Synthesis of hydroxyapatite based on coral Banyuwangi using sol-gel method: observe the effect of calcination temperature on its phase and crystallinity

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Abstract. A research on the effect of the calcination temperature on the hydroxyapatite phase and its crystallinity formed has been done. The synthesis method uses sol-gel, for the reason that it can precisely control the composition, the process using low temperature, can produce high purity and homogeneity. The material used is coral from Banyuwangi, East Java. To optimize the forming process, the coral powder was made of 54.84 nm using mechanical high energy milling (HEM-3D) method. Sol-gel methods include hydrolysis, condensation, aging, and drying. The calcination process was then carried out with temperature variations of 450°C, 550°C, 650°C, 700°C, 750°C, 80°C, 850°C and 900°C. The result of XRD observation shows that the temperature of 550°C gives the optimum hydroxyapatite phase which is 90.8%. In addition, at temperatures below 550°C formed Tricalcium phosphate (TCP), whereas above the temperature formed tetralkalium phosphate (TTCP). The lower the calcination temperature, the larger the TCP. Conversely, the greater the calcination temperature the greater the TTCP phase. Both phases, both TCP and TTCP are unstable calcium phosphate compounds. The observation results also show that the increase of calcination temperature can increase the degree of crystallinity. The degree of crystallinity of the sample at 900°C is 77.28%, twice the degree of crystallinity of 450°C. In addition, an increase in calcination temperature increases the size of the crystal as well, although the increase is not consistent as the degree of crystallinity

1. Introduction

Damage and disruption of bones can affect the activity and function of other body organs. In Indonesia, cases of bone disorders such as fractures continue to increase. Fractures can be caused by several factors including injury and mechanical collisions, traffic accidents, fatigue because the muscles can not absorb energy such as walking too far or bone weakness due to cancer and osteoporosis [1]. Traffic accidents contribute greatly to fractures, as data released by the Police Headquarters of 2014 show that of 61,616 cases of accidents in 33 provinces there were 32,232 fractured victims.

To overcome the various damage that occurs in bone, can be done some handleings either with therapy or by implant installation that aims to replace or support the actual bone function. Implantation is very well known in the medical world and specialized in bone, there are 3 kinds of biomaterial sources used in the implantation of autograft (derived from the patient's own body parts), allograft (derived from other individuals in one species) and xenografts (derived from body parts individuals of different species). Although the above three types of biomaterials can overcome the problem of bone implants
but the material also has weaknesses. Allograft has a weakness that it can causes an infection if the donor bone is not healthy. Xenograft has different bone mineral characteristics so it is less suitable for implant needs. Meanwhile, because the autograft originates from the bone in the other body part of the patient theirselves, it will provide an additional burden for the patient. Therefore, it is necessary to develop alternative biomaterials from natural or synthetic materials, especially that containing high calcium as a hydroxyapatite forming agent. The use of natural materials is safer compared to synthetic materials because of the lower risk of cross-reaction and other reactions [2].

Natural materials that can be utilized as a raw material for the formation of hydroxyapatite as a material that has a high calcium content. Some examples of such natural materials are limestone, egg shells, cuttle fish bones, crabs, and coral. Judging from the abundance of its availability, coral is one option because Indonesia is a maritime country. [3] showed that the content of CaCO₃ (Aragonite) from the highest corals of other compounds amounted to 92%. With certain heat treatment, then this aragonite can be synthesized into hydroxyapatite.

Hydroxyapatite (HA) with Ca₁₀(PO₄)₆(OH)₂ chemical formula is a bioactive ceramic with high biofinitry and it is a mineral component of bone because its composition and crystalinity is almost similar to human bone. Its crystal structure is hexagonal, and its ideal constituent composition is Ca 39.9% and P 18.5% with ratio of calcium-phosphate Ca / P equal to 1.67.

Synthesis of hydroxyapatite can be done by various methods. Some of those methods include precipitation, solid state (chemical precipitation), sol-gel, and hydrothermal method. Different synthesis process parameters will produce different quantities and quality of hydroxyapatite. The process parameters can be particle size, particle homogeneity, and particle shape obtained [4].

The sol-gel method has several advantages over other methods. The advantages of the sol-gel method are to control the composition precisely, using low temperature, high purity and homogeneity, and the granules obtained reach the nano size [5]. The sol-gel method begins with the process of changing from the solvent phase (sol) into a solid phase (gel), through the stages of formation of solution, gel formation, aging, drying and compaction (densification) [6]. The process for producing a hydroxyapatite powder by sol-gel method is influenced by several variables such as variation of precursor concentration, calcination temperature, catalyst concentration, solvent, and maturation time. This study focused on the influence of sintering temperature on the fraction of hydroxyapatite volume formed and its crystallinity.

2. Experimental Methods

Coral in this study came from the sea in Banyuwangi, East Java, Indonesia. Also used is 99.8% pure Phosphoric Acid (H₃PO₄) by Aldrich, distilled water and ethanol. The steps of sol-gel method include hydrolysis, condensation, maturation (aging), and drying. The hydrolysis process is carried out by reacting calcium hydroxide and phosphoric acid with a certain ratio. This process is carried out in a magnetic stirrer to generated homogeneous solution. In the next process, the condensation occurs the transition process from sol to gel by heating the solution at a temperature of 120°C until concentrated. At this stage also has formed anatase phase but still in an amorphous state. Furthermore, gel aging is formed (aging) by silencing the gel to change its properties for 24 hours. In this maturation process occurs the reaction of gel tissue formation is more rigid, strong, and shrink in the solution. After that, carried out drying stage at a temperature of 110°C then done the calcination process at a temperature variation between 450°C to 900°C with intervals of 50°C each for 5 hours.

3. Results and Discussion

The coral used in this study is a nanometer-sized powder. The process used HEM-3D (High Energy Milling-3Dimension) which has 3D motions that accelerate the nanoparticle process. The milling process is done for 20 hours and using PSA (Particle Size Analyzer), obtained the powder coral size is 54.84 nm (figure 1). The size of nanoparticles formed from this coral compound can accelerate the occurrence of hydroxyapatite formation.
Coral contains a large enough of CaCO3 compound is 94.3% while the rest is a Ca2O5Si compound of 5.7%. Through a heating process of 900°C, the CaCO3 compound turns into CaO. Furthermore, this compound reacts with water vapor transformed into Ca(OH)2 (equation 1). Through this reaction formed Ca(OH)2 of 95.8% and 4.2% CaCO3.

\[
\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2 \quad (1.a)
\]

\[
\text{CaO} + \text{H}_2\text{O} \rightarrow \text{Ca(OH)}_2 \quad (1.b)
\]

The formation of hydroxyapatite by sol-gel method begins to react the calcium hydroxide compound with phosphoric acid (equation 2). Furthermore, the formed solution is allowed to stand for 1 day to form a gel network that is more rigid, strong, and shrinks in solution. This process produces gel.

\[
\text{Ca(OH)}_2 + \text{H}_3\text{PO}_4 \rightarrow \text{CaHPO}_4 \cdot 2\text{H}_2\text{O} \quad (2)
\]

The formed gel was dehydrated in an oven at 110°C for 2 hours. The calcination performed on different temperature variations of 450 °C; 550°C; 650°C; 700°C; 750°C; 800°C; 850°C and 900°C to determine the optimum temperature of the formation of hydroxyapatite powder. The formed gel was dehydrated in an oven at 110°C for 2 hours. The, the calcination performed on different temperature variations of 450 °C; 550°C; 650°C; 700°C; 750°C; 800°C; 850°C and 900°C to determine the optimum temperature of the formation of hydroxyapatite powder.

The results of observations using XRD (figure 2) showed that the compounds formed are hydroxyapatite (HAp), tricalcium phosphate (TCP), and tetra calcium phosphate (TTCP) (table 1). At the calcination temperature of 450°C and 550°C, the compounds formed are HAp and TCP, while the calcination treatment at temperatures above 550°C produces HAp and TTCP. The optimal amount of HAp compound occurs at a calcination temperature of 550°C. The higher the calcination temperature decreases the HAp formed and the more TTCP compounds. The formation of these calcium phosphate phases can be chemically described as reaction equation (3)

\[
3\text{Ca(OH)}_2 + 2\text{H}_3\text{PO}_4 \rightarrow \text{Ca}_3(\text{PO}_4)_2 + 6\text{H}_2\text{O} \quad (3a)
\]

\[
10\text{Ca(OH)}_2 + 6\text{H}_3\text{PO}_4 \rightarrow \text{Ca}_10(\text{PO}_4)_6(\text{OH})_2 + 18\text{H}_2\text{O} \quad (3b)
\]

\[
2\text{CaHPO}_4 + 2\text{CaCO}_3 \rightarrow \text{Ca}_4(\text{PO}_4)_2 \text{O} + \text{CO}_2 + \text{H}_2\text{O} \quad (3c)
\]
Figure 2. The Difraktogram of sample with calciation temperature (a) 450°C, (b) 550°C, (c) 650°C, (d) 700°C, (e) 750°C, (f) 800°C, (g) 850°C, dan (h) 900°C

Table 1. Identification of sample content for various calcination temperature

| Calcination Temperature (°C) | Volume fraction (%) | HAp  | TCP | TTCP |
|------------------------------|---------------------|------|-----|------|
| 450                          | 86.4                | 13.6 | -   | -    |
| 550                          | 90.8                | 9.2  | -   | -    |
| 650                          | 42.4                | -    | 57.2|      |
| 700                          | 27.7                | -    | 72.3|      |
| 750                          | 27.6                | -    | 72.4|      |
| 800                          | 17.9                | -    | 82.1|      |
| 850                          | 12.9                | -    | 87.1|      |
| 900                          | 12.4                | -    | 87.6|      |

Table 2. The sample crystal size

| Calcination Temperature (°C) | Crystallinity | Crystal size (nm) |
|------------------------------|---------------|-------------------|
| 450°C                        | 38.86 %       | 32.38             |
| 550°C                        | 39.86 %       | 32.09             |
| 650°C                        | 40.90 %       | 38.29             |
| 700°C                        | 41.61 %       | 30.17             |
| 750°C                        | 43.80 %       | 53.39             |
| 800°C                        | 56.10 %       | 48.02             |
| 850°C                        | 61.65 %       | 63.37             |
| 900°C                        | 77.28 %       | 52.16             |

The crystalline phase corresponds to the size of the crystals formed. Using the Scherrer equation the sample crystal size can be expressed in table 2. The results show that the sample crystal size ranges from 30.17 nm - 63.37 nm. The samples at the calcined temperature of 700°C crystalline size were
smaller than in the other samples. These results show that there is no linear relationship between the size of the crystal and the temperature of calcination.

4. Conclusion
From the series of analysis and discussion that has been done, can be made some conclusions. First, In the sol gel method, variations in calcination temperature affect the formation of hydroxyapatite and increase the crystallinity of the content of the resulting compound. Secondly, The optimum hydroxyapatite was produced at 550°C calcined temperature with the most stable phase of hydroxyapatite of 90.8% with 39.8% crystallinity and 32.09 nm crystal size. However, the best degree of crystallinity was obtained at a 900 ° C calcination temperature of 77.28% owned by the TTCP phase

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