

Synthesis and Characterization of Hydroxyapatite from Green Mussel Shell with Sol-Gel Method

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Abstract

Hydroxyapatite (HAp) is a major component of bones and teeth. HAp is widely used to repair, fill, extend, and reconstruct damaged bone tissue. HAp is used for bone and dental implants, so it is necessary to synthesize HAp. HAp synthesis can utilize green mussel shell waste as a calcium precursor. This research synthesized HAp from a green mussel shell using the sol-gel method. The controlled synthesis parameter was pH, and the variable being compared was the heating temperature at 900 and 1100 °C. The HAp products were characterized by an X-ray diffractometer (XRD), Fourier-transform infrared spectrophotometer, and scanning electron microscope. The results showed that HAp was formed at alkaline pH, namely at pH 11. The XRD pattern showed that HAp was formed along with type A apatite carbonate, octacalcium phosphate, α - and β -tricalcium phosphate. The crystallinity was increased by raising the temperature and prolonging the heating time. The quality of HAp will improve with increasing crystallinity, and increasing the temperature will also raise the amount of HAp formed.

Keywords: Green mussels, hydroxyapatite, sol-gel.

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1. INTRODUCTION

Damage to the body's hard tissues in the form of bone structure defects is typical in Indonesia. The development of synthetic biomaterials for bone tissue and teeth rehabilitation has been expected to increase the growth of the cells, which will continue the tissue life cycle which had been replaced. One of the materials that have evolved is bio-ceramic. Bio-ceramic material that is commonly used for tissue rehabilitation is hydroxyapatite synthetic [HAp, $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$]. Hydroxyapatite (HAp) is inorganic material which chemically identical to the component of bone. It can be used as the coating material or artificial bone (Charlena *et al.*, 2015) to boost the growth of new bone cells from the bone receptor to the Hap implant (Salleh *et al.*, 2017). Thermodynamically, HAp has a stable crystal structure in the human body's fluids (Sadat-Shojai *et al.*, 2013). HAp can integrate with the bone without causing intoxication or inflammation (O'Hare *et al.*,

2010). It also has bio-active, bio-compatible, and non-toxic characteristics (Charlena *et al.*, 2015). Bio-active means could stimulate a cellular response in the body's tissue. Meanwhile, bio-compatible means could be received and well-functioned in the body's system without indicating inflammation or causing adverse reactions (Oladele *et al.*, 2018).

According to Arcos and Vallet-Regí (2020), the unit cell of HAp has a hexagonal crystal structure with lattice parameters of $a = 9.432 \text{ \AA}$ and $c = 6,881 \text{ \AA}$ with the formula $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ per unit cell. The molar ratio between calcium and phosphate (Ca/P) in hydroxyapatite is 1.67, close to the molar ratio of Ca/P in bone tissue (Rana *et al.*, 2017). The synthetic HAp compounds used nowadays are overpriced because they are imported from abroad. This disadvantage encourages finding other alternative materials to the low-cost synthetic HAp production, easy to get yet has

the same quality as the product of the synthetic HAp.

This research synthesis HAp used the green mussels' shells as the primary material. Green mussels (*Perna viridis*) are abundant commodities in Indonesia's waters. Based on previous studies, HAp has been synthesized from various materials containing calcium, such as golden apple snails shells with the constituent component in the form of Calcium carbonate (CaCO_3) in the amount of 48.02% (Siregar & Sulistyowati, 2019), chicken egg's shells by 94% (Gergely *et al.*, 2010), cow bone by 62.71% (Rana *et al.*, 2017), blood cockle shells (Khoirudin *et al.*, 2015), and rice field snail shells by 88.54% (Charlena *et al.*, 2015). Calcium carbonate's high consistency can be used as a calcium source in the synthesis of HAp.

Synthesis HAp can be done using precipitation methods (Cox *et al.*, 2014), hydrolysis (Pankaew *et al.*, 2010), sol-gel (Charlena, 2016), and hydrothermal (Wu *et al.*, 2013). In this research, HAp was synthesized using the sol-gel method. This method was chosen because the sol-gel method has high purity, homogeneous composition, and a smaller size (Vazquez *et al.*, 2005). This method received precursor calcium from green mussel shell waste through the calcination and hydration process. Therefore it produced starting material in the form of CaO and Ca(OH)_2 , and then it was reacted with Phosphoric acid (H_3PO_4). This synthesis is then characterized using XRD, SEM, and FTIR.

2. MATERIALS AND METHODS

Materials

The Materials used in this research are green mussel shells from Bogor traditional Market, ethanol 96% (Merck), H_3PO_4 80% (Merck), NH_4OH (Merck), Nitric acid (Merck), and distilled water.

Methods

Synthesis HAp in this research was conducted using a wet chemical technique (sol-gel method). There are five stages in this research, including (1) green mussel shells calcination, (2) hydration of CaO to Ca(OH)_2 , (3) determination of the consistency of Ca in the green mussel shells using AAS, (4) synthesis HAp using sol-gel method, and (5) characterization HAp using XRD, FTIR, and

SEM.

Calcination of Green Mussel Shell (Charlena 2015)

The green mussel shells are cleaned from contaminants and then dried. The calcination of the clam shells is processed at 1100 °C for 12 to 18 hours. The finely calcined products are analyzed using XRD to characterize CaO and AAS to determine calcium levels. The powder from the calcination process (CaO) is converted to Ca(OH)_2 by being hydrated for 1 night by being left in contact with air which contains water vapor at room temperature. The XRD analyzes the powder left in contact with the air to confirm the formulation of the Ca(OH)_2 diffraction pattern. Furthermore, the Ca level is determined using AAS.

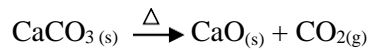
Synthesis of Hydroxyapatite using Sol-Gel Method (Modification of Charlena 2015)

The CaO powder from the calcination process or Ca(OH)_2 , the result of the hydration process, and phosphoric acid were dissolved in 50 mL of 96 % ethanol each. The precipitation process was carried out by dripping phosphoric acid into a solution of CaO or Ca(OH)_2 at 37 °C with stirring at 300 rpm and a flow rate of 1.0 mL/minute (pH was kept above 7 with 1 M NH_4OH). The compound was heated using a water bath at 60 °C for 1 hour and sediment for 24 hours. After that, it was stirred at 60 °C at 300 rpm until the solution turned into white gel. The gel was heated at 900 °C and 1100 °C for 2 hours. The same treatment was also conducted without pH control. Furthermore, the XRD, FTIR, and SEM characterized hydroxyapatite powder.

3. RESULTS AND DISCUSSIONS

The Calcination Result and Hydration

The green mussel shells must be calcined before being used as a calcium (Ca) precursor. Calcination is conducted at 1100 °C for 12 to 18 hours. Under this condition, all organic components of green mussel shells will burn down to CO_2 and H_2O (Adak & Purohit, 2011). This step also released CO_2 from aragonite. At the end of the calcination process, all green mussel shells can turn to CaO. The calcination result is a white powder. The reaction that occurs during calcination is:

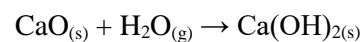


The presence of carbonate ions must be removed because it will affect the manufacture of HAp (Dahlan *et al.*, 2009). The presence of carbonate ions will fill 2 positions in the HAp structure, replacing OH- cluster configurations of Carbonate apatite type-a with the chemical formula $(\text{Ca}_{10}(\text{PO}_4)_6\text{CO}_3)$ or replacing PO_4^{3-} cluster configurations of Carbonate apatite type-b with the chemical formula $(\text{Ca}_{10}(\text{PO}_4)_3(\text{CO}_3)_3(\text{OH})_2)$.

The sample from calcination for 12 hours produced diffraction at angles of $2\theta = 32.27^\circ, 37.42^\circ, 53.92^\circ, 64.21^\circ,$ and 67.42° (**Figure 1a**). Meanwhile, the sample from calcination for 18 hours produced diffraction at angles of $2\theta = 32.34^\circ, 37.50^\circ, 53.99^\circ, 64.29^\circ,$ dan 67.52° (**Figure 1b**). Those diffraction patterns correspond to CaO compounds (JCPDS standard Number 37-1497).

The Crystallinity of the samples calcined for 18 hours (97.83%) was higher than that for 12 hours (91.85%). A longer calcination time will cause more crystals to form because the atomic arrangement in the material is getting more regular. Crystallinity is also influenced by the temperature in the heating process (Purnama, 2019). Based on the research result, calcined CaO for 18 hours can be used as one of the starting materials of HAp manufacturing.

Besides using CaO as the starting material, the researcher used $\text{Ca}(\text{OH})_2$. CaO was quickly converted to $\text{Ca}(\text{OH})_2$ through exothermic reactions with water.



Calcined CaO powders were hydrated by leaving them in contact with the air, which contains water vapor for 1 night at room temperature.

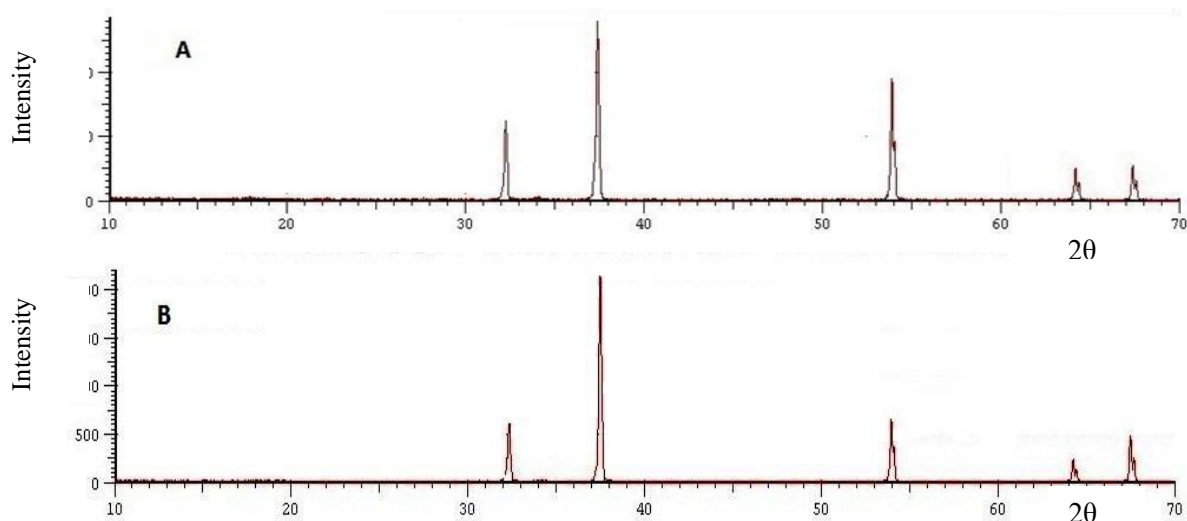


Figure 1. Diffractogram of the calcined clam shells at 1100 °C for 12 hours and 18 hours

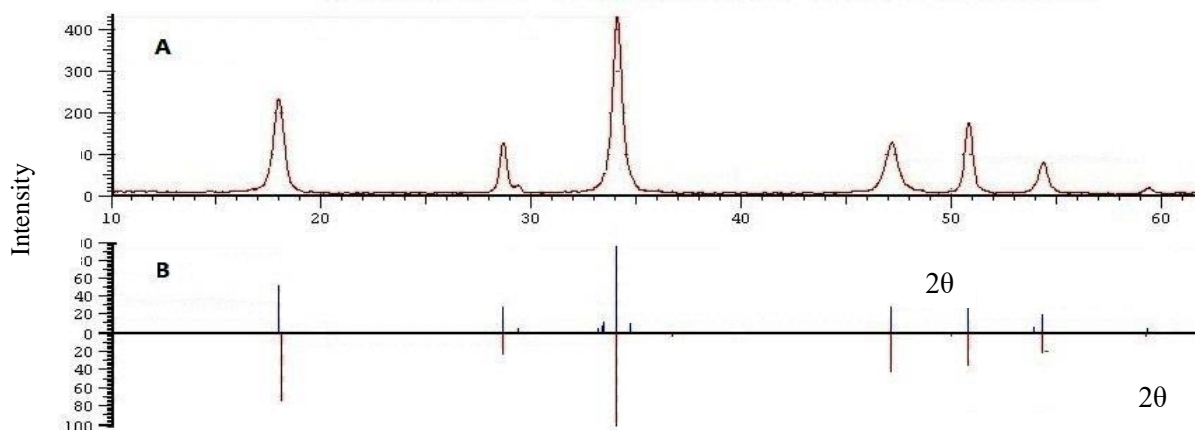


Figure 2. Diffractogram of the calcined clam shells (1100 °C, 18 hours) and hydrated (A); XRD sample pattern mirrored with $\text{Ca}(\text{OH})_2$ (JCPDS Standard Number. 44-1481) (B)

Figure 2 shows diffraction angle at $2\theta = 18.03^\circ, 28.70^\circ, 34.11^\circ, 47.14^\circ, 50.83^\circ,$ and 62.62° . The 2θ angles were suitable with Ca(OH)_2 (JCPDS standard Number 44-1481). The degree of crystallinity obtained was adequate, that is, 87.35%. However, it is lower than the crystallinity of CaO. Based on XRD results, the particle size of CaO is bigger than Ca(OH)_2 . Generally, the higher the crystallinity level, the more the particle size is prominent. The FTIR spectrum shows that Ca(OH)_2 contains higher carbonate than CaO. The formation of new structures during the conversion process from CaO to Ca(OH)_2 also increases the crystallinity levels.

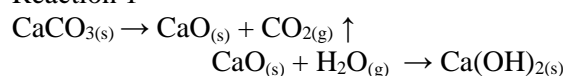
The calcium (Ca) in the calcified powder at 1100 °C for 18 hours was measured using AAS. The percentage of Ca was 45.62%. The percentage of Ca was lower than the calcium content of golden snail shells, chicken egg shells, beef bones, blood clam shells, and tutut shells. The presence of calcium in green mussel shells can be used as a source of calcium in the synthesis of HAp.

Hydroxyapatite

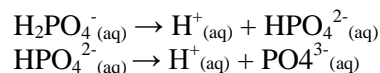
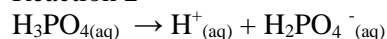
Hydroxyapatite is a Calcium phosphate compound containing hydroxide. The molecule formula is $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$. HAp can be made using wet chemical techniques. The primary advantage of synthesizing using a wet chemical technique is that the by-product is water. The contamination possibility during the processing is low, and the processing cost is low. The simple reaction is suitable for a big-scale industry and does not cause environmental pollution (Kehoe, 2008). The wet chemical technique of synthesis HAp, which has been chosen, is the sol-gel method that is expected to produce uniformity and controlled stoichiometry until the HAp is formed (Vazquez *et al.*, 2005).

CaO or Ca(OH)_2 powder was mixed with 80% of H_3PO_4 that dissolved to 50 mL of 96 % ethanol each (the pH was adjusted by adding 1 M NH_4OH). The ratio of Ca/P used is 1.67 (0.8 M Ca/0.5 M P). The reaction processes involved in the synthesis of HAp are as follows:

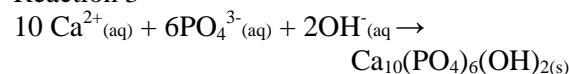
Reaction 1



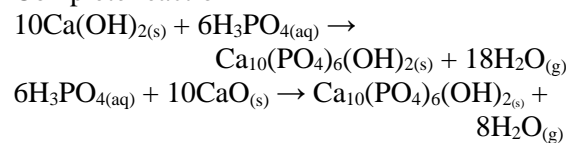
Reaction 2



Reaction 3



Complete reaction



The XRD Method can be used to determine the phase of a crystal sample. The obtained diffraction pattern was matched to the standardized data of HAp, JCPDS Number 09-0432. The HAp diffractogram from the obtained wet reaction of H_3PO_4 with CaO at 1100 °C (**Figure 3a**) shows the high intensity with the mostly peak from HAp phase, at $2\theta = 25.87^\circ, 31.78^\circ, 32.20^\circ, 32.92^\circ, 39.82^\circ,$ and 46.70° . Several other peaks with low intensity at $2\theta = 27.79^\circ, 29.63^\circ,$ and 31.04° . Referring to the data on JCPDS Number 29-0359, at 2θ angle is the tricalcium phosphate (TCP) phase with the molecule formula $\text{Ca}_3(\text{PO}_4)_2$. Besides, there is carbonate apatite phase type a ($\text{Ca}_{10}(\text{PO}_4)_6\text{CO}_3$), with low intensity at $2\theta = 35.47^\circ$. The peaks with very low intensity were considered as background or noise.

Diffractogram of HAp obtained from the reaction between H_3PO_4 and Ca(OH)_2 at 1100 °C (**Figure 3b**) also obtained peaks with high intensity from the HAp phase, at the angle of $2\theta = 25.90^\circ, 31.79^\circ, 32.22^\circ, 32.94^\circ, 39.83^\circ,$ and 46.73° . Apart from it, there are other phases with low intensity at $2\theta = 31.06^\circ$ and 43.90° at the TCP phase.

The calcined CaO at 900 °C, the diffractogram (**Figure 3c**) still shows HAp ($2\theta = 31.81^\circ, 32.96^\circ, 32.24^\circ, 46.75^\circ,$ and 25.88°) and TCP TCP ($2\theta = 31.06^\circ, 34.38^\circ, 27.83^\circ, 59.51^\circ,$ and 13.71°). The TCP phase in this sample brings out enough diffractogram peaks, several peaks with high enough intensity at $2\theta = 29.53^\circ$, and in the Calcium carbonate (CaCO_3) phase at $2\theta = 63.04^\circ$.

The diffractogram showed similar results from the reaction result of Ca(OH)_2 and H_3PO_4 at 900 °C (**Figure 3d**). The HAp phase at $2\theta = 31.80^\circ, 32.94^\circ, 32.19^\circ, 49.47^\circ,$ and 25.89° were obtained together with TCP phase at the angles of $2\theta = 31.05^\circ, 27.82^\circ, 34.36^\circ,$

and 37.35° . HAp phase was still more dominant than the TCP phase. Octacalcium phosphate (OCP) with molecule formula $\text{Ca}_8\text{H}(\text{PO}_4)_3 \cdot 25\text{H}_2\text{O}$ also appeared at $2\theta = 41.98^\circ$.

The XRD result from all samples in this research showed the HAp formulation from the reaction between Phosphoric acid and CaO and $\text{Ca}(\text{OH})_2$ as the starting materials. Several other phases were forming, such as OCP, TCP, Carbonate apatite type a, and CaCO_3 . The HAp phase is the most stable among other Calcium phosphate compounds at room temperature. However, at the heating process with high temperature (sintering), HAp can change the phase to other Calcium phosphate compounds. HAp was decomposed to tricalcium phosphate $\text{Ca}_3(\text{PO}_4)_2$ (α -TCP and β -TCP), Calcium oxide

(CaO), and tetra-calcium phosphate $\text{Ca}_4(\text{PO}_4)$ at a specific temperature and depending on the atmosphere around it (Bernache-Assolant *et al.*, 2002). All samples found the β -TCP phase. In this phase, with further heating, it can form α -TCP, seen in the HAp sample from CaO with the heating temperature at 1100°C . The conversion of HAp to TCP resulted from the release of the OH- cluster (and the release of water vapor); hence HAp was dehydrated and formed TCP. Based on research conducted by Bernache-Assolant *et al.* (2002), the TCP phase can be formed starting from the temperature of 600°C with calcium from Calcium nitrate tetrahydrate ($\text{Ca}(\text{NO}_3)_2 \cdot 24\text{H}_2\text{O}$) which was being reacted with diammonium hydrogen orthophosphate ($(\text{NH}_3)_2\text{HPO}_4$).

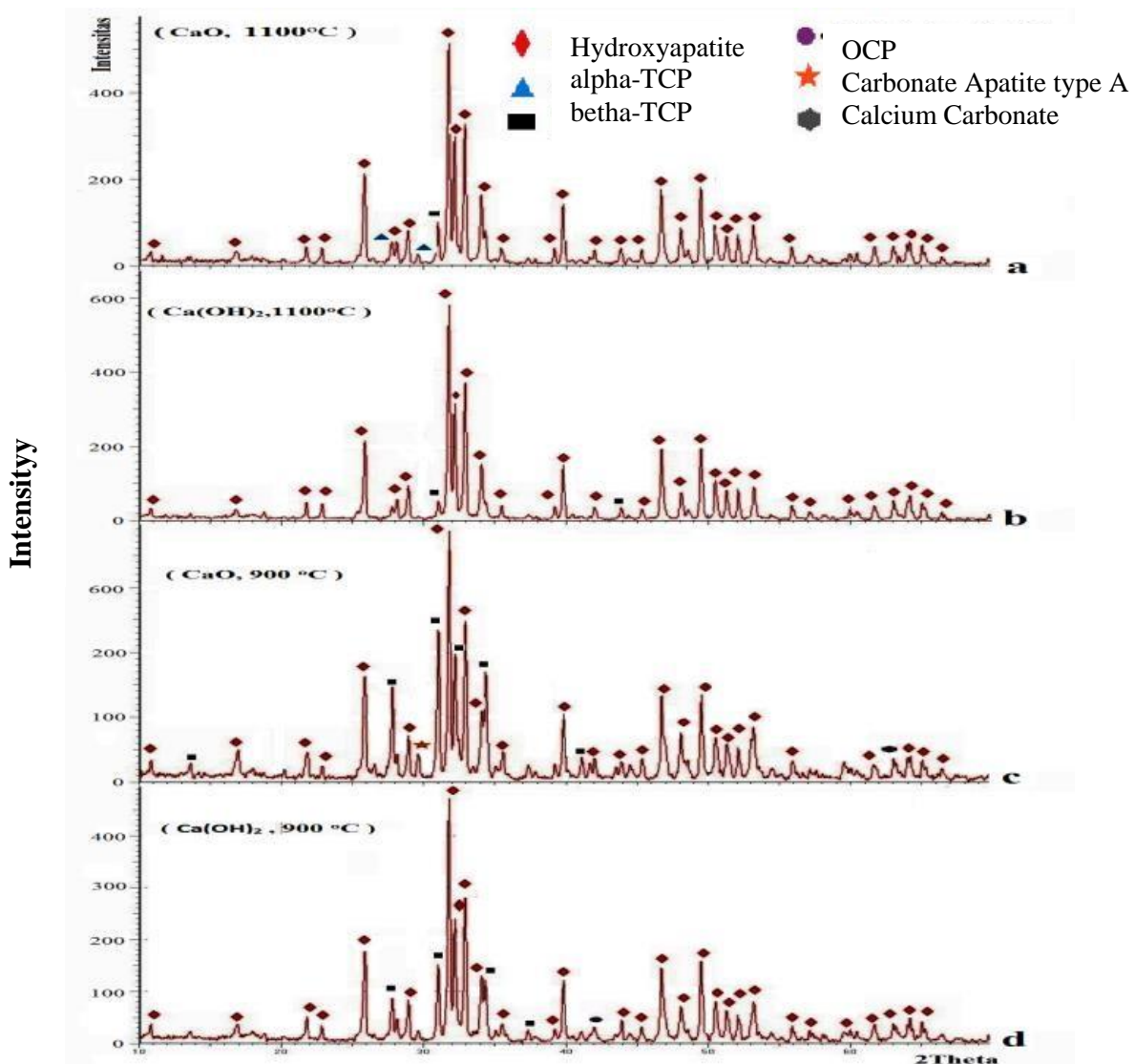


Figure 3. Diffractogram of HAp made of CaO and $\text{Ca}(\text{OH})_2$ 0.8 M with H_3PO_4 0.5 M at 1100°C (a and b) and 900°C (c and d)

To obtain HAp with high density and stability, it is necessary to do sintering until a specific temperature and must be kept. Therefore the HAp will not decompose to β -TCP or other compounds. The temperature at sintering is a factor that influences decomposition because the HAp surface can actively interact with the environment around it at a specific temperature.

The carbonate apatite type can be formed because of the high temperature that enables the carbonate ion to replace the OH-position on the HAp structure. The carbonate ion found on the clam shell's powder before it was calcined can also form from the air and get through after the calcination process. The trapped ion during this synthesis process will be hard to remove because it was attached to the HAp crystal. The presence of carbonate apatite type, a relatively small amount of HAp product, will not harm the human body because it is also the composite of Calcium phosphate. Therefore bone formation can be through carbonate apatite type a. This carbonate apatite type belongs to the mineral fraction of hard tissue, which will be implanted with HAp and will not harm the organism's body (Suchanek *et al.*, 2004).

The CaCO_3 phase is the most phase of the clam shells. If there is CaCO_3 detected in the process, it means that not all CaCO_3 is well converted to CaO in the calcination process. However, CaCO_3 also be generated from the reaction of CO_2 from the air with CaO during the synthesis process. Hidayat *et al.* (2006) explained that increasing carbonate will decrease the crystallinity process. In other words, the HAp crystal formation will be disturbed.

From the research result from the synthetic material, the conversion of calcium phosphate amorf to HAp is conducted through the non-apatite crystal formation, which is

OCP and dicalcium phosphate dihydrate (Soejoko, 1999). The presence of the diffraction peaks corresponds to the OCP crystal on the sample of Ca(OH)_2 and H_3PO_4 at 900 °C, shows that the HAp phase is not fully formed and also proves that the non-apatite crystal formation starts the HAp formation. The result of the synthesis of HAP in this research has a diffraction pattern that is relatively similar to the commercial HAP.

The XRD can determine the crystal system, lattice parameter, crystallinity, and sample phase (Cullity & Stock, 2001). Table 1 shows the influence of temperature and the starting material of the synthesis of HAp on the crystallinity of HAp that is produced. Crystallinity indicates the crystalline content of a material by comparing the width of crystal curves with the total width of amorf and crystal. The Percentage of crystallinity was found to increase along with the heating temperature rise. The higher the heating temperature causes the atomic arrangement to be more orderly. Thus more crystalline phases are formed. It is seen from the higher intensity and the narrower width of the half peak (full width at half maximum [FWHM]) at the angles of $2\theta = 31.78^\circ$ (CaO; 1100 °C) and 31.79° (Ca(OH)_2 ; 1100 °C) also at 31.81° (CaO; 900 °C) and 31.80° (Ca(OH)_2 ; 900 °C).

The difference in the starting materials of HAp synthesis contributed to the crystallinity. Calcium hydroxide provides higher crystallinity than Calcium dioxide. It is related to the size of crystal particles that have been formed. Generally, the higher crystallinity, the larger particle size. As shown in **Table 1**, using Ca(OH)_2 as the starting material of HAp synthesis produced an enormous crystal with high density and stability.

Table 1. Crystallinity, lattice parameter, and crystal size (d) of the synthesized HAP

Starting Material	T (°C)	Crystallinity(%)	Lattice parameter		d(002) (nm)
			a (Å)	c (Å)	
CaO	1100	84.47	9.417	6.881	86.66
Ca(OH)_2	1100	91.99	9.413	6.876	99.04
CaO	900	79.31	9.416	6.88	69.33
Ca(OH)_2	900	81.93	9.412	6.894	81.56

Dahlan *et al.* (2009) reported that the synthesis of HAp from egg shells used a dry method. The HAp phase was obtained from several other phases, with the heating temperature at 900 and 1000 °C that produced crystallinity between 84% and 94%. That crystallinity is higher than the wet chemical process (sol-gel) because it did not involve many reactors. Solihat (2008) synthesizes the HAp from egg shells using a hydrothermal method. The HAp phase was obtained with other phases, CaO, with 96% crystallinity. This result is also higher, either from the purity or the crystallinity. The hydrothermal method involves high pressure with a close synthesis condition, so it is possible to form a better apatite crystal.

The distance between unit cells in all directions is called the lattice parameter. Lattice parameters of the HAp crystal based on Aoki (1991) are $a = 9.432 \text{ \AA}$ and $c = 6.875 \text{ \AA}$. Based on the measurement result with XRD, the lattice parameter sample (Table 1) is in the range of the HAp parameter, thus proving that the HAp phase has been formed in the sample. The crystal size was calculated using the Scherrer equation and is directly proportional to the rising temperature (Table 1). However, it is inversely proportional to the FWHM value.

This research also conducted the synthesis of HAp without pH control during the mixing of H_3PO_4 with the calcium source. The measurable pH is around 3. Based on the diffractogram, the formed HAp compound is

minor. The dominant result is TCP. Tricalcium phosphate is also a bio-material commonly used to reconstruct the bone because the biodegradation level corresponds with the bone growth rate and has osteoconductive characteristics (Khrisna *et al.*, 2007).

Besides the influence of pH and temperature, the TCP formation can be caused by the influence of CO_2 during the synthesis process. Consequently, at the starting process of HAp manufacturing, it should be pre concerned that only the HAp phase was being formed. Suppose the α - and β -TCP phases appear at the beginning of sample formation, thus after the heating process. In that case, those phases will have peaks (XRD pattern) is getting stronger, which means the decomposition rates increase (Arifianto, 2006).

The result of this research showed the importance of pH adjustment during the synthesis process in order to form HAp. The pH is adjusted above 7 by adding NH_4OH 1 M. Previous kinds of research state that the content of apatite crystal phase on the sample was rising along with the pH rising and significant while the pH on the solution is above 7 (Soedjoko & Wahyuni, 2002).

The Spectrum of HAp

The FTIR analysis was used to identify the sample in OH^- , PO_4^{3-} , and CO_3^{2-} clusters. The synthesized HAp product spectrum from CaO 0.8 M and H_3PO_4 0.5 M at 1100 °C can be seen at **Figure 4a**.

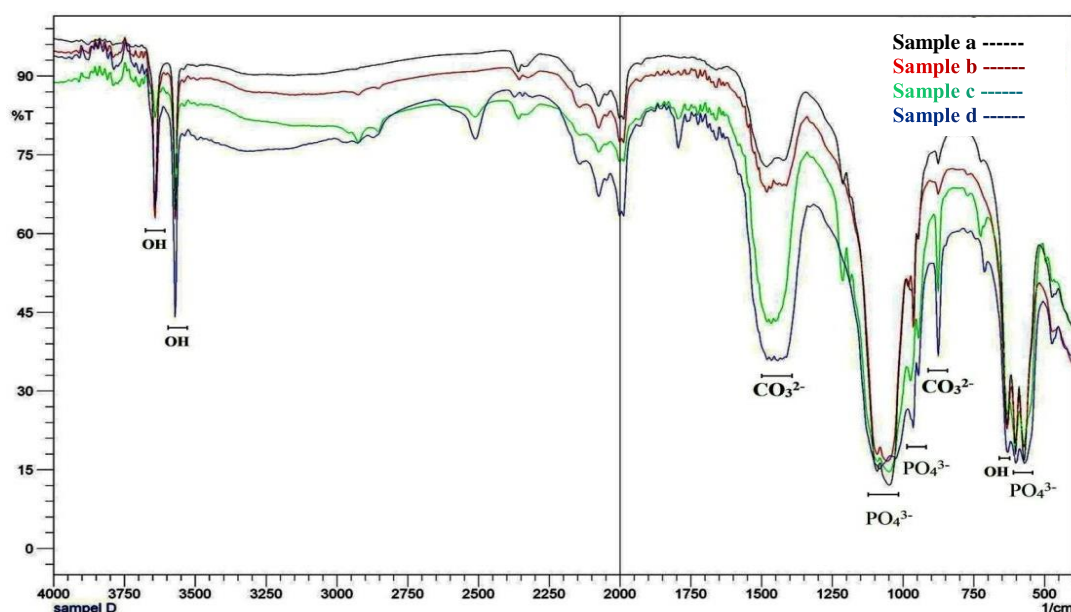


Figure 4. FTIR spectrum HAp synthesized from CaO 0.8 M and $\text{Ca}(\text{OH})_2$ 0.8 M with H_3PO_4 0.5 M at 1100 °C (a and b) and 900 °C (c and d).

There is an absorption band for asymmetric bending vibrations ($\bar{\nu}_4$) phosphate at wave number 570.93 and 601.79 cm^{-1} , asymmetric stretching vibrations ($\bar{\nu}_3$) phosphate at 1049.28 and 1091.71 cm^{-1} , stretching vibrations ($\bar{\nu}_1$) phosphate at 955.16 cm^{-1} . However, no absorption band was detected for bending vibrations ($\bar{\nu}_2$) phosphate. The wavenumbers show the OH-cluster at 3572.17, 3641.6, and 632.65 cm^{-1} . The presence of OH- clusters are typical for HAp. The presence of an absorption band of phosphate and hydroxyl proved that HAp was formed on the sample.

The absorption band of CO_3^{2-} is found in wave numbers 875.68, 1419.61, and 1481.33 cm^{-1} . Carbonate ion is the inhibitor of HAp manufacturing and comes from the reaction between CaO with CO_2 in the free air during the synthesis process (Dahlan *et al.*, 2009). Besides, CO_3^{2-} was assumed to exist before the synthesis process was produced or brought from the primary material. The presence of CO_3^{2-} can not be said as a worse condition because the human bones also have CO_3^{2-} as a natural substitution of PO_4^{3-} that is suitable with the molecule formula $\text{Ca}_{10}(\text{CO}_3)_x(\text{PO}_4)_{6(2/3)x}(\text{OH})$ or usually called carbonated HAp (Aoki, 1991).

The spectrum of synthesized HAp from $\text{Ca}(\text{OH})_2$ 0.8 M and H_3PO_4 0.5 M at 1100 $^\circ\text{C}$ (Figure 4b) also showed the phosphate absorption band at wave numbers 570.93 and 601.79 cm^{-1} ($\bar{\nu}_4$), 964.41 cm^{-1} ($\bar{\nu}_1$), 1056.99 and 1091.71 cm^{-1} ($\bar{\nu}_3$). The OH cluster brought up an absorption at 3572.17, 3641.6, and 632.65 cm^{-1} , while the absorption band of CO_3^{2-} occurred at 875.68, 1411.89, and 1481.33 cm^{-1} .

The product spectrum of synthesized HAp from CaO 0.8 M and H_3PO_4 0.5 M at 900 $^\circ\text{C}$ (Figure 4c) has an absorption band of vibration phosphate at the wave numbers 570.93 and 601.79 cm^{-1} ($\bar{\nu}_4$), 962.12 cm^{-1} ($\bar{\nu}_1$), 1049.28 dan 1091.71 cm^{-1} ($\bar{\nu}_3$). The OH-cluster is shown by the absorption at 3572.17, 3641.6, and 632.65 cm^{-1} , while the absorption band of CO_3^{2-} occurred at 875.68 and 1450.47 cm^{-1} .

The product spectrum of synthesized HAp from $\text{Ca}(\text{OH})_2$ 0.8 M and H_3PO_4 0.5 M at 900 $^\circ\text{C}$ (Figure 4d) showed the absorption band of vibration phosphate at the wave numbers 570.93 and 601.79 cm^{-1} ($\bar{\nu}_4$), 964.41 cm^{-1} ($\bar{\nu}_1$), 1026.13 and 1083.99 cm^{-1} ($\bar{\nu}_3$). The absorption of OH- clusters occurred at 3572.17, 3641.6, and 628.79 cm^{-1} . The absorption band of CO_3^{2-} obtained at 875.68 and 1442.75 cm^{-1} . The HAp compound can be recognized from the absorption band of the hydroxyl and phosphate cluster, while the Carbonate apatite gave an additional absorption band for the carbonate cluster (Nurlaela, 2009). Those four samples showed the existence of phosphate and hydroxyl. It showed that HAp was formed on the sample.

Morphology of HAp

The heating treatment at 900 $^\circ\text{C}$ produced a lumpy sample (Figures 5c and d) compared with the treatment at 1100 $^\circ\text{C}$ (Figures 5a and b). It was caused by the narrowing surface of the granules along with the increasing temperature; therefore, the lumpy was formed smaller. The crystal formation was also increasing.

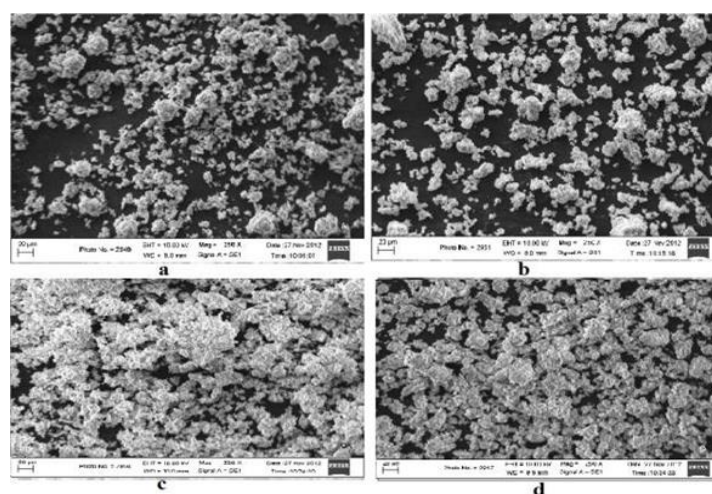


Figure 5. The morphology of HAp with CaO and $\text{Ca}(\text{OH})_2$ as the starting materials at 1100 $^\circ\text{C}$ (a and b) and 900 $^\circ\text{C}$ (c and d) heating treatment

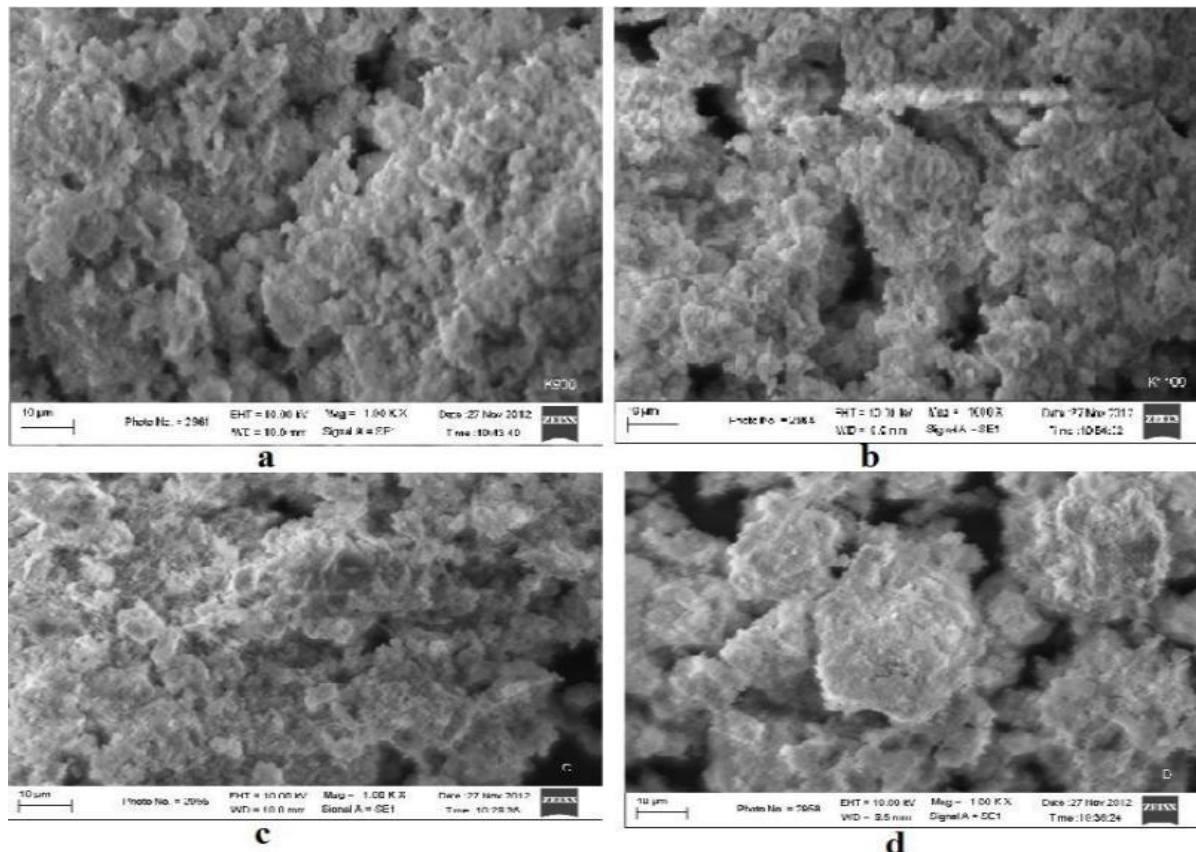


Figure 6. The morphology of HAp with CaO and Ca(OH)₂ as the starting material with heating treatment at 1100 °C (a and b) and 900 °C (c and d).

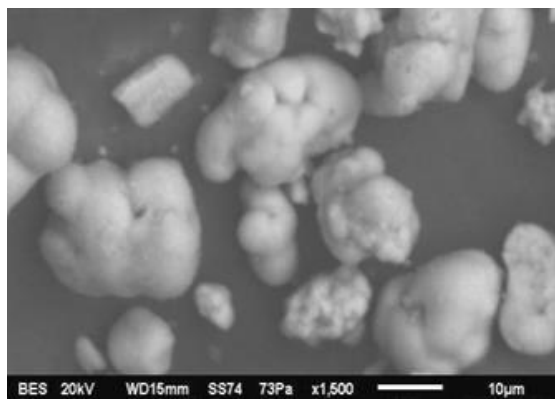


Figure 7. The result of SEM analysis of commercial HAp

4. CONCLUSIONS

The synthesis of HAp was successfully conducted with the sol-gel method from calcined CaO and Ca(OH)₂ as the starting material and hydration of green mussel shells. The pH adjustment to base at pH 11 is needed in the HAp formation. The XRD diffractogram showed HAp as the dominant phase with a few other phases. The FTIR spectrum showed the presence of Phosphate and Hydroxyl. The

Synthesis using Ca(OH)₂ as the starting material, and heating treatment at 1100 °C was the best condition because it produced HAp with crystallinity, lattice parameter, and high purity. The SEM picture showed some morphology, such as granules with a uniform grain but rough surfaces.

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