The effect of PVA addition as binders on the properties of hydroxyapatite sintered body

1st Ade Indra[1], 2nd Ronald Budi Setiawan[2], 3rd Ismet Hari Mulyadi[3], 4th Jon Affi[4], 5th Gunawarman[5]
gunawarman@eng.unand.ac.id[1]

[1,2] Mechanical Engineering Department, Institut Teknologi Padang, Padang, West Sumatera, Indonesia.
[3,4,5] Mechanical Engineering Department, Universitas Andalas, Padang, West Sumatera, Indonesia.

Abstract. Sintered body has been fabricated from Bio-ceramic Hydroxyapatite (HA) with having 2.5 µm of powder size. Initially, HA powder was mixed with varied polyvinyl alcohol (PVA) liquid that is played as binder. The addition of PVA aims to improve the tangential bond between HA powders. Subsequently, the uniaxial pressing method at a pressure of 200 MPa was applied to manufacture the green body. Meanwhile, the sintered body produced after sintering process conducted at 1150 ^{o}C with holding time of 120 minutes. Furthermore, X-Ray Diffraction (XRD), Scanning Electron Microscopy (SEM), density measurement, and Vickers Hardness Number (VHN) were utilized to characterize the product. The results indicate that PVA addition to HA powder enable to improve the physical and mechanical properties of the sintered body. It is due to have good tangential bond between HA powder thus increasing the strength mechanism. The finding would usefull for fabricating hard bone-implant products.

Keywords: *hydroxyapatite*; polyvinyl alcohol; uniaxial pressing; sintering, bone-implant.

1. Introduction

Ceramic products is generally produced by utilizing the powder metallurgy method [1-3] due to its natural conditions that make it difficult to perform by casting process. In powder metallurgy processing, the product produces through subsequent main stages which are including preparation of ceramic powders, compaction processes, and sintering [4]. Many research has been conducted in order to improve the quality of sintered body products. This can be classified in to several studies such asadjusting the composition between the matrix and the reinforced material to produced composites [5-8], and application of manufacturing methods such as hot pressing [9-12] and pressureless sintering [13,14].

Those studies are not limited for common ceramic production but also for coating implant products with bio-ceramic materials such as Hydroxyapatite (HA). HA is a coating substrate favourable for implants due to characterize as high biocompatible and adaptable to human bones [15-23]. However, as commonly known, products made of ceramics including bio ceramics pose low impact strength thus tending to produce a fragile product that is not suitable for medical application such as implant. Therefore, research on quality improvement of implant made of bio-ceramics such as HA are underway.

One of improvement strategy that has been taken into account is by composing HA with other suitable materials. Several investigation has been carried out for this objective such as HA/Al2O3 [24], HA/P2O5 [25], HA/silica-coated graphene (S-G) [26], HA/Ag [27]. The results indicated that HA composites with the addition of reinforcing material enable to

ICITID 2021, August 30, Yogyakarta, Indonesia

DOI 10.4108/eai.30-8-2021.2311514

improve its strength. However, the addition of other materials to HA have beyond expectancy effect on its biocompatibility.

Although, sintering process with appropriate temperature setting can improve the quality of bio-ceramics products [12,28]. But, by addition of a binder when making a green body has been proofed to enhance mechanical properties of HA-based products. The addition of the binder creates strong tangential bonds in the green body before the sintering process. Strong tangential contact between particles would facilitate sintering process easily. Several studies used binders to manufacture green body by employing uniaxial pressing. HA/bredigite and β-TCP/PEG were compacted by uniaxial pressing process at pressure of 200 MPa with 5% wt of polyvinyl alcohol (PVA) as binder and of 8 MPa with 10% wt of PVA as binder respectively [29]. Accordingly, Polyvinylpyrrolidone (PVP), polyacrylamide (PAM), and polyvinyl alcohol (PVA) are the binder oftenly used. These type of binders have good biocompatible properties, excellent biological inertia, good comprehensive performance, and positively interacts with HA [30]. Amongst, PVA is believed to have good binder quality [30]. However, to date, there is lack of information regarding the amount of PVA addition that is appropriate for producing improved quality of HA bio-ceramic green body has been reported.

Therefore, in this work, HA with having 2.5 μm of powder size was added with PVA that have varying amount. Furthermore, powder metallurgy method using uniaxial pressing at 200 MPa was applied to produce the green body. Subsequently, the green body was preheated at a temperature of 700 ^{o}C and with holding time of 60 minutes in order to remove the PVA. Eventually, sintering process in an air environment with a temperature of 1150 ^{o}C and with holding time of 120 minutes was finalized the stages. The sintered body was furthermore characterized in terms of occurence of linear shrinkages, density as well as its hardness.

2. Material and Method

2.1. Material

Bio-ceramics used in this study were commercial analytical HA with having powder size of 2.5 μm (Sigma-Aldrich Co., USA). Meanwhile technical PVA was used as binder material and alcohol was as a thinner. All the materials used was without having treatment and according to the initial conditions. Pure water (equates) was used throughout theresearch process.

2.2. Method

2.2.1. Powder characterization. X-Ray Diffraction (XRD-PANalytical, Type PW3040/60, Netherlands) was used to characterize the HA powder crystalline phase. XRD poses working conditions on Cu anode material at 40 kV and 30 mA. The steeply scanning time was 7.14 seconds. Characterisation of HA was performed before and after the sintering process.

2.2.2. Sample preparation. HA samples were prepared from powder having particle size of 2.5 μm that was added with PVA varied at percentage of 0% wt; 2.5% wt; 5% wt; 7.5% wt; 10% wt; 12.5% wt; and 15% wt. Each variation was mixed in a rotating drum for 60 minutes with assistance of steel balls. In advance, the green body was compacted with a pressure of 200 MPa in 8 mm of diameter and 5 mm of thickness of stainless steel mold. All green body products were then weighed and their diameters were measured. To remove PVA, a preheating process at a temperature of 700 ^{o}C and holding time of 60 minutes was performed before sintering at a temperature of 1150 ^{o}C and holding time of 120 minutes was carried out. Eventually, the sintered body was then left in the furnace to get cooled to room temperature. Illustration of sample preparation can be seen from Figure 1.

2.2.3. Characterization of sintered body.

Some physical and mechanical properties influenced by addition of PVA as a binder would be examined. Linear shrinkage was checked by comparing the weight and the diameter of the green body with the sintered body. Furthermore, the actual density was tested by adopting Archimedes' theory that further was going to be used to calculate relative density by comparing the actual density with the theoretical density of HA (e.g 3.156 g/cm^3 [28]). Finally, the hardness of sintered body was then measured by using Vickers HMV Shimadzu micron testing machine to obtain the Vickers Hardness Number (VHN). Meanwhile, the sintered body morphology was examined using SEM in order to observe the shape of the bond that is formed as addition of PVA binder. Beforehand, the sintered body crystal phase characterization was conducted by means of XRD-PANalytical, Type PW3040 / 60, Netherlands.

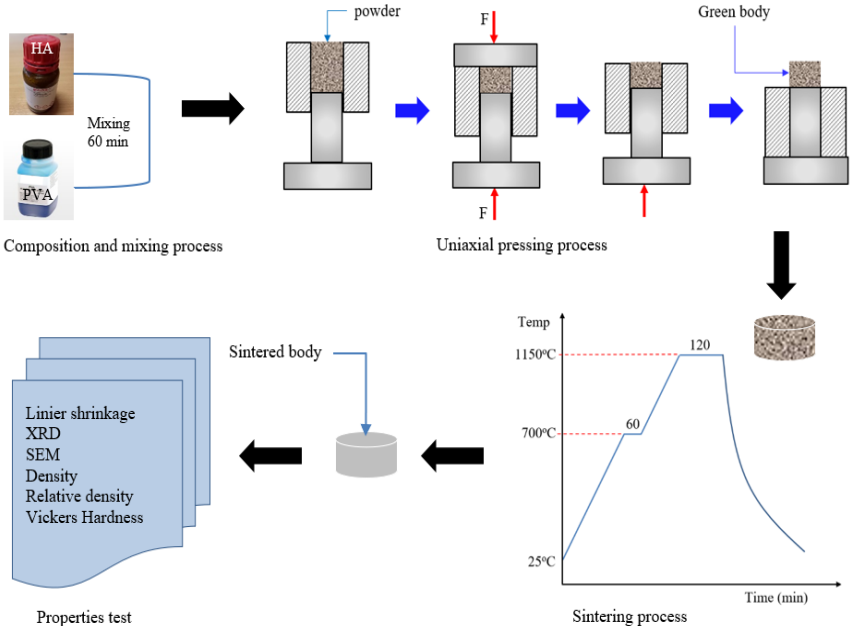


Fig. 1. Sample preparation Illustration

3. Results and Discussions

3.1. Crystalline phase

Before the changes in physical and mechanical characteristics of HA sintered body is discussed, The crystalline phase of used HA powder would be attested by performing XRD analysis. The results as depicted in see the main peaks at an angle of 31.74; 32.83; and 34.06. These results are also consistent with commercial HA as was done in previous studies [31]. Characterization of the crystalline phase performed on the HA sintered body showed no phase change after the sintering process. The main peaks at an angle of 2 thetas each; 31.76; 32.91; and 34.11. The PVA used as binders disappear after the sintering process. The results of XRD characterization, see Table 1 and Figure 2.

Table 1. XRD peak list of hydroxyapatite

HA 2,5 µm powder		HA comparator		HA 2,5 µm sintered body	
Position [°2Th]	Rel.Int. [%]	Position [°2Th]	Rel.Int. [%]	Position [°2Th]	Rel.Int. [%]
31.7403	100.00	31.741	100.0	31.7664	100.00
32.8353	54.38	32.179	45.3	32.9179	88.90
34.0639	24.62	32.868	56.4	34.1144	15.54

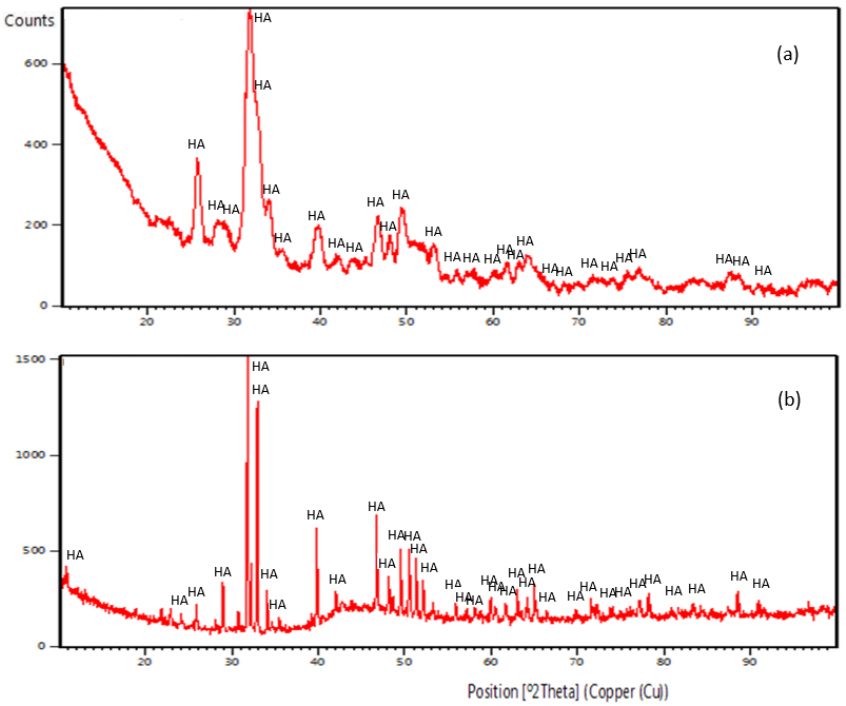


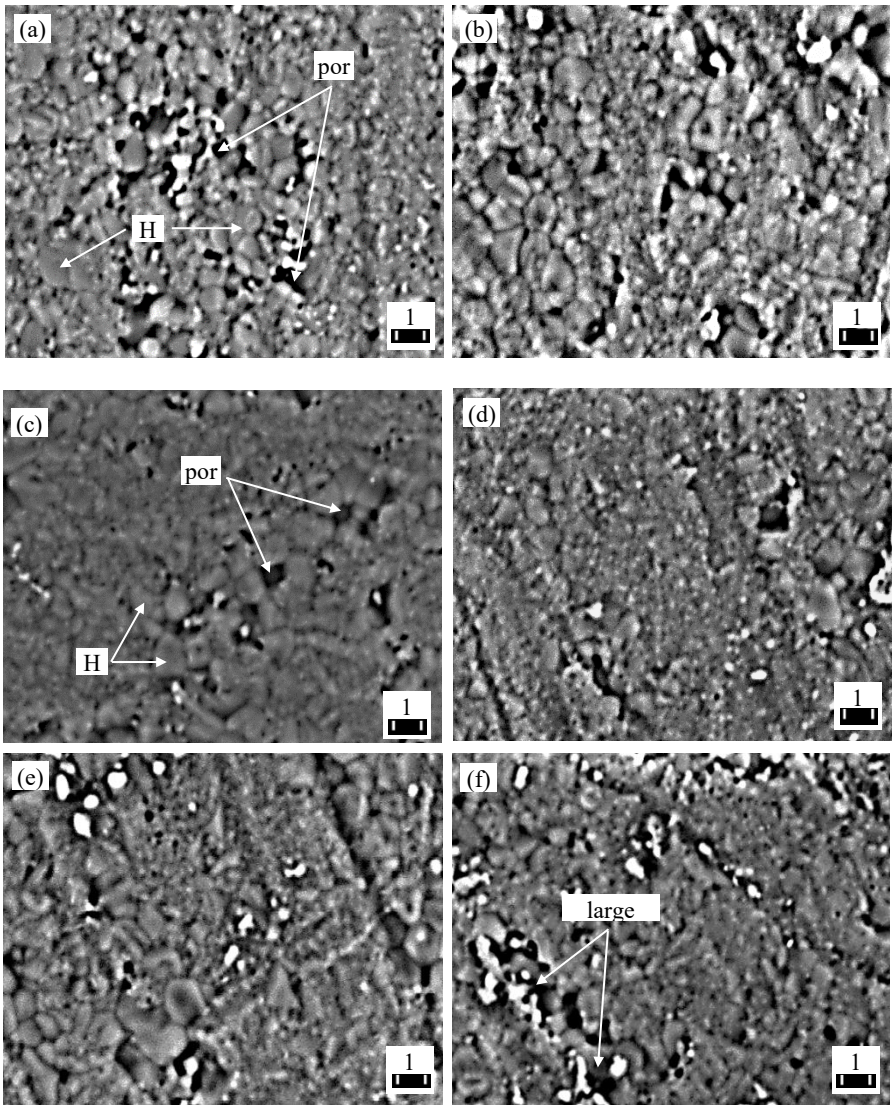
Fig. 2. XRD test of HA (a) HA powder, (b) HA sintered body, sintering 1150 °C

3.2. Microstructure morphology

The microstructure characterization on the surface of the HA sintered body can be seen in Figure 3. All SEM images show that the sintering temperature of 1150 °C has not been sufficient for a good bond between grains. Figure 3 (a) is HA sintered body without adding PVA as a lubricant and binder, seen many pores caused by the not yet perfect tangential bonding at the time of making the green body, so there is no good grain bonding in the sintering process, as well as several samples, broke after the sintering process.

Figure 3 (b) there are still many pores; it is suspected that the amount of PVA is not sufficient as a lubricant and binder in the manufacture of the green body. Figure 3 (c) - (e) is HA sintered body with the addition of PVA each; 5; 7.5; and 10% wt in the manufacture of green body, the results showed a decrease in the number of pores and increased grain bond. This condition shows the optimal amount of addition of PVA as a lubricant and binder when compacting of green body. Figure 3 (f) (g) is HA sintered body with the addition of 12.5 and

15% wt PVA, the amount of PVA is too much, evident the discharge of PVA when compacting green body, while the SEM image also shows a large pore size, this is thought to be the amount of PVA excessive so blocking tangential contact between particles. Figure 3 (h) shows a crack on the surface of HA sintered body, thought to be caused by an overly high heating rate and cooling rate. It is recommended for slow heating rates over a range 0.5-10 ^{o}C/min [32,33], and low temperature cooling rate [34].



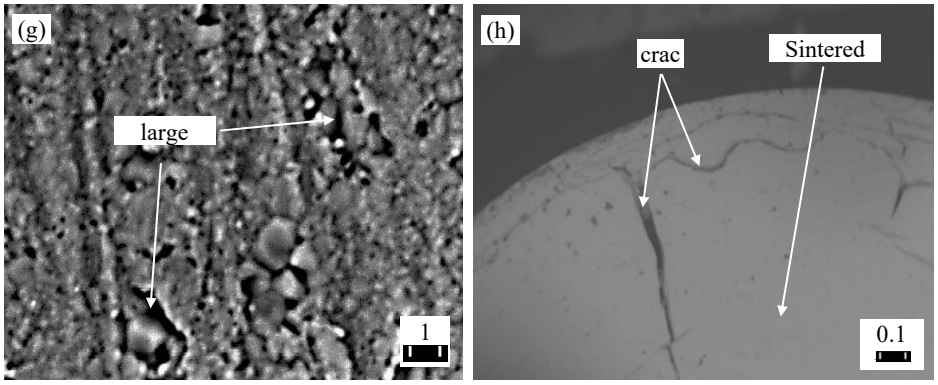


Fig. 3. SEM image of sintered body HA (a) without PVA (b) 2.5 % wt of PVA addition (c) 5 % wt of PVA addition, (d) 7.5 % wt of PVA addition, (e) 10 % wt of PVA addition, (f) 12.5 % wt of PVA addition, (g) 15 % wt of PVA addition, (h) crack occured at sintered body

3.3. Linear shrinkage

Linear shrinkage plays importance role in ceramic production due to Figure 4 shows the linear shrinkage that occurred. Linear shrinkage is observed in two ways namely weight shrinkage and diameter shrinkage. Percentage of diameter shrinkage decreased until the addition of PVA 10% wt, and this is due to the presence of PVA between particles that are part of the green body so that it can prevent the process of bonding occurs during the sintering process. On the addition of PVA 12.5-15% wt an increase in the percentage of diameter shrinkage, this is thought to be caused by the discharge of PVA during the compacting process due to excessive amount of PVA. The average percentage shrinkage diameter is 18% which is identical to other previous studies [28]. Percentage of weight shrinkage, there is an increase in the addition of 10% wt PVA. An increase in the percentage of weight shrinkage due to loss of PVA during the sintering process. This is also evidenced by the XRD test in Figure 2 (b), that there is no phase change in the sintered body. Addition of PVA 12.5-15% wt a decrease in the percentage of weight shrinkage, this is thought to be caused by the discharge of PVA during the compacting process due to excessive amount of PVA.

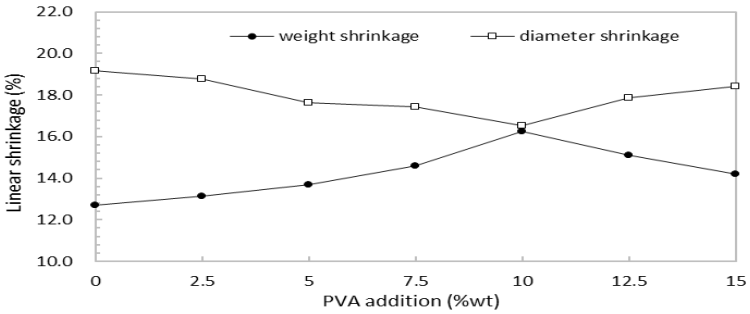


Figure 4. The effect of PVA addition on linear shrinkage of HA sintered body

3.4. Density and relative density

Density testing using Archimedes theory, results are shown in Figure 5. Addition of PVA to HA powder while compacting provides a good tangential bond between HA particles. There was a significant increase in density in the HA sintered body after the addition of 2.5 -5% wt PVA. While on the addition of 7.5-15% wt PVA, the density is constant, but the value is below the addition of 5% wt PVA. The highest relative density value is obtained at the addition of 5% wt PVA, and this shows the most optimal level of density with 2.5 µm HA particle size. Relative density HA sintered body with sintering temperature of 1150 ^{o}C identic with other studies that have been done [35].

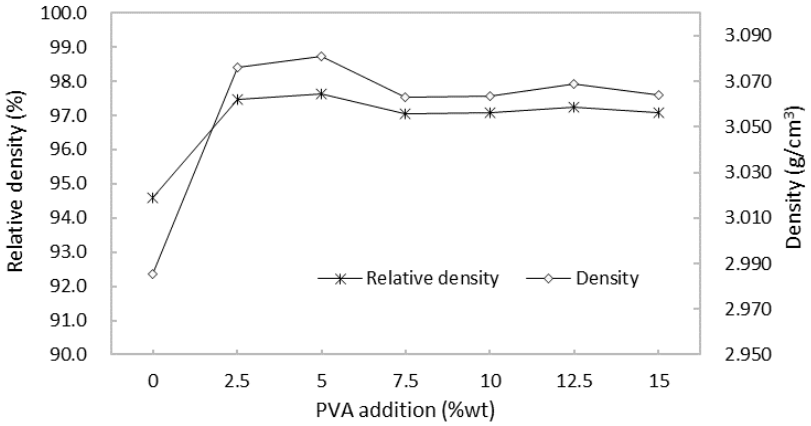


Fig. 5. The effect of PVA addition on density and relative density of HA sintered body

3.5. Hardness

The hardness of HA sintered body owing to different percentage of PVA addition was measured by Vickers Hardness tester. average hardness of HA sintered body with the addition of PVA varies, shown in Figure 6. The lowest hardness value is in the HA sintered body without the addition of PVA when making a green body.

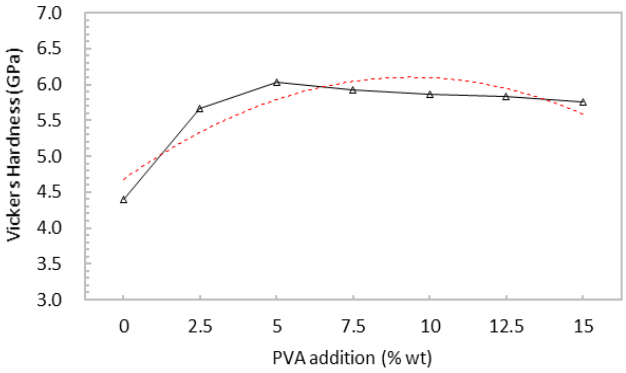


Fig. 6. The effect of PVA addition on Vickers Hardness of HA sintered body

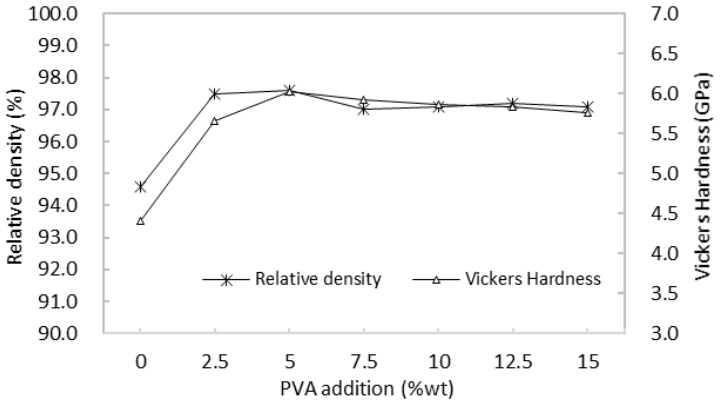


Fig. 7. The relationship between relative density and Vickers hardness

The hardness increases significantly with the addition of 2.5% wt PVA and slowly increases with the addition of 5% wt PVA, then decreases slowly with the addition of PVA up to 15% wt. This shows, that an increase in the density of sintered HA due to the addition of PVA as a binding material between HA powder when making a green body. The increase in hardness with the addition of 2.5-5% wt PVA is caused by the increased relative density value, as shown in Figure 7. Hardness correlates with the relative density value of a product [28,36]. In this study, the results of hardness and relative density also correlate with the addition of PVA as a binder when making a green body.

4. Conclusions

The addition of PVA to HA powder when making the green body can increase tangential bond between particles, so the strength of HA sintered body increases as evidenced by the increase in relative density and Vickers hardness. The addition of PVA is recommended at 2.5-10% weight. There is no phase change in the HA sintered body with the addition of PVA, and it is suspected that PVA has been burned out during the sintering process.

Acknowledgment

This research was funded from Hibah Penelitian Disertasi Doktor, Direktorat Riset and Pengabdian Masyarakat, Direktorat Jenderal Penguatan Riset dan Pengembangan, Kementerian Riset Teknologi dan Pendidikan Tinggi, Contract No: 051/SP2H/LT/DRPM/2019, Fiscal Year 2019. Thank you for the support given by the Mechanical Engineering Laboratory of Institut Teknologi Padang, Metallurgy Laboratory of Universitas Andalas, and Physics Laboratory of Universitas Negeri Padang.

References

[1] G. Xiong *et al.*, "Characterization of biomedical hydroxyapatite/magnesium composites prepared by powder metallurgy assisted with microwave sintering," *Curr. Appl. Phys.*, vol. 16, no. 8, pp. 830–836, 2016.

[2] M. Ashuri, F. Moztarzadeh, N. Nezafati, A. Ansari Hamedani, and M. Tahriri, "Development of a composite based on hydroxyapatite and magnesium and zinc-containing sol-gel-derived bioactive glass for bone substitute applications," *Mater. Sci. Eng. C*, vol. 32, no. 8, pp. 2330–2339, 2012.

[3] X. Gu, W. Zhou, Y. Zheng, L. Dong, Y. Xi, and D. Chai, "Microstructure, mechanical property, bio-corrosion and cytotoxicity evaluations of Mg/HA composites," *Mater. Sci. Eng. C*, vol. 30, no. 6, pp. 827–832, 2010.

[4] C. A. Vogiatzis, A. Tsouknidas, D. T. Kountouras, and S. Skolianos, "Aluminum-ceramic cenospheres syntactic foams produced by powder metallurgy route," *Mater. Des.*, vol. 85, pp. 444–454, 2015.

[5] K. Kanthavel, K. R. Sumesh, and P. Saravanakumar, "Study of tribological properties on Al/Al2O3/MoS2hybrid composite processed by powder metallurgy," *Alexandria Eng. J.*, vol. 55, no. 1, pp. 13–17, 2016.

[6] K. Soorya Prakash, P. M. Gopal, D. Anburose, and V. Kavimani, "Mechanical, corrosion and wear characteristics of powder metallurgy processed Ti-6Al-4V/B4C metal matrix composites," *Ain Shams Eng. J.*, vol. 9, no. 4, pp. 1489–1496, 2018.

[7] F. Erdemir, A. Canakci, and T. Varol, "Microstructural characterization and mechanical properties of functionally graded Al2024/SiC composites prepared by powder metallurgy techniques," *Trans. Nonferrous Met. Soc. China (English Ed.*, vol. 25, no. 11, pp. 3569–3577, 2015.

[8] K. Soorya Prakash, R. Sathiya Moorthy, P. M. Gopal, and V. Kavimani, "Effect of reinforcement, compact pressure and hard ceramic coating on aluminium rock dust composite performance," *Int. J. Refract. Met. Hard Mater.*, vol. 54, pp. 223–229, 2016.

[9] A. Goldstein, J. Raethel, M. Katz, M. Berlin, and E. Galun, "Transparent MgAl2O4/LiF ceramics by hot-pressing: Host-additive interaction mechanisms issue revisited," *J. Eur. Ceram. Soc.*, vol. 36, no. 7, pp. 1731–1742, 2016.

[10] K. Waetzig and T. Hutzler, "Highest UV–vis transparency of MgAl2O4 spinel ceramics prepared by hot pressing with LiF," *J. Eur. Ceram. Soc.*, vol. 37, no. 5, pp. 2259–2263, 2017.

[11] M. Buchi Suresh, P. Biswas, V. Mahender, and R. Johnson, "Comparative evaluation of electrical conductivity of hydroxyapatite ceramics densified through ramp and hold, spark plasma and post sinter Hot Isostatic Pressing routes," *Mater. Sci. Eng. C*, vol. 70, pp. 364–370, 2017.

[12] J. Dou, C. Zhang, C. Chen, and X. Zhang, "Effects of sintering temperature on the properties of alumina/hydroxyapatite composites," *J. Sol-Gel Sci. Technol.*, vol. 84, no. 1, pp. 23–27, 2017.

[13] M. J. Abden, J. D. Afroze, M. S. Alam, and N. M. Bahadur, "Pressureless

sintering and mechanical properties of hydroxyapatite/functionalized multi-walled carbon nanotube composite," *Mater. Sci. Eng. C*, vol. 67, pp. 418–424, 2016.

[14] M. Akmal, A. Raza, M. M. Khan, M. I. Khan, and M. A. Hussain, "Effect of nano-hydroxyapatite reinforcement in mechanically alloyed NiTi composites for biomedical implant," *Mater. Sci. Eng. C*, vol. 68, pp. 30–36, 2016.

[15] M. Wu, Q. Wang, X. Liu, and H. Liu, "Biomimetic synthesis and characterization of carbon nanofiber/ hydroxyapatite composite scaffolds," *Carbon N. Y.*, vol. 51, no. 1, pp. 335–345, 2013.

[16] A. Szcześ, L. Hołysz, and E. Chibowski, "Synthesis of hydroxyapatite for biomedical applications," *Adv. Colloid Interface Sci.*, vol. 249, no. April, pp. 321–330, 2017.

[17] C. Sharma, A. K. Dinda, P. D. Potdar, C. F. Chou, and N. C. Mishra, "Fabrication and characterization of novel nano-biocomposite scaffold of chitosan-gelatin-alginate-hydroxyapatite for bone tissue engineering," *Mater. Sci. Eng. C*, vol. 64, pp. 416–427, 2016.

[18] H. L. Kim *et al.*, "Preparation and characterization of nano-sized hydroxyapatite/alginate/chitosan composite scaffolds for bone tissue engineering," *Mater. Sci. Eng. C*, vol. 54, pp. 20–25, 2015.

[19] E. Quinlan, A. López-Noriega, E. Thompson, H. M. Kelly, S. A. Cryan, and F. J. O'Brien, "Development of collagen-hydroxyapatite scaffolds incorporating PLGA and alginate microparticles for the controlled delivery of rhBMP-2 for bone tissue engineering," *J. Control. Release*, vol. 198, pp. 71–79, 2015.

[20] S. Kulanthaivel *et al.*, "Cobalt doped proangiogenic hydroxyapatite for bone tissue engineering application," *Mater. Sci. Eng. C*, vol. 58, pp. 648–658, 2016.

[21] Y. Lei *et al.*, "Strontium hydroxyapatite/chitosan nanohybrid scaffolds with enhanced osteoinductivity for bone tissue engineering," *Mater. Sci. Eng. C*, vol. 72, pp. 134–142, 2017.

[22] D. Juliadmi, V. R. Fauzi, Gunawarman, H. Nur, and M. H. Idris, "Hydroxyapatite coating on titanium alloy Ti-6Al-4V with electrophoretic deposition (EPD) for dental root application," *Int. J. Adv. Sci. Eng. Inf. Technol.*, vol. 7, no. 6, pp. 2152–2158, 2017.

[23] N. F. Nuswantoro, I. Budiman, A. Septiawarman, D. H. Tjong, M. Manjas, and Gunawarman, "Effect of Applied Voltage and Coating Time on Nano Hydroxyapatite Coating on Titanium Alloy Ti6Al4V Using Electrophoretic Deposition for Orthopaedic Implant Application," *IOP Conf. Ser. Mater. Sci. Eng.*, vol. 547, p. 012004, 2019.

[24] V. R. Sivaperumal, R. Mani, M. S. Nachiappan, and K. Arumugam, "Direct hydrothermal synthesis of hydroxyapatite/alumina nanocomposite," *Mater. Charact.*, vol. 134, no. November, pp. 416–421, 2017.

[25] A. Harabi, E. Harabi, S. Chehlatt, S. Zouai, N. E. Karboua, and L. Foughali, "Effect of B2O3 on mechanical properties of porous natural hydroxyapatite derived from cortical bovine bones sintered at 1,050°C," *Desalin. Water*

Treat., vol. 57, no. 12, pp. 5303–5309, 2016.
[26] Z. Li, S. G. Bi, R. T. Li, and K. A. Khor, "Hydroxyapatite Bioceramics Reinforced with Silica-Coated Graphene," *Key Eng. Mater.*, vol. 758, pp. 150–154, 2017.
[27] B. T. Lee, N. Y. Shin, J. K. Han, and H. Y. Song, "Microstructures and fracture characteristics of spark plasma-sintered HAp-5 vol.% Ag composites," *Mater. Sci. Eng. A*, vol. 429, no. 1–2, pp. 348–352, 2006.
[28] G. Muralithran and S. Ramesh, "The Effects of sintering temperature on the properties of hydroxyapatite," *Ceram. Int.*, vol. 26, no. 2, pp. 221–230, 2000.
[29] F. Zhang, K. Lin, J. Chang, J. Lu, and C. Ning, "Spark plasma sintering of macroporous calcium phosphate scaffolds from nanocrystalline powders," *J. Eur. Ceram. Soc.*, vol. 28, no. 3, pp. 539–545, 2008.
[30] Q. Wei, Y. Wang, W. Chai, Y. Zhang, and X. Chen, "Molecular dynamics simulation and experimental study of the bonding properties of polymer binders in 3D powder printed hydroxyapatite bioceramic bone scaffolds," *Ceram. Int.*, vol. 43, no. 16, pp. 13702–13709, 2017.
[31] A. Shavandi, A. E. D. A. Bekhit, A. Ali, and Z. Sun, "Synthesis of nano-hydroxyapatite (nHA) from waste mussel shells using a rapid microwave method," *Mater. Chem. Phys.*, vol. 149, pp. 607–616, 2015.
[32] J. Wang and R. Raj, "Estimate of the Activation Energies for Boundary Diffusion from Rate-Controlled Sintering of Pure Alumina, and Alumina Doped with Zirconia or Titania," *J. Am. Ceram. Soc.*, vol. 73, no. 5, pp. 1172–1175, 1990.
[33] M. -Y Chu, M. N. Rahaman, L. C. De Jonghe, and R. J. Brook, "Effect of Heating Rate on Sintering and Coarsening," *J. Am. Ceram. Soc.*, vol. 74, no. 6, pp. 1217–1225, 1991.
[34] W. Ji, B. Parker, S. Falco, J. Y. Zhang, Z. Y. Fu, and R. I. Todd, "Ultra-fast firing: Effect of heating rate on sintering of 3YSZ, with and without an electric field," *J. Eur. Ceram. Soc.*, vol. 37, no. 6, pp. 2547–2551, 2017.
[35] M. Hidouri, S. V. Dorozhkin, and N. Albeladi, "Thermal Behavior, Sintering and Mechanical Characterization of Multiple Ion-Substituted Hydroxyapatite Bioceramics," *J. Inorg. Organomet. Polym. Mater.*, vol. 29, no. 1, pp. 87–100, 2019.
[36] J. Nie, J. Zhou, X. Huang, L. Wang, G. Liu, and J. Cheng, "Effect of TiO 2 doping on densification and mechanical properties of hydroxyapatite by microwave sintering," *Ceram. Int.*, vol. 45, no. 11, pp. 13647–13655, 2019.