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Synthesis of Hydroxyapatite from Duck Egg Shells by Precipitation Method for Bio-Ceramics Applications

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Abstract. Utilization of duck egg shells as a source of calcium for the synthesis of hydroxyapatite (HAp) has been carried out by precipitation method. The precipitation method is the most commonly used option in terms of its convenience. This study aims to determine the chemical components of duck egg shells before and after calcination, and to analyze the effect of variations in sintering temperature on HAp. Characterization carried out using XRF and XRD as well as testing the mass efficiency of HAp at sintering temperatures of 700ºC, 800ºC, 900ºC, and 1000ºC for 5 hours. XRF analysis showed that the main components of duck egg shells before and after calcination were 99.02% $CaCO_3$ and 93.95% CaO, and the main component of HAp contained CaO and P_2O_5. XRD analysis showed that the phase formed was HAp with a hexagonal crystal structure. The HAp sintered at various temperatures produced crystal sizes of respectively 14.18 nm; 20.87 nm; 30.56 nm; and 31.73 nm with a mass efficiency of 61.78%; 58.84%; 58.62%; and 57.47%. The best result was sintering at 800ºC, which give the optimum condition for HAp for application as bone and dental implants.

INTRODUCTION

The development of research in the fields of industry and technology has an impact on increasing material requirements. In the medical world, one of the uses of the material is an implant. Bio-ceramic is a synthetic biomaterial that is continuously developed and is a well-known implant material because it has several advantages compared to polymer or metal biomaterials, including having good biocompatibility with body cells, non-toxic and does not damage cells in the human body [1]. The advantages of bio-ceramics make it a material that continues used in the development of medical science, especially for bones and teeth caused by the increasing cases of fractures and tooth decay [2]. Bio-ceramics can be synthesized from materials rich in calcium, such as beef bones, fish bones, clam shells, and egg shells [3-7]. Duck egg shell is one of the materials that have the potential as a bio-ceramic material that is easily obtained.

Generally, duck egg shells are considered as unused waste and have no economic value, so most of them are just thrown away. Based on several references, duck egg shells contain high calcium carbonate ($CaCO_3$) up to 99% which can be used as a source of calcium for the synthesis of hydroxyapatite (HAp) [2, 8-9]. Hydroxyapatite ($Ca_{10}(PO_4)_6OH_2$) is a bio-ceramic compound formed from the main elements calcium and phosphorus with a Ca/P ratio of 1.667 [10-12]. The advantages of HAp are that it has biocompatibility, non-toxic, non-immunogenic, non-inflammatory, and bioactive properties and has the same crystal structure as hydroxyapatite in human bones and teeth [8,13-15].

The use of HAp material in the medical field has several characteristics such as crystal size, lattice parameters and crystal structure. HAp has the same crystal size as bone and tooth HAp crystal size, which is in the range of 20–50 nm [16-17]. The crystal structure of HAp can be monoclinic or hexagonal. The Hydroxyapatite with a monoclinic structure was obtained under pure conditions with a stoichiometric composition, with a Ca/P ratio of 1.667 [10,18]. HAp has a stable calcium phosphate crystal phase with lattice parameters, namely a = b = 9.42 Å and c = 6.88 Å [19].

Based on research conducted by Agbabiaka et al [11], chicken egg shells can be used as a source of calcium for the synthesis of HAp and orthophosphoric acid (H_3PO_4) as a source of phosphorus. The results showed that the best

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sample of HAp synthesized using the hydrothermal method was produced at a temperature of 1000ºC. At this temperature, the Ca/P stoichiometric ratio of 1.65 is close to the natural bone stoichiometric ratio of 1.667 [10].

Based on this explanation, a research was conducted on the synthesis of HAp from duck eggshell as a source of calcium and di-ammonium hydrogen phosphate ($(NH_4)_2HPO_4$) as a source of phosphorus using the precipitation method by varying the sintering temperature. The precipitation method is part of the well-known and most widely used wet chemical method. It has several advantages, such as the price of the raw materials needed is cheaper, the chemical reaction is relatively simple, the size and homogeneity of the particle size obtained tend to be better. The byproduct is only water, does not pollute the environment and contamination during processing is very low so that in the production process it produces a high level of purity [14, 20]. The presence of diffusion events at high sintering temperatures causes the incorporation of powder particles, fine particle bonds formed between the powder surfaces. The bond can increase the strength and physical properties of a sample. The sintering process is by heating the HAp below its melting point of 1250ºC [16, 21-22].

This study aimed to determine the chemical composition of duck egg shells and the resulting HAp, as well as to analyze the effect of sintering temperature on the structural properties and mass efficiency of HAp. To determine the chemical composition, structure, crystal size, elements, and lattice parameters, analysis was using X-ray fluorescence (XRF) and X-Ray Diffraction (XRD), as well as testing the mass efficiency of HAp. The resulting HAp is expected use in the medical world as a bio-ceramic application.

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MATERIAL AND METHODS

The duck egg shell, di-ammonium hydrogen phosphate ($(NH_4)_2HPO_4$), and distilled water are used as raw material. Duck egg shells are washed thoroughly to remove dirt that is still attached to the shell. Clean egg shells are boiled for 30 minutes. Furthermore, in a warm state, the white layer (mammary layer and membrane layer) is separated from the egg shell. Then, the egg shells are dried for 24 hours. The dried egg shells were mashed using a mortar and then sieved using a 200 mesh. Furthermore, the egg shells were calcined in a furnace at a temperature of 800ºC for 3 hours to produce CaO.

A 2.83 grams of CaO was dissolved in 100 ml of distilled water was marked as the first solution. Then 3.97 grams ($(NH_4)_2HPO_4$) was also dissolved in 100 ml of distilled water and marked as the second solution. The first solution was stirred for 10 minutes at a speed of 350 rpm, the same treatment applies to the second solution. After that, the phosphate precursor solution was slowly mixed into the calcium hydroxide ($Ca(OH)_2$) suspension. The second solution added by titration method at a rate of 10 ml/min into the first solution at 350 rpm until well mixed. After the $(NH_4)_2HPO_4$ solution mixed, the mixture covered with aluminum foil and allowed to stand for 18 hours to form a precipitate. The resulting precipitate was then filtered using filter paper and washed with distilled water 3 times. After that, it dried at 110ºC for 3 hours. The sintering process carried out at 700ºC, 800ºC, 900ºC, and 1000ºC for 5 hours. Hydroxyapatite that has synthesized using the precipitation method is then calculated using the equation [23-26]:

$$\text{Hydroxyapatite mass efficiency} = \frac{\text{Hydroxyapatite mass}}{\text{initial mass of calcium and phosphoric acid}} \text{ x } 100\% \quad (1)$$

To determine the chemical composition, analysis using X-ray fluorescence (XRF) carried out on the entire sample. The analysis uses an X-Ray Diffraction (XRD) instrument to identify the structure, crystal size, elements, and lattice parameters of a material through the intensity peaks that appear. Crystal size can be calculated using Debye Scherrer's equation as follows [27]:

$$D = \frac{0{,}9\,\lambda}{\beta \cos\,\theta} \quad (2)$$

Debye Schrerrer's equation shows the relationship between crystal size values and FWHM values.

RESULTS AND DISCUSSION

The results of the preparation of duck egg shells were characterized using X-Ray Fluorescence (XRF) to determine the chemical components contained in the egg shells. Based on the results of XRF analysis, duck egg shells contain 99.02% calcium carbonate ($CaCO_3$) as the main component. These r esults are in accordance with research conducted

by Sabir et al (2020) who reported that the main content of duck egg shells was $CaCO_3$ 99.63% [2]. The high $CaCO_3$ content can be used as a source of calcium for the synthesis of HAp.

Calcium contained in duck egg shells is a compound of calcium carbonate ($CaCO_3$), and needs to be calcined to obtain calcium oxide (CaO) [28, 29]. The CaO used as a calcium (Ca) precursor in the HAp synthesis process. The reaction shown in the following equation [30]:

$$CaCO_3 \rightarrow CaO + CO_2 \quad (3)$$

The reaction shows that $CaCO_3$ decomposes into CaO and CO_2, the carbon dioxide will evaporate in the air. Duck egg shell calcination in this study was carried out using a furnace at a temperature of 800°C for 3 hours. The calcium oxide powder produced from the calcination process characterized using XRF. Based on the results of XRF analysis, duck egg shells after being calcined contained 93.95% CaO compounds and 6.05% other oxide compounds, namely MgO, P_2O_5, SrO, TiO_2, Nb_2O_5, and MoO_3. The presence of oxide compounds other than CaO caused by the presence of other compounds that react when the synthesis process takes place [31]. In addition, during the synthesis process, duck eggshell powder may contaminated with other materials found in the laboratory.

The synthesis of hydroxyapatite (HAp) was carried out using calcium oxide (CaO) compounds from calcined duck egg shell powder. The CaO compound was reacted with $(NH_4)_2HPO_4$ as a source of phosphorus using the precipitation method. The precipitation method is a HAp synthesis method in which an acid-base reaction occurs and produces a crystalline solid [32]. The reaction for the formation of HAp described in the following reaction equation [33]:

$$10Ca(OH)_2+6(NH_4)_2.HPO_4+2H_2O \rightarrow Ca_{10}(PO_4)_6(OH)_2+6H_2O+12NH_4OH \quad (4)$$

The results of XRF analysis for HAp synthesis carried out with several variations of sintering temperature shown in Table 1.

TABLE 1. Results of XRF analysis of HAp powder

Sintering Temperature (°C)	Oxide Compounds (%)						CaO/P_2O_5 Ratio
	CaO	P_2O_5	SrO	ZnO	Nb_2O_5	Other	
700	60.56	39.36	0.04	0.01	0.01	0.02	1.538
800	62.56	37.29	0.06	0.03	0.01	0.05	1.677
900	62.52	37.15	0.06	0.25	0.01	0.02	1.682
1000	61.68	38.19	0.06	0.04	0.01	0.01	1.615

Based on the results of XRF analysis in Table 1, the chemical composition of HAp contains the main chemical compounds CaO and P2O5. HAp sintered at 800ºC for 5 hours produced a CaO/P_2O_5 ratio of 1.677, which was close to the HAp stoichiometric ratio value, which was 1.667 [10]. This value is a specification of HAp is identical to calcium apatite in bones and teeth [8, 13-15]. The table show the sintering temperature affects the ratio of CaO/P_2O_5, this is because CaO and P_2O_5 at increasing sintering temperature are unstable [11].

HAp powder synthesized by precipitation method was analyzed using X-Ray Diffraction (XRD) is shown in Fig.1. XRD characterization results show diffraction peaks in the form of hexagonal structures formed at 2Θ = 31.766º; 32.195º; 32.897º; 34.063º; and 39.791º with hkl (211), (112), (300), (202), and (130) (JCPDS No. 01-074-0566). The dominant phase formed is HAp which is indicated by the numbers 1,2,3,4,5 on the curve and the lattice parameters formed are a = b = 9.424 Å and c = 6.879 Å.

Based on the results of the study, HAp which was sintered at 900ºC and 1000ºC produced new peaks formed in the 2θ range between 30º-34º which was also HAp (5). This is evidenced by the research of Charlena et al [34] which states that the higher the sintering temperature, the more HAp formed, this result is due to the more regular arrangement of atoms.

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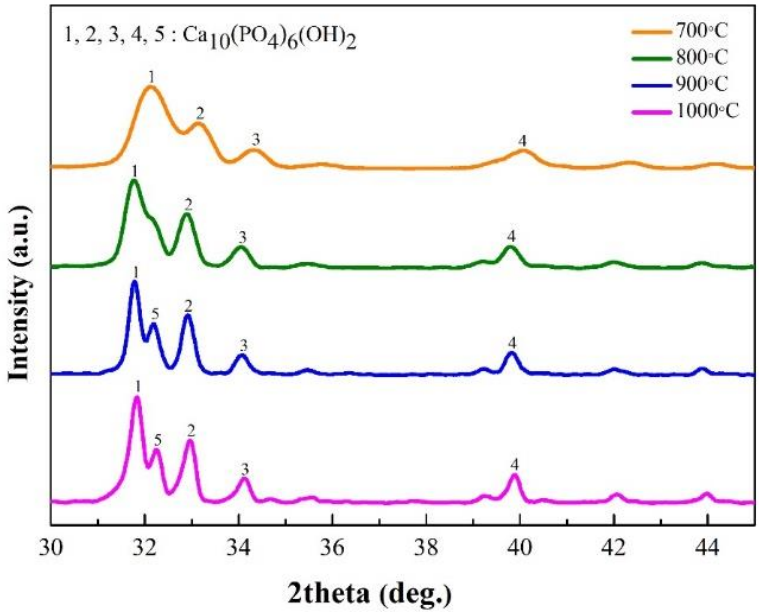

FIGURE 1. HAp diffractogram at sintering temperatures of 700ºC, 800ºC, 900ºC, and 1000ºC for 5 hours

Debye Schrerrer's equation shows the relationship between crystal size values and FWHM values. The smaller the crystal size value, the higher the FWHM value, and vice versa [28]. The crystal size of HAp sintered at several temperatures was calculated using equation 2.

TABLE 2. Crystalline size of hydroxyapatite (HAp)

Sintering Temperature (°C)	Crystal Size (nm)
700	14.18
800	20.87
900	30.56
1000	31.73

Based on Table 2, the variation of the sintering temperature carried out has an effect on the size of the resulting crystal. HAp crystal size has the same size as HAp crystal size in teeth and bones, which is in the range of 20–50 nm [16]. The table also shows that the increase sintering temperature will increase the size of the crystals formed, because the energy received by the atoms is greater for diffusion and agglomeration. The size of the crystals formed is getting bigger and the bonds between atoms are getting stronger and more regular [16].

The mass efficiency of the resulting HAp was calculated using equation 1 with an initial mass of calcium and phosphoric acid of 6.8 grams.

TABLE. 3. Effect of sintering temperature on mass efficiency of HAp

Sintering Temperature (°C)	Hydroxyapatite Mass (gr)	Hydroxyapatite Mass Efficiency (%)
700	4.2008	61.78
800	4.0010	58.84
900	3.9859	58.62
1000	3.9077	57.47

Based on Table 3, the mass of HAp after sintering was smaller than the initial mass of calcium and phosphoric acid because during the washing process there was wasted HAp. This shows that the higher the sintering temperature, the lower the mass efficiency of the HAp produced, and vice versa. The decrease in efficiency is due to the water

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content and organic matter lost during the sintering process [35]. The mass efficiency value of HAp in the range of 60% or less will be white which indicates that the resulting HAp is purer [36]. These results are in accordance with the research conducted by Yuliana et al. who reported that the sintering temperature affected the mass efficiency of the HAp produced [35].

CONCLUSION

The results of XRF analysis showed that the main component in duck eggshell before calcination was calcium carbonate ($CaCO_3$), and after calcination it produced calcium oxide (CaO) compounds, and the main component of HAp contained chemical compounds CaO and P_2O_5. Based on the results of XRD analysis, the formed HAp has a hexagonal crystal structure with lattice parameters a = b = 9.424 Å and c = 6.879 Å. The sintering temperature affects the crystal size and mass efficiency of the resulting HAp. The increase the sintering temperature will increase the crystal size and decrease the HAp mass efficiency. The best HAp was produced at a sintering temperature of 800^{o}C with a crystal size of 20.87 nm and a CaO/ P_2O_5 ratio of 1.677. This value is a specification of HAp, which is identical to calcium apatite in bones and teeth.

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