Synthesis of Tricalcium Phosphate From Eggshells with Precipitation Method

S Sani, S Muljani*, D Astuti, R Mardayana, V D Alfiyani

Chemical engineering Department, Engineering Faculty, University of Pembangunan Nasional “Veteran” East Java, Jl. Rungkut Madya, Gunung Anyar, Surabaya, East Java, Indonesia 60294

*sriemuljani.tk@upnjatim.ac.id

Abstract. Calcium phosphate compounds are one of the biomaterials that are widely used for bone reconstruction because they are biocompatible and have a chemical composition that is close to the inorganic components present in the bone. Two types of calcium phosphate that are widely applied to the bone reconstruction process are hydroxyapatite (Ca\(_{10}\) (PO\(_4\))\(_6\) (OH)\(_2\)) and \(\beta\)-Tricalcium Phosphate (Ca\(_3\) (PO\(_4\))\(_2\)). This research develops the manufacture of \(\beta\)-Tricalcium Phosphate by reacting calcium compounds derived from chicken eggshells and phosphate sources derived from dinatrium phosphate (Na\(_2\)HPO\(_4\)) using precipitation method which is carried out with variations in sintering temperature 600 to 1000 °C and sintering time of 1 to 5 h. The results of X-Ray fluorescence (XRF) analysis showed that the Ca / P ratio obtained was 1.74, at the sintering temperature of 1000 °C and the sintering time for 5 h. These results have approached a standard where the ratio of Ca / P on Tricalcium Phosphate is 1.5. While based on the results of X-Ray Diffraction (XRD) analysis that in the sample formed two types of Calcium Phosphate namely \(\beta\)-Tricalcium Phosphate and Hydroxyapatite so that it can be said that the product produced is Biphase Calcium Phosphate. The high percentage of \(\beta\)-Tricalcium Phosphate is 81.9% with the 3 highest peaks, namely at the angle 2\(\theta\) of 27.83; 31.03; 34.42 is obtained at the sintering temperature of 1000 °C and at the sintering time is 5 h.

1. Introduction
Bone in the human body is very important because it is a skeleton that gives shape to the human body and supports the human body so that its strength must be maintained. Damage to bones causes disruption of bodily functions. An increase in the number of people with bone damage in Indonesia, one of which is triggered by accidents in traffic which result in fractures.

To replace or speed up the process of repairing a damaged part of the bone, it is necessary to have a material that is expected to be a very appropriate alternative to be used as an implant material. This material is commonly referred to as biomaterial bone implantation. Biomaterials are natural or artificial materials (syntheses) that can be implanted into living systems or tissues instead of damaged tissue functions. The selection of the right biomaterial is needed in the implantation process. The materials chosen for biomaterials are those that are easy to obtain, biocompatible, bioactive, and no toxic [1-4].
The biomaterial that will be used for bone implantation must have a composition that resembles bone composition. In general, biomaterials that are widely used for implants are Tricalcium Phosphate (Ca₃(PO₄)₂) and Hydroxyapatite (Ca₁₀(PO₄)₆(OH)₂). Hydroxyapatite (HA, Ca₁₀(PO₄)₆(OH)₂), β-tricalcium phosphate (β-TCP, Ca₃(PO₄)₂), and biphasic calcium phosphates (BCP) are the most commonly employed forms of calcium ceramics [5-7]. TCP is a calcium phosphate compound which has a Ca/P molarity ratio of 1.50 with a density of 3.07 g/cm³ [8]. Tri calcium phosphate (TCP) polymorph which is often used in bone implantation studies, namely α-TCP and β-TCP. The α-TCP crystal has a monoclinic cell shape with lattice parameters a = 1.2887 nm, b = 2.7280 nm, and c = 1.5219 nm while β-TCP has a hexagonal cell shape with a lattice parameter a = 1.0439 nm and c = 3.7375 nm. When heated at a higher temperature HA will transform into TCP. Therefore, to synthesize TCP high temperatures are needed. α-TCP has lower mechanical properties. The properties of β-TCP are porous and capable of being degraded biologically at a high rate, bioresorbable (easily absorbed), bioactive, biocompatible, osteoconductivity. One of the mechanical properties of β-TCP is relatively not easily broken compared to α-TCP [9,10]. Tricalcium Phosphate synthesis has been studied using several methods and various types of raw materials that contain very high calcium [9-13]. The many factors that influence the formation of TCP are the reason why TCP-related research is still being developed. Synthesis of TCP from natural ingredients is better because it can improve bioactive and biocompatible properties. Natural materials commonly used are coral, shellfish, and eggshells. The use of these materials as a source of calcium because most of the content contained in these materials is calcite (CaCO₃). The morphology and characteristics of TCP have been widely reported and to get it is highly dependent on operating conditions including the type of raw material, temperature and concentration of phosphoric acid [14-19]. Anne [20] reported that the absence of a brushite phase or α or β tricalcium phosphate in the product when synthesized at relatively low temperatures (85°C). While at high sintering temperatures (> 1200 C) there will be a phase change in TCP. The synthesis of Tricalcium Phosphate in this research was carried out by studying the effect of temperature and time of sintering on the characteristics of Tricalcium Phosphate (Ca₃(PO₄)₂) by precipitation method using natural calcium sources from egg shells.

2. Materials and Methods
The materials used in this study were chicken eggshell, disodium phosphate (Na₂HPO₄), sodium hydroxide (NaOH), hydrochloric acid (HCl) and demineralized water.

2.1. Preparation of calcium chloride (CaCl₂)
Eggshell is washed and cleaned using clean water and then dried. After drying the eggshell is crushed into powder, then filtered using a 100 mesh filter. The powder is then analyzed using X-Ray Fluorescence (XRF) to determine its chemical composition. Preparation of calcium chloride (CaCl₂) is done by reacting eggshell powder with 1M HCl in a stirring reactor at room temperature. Stirring speed is set at 300 rpm for 60 min.

2.2. Preparation of Tricalcium phosphate (Ca₃(PO₄)₂)
Preparation of tricalcium phosphate was carried out by mixing 90 cc of CaCl solution and 0.3 M of sodium phosphate (Na₂HPO₄) solution of 100 cc. The two solution mixture was stirred with a magnetic stirrer at a stirring speed of 300 rpm for 60 minutes at room temperature. Next, 1 M NaOH solution is added as a pH controller until it reaches pH 8 and to form deposits (Ca₃(PO₄)₂). Deposition of Ca₃(PO₄)₂ is separated from the solution by filtration then the precipitate is washed with demineralization water. The precipitate formed is then dried using an oven for 2 h followed by drying in the furnace with variations in temperature of 600, 700, 800, 900, 1000°C and sintering time in the range of 1-5 h.

2.3. Characterization
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3. Result and Discussion

Table 1 showed the element composition in egg shells from XRF analysis. Based on the results of the analysis, the content of Calcium (Ca) is quite high at 99.61%. This supports that this eggshell has the potential to be used as a raw material in the synthesis of Tricalcium Phosphate. wishes to divide the paper into sections the formatting shown in table 2 should be used.

| Component | Concentrations (%) |
|-----------|--------------------|
| S         | 0.16               |
| Ca        | 99.61              |
| Fe        | 0.033              |
| Cu        | 0.077              |
| Sr        | 0.12               |

3.1. Effect of sintering temperature on Ca/P ratio.
The results showed that the Ca / P ratio decreased with increasing temperature and sintering time. The Ca / P values ranged from 1.74 to 3.22 for the sintering temperature range from 600 to 1000 C and for the period of 1 to 5 hours. The lowest Ca / P of 1.74 was achieved at 5 hours sintering time and 1000 C temperature, but still greater than the Ca / P standard for tricalcium phosphate ie 1.5.

3.2. Effect of sintering time on Ca/P ratio
Wherever possible try to ensure that the size of the text in your figures (apart from superscripts/subscripts) is approximately the same size as the main text (11 points).

3.3. Diffraction patterns of Tricalcium Phosphate (Ca3 (PO4) 2)
The XRD characteristics of the sample showed that the most dominant type formed was β-Tricalcium Phosphate (β-TCP) and hydroxyapatite (HA). Identification of the type of compound in the sample was
carried out by matching the diffraction pattern with the Joint Committee for Powder Diffraction (JCPDS) where B-TCP corresponds to No. 09-0169 while for HA according to No. 09-0432.

Figure 3 correlation with Figure 6 showed diffraction patterns of the samples sintered at 600 to 1000 °C for 1h sintering time. The diffraction pattern depicted in Figure 3a of the sample sintered at 700 °C for 1h formed β-TCP at 61.4% with 3 highest peaks at an angle of 2θ at 27.83; 31.04; 34.35 while HA with a percentage of 38.5% has 3 highest peaks, namely at the angle 2θ of 25.89; 31.76; 32.84. The XRD pattern shown in Figure 3b showed that the sample sintered at 800 °C for 1h formed β-TCP at 67.4% with 3 highest peaks at 2θ at 27.81; 31.02; 34.41 while HA with a percentage of 32.6% and has the 3 highest peaks, namely at the angle 2θ of 25.87; 31.79; 32.86. The XRD pattern depicted in graph 3c showed that the sample sintered at 900 °C for 1h formed β-TCP at 72.2% with 3 highest peaks at 2θ at 27.79; 31.09; 34.39 while HA with a percentage of 27.8% and has the 3 highest peaks, namely at the angle 2θ of 25.95; 31.87; 32.94. The diffraction pattern depicted in graph 3d shows that the sample sintered at 1000 °C for 1h formed β-TCP at 77.4% with 3 highest peaks at 2θ at 27.85; 31.05; 34.44 while HA with a percentage of 22.6% and has the 3 highest peaks, namely at the angle 2θ of 25.88; 31.74; 32.86.
Figure 4 corelation with Figure 6 showed diffraction patterns of the samples sintered at 600 to 1000 °C for 3h sintering time. The diffraction pattern depicted in Figure 4a of the sample sintered at 700 °C for 3h formed β-TCP at 63.9% with 3 highest peaks at an angle of 2θ at 27.85; 31.05; 34.44 while Hydroxyapatite (HA) with a percentage of 36.1% has 3 highest peaks, namely at the angle 2θ of 25.91; 31.82; 32.89. The XRD pattern shown in Figure 3b showed that the sample sintered at 800 °C for 3h formed β-TCP at 67.9% with 3 highest peaks at 2θ at 27.87; 31.07; 34.37 while HA with a percentage of 32.1% and has the 3 highest peaks, namely at the angle 2θ of 25.92; 31.84; 32.91. The XRD pattern depicted in graph 4c showed that the sample sintered at 900 °C for 3h formed β-TCP at 73.5% with 3 highest peaks at 2θ at 27.86; 31.06; 34.36 while HA with a percentage of 26.5% and has the 3 highest peaks, namely at the angle 2θ of 25.92; 31.84; 32.90. The diffraction pattern depicted in graph 4d shows that the sample sintered at 600 °C for 3h produced β-TCP at 60.9% with 3 highest peaks at 2θ at 27.82; 31.08; 34.38 while HA reached of 39.1% and has the 3 highest peaks, namely at the angle 2θ of 25.84; 31.78; 32.85. and the sample sintered at 1000 °C for 3h formed β-TCP at 78.6% with 3 highest peaks at 2θ at 27.84; 31.03; 34.52 while HA with a percentage of 21.4% and has the 3 highest peaks, namely at the angle 2θ of 25.90; 31.71; 32.87.
Figure 4c. Diffraction pattern of sample at 900°C sintering temperature for 3h

Figure 4d. Diffraction pattern of sample at 600 and 1000°C sintering temperature for 3h

Figure 5a. Diffraction pattern of sample at 700°C sintering temperature for 5h

Figure 5b. Diffraction pattern of sample at 800°C sintering temperature for 5h

Figure 5c showed that the sample sintered at 700 °C for 5 h formed β- TCP at 66.2% with 3 highest peaks at angle2θ of 27.87 ; 31.07 ; 34.37 while hydroxyapatite (HA) with a percentage of 33.8% and has the 3 highest peaks, namely at the angle 2θ of 25.92 ; 31.84 ; 32.91 .The XRD pattern depicted in Figure 5b showed the sample sintered at 800 °C for 5 h formed β-TCP at 70.3% with 3 highest peaks at angle 2θ of 27.86 ; 31.06 ; 34.36 while hydroxyapatite with a percentage of 29.7% and has the 3 highest peaks, namely at the angle 2θ of 25.92 ; 31.84 ; 32.90 . Figure 5c showed that the sample sintered at 900 °C for 5 h can produce β- TCP at 74.9% with 3 highest peaks at angle 2θ of 27.86 ; 31.06 ; 34.36 while HA with a percentage of 25.1% and has the 3 highest peaks, namely at the angle 2θ of 25.82 ; 31.84 ; 33.00. Figure 5d showed the diffraction pattern of the samples sintered at 600 and 1000 °C for 5 h. At 600 °C β-TCP formed at 61.4% with 3 highest peaks at an angle of 2θ at 27.82 ; 31.02 ; 34.38 while HA with a percentage of 38.6% has 3 highest peaks, namely at the angle 2θ of 25.83 ; 31.81 ; 32.87, while the sample sintered at 1000 °C for 5 h formed β- TCP at 81.9% with 3 highest peaks at angle 2θ of 27.83 ; 31.03 ; 34.42 while HA with a percentage of 18.1% and has the 3 highest peaks, namely at the angle 2θ of 25.90 ; 31.71 ; 32.97.
4. Conclusion

The β-TCP synthesis of eggshell by precipitation method was successfully carried out. Temperature studies (6000-10000C) and sintering time (1-5 h) show a significant effect of both on β-TCP composition and Ca / P ratio on the product. The highest yield of β-TCP composition was 81% obtained at 1000C for 5 hours sintering but Ca / P of 1.74 still did not reach the desired Ca / P value of 1.5.
5. References

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