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Effect of sintering on the mechanical properties of hydroxyapatite from fish bone (*Pangasius Hypophthalmus*)

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Abstract. Hydroxyapatite was synthesized from materials containing calcium. The aim of this research is to determine the effect of sintering i.e. temperature and duration on mechanical properties of hydroxyapatite from paten fish *(Pangasius hypophthalmus)* bone. The calcium content of fish bone was analyzed by using atomic absorption spectroscopy. Hydroxyapatite synthesis was conducted by hydrothermal method followed by a sintering process at various temperatures 800, 900, 1000, 1100 and 1200°C for 2 hours. The optimum temperature for sintering hydroxyapatite was used for further synthesis by varying duration i.e. 1, 2, 3, 4 and 5 hours. The result shows that increasing temperature and duration of sintering enhanced Vickers Hardness and Modulus Young of hydroxyapatite product before it decreases subsequently. The optimum sintering condition was obtained at 1100°C and 2 hours with mechanical properties represent by Vickers Hardness 20.6±0.62 VHN and Modulus Young 3.23±0.11 GPa. The hydroxyapatite obtained has an average crystallite size of 45.68 nm and crystallinity of 87.31%. SEM-EDS analysis indicates the hydroxyapatite was porous and has an irregular shape with O, Ca and P content 33.12; 21.35 and 45.53%, respectively.
Keywords: hydroxyapatite, fish bone, sintering, mechanical properties

1. Introduction

Hydroxyapatite is an apatite mineral compound having general formula $Ca_{10}(PO_4)_6(OH)_2$. The mineral shows the hexagonal structure and contains a stoichiometrically Ca/P element ratio 1.667 [1]. Hydroxyapatite is a biomaterial that has the potential to be used in biomedical applications such as tissue engineering, teeth and maxillofacial [2-4]. Hydroxyapatite can also be used in the water treatment process for pollutants removals such as Pb [5], nitrobenzene [6], and dye [7].

Hydroxyapatite has a composition like bone and teeth [1]. The mineral shows biocompatibility and able to form bonds with living tissue, it also can integrate with a bone to form new tissue. It displays antimicrobial property as well as osteoconductivity and osteoinductivity [3]. In addition to the properties mention above, hydroxyapatite can be made in form of powder with a porous structure and good mechanical strength hence it suitable for medical application [8]. Biomaterial contained calcium such as star fish [3], egg shell [9], bovine bone [10] and phosphogypsum waste [5] can be used as raw material for hydroxyapatite.

One of the fish types that are cultivated and consumed by the people in Indonesia is paten fish *(Pangasius Hypophthalmus)*. Paten fish production in Indonesia continues to increase annually due to

increased demand for both domestic and export consumption. The increased number of paten fish consumed also increases the solid waste produced i.e. fish bones. Fish bone composes approximately 10-15% of the fish body [11]. Calcium content in fish bone is a potential resource for hydroxyapatite synthesis due to its cheapness and availability [12]. Synthesis of hydroxyapatite using fish bones also provides benefit for the environment because it solves the solid waste problem from paten fish consumption [13].

Several methods had been developed for hydroxyapatite synthesis such as sol-gel method [8], hydrothermal [10], wet-precipitation [4] and microwave processing [14]. The difference in synthesis method can result in different degree of crystallinity, particle size, morphology, homogeneity, and stoichiometry of resulting product. The hydrothermal method shows a high success rate among other methods not to mention its simplicity. Proper condition of sintering process plays important role in producing high quality of hydroxyapatite. Temperature selection and duration time of sintering impacts on the crystallinity and mechanical property i.e. Vickers Hardness and Modulus Young [15].

The aim of the research is to synthesis hydroxyapatite from raw materials of paten fish *(Pangasius Hypophthalmus)* bone by hydrothermal method. Optimum temperature and sintering duration will be evaluated. $CaCO_3$ from fish bone was converted to CaO through calcination process at 900°C. CaO compound was further converted into hydroxyapatite through a chemical reaction with $(NH_4)_2HPO_4$ in alkaline condition.

2. Material and Methods

2.1. Materials

A sample of fish bone was obtained from Palembang, South Sumatera Indonesia. Chemicals used in this research were distilled water, HNO_3 (65%), NH_4OH (NH_3 in H_2O 28-30%) both were purchased from Sigma-Aldrich (65%) and $(NH_4)_2HPO_4$ purchased from Merck.

2.2. Determination of calcium in fish bone

The fish bone powder (0.142 g) poured into the flask, added by 10 mL HNO_3 36% and deionized water 50 mL. The mixture was heated by using an electric mantle at 180°C for 2 hours. The resulting filtrate was transferred into a volumetric flask of 50 mL and then diluted using deionized water. The Ca contents were determined by using Atomic Absorption Spectroscopy Shimadzu AA 7000.

2.3. Synthesis of Hydroxyapatite

Fish bones were cleaned from dirt, washed with distilled water, then boiled for 3 hours. The bones were dried in an oven at 110°C for 2 hours. About 250 g of fish bone powder was heated at 900°C for 2 hours to convert $CaCO_3$ to CaO and then it was crushed into powder using ball milling to obtain nano size.

The mixture of 12 g CaO and 100 mL HNO_3 2 M stirred at 70°C for an hour. The precipitate was filtered and washed using distilled water until pH neutralized. The precipitate was dried in an oven at 110°C for 2 hours. This dried powder of 6.0 g was added into 250 mL $(NH_4)_2HPO_4$ 0.9 M, mixed by using shaker at 120 rpm and NH_4OH 1 M was added dropwise to obtain pH±10. Mixing was continued for 24 hours, then the mixture was washed with distilled water to remove NH_4^+ and NO_3^-. The materials were dried in an oven at 110°C for 3 hours.

The powder was then solidified using the hydraulic machine at 20 MPa on cylinder specimen with 38 mm diameter and 40 mm length. The sintering process was conducted at 800, 900, 1000, 1100 and 1200°C for 2 hours, and then by using optimum sintering temperature, the calcination was carried out for various duration time (1, 2, 3, 4 and 5 hours).

2.4. Characterization of Hydroxyapatite

Hardness test was conducted using the Vickers method with 50 g load for 10 seconds and 5 different points of measurement were chosen. The test repeats for 3 times to estimate the deviation standard. Modulus Young is measured using the same instrument. Hydroxyapatite powder was characterized to

determine the crystallinity using X-ray diffractometer (XRD Miniflex 600) the 2θ at a range of 0-90° using CuKα=1.5418 Å, voltage 45 kV, and 100 mA. XRD data were used to calculate crystallite size and crystallinity using Scherrer equation. The morphology and elemental composition were evaluated by using SEM-EDS JEOL JSM 6510 LA.

3. Results and Discussion

This study report that paten fish *(Pangasius Hypophthalmus)* bone contained calcium 18.30%. This amount of calcium has the potential as raw materials resources for hydroxyapatite synthesis. The synthesis was conducted via a hydrothermal method. Calcination of fish bone to convert $CaCO_3$ into CaO was carried out through chemical reaction as follows:

$$CaCO_3 \rightarrow CaO + CO_2 \quad (1)$$

$$CaO + 2HNO_3 + 3H_2O \rightarrow Ca(NO_3)_2 + 4H_2O \quad (2)$$

$$10Ca(NO_3)_2 + 6(NH_4)_2HPO_4 + 2NH_4OH \rightarrow Ca_{10}(PO_4)_6(OH)_2 + 14NH_4NO_3 + 6HNO_3 \quad (3)$$

The XRD pattern of hydroxyapatite synthesized at different temperatures 800, 900, 1000, 1100 and 1200°C depicted in Fig. 1. The sintering temperature at 800°C shows broad peaks represents an amorphous structure. The broad pattern indicates the existence of protein and collagen [13]. As the temperature got higher, sharp and narrow peaks resulted. Even though, at 1200°C the peak intensity is decreased. At a temperature <1250°C, α-TCP was formed which is converted into β-TCP and tetra calcium phosphate at a higher temperature [8]. β-TCP can reduce the mechanical property of hydroxyapatite [15]. The sintering temperature at 1250°C can not attain pure hydroxyapatite but it will contain potassium calcium phosphate with crystalline size quite large i.e. 1224 nm [16].

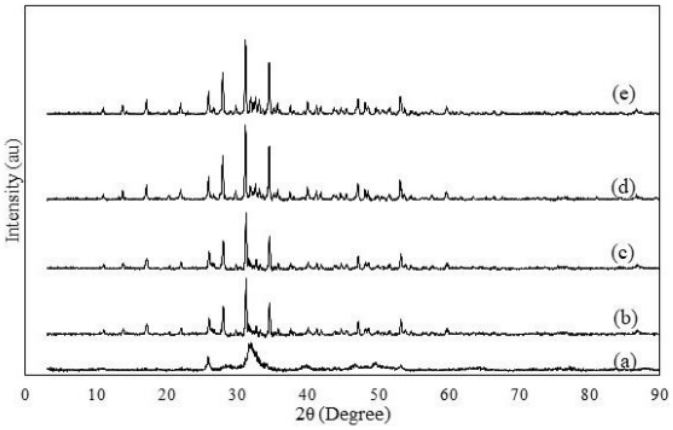

Figure 1. XRD pattern of hydroxyapatite sintered at (a) 800°C (b) 900°C (c) 1000°C (d) 1100°C and (e) 1200°C.

Based on JCPDS No. 09.0432, characteristic peak of hydroxyapatite at 2θ=25.8 (002); 31.7 (211); 32.1 (112); 32.9 (300); 46.7 (222) and 49.4° (213). The peaks shown is for synthetic hydroxyapatite in different intensity. The average crystalline size and crystallinity shown in table 1. Crystallite size is proportional to the crystallinity. The similar result of hydroxyapatite synthesis using calcium nitrate and potassium dihydrogen phosphate precursors [17]. In this study, we report that the sintering process at 800°C produced lowest crystallite size and crystallinity whereas sintering process at 1100°C obtained highest crystallite size and crystallinity. The other research described increased of crystallite size

accompanied by a decrease of the amorphous phase [18]. The hydroxyapatite of our synthesis indicates a similarity between hydroxyapatite from human bone i.e. 20-80 nm [19].

Table 1. The average crystallite size and crystallinity of hydroxyapatite.

Sintering temperature (°C)	Average crystallite size (nm)	Average crystallinity (%)
800	24.16	66.78
900	31.26	73.56
1000	38.89	80.20
1100	45.68	87.31
1200	42.46	85.19

Process duration affected the optimum condition for sinter completion. Fig. 2 shows various duration time of sintering at 1100°C. Optimum time obtained is 2 hours while 1 hour duration still displayed low peaks and longer duration (3 and 4 hours) indicates a decrease in intensity at 2θ=31.7°. The long heating process during sintering caused decomposition of hydroxyapatite product henceforth decreased its intensity.

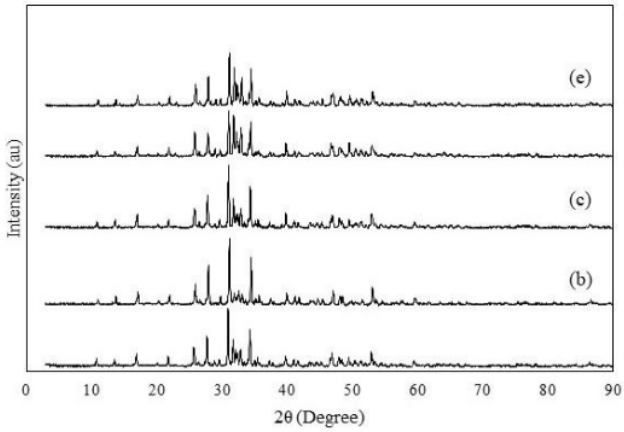

Figure 2. XRD pattern of hydroxyapatite sintered for (a) 1 (b) 2 (c) 3 (d) 4 and (e) 5 hours.

Table 2 displays crystallite size and crystallinity of hydroxyapatite which was synthesized at various duration time and 1100°C. While 3 hours duration shows slight different with 2 hours, sintering duration for 4 and 5 hours resulted in lower crystallite size and crystallinity. Longer heating duration on sintering triggered contraction and expansion which caused damaged materials.

Table 2. The average crystallite size and crystallinity of hydroxyapatite at various sintering duration.

Time (hour)	Average crystallite size (nm)	Average crystallinity (%)
1	42.16	85.78
2	45.68	87.31
3	44.76	86.69
4	36.89	78.89
5	34.67	74.90

The temperature used in sintering affect the mechanical property of hydroxyapatite. This material's drawback inhibits its utilization in bone implants due to fragility. One way to overcome this situation is by controlling the sintering process i.e. temperature [20]. Mechanical property can be measured by hardness value and Modulus Young. Material hardness defined as material hardness against deformation on the local area while Modulus Young indicates stiffness measure of materials. The high temperature of the sintering process induced microstructure alteration of hydroxyapatite as well as pore size. Increase hardness of crystal can be encouraged by positioning atoms in crystal lattice which is highly ordered. Increased sintering temperature enhanced crystal size and crystallinity but decreased porosity and surface area [16]. The porosity deceased will affect hardness by increase it. Fig. 3 and 4 shows the effect of sintering temperature on hardness and Modulus Young.

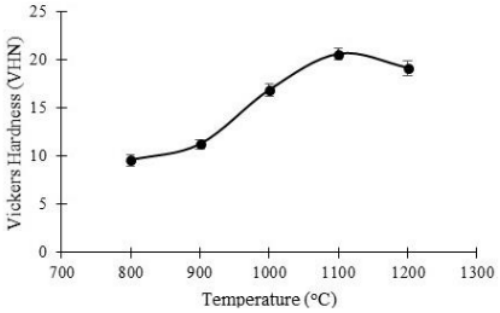

Figure 3. Vickers Hardness of hydroxyapatite sintered at various temperatures.

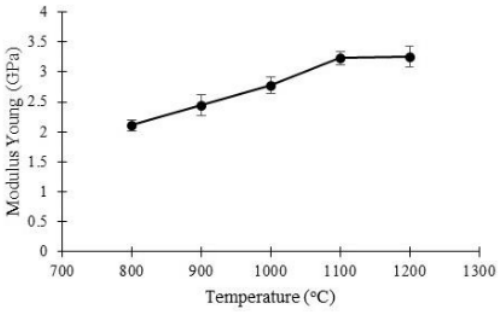

Figure 4. Modulus Young of hydroxyapatite sintered at a various temperature.

Hardness decrease was observed at 1200°C as well as Modulus Young even though just a bit. The hydroxyapatite synthesis by using wet precipitation method and wet mechanochemical result in a similar trend which is increased sintering temperature up to certain degree will cause increased hardness and then decreased at a higher temperature [21]. The hardness is not only affected by solid density but also grain size [20]. The largest hardness value obtains at 1100°C. For to the same temperature (1100°C) on his hydroxyapatite synthesis by using precursors of calcium hydroxide and orthophosphoric acids [22]. The increase of sintering temperature also increasing Modulus Young. The Modulus Young for 1100 and 1200°C sintering temperature shows a slight discrepancy i.e. 3.23 and 3.26 GPa.

The effect of sintering duration to Vickers Hardness and Modulus Young is shown on Fig. 5 and 6. The Fig. depicted the rise of Vickers Hardness and Modulus Young at 1 and 2 hours duration which is decreased afterward. Optimum values obtained after 2 hours duration are 20.6±0.62 VHN and 3.23±0.11 GPa for Vickers Hardness and Modulus Young, respectively.

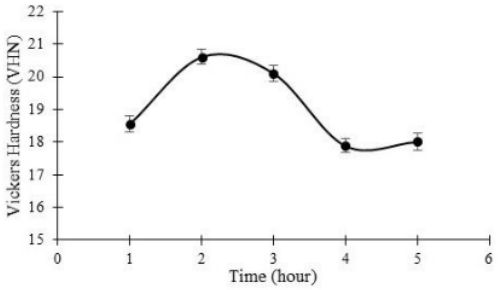

Figure 5. Vickers Hardness of hydroxyapatite sintered at the various duration of time.

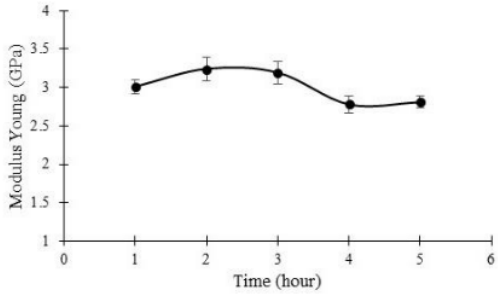

Figure 6. Modulus Young of hydroxyapatite sintered at the various duration of time.

The morphological of hydroxyapatite synthesized at 1100°C and 2 hours sintering temperature and duration is shown in Fig. 7. The studied the effect of sintering on the transformation of hydroxyapatite micro structure, finds out that change of pore began above 1260°C, pore shape became roundish, obtrusive and solid [23]. The temperature creates a condition which plays an important role in the morphologic formation, temperature control undoubtedly vital to the size and shape of crystal formed [24]. In this report, we obtained that hydroxyapatite has an oval shape, agglomerated and display porous structure. This result is alike what has been reported the other author which was hydroxyapatite synthesis from calcium nitrate and diammonium hydrogen phosphate using the same method [25]. Table 3 shows an elemental analysis result by the EDS method. Based on the data displayed, hydroxyapatite is purified

comprised of Ca, P and O and shows the molar ratio of Ca/P 1.654 approach standard ratio of synthetic hydroxyapatite 1.667.

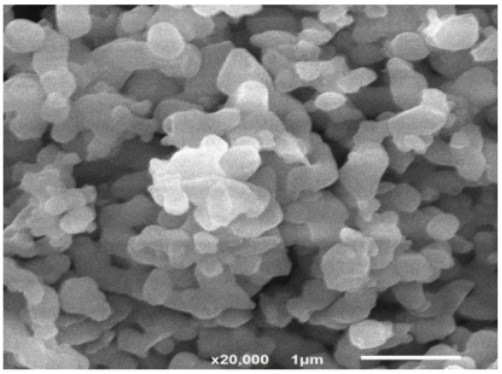

Figure 7. Hydroxyapatite morphology sintered at 1100°C for 2 hours.

Table 3. Elemental composition of hydroxyapatite sintered at 1100°C for 2 hours.

Elements	Mass (%)
O	33.12
P	21.35
Ca	45.53

4. Conclusions

This work shows that temperature and duration of sintering affect hydroxyapatite product prepared from paten fish *(Pangasius Hypophthalmus)* bone using the hydrothermal method. Using various temperature (800-1200°C) and sintering duration (1-5 hours) hydroxyapatite were obtained having best Vickers Hardness and Modulus Young value i.e. 20.6±0.62 VHN and Modulus Young 3.23±0.11 GPa at 1100°C after 2 hours sintering process. XRD pattern supported this result by sharp and narrow peaks with high intensity. The average crystallite size obtained of 45.68 nm and 87.31% of crystallinity. Elemental analysis shows no impurity in the product with Ca/P ratio 1.654 approaches the standard ratio of pure hydroxyapatite 1.667.

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