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THE EFFECT OF VARIATIONS OF HYDROTHERMAL TEMPERATURES ON EX-Situ HYDROXYAPATITE/AL_2O_3 DOPING PROCESS FROM PAPAI SHRIMP (*Acetes erythraeus*)

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Abstract

Hydroxyapatite (HA) is an alloplastic material that is commonly used as a substitute for bone grafts or bone grafts because it has bioactive properties, namely osteoconduction. This study aims to improve or develop the function of hydroxyapatite to become a strong and resilient biological device that can withstand loads for appropriate functions such as bone implants. Therefore, it is necessary to modify the structure, among others, by the reinforcement process (composite formation) with other materials. The doping of hydroxyapatite/Al_2O_3 in this study was carried out using the hydrothermal method. The hydrothermal method is one of the hydroxyapatite synthesis methods carried out at high pressure and temperature to achieve equilibrium. The material used in this study was papai shrimp as a source of calcium. The temperature has an effect in this study where the higher the doping temperature used, the higher the degree of crystallinity, particle size homogeneity, and porosity value. From the doping results, it is known that a temperature of 300°C produces a degree of crystallinity of 54.32% and a crystal size of 3.75 nm with a porosity value of 99.38%. This result is much better than the undoped hydroxyapatite in the previous study.

INTRODUCTION

Calcium phosphate (CaP) salts are the main minerals that form bones and teeth. Among the types of CaP salts, hydroxyapatite is the most similar to the mineral portion of bone. Having the chemical formula $Ca_{10}(PO_4)_6(OH)^{2-}$, hydroxyapatite is the most thermodynamically stable crystalline phase of CaP [1]. Hydroxyapatite (HA) is an alloplastic material that is commonly used as a substitute for bone grafts or bone grafts because it has bioactive properties, namely osteoconduction. The advantage of using hydroxyapatite as a bioceramic or biomaterial compared to other bioceramics is its itribbonilarity to the inorganic components of bone and teeth [2]. Shrimp rebon or in a dried form called shrimp papai is one of the marine products of the type of crustaceans but with a very small size compared to othrebornpes of shrimp. Because of this small size, this shrimp is called "rebon" shrimp [3]. Papai shrimp has a length of about 1-1.5 ,cm from the *Acetes* sp. [4]. In 100 g of papaw shrimp (*Acetes erythraeus*) there are 59.5 g of protein, 3.6 g of fat, 2.306 mg of calcium, 625 g of phosphorus, and 21.4 g of iron [5]. The calcium content in papai shrimp (*Acetes erythraeus*) is the largest mineral content compared to other minerals. Based on this, it is necessary to make efforts to utilize papai shrimp as a source of calcium for the manufacture of bone implants. To improve or develop the function of hydroxyapatite to become a strong and resilient biological device that accepts loads for appropriate functions such as bone implants, it is necessary to modify the structure, including reinforcement (composite formation) with other materials [6].

One of the metals that have been used in hydroxyapatite composites is Al_2O_3 or alumina. Alumina has good mechanical properties and is compatible so the combination of the mechanical characteristics of alumina with the characteristics of hydroxyapatite can be attractive to produce alumina-hydroxyapatite composites that can be used as bone implant biomaterials [7].

EXPERIMENT

The doping of hydroxyapatite/Al_2O_3 in this study was carried out using the hydrothermal method. The hydrothermal method is the most appropriate method to get results with good quality, purity, reactivity, and high yield. In addition, previous studies reported that the hydroxyapatite produced by the hydrothermal method was the most homogeneous [8].

The hydrothermal method is one of the methods for the synthesis of Hydroxyapatite which is carried out at high pressure and temperature to achieve equilibrium [9].

Material

The materials used in this study were Papaya Shrimp, HNO_3, NH_4OH, baking soda, citric acid, distilled water, $(NH_4)_2HPO_4$, and Aluminum Nitrate $Al(NO_3)_3$.

Instrumentation

The instruments used in this research are Fourier Transform Infrared (FTIR), X-ray Diffraction (XRD), and Scanning Electron Microscope (SEM).

Procedure

This study refers to research on the effect of variations in synthesis temperature and characterization of hydroxyapatite.

Papai Shrimp Preparation

Papai shrimp are dried in the sun to dry, after drying, they are mashed using a blender until they become dry powder, then followed by sifting using a 30 mesh sieve. Papai shrimp powder was calcined using a furnace for 3 hours at a temperature of 900°C.

Precipitated Calcium Carbonate Preparation

Synthesis of Precipitated Calcium Carbonate (PCC) refers to research [10] by converting CaO into Precipitated Calcium Carbonate (PCC) using the carbonation method. This process was carried out by dissolving 34 g of CaO in 600 ml of 2M HNO_3 and then stirring using a magnetic stirrer for 1 hour. The resulting mixture was filtered using filter paper. The filtrate was obtained from the filtering at hot conditions of 60°C and adjusted at pH 12 with the addition of concentrated NH_4¬OH solution slowly. Then filtered again. The results obtained are in the form of filtrate and CO_2 is added slowly until the pH becomes 8. When the gas has been added properly, a white precipitate will be formed which is called PCC. The PCC precipitate obtained was filtered again and washed with distilled water until the pH of the mixture became 7. Then it was placed in an oven at 110°C.

Synthesis of Hydroxyapatite from PCC

The hydroxyapatite synthesis step was carried out by mixing 2 g of PCC and 1.526498 g $(NH_4)_2HPO_4$ with a variation of the Ca/P precursor ratio of 1.73 with a pH of 11 in 100 mL distilled water. Then added NH_4OH solution. This mixing process is carried out in a hydrothermal vessel at a temperature of 150°C with a reaction time of 6 hours in the oven. The last step in the synthesis of hydroxyapatite is the purification step which is carried out to separate hydroxyapatite from the rest of the reactants with water. This purification process is carried out by filtering the hydroxyapatite mixture from the rest of the reactants with filter paper. The precipitate obtained was dried in an oven at a temperature of 110°C.

Making Alumina Solution (Al_2O_3) from Aluminum Nitrate

The first step is to make an alumina solution by mixing Aluminum Nitrate $Al(NO_3)_3$ with 250 mL of distilled water. Then an ammonia solution (25% ammonia) was added to increase the pH to 11. After that, the prepared solution was allowed to stir for 12 hours using an orbital shaker before use.

Hydroxyapatite/Alumina (Al_2O_3) Doping

Hydroxyapatite/Alumina (HA/Al_2O_3) composite was synthesized using the hydrothermal method. Mixing 2 g of hydroxyapatite with 250 mL of alumina solution with a concentration of 0.05M which has been stirred using an orbital shaker for 12 hours. Then the mixture was heated with temperature variations at 200°C, 250°C, and 300°C for 5 hours. After 5 hours cool to room temperature. After that, the results obtained are washed with water so that the results are purer. Then filtered and then heated again to remove the remaining water at a temperature of 60°C so that it can be further characterized. The results of hydroxyapatite doping using Al_2O_3 were characterized using Fourier Transform Infrared (FTIR), X-ray Diffraction (XRD), and Scanning Electron Microscope (SEM).

RESULTS AND DISCUSSION

Papai Shrimp Preparation

Papai shrimp serves as a source of $CaCO_3$ which will be decomposed into CaO in the process of making hydroxyapatite. After being dried, the Papaya shrimp were mashed using a blender and then sieved using a 30-mesh sieve. The purpose of this refining is to obtain papai shrimp powder to facilitate the calcination process. Calcination is heating at high temperatures to remove certain compositions and remove water molecules [11]. Papai shrimp calcined result can be see at **Figure 1**. The reactions that occur during the calcination process are as follows:

$$CaCO_{3(s)} \longrightarrow CaO_{(s)} + CO_{2(g)}$$

Figure 1. Papai Shrimp Calcined Results.

Precipitated Calcium Carbonate Preparation

Precipitated Calcium Carbonate is calcium carbonate with the chemical formula $CaCO_3$ produced from the precipitation process with high purity [10]. Preparation of Precipitated Calcium Carbonate refers to research [10] by dissolving 34 g of CaO in 600 mL of 2M HNO_3. The best conditions in the manufacture of Precipitated Calcium Carbonate were obtained at the concentration of 2M HNO_3, where the HNO_3 solution served as a solvent to dissolve the calcined calcium oxide [12]. After that, the solution was stirred using a magnetic stirrer at a constant speed for 60 minutes on a hot plate at 60°C so that the solution was homogeneous. The reactions that occur are as follows:

$$CaO_{(s)} + 2HNO_{3(aq)} \longrightarrow Ca(NO_3)_{2(aq)} + H_2O$$

After obtaining a homogeneous solution, filtered to obtain the filtrate. The filtrate obtained was adjusted by adding NH4OH until the pH of the solution changed to 12. The filtrate was filtered again to obtain the filtrate. The reaction that occurs is as follows:

$$Ca(NO_3)_{2(aq)} + NH_4OH_{(aq)} \longrightarrow Ca(OH)_{2(aq)} + 2NH_4NO_{3(aq)}$$

The obtained filtrate is then converted into $CaCO_3$ by the carbonation method. This process aims to purify calcium carbonate by binding CaO in the material using CO_2 gas. The carbonation process is carried out by reacting commercial citric acid and commercial baking soda to form CO_2 gas. The formation of Precipitated Calcium Carbonate is indicated by the presence of a white precipitate in the solution. Then the solution is filtered to separate the precipitated Precipitated Calcium Carbonate from the filtrate. Precipitated Calcium Carbonate precipitate was washed using distilled water to pH 7 and dried in an oven at 110°C to remove residual water from the precipitation process. The reaction that occurs is as follows:

$$Ca(OH)_{2(aq)} + CO_{2(g)} \longrightarrow CaCO_{3(s)} + H_2O_{(l)}$$

Synthesis of Hydroxyapatite from PCC

The process of hydroxyapatite synthesis requires a phosphate source derived from diammonium hydrogen phosphate $(NH_4)_2HPO_4$ [13]. The synthesis of hydroxyapatite was carried out by mixing 2 g of Precipitated Calcium Carbonate and 1.526498 g $(NH_4)_2HPO_4$ with a variation of 1.73 Ca/P precursors in 100 mL distilled water. This refers to the study [14] where the 1.73 precursor was the optimum precursor for the synthesis of hydroxyapatite. After the solution is mixed, NH_4OH solution is added to a pH of 11. This is because the formation of hydroxyapatite occurs at pH 10-12 [13] The mixing process is carried out in a hydrothermal vessel. The temperature used for the synthesis of hydroxyapatite is 150°C, this refers to research conducted where this temperature is the optimum temperature for the synthesis of hydroxyapatite because the percentage of the product content of the synthesis is 88% and calcite is 12%. The time required for this synthesis process refers to research [14] where the optimal time for the synthesis of hydroxyapatite is 6 hours.

Making Alumina Solution (Al_2O_3) from Aluminum Nitrate

A 0.05 M alumina solution was prepared by dissolving aluminum nitrate $Al(NO_3)_3$ with 250 mL of distilled water. Then the pH of the solution was increased to 11 with the addition of a solution of ammonia (ammonia 25%). Then the alumina solution was stirred using an orbital shaker to make it homogeneous for 12 hours.

Hydroxyapatite/Alumina (Al2O3) Doping

Doping is the addition of another material to a material. The purpose of doping is to optimize the properties of a material [15]. Hydroxyapatite doped using ex-situ hydrothermal method. The ex-situ process was carried out by forming the HA-Al_2O_3 composite directly after the hydroxyapatite was formed. Hydrothermal doping with the ex-situ hydrothermal method has higher purity and crystallinity than in-situ results [16].

Hydroxyapatite/alumina doping was done by mixing 2 g of hydroxyapatite with 250 mL of alumina solution with a concentration of 0.05 M. This mixing was carried out in a hydrothermal

vessel. The principle of the hydrothermal method is heating the reactants in a closed container using a medium of water where this closed system allows the pressure and temperature to increase rapidly. This results in high purity and crystallinity. The reaction mechanism that occurs in the doping process is as follows [17]:

$$Ca_{10}(PO_4)_6(OH)_2 + Al_2O_{3(aq)} \longrightarrow 3Ca_3(PO_4)_{2(s)} + CaAl_2O_{4(aq)} + H_2O_{(l)}$$

The doping process was carried out with temperature variations of 200°C, 250°C, and 300°C for 5 hours. After the doping process is complete, the hydrothermal vessel is cooled to room temperature. After that, the results obtained were washed with distilled water and filtered to obtain a hydroxyapatite/alumina precipitate. The precipitate was dried again in the oven at a temperature of 60°C to remove the remaining water molecules that were still present in the doped product. The doping results were characterized using Fourier Transform Infrared (FTIR), X-ray Diffraction (XRD), and Scanning Electron Microscope (SEM).

Fourier Transform Infrared (FTIR) Characterization Results

Characterization using Fourier Transform Infrared (FTIR) aims to identify the presence of certain groups or components contained in hydroxyapatite/alumina samples as indicated by the presence of peaks at certain wave numbers.

Fourier Transform Infrared (FTIR) spectra analysis was carried out at wave numbers from 4000-400 cm^{-1}. Spectra FTIR hydroxyapatite/Al_2O_3 result in **Figure 2**. To process the Fourier Transform Infrared analysis data in this study, the OiginLab 2022 application was used. From the three variations of the hydroxyapatite doping temperature, the results of the FTIR spectra were not much different. The results obtained are by research [18] where the absorption band at wave number 3700-3200 cm^{-1} is related to the hydroxyl group (-OH). There are H_2O compounds at wave number 2083-2318 cm-1 which indicates that there are still water molecules in the sample due to poor drying or storage [19]. There is another functional group, namely CO_3^{2-} which is usually found in the wave number range of 1390-1630 cm-1 [20]. There is also a functional group PO_4^{3-} at the wave number 873-1055 cm^{-1}.

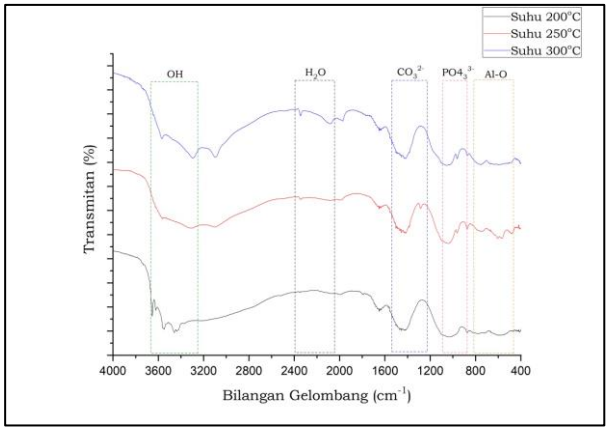


Figure 2. Spectra FTIR hydroxyapatite/Al_2O_3 result.

X-Ray Diffraction (XRD) Characterization Results

Based on the Match 3 database! 96-900-1234 and 96-900-3549 formed two compounds, XRD Hydroxyapatite/Al_2O_3. The result in **Figure 3** namely hydroxyapatite and AlOH. From the graph of the diffraction pattern X-Ray Diffraction analysis shows the highest 2θ angle for each sample, namely 31.85°; 31.87°; and 31.86°. The results of the diffractogram analysis for each temperature variation of hydroxyapatite/alumina show that the peaks are not much different from the hydroxyapatite and alumina phases according to JCPDS standard data 09-0432, the three main peaks of hydroxyapatite are at 2θ ie 31.77°; 32.90° and 32.19 [21]. From the diffraction pattern data, it is clear that temperature affects the hydroxyapatite/alumina doping process. Where the higher temperature is used in the doping process, it is characterized by a narrower peak difference and an increase in the intensity of the hydroxyapatite/alumina peak. The peaks are narrowed, indicating increased crystallinity of hydroxyapatite/alumina [22].

From the X-Ray Diffraction analysis data, it can be determined the degree of crystallinity of the crystal size of the hydroxyapatite/alumina. The degree of crystallinity was calculated by comparing the crystalline area fraction with the sum of the crystalline area fraction and amorphous area fraction [23]. The width of each X-ray diffraction peak indicates the crystal size. To determine the crystal size, you can use the Scherrer equation, therefore the FWHM (Full Width High Maximum) value is needed for each highest peak of each diffractogram [24].

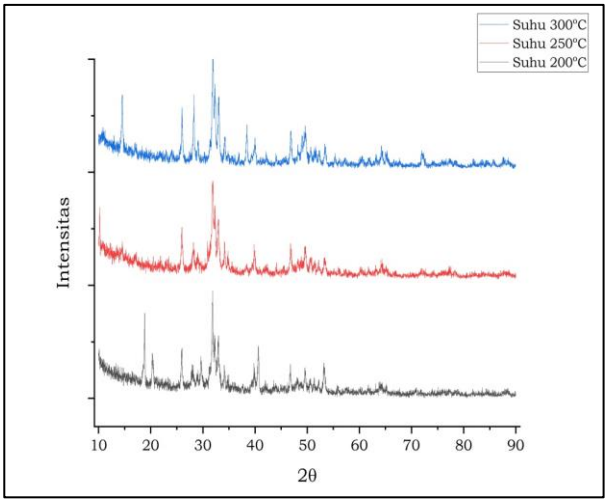


Figure 3. XRD Hydroxyapatite/Al_2O_3. Result.

$$D = \frac{k\lambda}{\beta \cos\theta} \quad (1)$$

Where D is the crystal size, the X-ray wavelength used is 0.154056 nm, is the peak width at half maximum (Full-Width High Maximum), is the Bragg angle and k is a constant with a value of 0.9. Determination of the degree of crystallinity and crystal size was also analyzed using OriginLab 2022. At a temperature of 200°C, it has a crystallinity degree of 37.46% with a crystal size of 5.07 nm. At a temperature of 250°C has a degree of crystallinity of 41.31% with a crystal size of 3.84 nm. At a temperature of 300°C has a degree of crystallinity of 54.32% with a crystal size of 3.75 nm. From the analysis data, it can be concluded that the higher the doping temperature of the hydroxyapatite/alumina, the higher the degree of crystallinity and homogeneity of the particle size of the hydroxyapatite/alumina. The smaller hydroxyapatite particle size will expand the contact area with the surrounding tissue so that the bond obtained can be better [24].

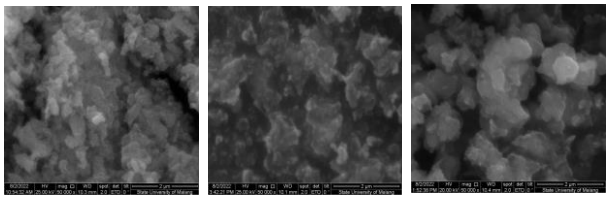
Table 1. Degree of Crystallinity and Crystal Size.

Temperature	FWHM (rad)	θ(°)	Crystallinity (%)	*D* (nm)
200°C	0,02076	32,12452	37,46	5,07
250°C	0,02764	32,11397	41,31	3,84
300°C	0,0278	32,13594	54,32	3.75

Table 1 shows the degree of crystallinity and crystal size of hydroxyapatite/alumina calculated by the Scherrer equation. The temperature increase in the doping process is directly proportional to the degree of crystallinity of the hydroxyapatite/alumina. This is caused by the increase in temperature in the doping process where the higher temperature causes the atomic arrangement to be more regular, causing many crystal phases to form. At lower temperatures, the hydroxyapatite/alumina doping process is slower. The crystal size obtained in hydroxyapatite/alumina is inversely proportional to the Full-Width High Maximum (FWHM) value. If the Full-Width High Maximum value is small, the crystal size will be large, otherwise, if the Full-Width High Maximum value is large, the crystal size will be smaller [25]. The table above states that 300°C is the optimum temperature for hydroxyapatite/alumina doping.

Scanning Microscope Electron (SEM) Characterization results

Based on the **Figure 4** results of the morphological analysis of the Scanning Electron Microscope, hydroxyapatite/alumina at a temperature of 300°C showed a shape that was not much different. In the SEM results, the morphology results can be observed more clearly because the particles shown are getting bigger [26]. The porosity value obtained from the results of hydroxyapatite/alumina doping at a temperature of 300°C which was analyzed with the help of OriginLab 2022 software was 99.38%. The porosity value obtained was higher than the porosity value of hydroxyapatite/alumina doped at 200°C and hydroxyapatite/alumina doped at 250°C. This proves that the doping temperature affects increasing the porosity value of hydroxyapatite/alumina. The higher the doping temperature used, the higher the porosity value obtained. This is because the higher temperature causes the molecules to move faster or the kinetic energy of the reacting molecules is getting bigger so that the collisions between the reactant molecules also increase. This is to the Arrhenius equation which states that with increasing temperature the reaction rate will also increase [27]. The results of the Scanning Electron Microscope showed that the optimum temperature for hydroxyapatite/alumina doping in this study was at a temperature of 300°C.



(a) (b) (c)

Figure 4. SEM hydroxyapatite/Al_2O_3 (a) temperature 200°C; (b) temperature 250°C; (c) temperature 300°C results.

CONCLUSION

The temperature has an effect in this study where the higher the doping temperature used, the higher the degree of crystallinity, particle size homogeneity, and porosity value. From the doping results, it is known that a temperature of 300°C produces a degree of crystallinity of 54.32% and a crystal size of 3.75 nm with a porosity value of 99.38%. This result is much better than the undoped hydroxyapatite in the previous study.

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