Advanced Materials Research Vols. 93-94 (2010) pp 405-408
Online available since 2010/Jan/12 at www.scientific.net

doi:10.4028/www.scientific.net/AMR.93-94.405

Concentration Effect of Aqueous Synthesis on Biphasic Hydroxyapatite – β-Tricalcium Phosphate Composition

A.S.F. Alqap[1,2], I. Sopyan[1,a] and S.A. Zubir[1]

[1]Department of Manufacturing and Materials Engineering, International Islamic University Malaysia, P.O. Box 10, Kuala Lumpur 50728, Malaysia

[2]Mechanical Engineering Program, Faculty of Engineering, University of Bengkulu, Indonesia

[a]sopyan@iiu.edu.my

Keywords: Hydroxyapatite, β-tricalcium phosphate, calcium phosphate, suspension concentration, phase behaviour, calcination

Abstract. Hydroxyapatite of calcium phosphate materials, one of the most frequently used ceramic material in biomedical application, has been produced via chemical reaction involves both calcium and phosphorus precursors. Effect of suspension concentration on available phases was investigated using a basis of 2 mole % excess of calcium oxide. The synthesis was performed at 90°C until paste was obtained. To improve crystallinity, hydroxyapatite was calcined at 900°C. However, β-TCP appeared as trace which varied in fraction with suspension concentration. Varying concentration is then one approaching method in designing phase composition through which a functional material could be attained.

Introduction

As the main mineral constituent of human bones and teeth, hydroxyapatite (HA, $Ca_{10}(PO_4)_6(OH)_2$) has attracted strong interest as a bone substitute over the past few decades. Comprehensive studies have confirmed that HA is bioactive and can stimulate new bone formation. It has been successfully used in various implant applications [1]. There are many possible reactants to obtain HA; they would be from calcium phosphate compounds such as mono, di, tri, or tetra -calcium phosphate [2], or from calcium and phosphorus precursors [3]. An important thrust of current research with calcium phosphate bioceramics is focused on biphasic that composes of non-degradable HA and degradable phase like β-tricalcium phosphate (β-TCP) ($Ca_3(PO_4)_2$). The partial dissolution of the bio-degradable phase in coatings is beneficial to stimulate bone-like apatite formation at the interface between implant and bone [4]. Biphasic calcium phosphate (BCP) ceramics of HA and β-TCP phases are considered as an ideal bone graft substitution and have recently attracted great attention due to their similarity in chemical composition of HA with bone mineral and readily degradable property of β-TCP in human body fluid. The synthesis involving calcium nitrate and di-ammonium hydrogen phosphate suspension may produce calcium deficient apatite; if it is heated at 950°C or more, BCP may be obtained [5]. If the same precursors are added with Mg-Nitrate and the as-synthesized powder heated at 800°C BCP is obtained with low crystallinity [6]. In fact, the product of HA with some traces such as β-TCP and CaO are possible. Fortunately, these traces are biodegradable phases and the biodegradable property is a key in the promotion of bone-like cell growth over the bone implant surface even in nanophase HA [7]. In present study ammonium di-hydrogen phosphate and calcium oxide produced from cockle shells have been employed as precursors to produce HA with β-TCP as trace. To investigate phase behaviour available in BCP produced from these precursors, the suspension concentration is varied and the formation of the phases reported.

Experimental Procedures

The cockle shells were washed with water, immersed overnight in acetone to remove all the dirt and other materials, and then dried overnight another in oven at 80°C. The shells were crushed by the

pestle in mortar, and then ball-milled for 5 hours into powder. The powder was heated at 1000°C to form calcium oxide (CaO). CaO was reacted with reagent grade ammonium di-hydrogen phosphate (Systerm, Malaysia) at 90°C. Based on the reaction of $5CaO + 3NH_4H_2PO_4 + H_2O \rightarrow Ca_5(PO_4)_3 \cdot OH + 3NH_4OH + H_2O$, 2 mole% excess CaO of the stoichiometric weight was chosen, while keeping the mole ratio of 1.67 Ca/P precursors, with varying the system as shown in Table 1.

Table 1. Variation of precursors' concentration and corresponding HA/ β-TCP after calcination

CaO		$NH_4H_2PO_4$		water	Fraction of HA/ β-TCP		Observed HA peaks, cps	
(mole)	(g)	(mole)	(g)	(ml)	$HA_{(211)}$	$\beta\text{-TCP}_{(0210)}$	$\sim I_{(002)}$	$\sim I_{(300)}$
0.125	7.14	0.075	8.627	150	0.96	0.04	340	500
0.25	14.28	0.15	17.26	150	0.71	0.29	300	420
0.38	21.71	0.23	26.46	200	0.69	0.31	280	380
0.5	28.56	0.3	34.51	200	0.41	0.59	240	240

The process continued at that temperature up to paste obtained. The paste was dried overnight at 80°C and then crushed into powders. The powders were calcined at 900°C (Protherm, PLF 160/5) by heating rate of 10°C/minute for evaluation of phases using X-ray diffractometer (Shimadzu, X-Lab XRD 6000) and for the general feature of powders using FESEM (JEOL, JSM 6700 F).

Results and Discussion

The 2 mole % excess CaO is the basis of the suspension concentration to which phase variation is investigated in the calcium phosphate powder calcined at 900°C. Fig. 1 shows that the main phase of the product is HA with traces of β-TCP and CaO ($2\theta \approx 37.30°$). From the intensity of the main peaks of β-TCP (0 2 10) at $2\theta \approx 31.03°$ and HA (211) at $2\theta \approx 31.8°$, the fraction of each phase can be calculated as detailed in Table 1.

β-TCP which appears as the secondary phase along with HA can be explained by two possible sources. First of all, there will be phosphoric acid in the solution from ammonium di-hydrogen phosphate decomposition. CaO reacts with the phosphoric acid to form $Ca(H_2PO_4)_2$ and water. $Ca(H_2PO_4)_2$ decomposes to $CaHPO_4$ and phosphoric acid and finally $CaHPO_4$ transforms to $Ca_2P_2O_7$ and water. In the presence of OH and calcium ions, $Ca_2P_2O_7$ may transform to TCP. This possibility may occur during synthesis and heating. The second possible source i.e., in the solid state reaction, calcium deficient apatite which appears during heating between 500-700°C would transform to β-TCP at further heating at 750°C or above [13]. The higher the concentration the more difficult the process to dilute the monomers, and the higher the concentration the more the traces available in the suspension or solution could be. Any intermediate phases which possibly appear during the aqueous or solid state reaction readily dissolve during the heating therefore, those are not observed in the X-ray patterns as shown in Fig. 1.

There is also another possibility to explain the appearance of β-TCP in higher temperature. HA may decompose into calcium deficient apatite and then, the calcium deficient apatite decomposes into β-TCP. This is true, even one mixes pure HA with pure β-TCP and heats the mixture, he would observe some portions of HA decomposes into β-TCP [8]. The decomposition of HA into calcium deficient apatite may be altogether with water or calcium hydroxide. The presence of this calcium hydroxide is source of calcium oxide that presents in high temperature while the presence of water promotes the decomposition of HA into calcium deficient apatite and then β-TCP. In fact, the formation of CaO is possible due to the Ca/P ratio higher than 1.67. The source of CaO is not only calcium hydroxide formed at high temperature but also from the suspension at ambient temperature.

Using different precursor materials, authors [9] obtained HA with brushite as traces at all Ca/P ratios employed after they had calcium deficient precipitate. But in this study the traces are β-TCP and CaO. Compared to brushite, β-TCP is stronger and less degradable. The presence of β-TCP favors the formation of bone-like apatite when this composite is soaked under the synthetic human

body fluid. It was elsewhere mentioned, a minor phase like β-TCP contributes to the dissolution of the granules and to the precipitation of the bone-like apatite. The exposition of the biphasic (HA – β-TCP) to medium culture leads to precipitation of a bone-like apatite more than pure TCP or pure HA [10].

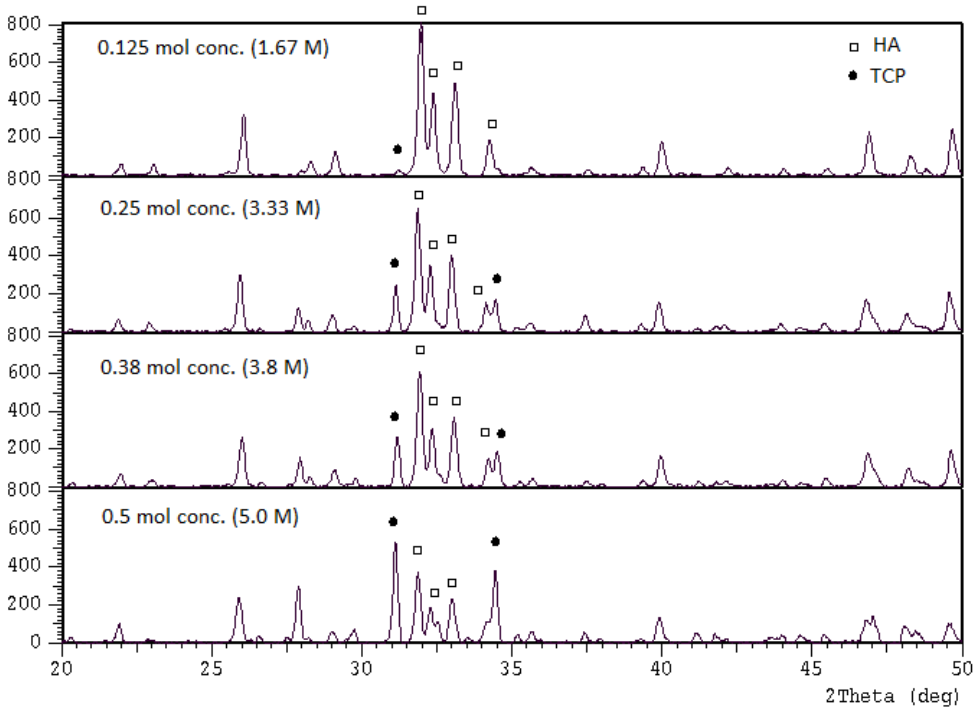

Fig. 1: XRD pattern for cockle shell derived HA powder of 0.125, 0.25, 0.38 and 0.5 mole concentration of CaO after 900°C calcinations.

It is interesting to note that the concentration variation also influences the geometrical aspect of HA. The peak of HA (002) at 2θ ≈ 25.88° and (300) at 2θ ≈ 32.90° represent the *c* and *a*- lattice parameters respectively. From table 1 and Fig. 1, their intensities (cps) suggest that the more equidistance in the z and x space of the HA crystal geometry is obtained at the higher suspension concentration. It suggests that the amount of β-TCP can suppress the growth of HA in x direction.

The phase solubility in aqueous solution decreases in the sequence of CaO >> β-TCP > HA. The composite containing phases of HA and β-TCP as graded in solubility is a key of the material that can function gradually the degradability property with respect to bone tissue by gradually changing the solubility of phases in the aqueous solution. When it is implanted and soaked in cell fluid, it is expected to improve the promotion of bone-like apatite cell growth over an implant surface. Fig. 2 shows the product in agglomerated powders which consist of particles in nano scale. The aglomerated material is a typical product one can obtain from the synthesis like hydrothermal and sol-gel methods [7,11]. The nano size is preferred because it favors in promotion of cell growth [7,12].

Summary

A phase graded bioceramic material that can function gradually with respect to bone tissue by gradually changing the degradable property of phase to phase of the calcium phosphates material was successfully synthesized. The control of suspension concentration is one feasible procedure in adjusting a portion of biphasic bioceramic material.

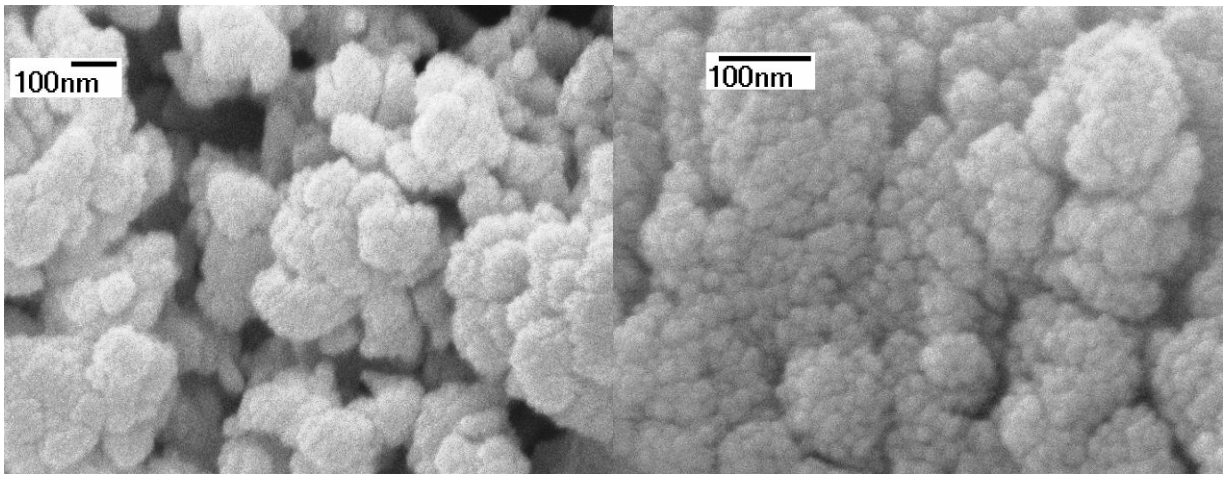

Fig. 2: FESEM of HA powders of 0.125 mole at 2 different magnification: 50,000 (left) and 100,000x (right).

Acknowledgement

ASFA, one of authors, thanks the Ministry of National Education the Republic of Indonesia for the scholarship (No. 2865.33 & 2866.38/D4.4/2008).

References

[1] H. Ye, X.Y. Liu and H. Hong: J. Mater. Sci: Mater. Med. Vol. 20 (2009), p. 843

[2] T. Nomoto, K. Haraguchi, S. Yamaguchi, N. Sugano, H. Nakayama, T. Sekino and K. Niihara: J. Mater. Sci: Mater. Med. Vol. 17 (2006), p. 379

[3] M.P. Ferraz, F.J. Monteiro and C.M. Manuel: J. App. Biomater. Biomech. Vol. 2 (2004), p. 74

[4] H. Kim, R.P. Camata, Y.K. Vohra and W.R. Lacefied: J. Mater. Sci: Mater. Med. Vol. 16 (2005), p. 961

[5] B. Li, X. Chen, B. Guo, X. Wang, H. Fan and X. Zhang: Acta Biomaterialia Vol. 5 (2009) p. 134

[6] S. Kannan, I.A.F. Lemos, J.H.G. Rocha and J.M.F. Ferreira: J.Solid State Chem. Vol. 178 (2005), p. 3190

[7] S. Murugan and S. Ramakrishna: Am. J. Biochem. & Biotechnol. Vol. 3(3) (2007), p. 123

[8] Y-M. Kong, H-E. Kim and H-W. Kim: J. Biomed. Mater. Res. Appl. Biomater. Vol. 84B (2008) p.334

[9] K.J. Lilley, U. Gbureck, A.J. Wright, D.F. Farrar and J.E. Barralet: J. Mater. Sci. Mater. Med. Vol. 16 (2005), p. 1185

[10] F.Z. Mezahi, H. Oudadesse, A. Harabi, A. Lucas-Girot, Y.Le Gal, H. Chaair and G. Cathelineau: J. Therm. Anal. Cal. Vol. 95(1) (2009), p. 21

[11] I. Sopyan, R. Singh and M. Hamdi: Indian J. Chem. Vol. 47A (2008), p. 1626

[12] Z. Shi, X. Huang, Y. Cai, R. Tang and D. Yang: Acta biomaterilia vol. 5 (2009) p. 338

[13] A.S.F. Alqap and I. Sopyan: Indian Journal of Chemistry Part A, In press (2009)

Functionalized and Sensing Materials
doi:10.4028/www.scientific.net/AMR.93-94

Concentration Effect of Aqueous Synthesis on Biphasic Hydroxyapatite – β-Tricalcium Phosphate Composition
doi:10.4028/www.scientific.net/AMR.93-94.405

References
[1] H. Ye, X.Y. Liu and H. Hong: J. Mater. Sci: Mater. Med. Vol. 20 (2009), p. 843
doi:10.1007/s10856-008-3647-3
PMid:19034619

[2] T. Nomoto, K. Haraguchi, S. Yamaguchi, N. Sugano, H. Nakayama, T. Sekino and K. Niihara: J. Mater. Sci: Mater. Med. Vol. 17 (2006), p. 379
doi:10.1007/s10856-006-8242-x
PMid:16617417

[3] M.P. Ferraz, F.J. Monteiro and C.M. Manuel: J. App. Biomater. Biomech. Vol. 2 (2004), p. 74

[4] H. Kim, R.P. Camata, Y.K. Vohra and W.R. Lacefied: J. Mater. Sci: Mater. Med. Vol. 16 (2005), p. 961
doi:10.1007/s10856-005-4430-3
PMid:16167104 PMCid:2430512

[5] B. Li, X. Chen, B. Guo, X. Wang, H. Fan and X. Zhang: Acta Biomaterialia Vol. 5 (2009) p. 134
doi:10.1016/j.actbio.2008.07.035
PMid:18799376

[6] S. Kannan, I.A.F. Lemos, J.H.G. Rocha and J.M.F. Ferreira: J.Solid State Chem. Vol. 178 (2005), p. 3190
doi:10.1016/j.jssc.2005.08.003

[7] S. Murugan and S. Ramakrishna: Am. J. Biochem. & Biotechnol. Vol. 3(3) (2007), p. 123

[8] Y-M. Kong, H-E. Kim and H-W. Kim: J. Biomed. Mater. Res. Appl. Biomater. Vol. 84B (2008) p.334
doi:10.1002/jbm.b.30876

[9] K.J. Lilley, U. Gbureck, A.J. Wright, D.F. Farrar and J.E. Barralet: J. Mater. Sci. Mater. Med. Vol. 16 (2005), p. 1185
doi:10.1007/s10856-005-4727-2
PMid:16362220

[10] F.Z. Mezahi, H. Oudadesse, A. Harabi, A. Lucas-Girot, Y.Le Gal, H. Chaair and G. Cathelineau: J. Therm. Anal. Cal. Vol. 95(1) (2009), p. 21
doi:10.1007/s10973-008-9065-4

[11] I. Sopyan, R. Singh and M. Hamdi: Indian J. Chem. Vol. 47A (2008), p. 1626

[12] Z. Shi, X. Huang, Y. Cai, R. Tang and D. Yang: Acta biomaterilia vol. 5 (2009) p. 338

[13] A.S.F. Alqap and I. Sopyan: Indian Journal of Chemistry Part A, In press (2009)