Synthesis and Characteristics of β-Tri-Calcium Phosphate from Green Mussel Shell

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Synthesis and Characteristics of β-Tri-Calcium Phosphate from Green Mussel Shell

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Abstract. The β-tri-calcium phosphate (β-TCP) is a calcium phosphate compound also called whitlockite. This form is more widely used because of its chemical stability, high mechanical strength and better bio-sorption when compared with α-Tri-calcium-phosphate. β-tri-calcium phosphate in this study was obtained from reactions of calcium oxide and phosphoric acid by precipitation method. Precipitation at 50 °C while sintering at 600, 700, 800, 900, and 1000 °C, in the sintering range of 1-5 hours. Green mussel shell has calcium carbonate ($CaCO_3$) content 60-70 % then calcined at 1000 °C to get calcium oxide (CaO). The result shows that β-tri-calcium phosphate optimum reached of 72% at sintering temperature 1000 °C for 5 hr sintering time. The crystal structure of β-tri-calcium phosphate formed is a rhombohedral crystal with a Ca / P ratio mole of 2.72

Key words: β tri-calcium phosphate, green mussel shell, sintering, precipitation.

1. Introduction

Calcium phosphate ($Ca_3(PO4)_2$) is a mineral containing calcium (Ca^{2+}) ions and orthophosphate ions (PO_4^{3-}), meta-phosphate or pyrophosphate ($P_2O_7^{4-}$). Sources of calcium are very much found in nature, among others, from lime, various shells such as mussel, crabs or eggshells. Calcium phosphate was prepared from phosphoric acid and oyster shells [1] and other composite as its function and characteristic development. [2-7]. Calcium phosphate have biological and chemical properties [2-4] and mechanical properties [5-6] similar to mineral phase of bone, and ability to bond to the host tissue, although it can disperse from where it is applied. Studies on the synthesis of calcium phosphate have been carried out [8-15], but many factors affect the production process so that research on tricalcium phosphate is still being developed. Calcium Phosphate ceramics have been widely used in tissue engineering due to their excellent biocompatibility and biodegradability. Ultimately, they are capable of replacing damaged bone with new tissue [3,6]. The application of calcium phosphate ceramics has become relatively so far and wide in the biomedical materials field, due to their biocompatibility with human hard tissue. Pure calcium hydroxyapatite (HA, $(Ca_{10}(PO_4)_6(OH)_2)$) and β-tricalcium phosphate (β-TCP, $Ca_3(PO_4)_2$) bioceramic powders, that have been synthesized via chemical precipitation techniques [13,14]. Various factors that affect the production of calcium phosphate include: degree of acidity (pH), combustion temperature (sintering [15]), raw material composition, and the source of calcium is organic or inorganic. Nanocomposites based on of β-tri calcium phosphate (β-TCP) and 2.5-10 wt% merwinite nanoparticles were prepared and sintered at 1100-1300°C [16,19]

The Ca/P [7] calcium phosphate usually in the range of 1.63 to 1.67 [7]

The calcium phosphate prepared by following reaction :

$$3\ CaO + 2\ H_3PO_4 \rightarrow Ca_3(PO_4)_2 + 3\ H_2O \quad (1)$$
$$3\ CaCl_2 + 2\ Na_2HPO_4 \rightarrow Ca_3(PO_4) + 4\ NaCl + 2\ HCl \quad (2)$$

To be able to get β-TCP, it is necessary to study the effect of sintering temperature and sintering. The purpose of this study was to produce the β-TCP from green mussle shell and to study the characterization by X-ray Diffraction (XRD) [20,21]and prepared by heating an equimolar mixture of $CaHPO_4$ and $CaCO_3$.

2. Materials and Method

This research is divided into two processes, the first process is the calcium production from green mussel shell and the second process is the calcium phosphate production. There are two process variables: temperature sintering in the range of 600, 700, 800, 900 and 1000 ° C and time of sintering in the rangeof 1, 2, 3, 4, and 5 min. The diagram of the research procedure as showed in Figure 1.

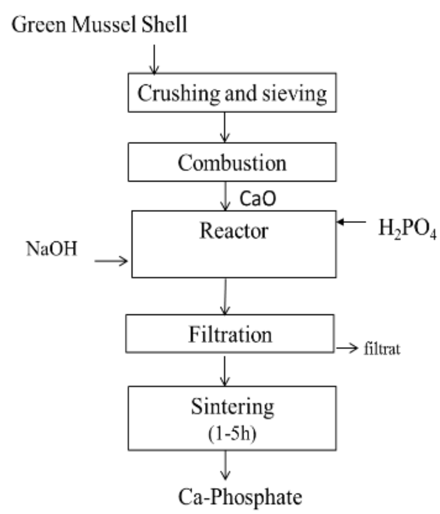

Figure 1. Schematic diagram of research procedure

3. Result and Discussions

a. The effect of time and sintering temperature on Ca/P ratio calcium phosphate product

Figure 2 showed the effect of time and sintering temperature on Ca/P ratio of calcium phosphate product. The Ca / P ratio tends to decrease with increasing sintering time from 1 to 5 h. A sharp decrease in Ca / P from 4 to 3.14 occurs in an increase in sintering time from 1 to 5 h at a temperature of 800 °C. The increasing of sintering temperature from 600 to 1000 °C tend to decrease the Ca/P ratio except for temperature rise from 700 to 800 °C, Ca / P increases but then Ca / P decrease again until reached temperature of 1000 °C. The lower Ca/P obtained in sintering temperature 1000 C in the range of 3.04 to 2.72 for 1to 5 h.

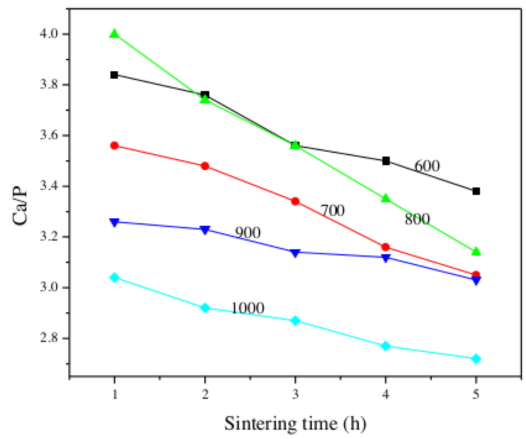

Figure 2. Effect of time and sintering temperature on Ca/P ratio of calcium phosphate product

b. The XRD characterization of β-Tri-calcium phosphate product at temperature 600 C

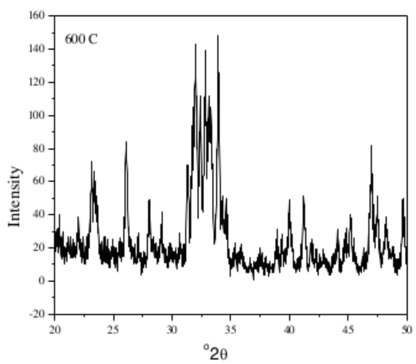

Figure. 3a. XRD pattern for TCP product at 600 °C

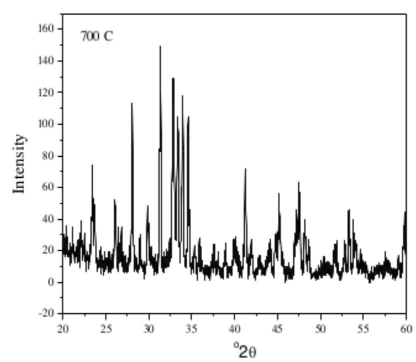

Figure. 3b. XRD pattern for TCP product at 700 °C

Figure 3 showed XRD pattern for TCP product at temperature 600 and 700 °C. There are two phases that occurred to Tri-calcium Phosphate (TCP) and Calcium oxide Phosphate (COP). The result found the pattern (Figure 3a) as COP and CP, then obtained about 90% of TCP and 10% of COP at 600 °C and about 82% of TCP and12% of COP at 700 °C (Figure 3b). No β-TCP appeared in both samples β tri-calcium phosphate.

c. *The XRD characterization of β-Tri-calcium phosphate product at temperature 800 C .*

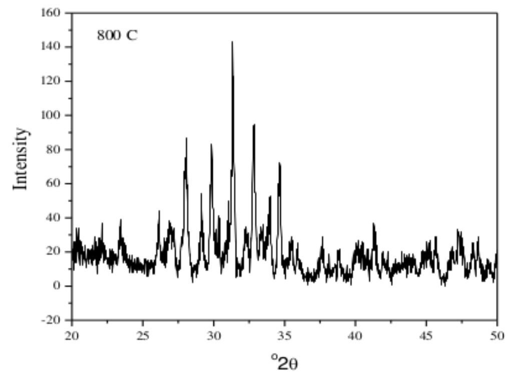

Figure. 4. The XRD pattern of TCP product at 800 ˚C

Figure 4 showed XRD pattern of TCP product at 800 ˚C. at the sintering temperature 800 C for 5 h begin to form β Tri-calcium Phosphate. β tricalcium phosphate (TCP) characterized by the red line, which has 2 highest peaks at 2θ angles of 27.25, and 29.27°.

d. The XRD characterization of β-Tri-calcium phosphate product at temperature 900 C

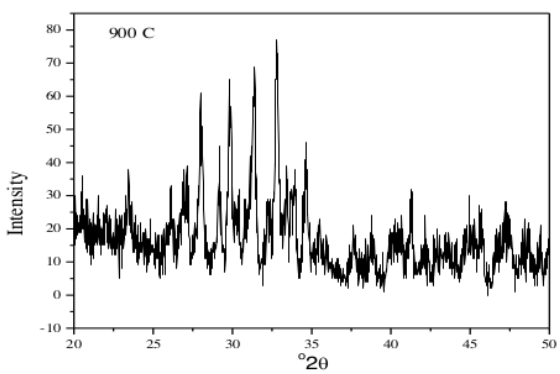

Figure. 5. XRD pattern of TCP product at 900 ˚C

Figure 5 showed the XRD pattern of TCP product at sintering temperature 900 ˚C. There are two phases that occur are Tricalcium Phosphate (TCP) and Calcium oxide Phosphate (COP). TCP value of 76% and COP 24%. In this sample phase β-TCP there are 3 highest peaks at 2θ angles of 25.95°, 27.22° and 29.24°.

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e. The XRD characterization of β-Tri-calcium phosphate product at temperature 1000 ˚C

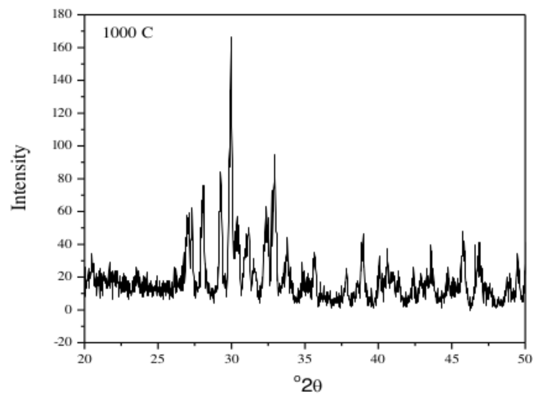

Figure. 6. The XRD pattern of β-Tricalcium phosphate product

Figure 6 showed the XRD pattern of β-TCP product at the sintering temperature of 1000 ˚C.. There are two phases that occur are TCP and COP. TCP value of 72% and COP 28%. Phase β-TCP appears characterized by four peaks at 2θ angle of 27.41, 29.37, 37.92 and 45.51°.

4 Conclusions

β-Tricalcium Phosphate from green mussel shell with Ca / P = 2.72 can be obtained at sintering temperature of 1000°C for 5 h, the content element is Calcium (Ca) of 74,28% and Phosporic (P) of 21,26%, The β-TCP crystal form indicates the rhombohedral.

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