

Optimization of Nano Coral-Based Synthesis Calcium Phosphate with Concentration Variation of Phosphoric Acid and Sintering Temperature

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Abstract: Research on the optimization of calcium phosphate formation has been carried out. The material used is nanocoral with varying concentrations of phosphoric acid and sintering temperature. The method used is precipitation method. There were three variations of molar concentration of phosphoric acid used, namely 1M; 1.5M; and 2M. While the variations in sintering temperature were 800°C, 850°C, 900°C and 950°C respectively. Nano-sized powders were obtained through mechano-chemical processes of fossilized corals using High Energy Milling (HEM) for 20 hours, which is 64.93nm. X-Ray Diffraction (XRD) observation results showed that the Calcium Phosphate phase formed is Hydroxyapatite (HAp), β -Tricalcium Phosphate (β -TCP) and Tetra Calcium Phosphate (TTCP). The TTCP phase only occurred at 950°C. The largest volume of HAp fraction occurred at the molar concentration of 1.5 M of phosphoric acid with sintering temperature of 850°C, which is 70.7% and the remaining β -TCP phase is 29.2%. The crystallinity percentage that occurred in these conditions is 94.95%.

1 INTRODUCTION

The Indonesian Ministry of Health Research and Development Agency (RISKERDAS, 2013), stated that there was approximately 5.8% of fractured injury sufferers in Indonesia. This figure increased by 0.7% compared to the same incident in 2007. Those injury cases are caused by various factors including traffic accidents, natural disasters and bone cancerous.

Improvements to bone injury can be done by using filler, scaffold or implant. Until now, 90% of the material is still imported. Someone who has bone damage spends about 70% of treatment cost for implants. This fact shows the importance of independence in providing medical materials including calcium phosphate biomaterials.

Calcium phosphate is the main mineral constituent of bones and teeth. Calcium phosphate can induce a biological response during bone renewal or formation by performing bone mineral absorption. When absorption occurs, the results of calcium phosphate degradation (calcium and phosphate ions) will be metabolized by the body naturally. In general, human bones consist of 60%

inorganic ingredients, 30% organic matter, and 15% water (Krishna *et. al.*, 2007). Inorganic material is bone mineral containing sub-microscopic Hydroxyapatite [$\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$]. Other inorganic minerals are magnesium (Mg), fluoride (F), Chloride (Cl), sodium (Na) and potassium (K). There is about 34.00% of calcium (Ca) compounds and 15% of phosphorus (P) compounds in human bones (Darwis, D. & Warastuti, Y., 2008). Calcium phosphate can be obtained from the synthesis of natural materials with high calcium, one of which is coral.

Research on coral rock used for raw materials implant has been carried out by previous researchers. A research conducted by Indarwati (2007) on coral rock analysis using XRD (X-Ray Diffraction) test showed that the composition of the coral is 91.696% CaCO_3 (Aragonite) compound, 3.677% MgSiO_3 , and 4.626% FeSi . From the results of the analysis, it appears that the coral contains very high calcium carbonate (CaCO_3) compounds. Calcium carbonate compounds (CaCO_3) can be converted into HAp through various processes. One of them is through the calcination process to form CaO and $\text{Ca}(\text{OH})_2$ compounds. Furthermore, calcium phosphate compounds can be formed by

reacting them with phosphoric acid which is sintered at a certain temperature.

Therefore, this study focused on the formation of calcium phosphate by optimizing the process parameters of phosphoric acid's molar concentration and sintering temperature variations. This is based on the fact that coral is a natural mineral that contains many compounds so that the right molar concentration of phosphoric acid is needed. In addition, the formation process also requires the right sintering temperature. To accelerate the reaction process of calcium phosphate formation in this study, the expansion of surface area of the touch reaction through the size of nanoparticles was carried out. The smaller the particle size, the wider the surface area of the touch (Ferraz, 2014).

2 MATERIAL AND METHODS

Coral used in this study came from the sea in Banyuwangi, East Java, Indonesia. Phosphoric acid (H^3PO^4) with a purity of 99.8% Aldrick, aquadest and glycerol.

This research was done through two stages of nano coral and calcium phosphate formation. The first stage was the formation of nano coral using top down method, which converts large particles into nano-sized particles through the milling process. The corals were cleaned from dirt and dried in the open space. Then, the coral was destroyed manually to be smaller particles. Once becoming sufficiently smooth, the sample was sieved using a 200 mesh sieve to facilitate the milling process. Then, the result of the sieve was milled using HEM-3D (High Energy Milling-3 Dimension) for 20 hours with comparison between samples of 1:20 to ball mill.

The formation of calcium phosphate based on nano coral was performed using precipitation method. The molarity of phosphoric acid used varies *i.e.* 1.0M; 1.5M; 2.0M, while the sintering temperature was carried out at four different temperatures *i.e.* 800°C; 850°C; 900°C; and 950°C. So, there were 12 samples used in this research.

3 RESULT AND DISCUSSION

The corals used in this study came from the Banyuwangi sea of East Java (figure 1a). The type of coral is fossilized coral. The coral was then broken into small sizes using a hammer (Figure 1b). To facilitate the milling process, the results of the

coral pieces were crushed using a mortar then filtered using a 200 mesh sieve (Figure 1c). The results of the filter were milled using HEM-3D for 20 hours to change the size of the nanoparticles. The results of the observation of Particle Size Analyzer (PSA) on the results of the treatment showed that the size obtained was 64.93 nm (Figure 2).



Figure 1: The process of sample preparation (a) coral has been cleaned, (b) coral has been dissolved, (c) coral has been refined.

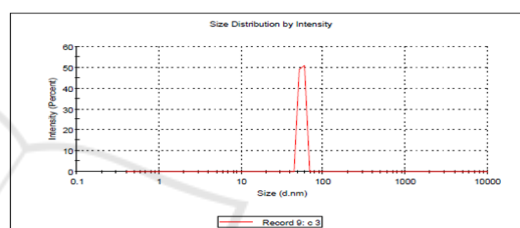
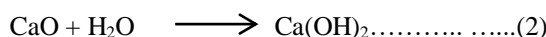


Figure 2: The results of PSA test of coral powder

Nano coral XRD diffractogram was done to determine the content of the compound. Figure 3 shows a sample of nano coral diffractogram. By using the Search-Match program (see Figure 3), it can be found that the coral consists of 78.6% $CaCO_3$ (calcite) compounds and 21.4% Ca_2O_5Si compounds. The $CaCO_3$ calcination process causes the change of the compound to CaO and CO_2 as shown in Equation 1. Furthermore, the milling process of calcined coral can cause a thermal reaction that produces water vapor. In the vial, the moisture formed can react with CaO which produces $Ca(OH)_2$, as stated in Equation (2). This can be seen in Figure 4 diffractogram, the coral produced 95.8% $Ca(OH)_2$ and 4.2% CaO . The presence of CaO is still suspected because the reaction process in the vial is still less than optimal. This can be caused by short time for milling and improper comparison of ball vials.



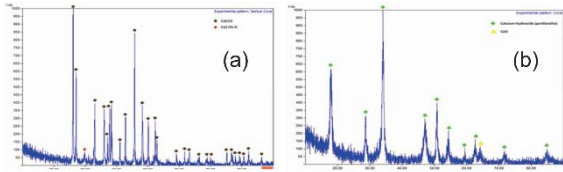


Figure 3: The results of XRD observation (a) nano coral (b) nano coral calcined at 900°C

Calcium phosphate was formed by the reaction of calcium hydroxide (Ca(OH)₂) and phosphoric acid (H₃PO₄), as shown in Equation (3). The treatment of phosphorus acid molar variation was done because the results of XRD (see Figure 4) still contained CaO as impurity form of Ca(OH)₂. In this study, there were 3 variations of phosphoric acid molarity used *i.e.* 1M, 1.5M and 2M. In addition, the process of ceramic formation generally is strongly influenced by the sintering temperature. In this study, four variations of sintering temperature were carried out. Therefore, every variation of molar above was performed by four variations of sintering temperature which are 800°C; 850°C; 900°C; and 950°C, so there were total of 12 samples used in this study. The results of observations of 12 samples are displayed in Figure 5, Figure 6, and Figure 7.

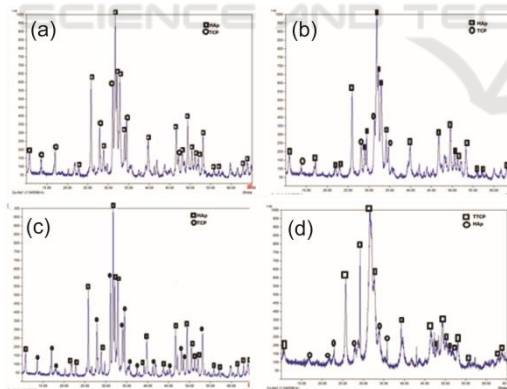
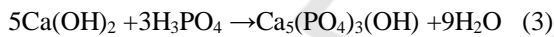


Figure 4: XRD observations of 1 M calcium phosphate sample with sintering temperature at (a) 800°C, (b) 850°C, (c) 900°C, and (d) 950°C

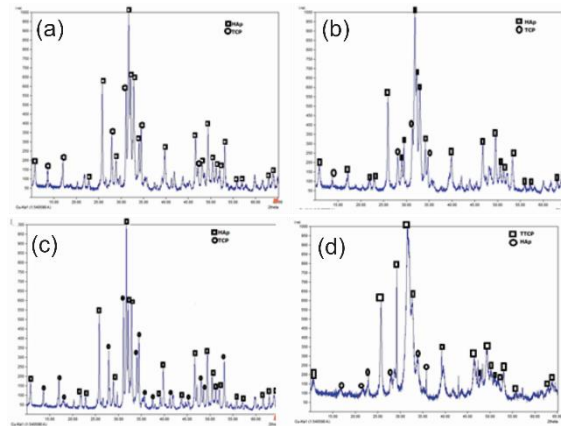


Figure 5: XRD observations of 1.5M calcium phosphate sample with sintering temperature at (a) 800°C, (b) 850°C, (c) 900°C, and (d) 950°C

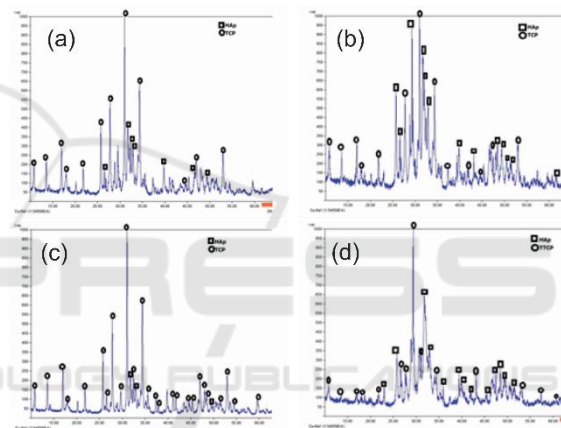


Figure 6: XRD observations of 2 M calcium phosphate sample with sintering temperature at (a) 800°C, (b) 850°C, (c) 900°C, and (d) 950°C

The identification of the XRD in Figure 4, Figure 5, and Figure 6 shows that the calcium phosphate formed is the HAp (Hydroxyapatite), TCP (Tri Calcium Phosphate), and TTCP (Tetra Calcium Phosphate) phases. In full, the volume fraction from these three phases for various molar concentration and sintering temperature are shown in Table 1.

Table 1: The volume fraction of calcium phosphate for various molar concentration and sintering temperature

temperature (°C)	Volume fraction (%) 1M			Volume fraction (%) 1,5M			Volume fraction (%) 2M		
	HA	β-TCP	TTCP	HA	β-TCP	TTCP	HA	β-TCP	TTCP
800	28,30	71,70	0,00	65,40	34,60	0,00	38,80	61,20	0,00
850	37,50	62,50	0,00	70,70	29,30	0,00	44,60	55,40	0,00
900	68,60	31,40	0,00	62,50	37,50	0,00	13,40	86,60	0,00
950	50,80	0,00	49,2	47,70	0,00	52,30	47,20	0,00	52,8

From Table 1, it appears that the stable calcium phosphate phase, Hap, is highly dependent on molarity of phosphoric acid and sintering

temperature. This optimum phase occurred at a sintering temperature of 900°C with molarity of 1M phosphoric acid. In addition, this phase is also optimized at 850°C sintering temperature with 1.5M phosphoric acid molarity. This also occurred with the crystallinity formed, as stated in Table 2.

Human bone crystallinity is in the range of 69% to 87% (Balgies, 2011), while the dominant phase of calcium phosphate in bone is HAp with a Ca / P ratio of 1.67. The Ca / P ratio of β-TCP and TTCP compounds are 1.50 and 2.0, respectively (Kerry L. and Hull, P., 2011). Based on these references, there are five crystallinity samples that fulfil the requirements as bone filler. Based on the heating process, 950°C sintering temperature is the most effective compared to other sintering temperatures. Based on its molarity, the 2M molar concentration of phosphoric acid is the most effective. This is allegedly caused by chemical reactions that occur between CaO and H₂O is less than perfect, so that Ca(OH)₂ is formed and there is still residual CaO (Sokolova,2012). The number of HAp phases, β-TCP phase and TTCP phase affect the Ca / P ratio of the material. The ratio of the three phases in a row is 1.67, 1.50 and 2.00. By using the mean principle from Table 1, the ratio of Ca / P of the sample can be determined. When viewed from the molarity of phosphoric acid, the 1.5M molarity has the best value of 1.67. However, when viewed from the sintering temperature, 900°C is the most optimal temperature, which gives a Ca / P ratio of 1.61

Tabel 2 : Crystallinity of Hydroxyapatite

Molarity of phosphoric acid	Crystallinity(%)			
	800°C	850°C	900°C	950°C
1 M	82,07	92,22	92,34	70,93
1,5M	94,75	94,95	89,40	86,17
2M	86,31	87,64	79,41	87,80

From the series of analysis and discussion that has been done, some conclusions can be drawn. First, the sintering process causes the transformation of the structure phase from amorphous to crystal. The crystallinity of calcium phosphate is influenced by the sintering temperature and the molar concentration of phosphoric acid. The sintering temperature of 800°C and 850°C give the optimum crystallinity. Second, the mole amount of phosphoric acid greatly influences both the phase and crystallinity. Finally, the stable phase of HAp was optimally formed at 850°C with 1.5M phosphate molarity of both volume fraction and crystallinity.

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