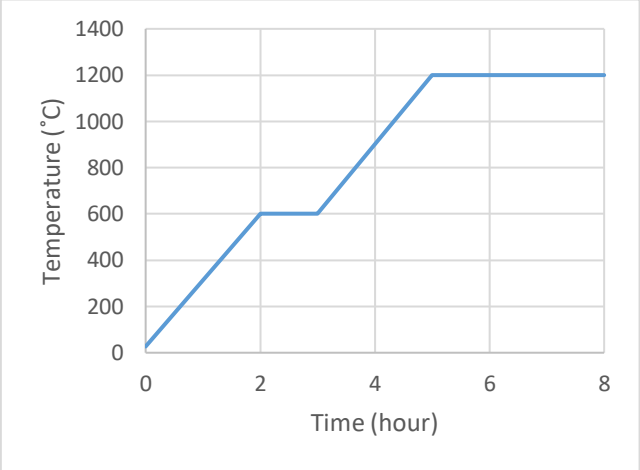


Figure 1. Heating schema in sintering process

Various experimental method has been done to characterize powder green bean, HA and Al_2O_3 as well as porous HA- Al_2O_3 composite including SEM evaluation using FEI Inspect S50, analyze decreasing weight of space holder via thermo gravimetric analyzer from TA Instruments TGA Q500, phase formed during syntheses using an X-Ray Diffraction of Rigaku MiniFlex 600 and compression strength tested using Bongshin Hydraulic Universal Material Tester

3. Results and Discussion

Thermo gravimetric analyzer (TGA) testing was carried out to determine the rate of weight change in the temperature function of rubber powder from room temperature to a temperature of 600°C as can be seen based on figure 2. Up to the temperature of 140°C the rubber powder material begins to experience a weight reduction caused by evaporation of the moisture content. The decomposition process occurs until the temperature of 300°C that temperature susceptible to a drastic decrease weight from 98.51% to 43.08%. Mass reduction continued to temperature of 580°C rubber powder remained 23.032% by weight where the rubber powder sample has not burned out completely and formed ash.

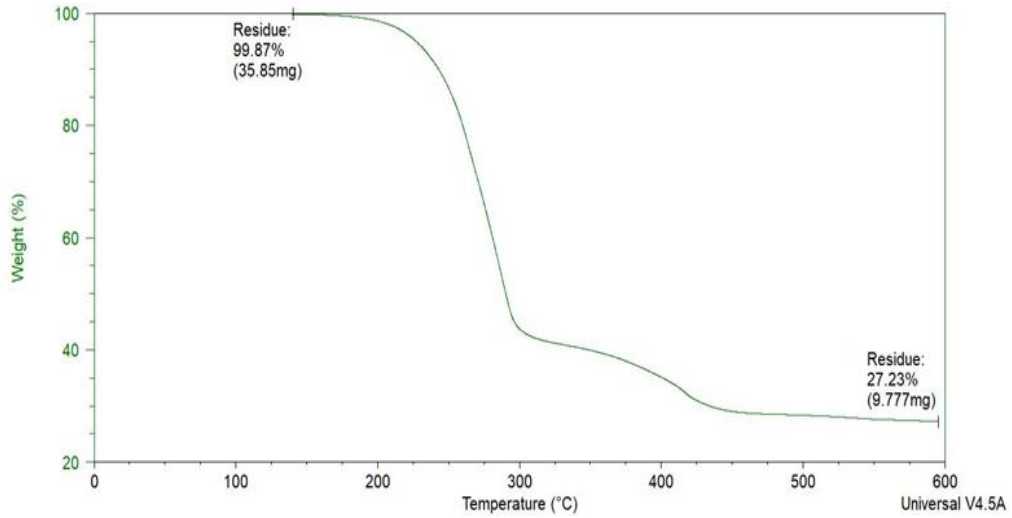
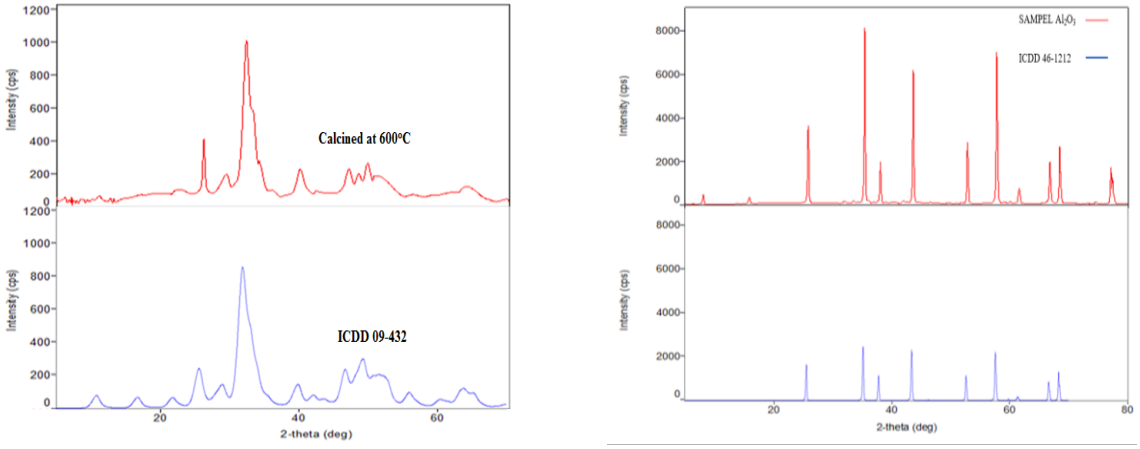


Figure 2. TGA result of latex powder

As can be seen from figure 3 (a), the XRD results of calcined bovine bone at a temperature of 600°C in the red graph while hydroxyapatite standard according to ICDD 09-432 in the blue graph. It can be

seen that the XRD graph of the sample close to the ICDD standard 09-432 at 2θ of 26.270, 29.61, 32.43, 33.31, 35.41, 40.19, 51.52, and 64.65°. Figure 3.b shows XRD pattern of alumina powder, as it can be seen that the result of XRD match perfectly with peak of alumina according to ICDD 46-1212 card. also XRD result depict high crystallinity of powder alumina.

XRD results on porous HA-Al2O3 sintered at 1200°C are shown in Figure 4 producing a more crystalline hydroxyapatite phase characterized by higher peak intensities than calcined powders. In addition, the β-TCP phase (ICDD 09-169) was also detected due to partial dehydration which caused the decomposition of hydroxyapatite to TCP due to the CaO reaction and water vapor which changed the location of the phase boundary. Third phase detected is the phase of alumina powder however another phase resulted from latex powder is not detected.



a) b)

Figure 3. a). XRD results of calcined bovine bone temperature 600°C
b). XRD result of as received Al_2O_3

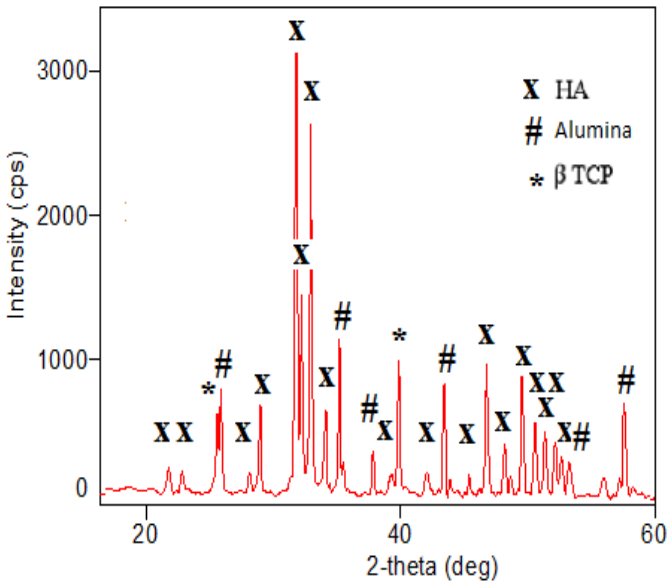
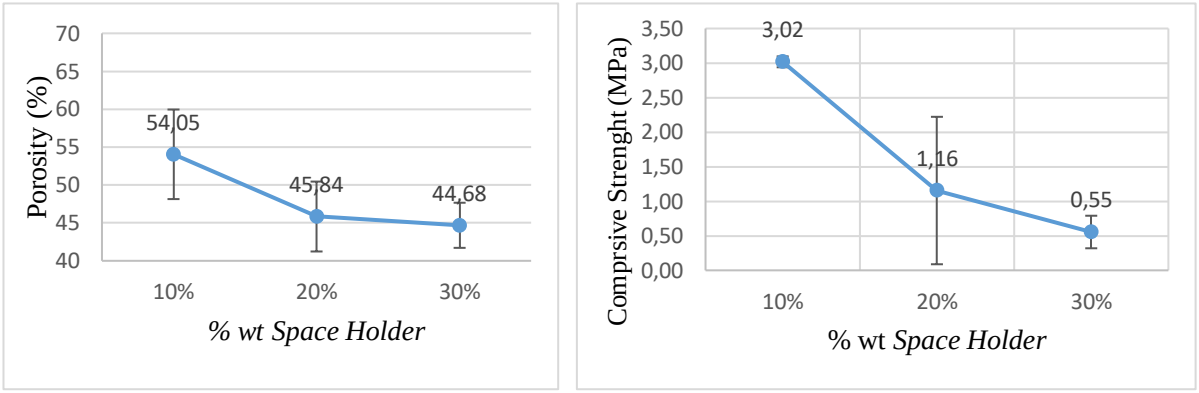


Figure 4. XRD result of Porous HA-Al_2O_3 Composite Sintering Temperature 1200°C

Figure 5.a depict the average percentage porosity HA/Al_2O_3 composite. The higher porosity was obtained in samples with a weight fraction of 10% space holder that was equal to 54.49%. However, the addition of space holder weight fraction up to 30% will reduce its porosity by 45.21%. The trend can be

confirmed by the TGA results in which the weight percentage of latex powder that remains when burned at 600°C is 27.23% in the form of ash. Increasing the percentage of space holder will accumulate and increase the amount of ash remaining.

The remnants of this ash will fill the space between the grains formed by the burning of latex powder. Increasing percentages the weight of the space holder from 10 to 30 has an undesirable effect on the porosity in term of height porosity material design. The addition of space holders is not able to increase porosity but decreases.



a) b)

Figure 5. a) Average porosity correspond to weight fraction of space holder
b) Compressive Strength Results of Composite at Various Weight Fraction of Space holder

The results of compressive strength test of HA-Al2O3 composites can be seen in Figure 5.b. From the results show that the compressive strength at 30% weight fraction space holder is the lowest compared to the variation of 10% and 20% space holder weight fraction. In contrast, the 30% weight fraction has the lowest porosity compared to other samples. The low compressive strength of this 30% sample indicates that accumulation of ash residual latex powder is more numerous than in samples with less space holders. In the ash sintering process the remaining space holder fills the space between HA grain boundary and interferes with the diffusion process between HA particles thereby reducing the amount of diffuse HA particles which in turn reduces the compressive strength.

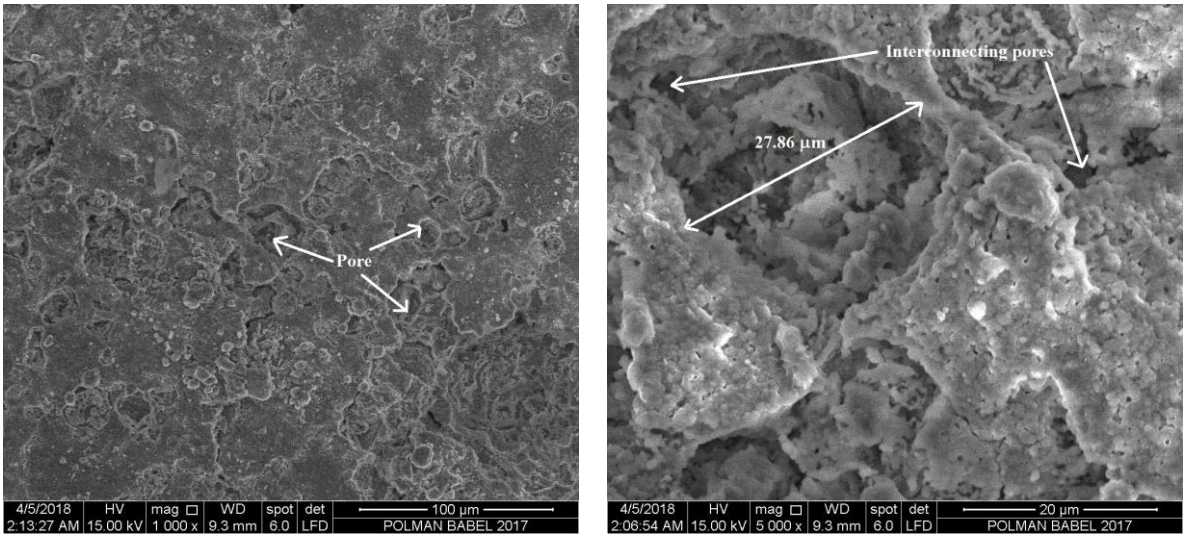


Figure 6. SEM Results of HA-Al_2O_3 Composite at Two Different Point

Figure 6 shows the observation of microstructure using SEM on a sample of 30% space holder. As can be seen, in two different observation points with magnification of 1000 and 5000, porosity formed has varying sizes with a maximum size of 27.86 μm. The large porous size is formed due to the process of burning down the space holder, while there are also smaller pores associated with particle diffusion in the sintering process. In addition, interconnected porous can also be seen clearly in the sample.

4. Conclusion

The conduct of the study as described turn to conclusion that Porous structure of hydroxyapatite-alumina composite has successfully produced using latex as space holder. Porosity characteristics of the sample show that density of the composite decreased with increased latex space holder. Increasing the percentage of latex space increase the amount of ash remaining that will fill the space between the grains formed by the burning of latex powder. Compressive strength results show that the addition of space holder weight fraction decreased the compressive strength of porous hydroxyapatite/Al_2O_3 composites. Increasing latex ash in the sintering process interferes diffusion process between HA particles. SEM observations of microstructure confirm that porous structure formed due to the process of burning down the space holder and an interconnected porous structure detected.

Acknowledgment

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References

[1] D. Shi, D. Shi, and G. Jiang, “Introduction to Bioceramics,” *Introd. to Biomater.*, pp. 3–12, 2010.
[2] T. Kanazawa, *Inorganic phosphate materials*, vol. 52. 1989.
[3] K. Usami and A. Okamoto, “Hydroxyapatite: Catalyst for a one-pot pentose formation,” *Org. Biomol. Chem.*, vol. 15, no. 42, pp. 8888–8893, 2017.
[4] R. Choudhary *et al.*, 2016 “In-vitro bioactivity, biocompatibility and dissolution studies of diopside prepared from biowaste by using sol-gel combustion method,” *Mater. Sci. Eng. C*, **68** pp. 89–100
[5] Z. Wu, Z. Zhou, and Y. Hong, 2019 “Isotropic freeze casting of through-porous hydroxyapatite ceramics,” *J. Adv. Ceram.*, **8** pp. 256–264
[6] H. Yoshikawa, N. Tamai, T. Murase, and A. Myoui, 2009 “Interconnected porous hydroxyapatite ceramics for bone tissue engineering,” *J. R. Soc. Interface*, **6** 3
[7] H. Noguchi, M. Sakane, A. Watanabe, T. Tsukanishi, Y. Wadano, and M. Yamazaki, 2014 “A novel unidirectional porous hydroxyapatite in canines,” *Bioinspired, Biomim. Nanobiomaterials*, **3** pp. 228–234
[8] L. Stanev, M. Kolev, B. Drenchev, and L. Drenchev, 2016 “Open-Cell Metallic Porous Materials Obtained Through Space Holders—Part I: Production Methods. A Review,” *J. Manuf. Sci. Eng.* **139** 050801