Synthesis of β-TCP by sol-gel method: variation of Ca/P molar ratio

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Synthesis of β-TCP by sol-gel method: variation of Ca/P molar ratio

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Abstract. Beta-TCP has been synthesized by sol-gel method in ethanol media with Ca/P molar ratio of 1.0–1.5. Phosphorous pentoxide solution was slowly added into calcium nitrate tetrahydrate solution with gentle stirring to produce white gel. The white gel was dried at 80°C for 20 hours and continued by calcination process at 800°C for 30 minutes. The results showed that pure β-TCP powders was obtained from Ca/P molar ratio of 1.3. For Ca/P of 1.0-1.2, beside β-TCP, a little amount of β-CPP were found and for Ca/P ratio of 1.4–1.5, hydroxyapatite was formed as secondary product. The crystallite size of β-TCP was in a range of 32.96-47.82 nm. Morphology changed due to Ca/P molar ratio in which the size of irregular shape β-TCP became bigger as Ca/P molar ratio increased from 1.0 to 1.3. The presence of hydroxyapatite in the product has not changed the morphology shape but reduced its grain size.
Keywords: β-TCP, sol-gel method, calcium phosphate

1. Introduction

Beta-tricalcium phosphate (β-TCP, β-$Ca_3(PO_4)_2$) has been used as powder phase in the production of calcium phosphate cement (CPC) due to its excellent properties such as biocompatible, bioactive, and osteoconductive [1-3]. CPC is a kind of bone filler that has been developed to maintain bone damage with minimally invasive surgery procedure. Hydrolysis of β-TCP by water in liquid phase will produce brushite paste (dicalcium phosphate dihydrate/DCPD, $CaH(PO_4).2H_2O$) that can be injected. This kind of CPC has adsorption rate better than other types of CPC [4]. DCPD is a metastable phase that will be transformed into mineral apatite in human bone [5]. DCPD cement can has compressive strength about 10 MPa [4] that similar to trabecular bone [5].

As a basic ingredient of CPC, there are several important characters of β-TCP that should be considered such as chemical composition, homogeneity, phase distribution, morphology, grain size, grain shape, grain boundaries, crystallite size, crystallinity, porosity, and surface roughness [6]. Those characters were depended on the synthesis method that used. There are several methods that can be used, including sol-gel [7], solid state reaction [8], wet precipitation [9], hydrothermal [10], mechanochemical [11] and electrochemical deposition [12]. Sol-gel method is considered as the best β-TCP synthesis method. Slow reaction between precursors enable Ca and P atoms to be arranged orderly by controlling some reaction factors. These factors are including the molar ratio of Ca/P reactants, ageing time, firing temperature and firing time [13]. The molar ratio of Ca/P reactants is related to the supply of Ca and P according to the expected ratio Ca/P of the product. Aging time is the time needed to form a stable gel structure. While firing temperature and firing time are related to energy supply for the formation of β-TCP's crystal nucleus and crystal growth of β-TCP.

In this study, calcium nitrate tetrahydrate [$Ca(NO_3)_2.4H_2O$] and phosphorus pentoxide [P_2O_5] were used as calcium and phosphorus precursors, respectively. Both of them were dispersed in pure ethanol.

The mixture of calcium and phosphorus precursors in ethanol media and ageing at proper time would produce stable gel as polymerization condensation product. Drying process of the gel at 80°C would produce amorphous calcium phosphate powder (ACP). Transformation of ACP into crystalline phase of β-TCP were conducted by firing process. The effect of molar ratio of Ca/P reactants to the product's purity, β-TCP's crystallite size and morphology were studied by varying the molar ratio of Ca/P reactants in a range of 1.0-1.5. All reactions were conducted with aging time of 1 day and firing temperature at 800° C for 30 minutes.

2. Experimental Procedures

The starting material for this work were commercially available phosphorus such as pentoxide (Merck), calcium nitrate tetrahydrate (Merck), ethanol (Merck), and proinjection distilled water (Ikaparmindo Putramas). Appropriate amounts of phosphorus pentoxide were dissolved in ethanol to obtain a solution with a concentration of 0.5 M. Meanwhile, solution of calcium nitrate tetrahydrate in ethanol was prepared in different concentration of 1.0; 1.1; 1.2; 1.3; 1.4 and 1.5 M. Then 100 mL of phosphorus pentoxide solution was slowly added into beaker glass containing 100 mL calcium nitrate tetrahydrate 1 M to give a Ca/P ratio of 1.0. The solution mixture was stirred at moderate rate until a constant gel formed. The gel was washed with aquabidest and then dried in air atmosphere at 80°C for 20 hours. The dried powder named amorphous calcium phosphate (ACP) was then heated (firing process) at 800°C for 30 minutes. The final product was named calcium phosphate (CP). Same steps were done with different calcium nitrate tetrahydrate concentration to get Ca/P ratio of 1.1; 1.2; 1.3; 1.4 and 1.5. The products were analysed with FTIR (Shimadzu Frontier FT-IR 96772), XRD (Shimadzu XRD-7000) and SEM-EDS (JSM-6510LA). FTIR and XRD data analysis were performed with Origin 8 software. The crystallite size was calculated with Scherrer equation.

3. Results and Discussion

FTIR spectra of ACP and CP for Ca/P ratio=1.5 can be seen in Fig. 1. For ACP spectra, it can be seen a peak at 532.73 cm^{-1} that is characteristic energy of bending vibration of O-P-O group (v4). Peak at wave number of 1011.72 cm^{-1} addressed to asymmetric stretching vibration of O-P-O (v3). Meanwhile for symmetric stretching vibration (v1) appears at 961.72 cm^{-1}. Those peaks are indicating that ACP contains PO43-group. XRD diffractogram of ACP confirmed that the structure is amorphous, so the calcium phosphate type of ACP cannot be ascertained. According to Ca/P ratio of the precursors, it could be brushite ($CaH(PO4).2H_2O$) [5]. ACP spectra also showed a broad peak around 3500 cm^{-1} that related to energy vibration for –OH groups with hydrogen bonding. Peak at 2983.1 cm^{-1} (C-H bond vibration) indicated that ethanol was not completely removed from the sample. For CP spectra, the peaks for v1 and v4 vibrations appear at 961.72 cm^{-1} and 567.31 cm^{-1}, respectively. The –OH peak become sharper and appear at 3436.44 cm^{-1}. No longer found C-H vibration in the CP indicated that ethanol was degraded by firing process.

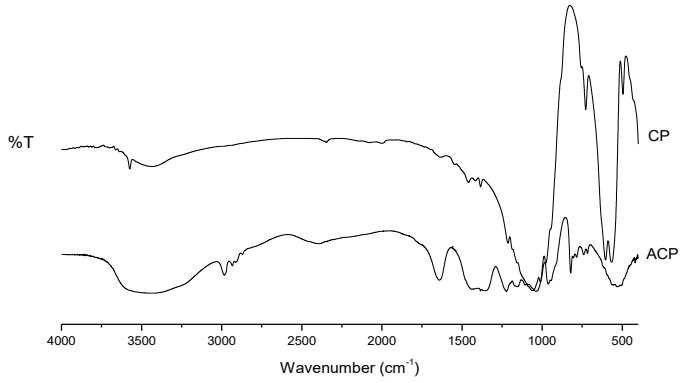

Figure 1. FTIR spectra of ACP and CP for Ca/P=1.5.

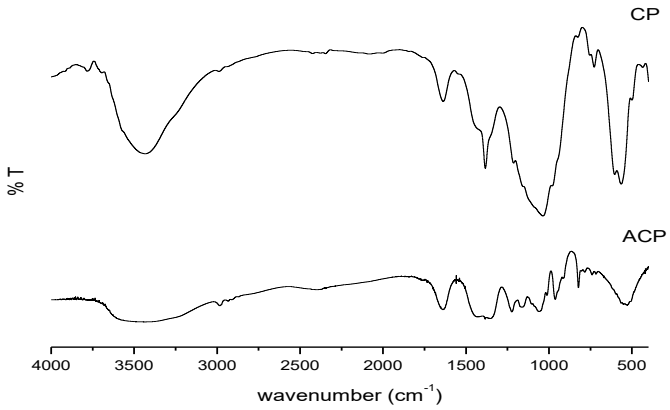

Figure 2. FTIR spectra of ACP and CP for Ca/P=1.3.

Fig. 2 showed FTIR spectra of ACP and CP for Ca/P=1.3. For ACP, the pattern is looked very similar with ACP for Ca/P=1.5. For CP spectra a sharp peak at 565.02 cm^{-1} and 1037.02 cm^{-1} are indicating the presence of asymmetric bending vibrations (v4) and asymmetric stretching vibrations (v3). The presence of water at the wave number of 1637.96 cm^{-1} is reinforced with a widening peak in the area of 3433.77 cm^{-1}. This data is indicating that the resulted calcium phosphate can absorb water with pretty much amount.

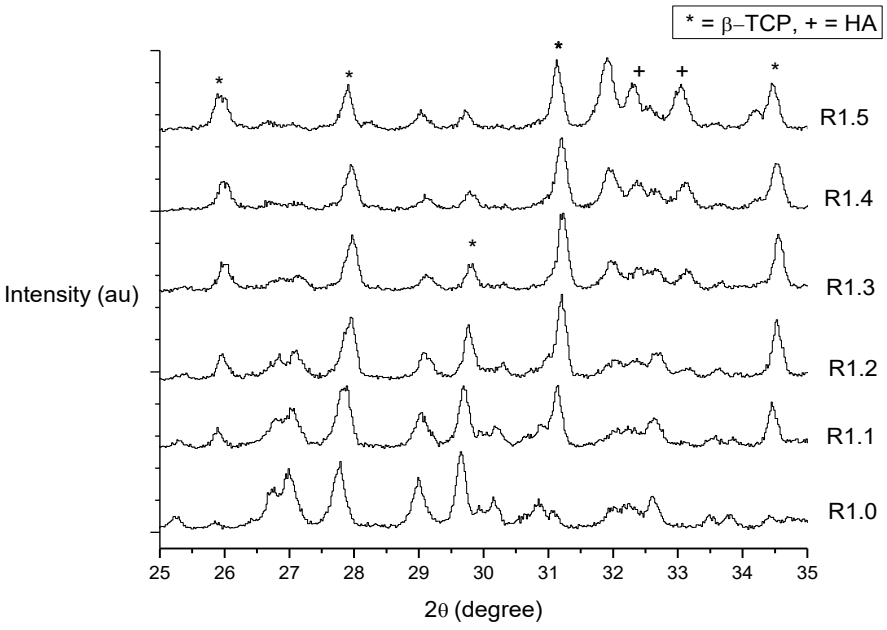

Figure 3. XRD diffractogram of CP at different Ca/P ratio.

XRD diffractogram of CP at different Ca/P ratio be seen on Fig. 3. The diffraction patterns for 2θ=25-35° has been compared to JCPDS no 09-0169 for β-TCP, JCPDS no 09-0432 for hydroxyapatite (HA, Ca10(PO4)6(OH)2) and JCPDS no 09-0346 for β-calcium pyrophosphate (β-CPP, Ca2P2O7). The result showed that for low Ca/P ratio (1.0-1.2) the products are β-TCP with a little amount of β-CPP, meanwhile for high Ca/P ratio (1.4 to 1.5) the products are β-TCP and HA. Pure β-TCP was formed at Ca/P ratio=1.3. The crystallite size of β-TCP for all Ca/P ratio are in a range of 32.965–47.819 nm. Fig. 4 shows that the crystallite size is increased with the increasing of Ca/P ratio until Ca/P=1.3 and then decreased at Ca/P=1.4. The crystallite size is increased again as Ca/P increase to 1.5. It can be said that

crystallite size of β-TCP increase as Ca/P is increased, but the present of HA in the product is reduced β-TCP's crystallite size. When HA become much more produced, β-TCP's crystallite size is increased again. The biggest crystallite size was obtained at Ca/P=1.3 which was 47.819 nm. The size is in accordance with the size of calcium phosphate in human bones ranging from 40-60 nm [14].

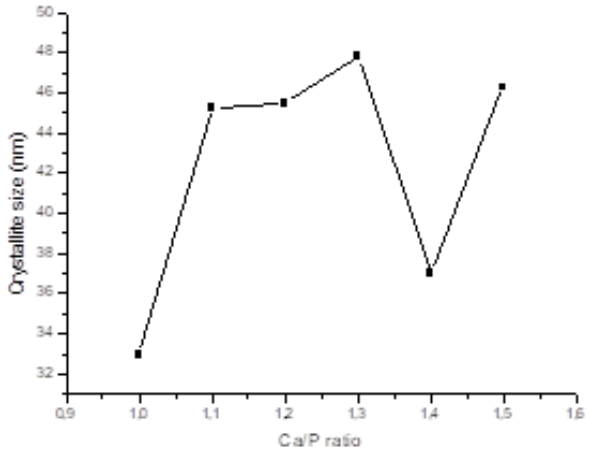

Figure 4. Crystallite size of β-TCP at different Ca/P ratio.

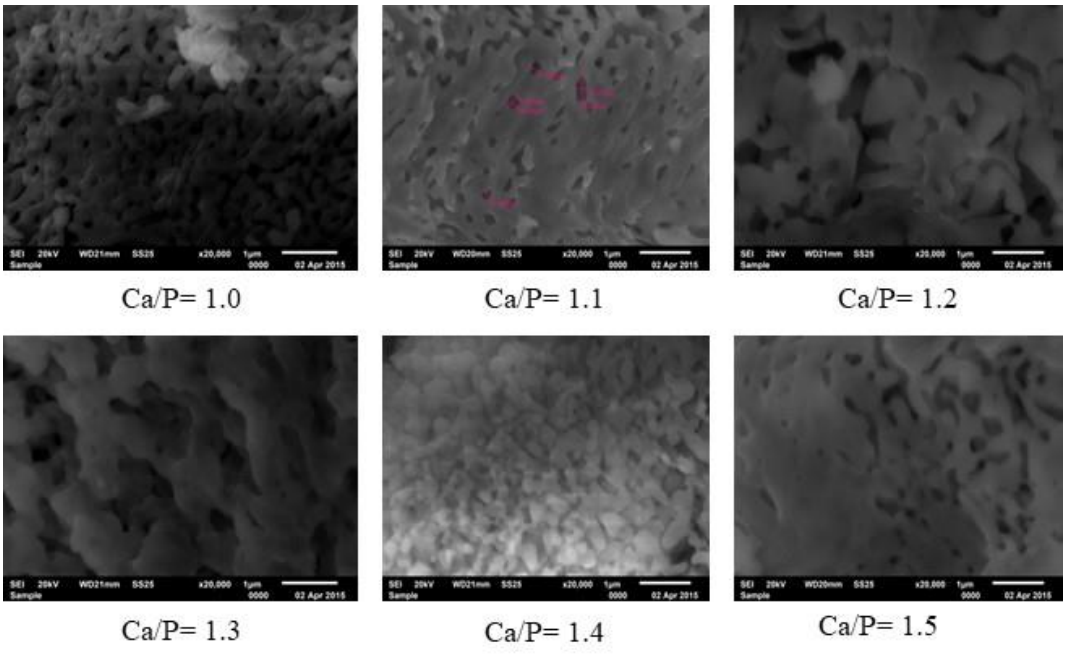

Figure 5. Morphology of CP at different Ca/P ratio.

Fig. 5 shows porous surface morphology in all Ca/P ratios. Irregular shape of products is connected each other's and produced a porous structure. It would be very useful in application because pores will increase cell proliferation so that bone regeneration can be proceed [15]. From Ca/P=1.0–1.3 the grains size is increased and then decreased at Ca/P=1.4. The grains size became bigger again as Ca/P increase to 1.5. This data is relevant with crystallite size of β-TCP (Fig. 4). Although for each Ca/P ratio the grains has different shape, it can be said that the largest agglomeration was produced at Ca/P=1.3. This is probably due to its highest purity.

Table 1. Element composition of CP from different Ca/P ratio of precursors.

Element	Atomic Percentage (%)					
	Ca/P molar ratio of precursors					
	1.0	1.1	1.2	1.3	1.4	1.5
C	-	13.80	14.94	12.71	13.86	14.49
O	75.69	64.37	61.91	53.42	66.39	70.71
Al	-	0.22	0.22	0.34	-	0.16
P	13.47	11.49	11.84	10.20	10.18	8.06
Ca	10.84	10.13	11.09	23.33	9.58	6.58
Ca/P	0.80	0.88	0.94	2.29	0.94	0.82
Ca/O	0.14	0.16	0.18	0.44	0.14	0.09

EDS data (table 1) shows the Ca/P products present in a range of 0.80-0.94 for all Ca/P ratio except for Ca/P ratio of 1.3. For Ca/P=1.3, the EDS data is showed that the product has Ca/P molar ratio of 2.29 deviates from the ratio of Ca/P of β-TCP that is equal to 1.5. From table 1, it can be found that Ca/O ratio of products are varied greatly. The unique data is coming from Ca/P=1.3 with Ca/O=0.44 which is close to Ca/O ratio of β-TCP of 0.375. The others Ca/P ratio are produced Ca/O ratio in a range of 0.09–0.18. The EDS data is showed that the products contain of carbon and alumina in a range of 0–14.94% and 0.16–0.34%, respectively. Carbon may exist in the products due to the use of ethanol as reaction media, meanwhile alumina was produced as impurities. However, the produced β-TCP meets the standard specification of β-TCP which can be used in implantation surgery (ASTM F 1088-04a). This study successfully synthesized β-TCP at relatively low temperature and very short time.

4. Conclusion

Pure β-TCP can be obtained by using Ca/P ratio of reactants 1.3. For Ca/P of 1.0-1.2, beside β-TCP a little amount of β-CPP was found and for Ca/P ratio of 1.4–1.5, hydroxyapatite was formed as secondary product. The crystallite size of β-TCP was in a range of 32.96-47.82 nm. Morphology changed due to Ca/P molar ratio in which the size of irregular shape β-TCP became bigger as Ca/P molar ratio is increased from 1.0 to 1.3. The presence of hydroxyapatite in the product has not changed the morphology shape but reduced its grain size.

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