Morphology and Chemical Compositions of Hydroxyapatite Powder Synthesized by Solution Combustion and Solid State Reaction Techniques

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Abstract

Hydroxyapatite (HAp) has been widely recognized as a biomaterial for repairing or substituting human hard tissues such as scaffolds and artificial bones. To utilize hydroxyapatite in practical applications, desired chemical compositions, and crystal structure, and microstructure are required. Hydroxyapatite is generally obtained from porcine bones and through chemical synthesis. The aim of this study was to synthesize hydroxyapatite powder by solution combustion and solid-state reaction techniques, and to examine the effects of synthesis techniques on chemical compositions, crystallinity, crystal structure, size and morphology of the synthesized powders. Experimental results revealed that hydroxyapatite was presented as the main phase in the synthesized powders, along with biocompatible β-tricalcium phosphate (β-TCP) phase. An additional phase corresponding to calcium oxide was evident in the powders synthesized by solid-state reaction. The results also revealed that synthesis techniques had apparent effects on structure and microstructure of the powders. While the solution combustion technique was able to produce finer platelet B-type hydroxyapatite powders of lower crystallinity, the solid-state reaction technique produced coarser spherical A-type hydroxy-apatite powders of higher crystallinity.

Keywords :

hydroxyapatite; combustion synthesis; solid-state reaction; crystallinity; morphology

1. Introduction

Synthetic hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$ is a common material employed in the fabrication of artificial bone since its chemical composition is similar to that of the bone. In addition, its high osteoconductive property enables it to bind to the bone quite well. Its chemical composition and other properties of the hydroxyapatite powder, including crystallinity, crystal structure, morphology, and particle size also contribute to its applications.

It is generally accepted that the lower degrees of crystallinity in hydroxyapatite lead to osteoconductive property [1, 2], and that the crystal structure of the hydroxyapatite is strongly related to the morphology of the particles [3, 4]. Furthermore, it has been reported that microstructure could also affect its mechanical properties [5].

To obtain hydroxyapatite powders with the desired characteristics and properties, the careful selection of the synthesis techniques and monitoring of the process are required. Common techniques of synthesizing hydroxyapatite include: hydrothermal, sol-gel, solid-state reaction, and solution combustion technique [1, 2, 5-7]. As the above mentioned, solid-state reaction is the simplest, while solution combustion method is known to effectively produce fine powders of highly homogeneous chemical compositions. Additionally, both techniques use cost-effective reagents, use low temperature and no need high technology. For these reasons, Solid-state reaction and solution combustion techniques are selected to synthesize hydroxyapatite powders in this study. This work also aimed at examining the effects of synthesis techniques on chemical compositions, crystallinity, crystal structure and microstructure of hydroxyapatite.

2. Method

2.1 Hydroxyapatite preparations

For solid-state reaction, hydroxyapatite powders were prepared by mixing reagent grade calcium nitrate $Ca(NO_3)_2 \bullet 4H_2O$ (Daejung, 97%) with ammonium dibasic $(NH_4)_2HPO_4$ (Daejung, 98.5%) at 1.9 and 21 Ca/P ratios respectively for 24 hours using a ball mill. The mixtures were later calcined at 1150 ˚C for 3 hours.

For solution combustion technique, $Ca(NO_3)_2 \bullet 4H_2O$ and $(NH_4)_2HPO_4$, at Ca/P ratios of 1.9 and 2.1 were mixed using a magnetic stirrer at a speed of 100 rounds per minute for 20 minutes. Glycine, at the ratio of 1:1 glycline:reagents, which serves as combustion fuel, was then added to the mixture that was being stirred. To initiate combustion, the mixture was heated to a temperature of less than 400 ˚C. Upon combustion reaction completion, the powder product was collected and calcined at 900 ˚C for 6 hours.

2.2 Characterizations

Chemical composition of the calcined powders was investigated using an X-ray diffractometer (Bruker, D8 Advance), at angles ranging from 20 to 60 in 2θ, at a 0.021 step size increment and a scanning rate of 1.31/min. The absolute values of crystallinity (Xc) of the hydroxyapatite particles were determined from X-ray diffraction pattern, following equation 1:

$$X_c \approx 1 - (V_{112/300}/I_{300}) \qquad \text{Equation 1}$$

where, I_{300} is the intensity of (300) diffraction peak, and $V_{112/300}$ is the intensity of the hollow between (112) and (300) diffraction peaks.

The analysis of the functional groups of the hydroxyapatite powder were made at the spectral range of 4000-500 cm^{-1}using an FTIR spectrophotometer (Bruker,Alpha-E) with a resolution of 4 cm^{-1}. A scanning electron microscope (FEI Quanta 450) was employed in examining the morphology of particles. Average sizes of the particles and grains were determined using an Image J Software.

3. Results and Discussion

3.1 Effects of synthesis techniques on chemical compositions

An X-ray diffraction technique was employed in identifying chemical compositions of the synthesized powders. X-ray diffraction analysis of the hydroxyapatite powders, shown in Fig. 1, indicated that all powders contained hydroxyapatite (JCPDS 01-075-9526) with the predominant peaks at 26.4°, 31.8°, 32.2°, 32.8° and 34.0° under 2θ and β-tricalcium phosphate (β-TCP) (JCPDS 01-086-1585) with the predominant peaks at 31.1°, 34.4°, 37.4° and 59.7° under 2θ [8]. β-TCP is a biocompatible material with biocompatibility property similar to that of the hydroxyapatite [9], though its mechanical properties i.e. strength are slightly inferior [10, 11].

For the powder synthesized by the solid-state reaction technique, an additional phase corresponding to calcium oxide (CaO) (JCPDS 01-037-1497) was also evident, which might be related to the heterogenous mixing of the initial reagents that consequently resulted to incomplete chemical reaction and formation of secondary phases. For both technique, the Ca/P ratio at 2.1 showed significantly higher β-TCP phase than the Ca/P at 1.9 as increasing of calcium content in system. In general, calcium oxide phaseis also biocompatible but its formation couldalso potentially result in the reduction of strength [8]. Thus, its presence in the synthesized powders is not that desirable.

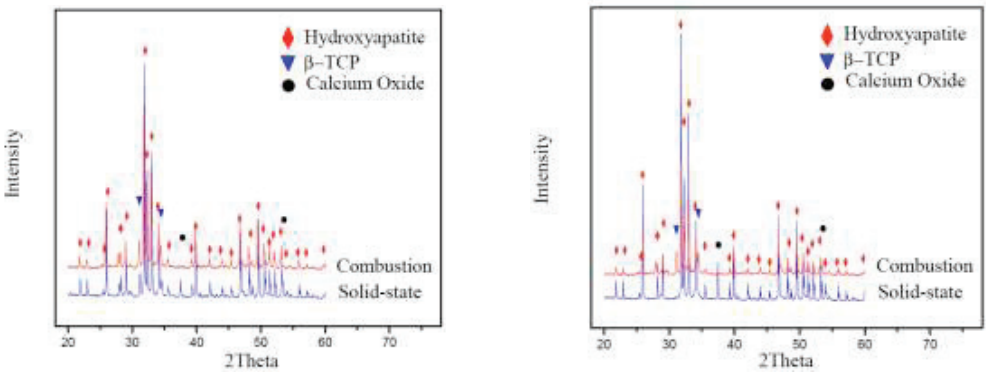


Figure 1. X-ray diffraction patterns of hydroxyapatite powders synthesized by solution combustion and solid-state reaction at (a) Ca/P ratio = 1.9 and at (b) Ca/P ratio = 2.1

3.2 Effects of synthesis techniques on crystallinity

In the previous section, X-ray diffraction was employed in phase identification. In this section, X-ray diffraction was employed in the analysis of crystallinity. It has been established that high crystallinity leads to superior mechanical properties, whereas low crystallinity has been associated to superior osteoconductive property, bone-bonding ability, and biodegradability [9, 11, 17]. Natural bones generally retain high crystallinity, ranging from 94 to 96% [4].

Crystallinity of the hydroxyapatite particles was evaluated using intensity of (300) peak and the intensity of the hollow between (112) and (300) peaks. The results of the analysis showed higher crystallinity in powders prepared by the solid-state reaction that ranged from 92.01 to 94.78%, than in powders prepared by the solution combustion technique, which ranged between 85.35 and 89.11% (Table 1).

According to Liu *et al*. (2014), crystallinity increased with a decrease in water content [12]. While the solution combustion technique involved mixing of initial reagents in the liquid form, the solid-state reaction technique involved solid state mixing and calcination at high temperature. Additionally, high calcination temperature also promotes crystal growth, which thus account for the higher crystallinity obtained for the powders prepared by the solid-state reaction.

Table 1. Crystallinity of the hydroxyapatite powders synthesized by solution combustion and solid-state reaction

	Crystallinity, X_c (%)
HApCS1.9	88.15
HApCS2.1	88.40
HApSS1.9	93.43
HApSS2.1	94.40

3.3 Effects of synthesis techniques on crystal structure

Structure and arrangement of the functional groups in the synthesized powders are closely related to their particle morphology. Hydroxyapatite consists of CO_3^{2-}, PO_4^{3-} and OH^- functional groups arranged in hexagonal structure. The carbonate-substituted hydroxyapatite is categorized into 3 types, including A-, B- and mixture of the A and B-types, as shown in Fig. 3. For the A-type hydroxyapatite, OH^- group is substituted by CO_3^2, while in the B-type hydroxyapatite, PO_4^{3-} is substituted by CO_3^{2-}.

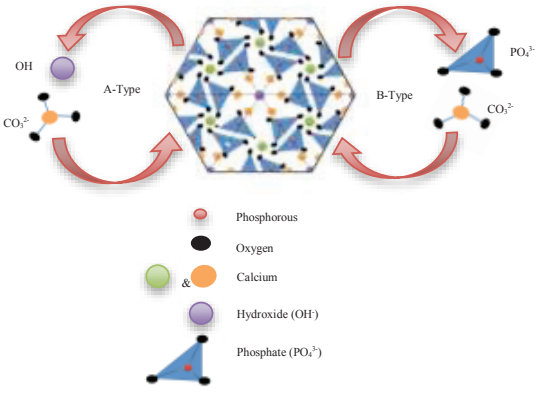
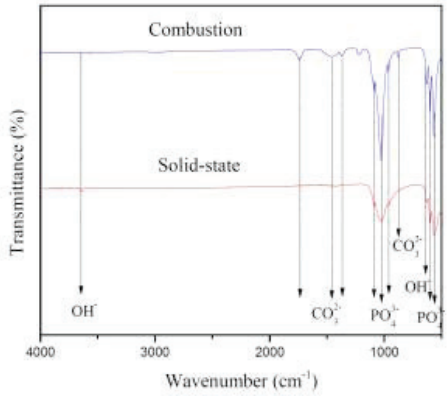


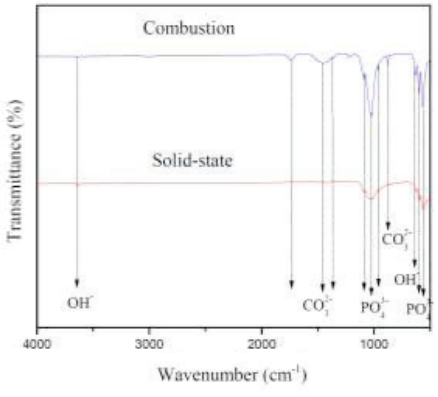
Figure 2. Structure of an A-type and B-type carbonate-substituted hydroxyapatite

The structures, of the hydroxyapatite functional group, were analyzed by Fourier transformed infrared (FTIR) spectrophotometer. FTIR patterns of the powders prepared by the solution combustion technique indicated the characteristic of B-type hydroxyapatite with prominent peaks corresponding to CO_3^{2-} at 875 cm^{-1} and PO_4^{3-} at 1040 and 560 cm^{-1}, respectively. For the powders prepared by solid-state reaction, the peaks corresponded to CO_3^{2-} at 1550 and 1457 cm^{-1} was diminished. The CO_3^{2-} peak at 1550, 1457 and 880 cm^{-1} is characteristic of an A-type carbonate-containing hydroxyapatite [14].

Both A- and B-type hydroxyapatites are biocompatible and can be utilized in the production of artificial bone [1, 4, 9]. A minor distinction between these two though, lies on their particle morphological structures.



(a)



(b)

Figure 3. FTIR patterns of hydroxyapatite powders by solution combustion and solid-state reaction processes at (a) Ca/P ratio = 1.9 and at (b) Ca/P ratio = 2.1

3.4 Effects of synthesis techniques on particle size and morphology

Several researchers have shown that the mechanical properties of fabricated hydroxyapatite could be significantly enhanced by controlling the important parameters like particle size, shape, its distribution and agglomeration.

Morphology of hydroxyapatite powders was examined by Scanning Electron Microscope (SEM), as shown in Figs 4 and 5. SEM micrographs revealed that particle morphology was strongly dependent on synthesis techniques. While hydroxyapatite particles synthesized by the solution combustion technique appeared to be platelet-like, the particles prepared by solid-state reaction were equiaxial. The equiaxial morphology in the A-type hydroxyapatite was commonly observed [3]. For the B-type hydroxyapatite, PO_4^{3-} is substituted by CO_3^{2-}. While PO_4^{3-} has a tetrahedral structure, CO_3^{2-} has a trigonal planar structure. Substitution of tetrahedral PO_4^{3-} by trigonal planar CO_3^{2-} potentially resulted in planar-like structure, leading to plate-like morphology [3, 4].

Image analysis was a tool employed in particle size analysis. The results indicated that the average sizes of hydroxyapatite particles ranged from 0.35 to 0.74 micrometers. The analysis also revealed that powders from solution combustion technique were finer than those from solid-state reaction. It is generally accepted that solution combustion is the technique capable of producing nano-sized powder [18, 19]. On the other hand, the powder synthesized by solid-state reaction usually appeared to be highly agglomerated due to solid state mixture and high temperature calcination [5].

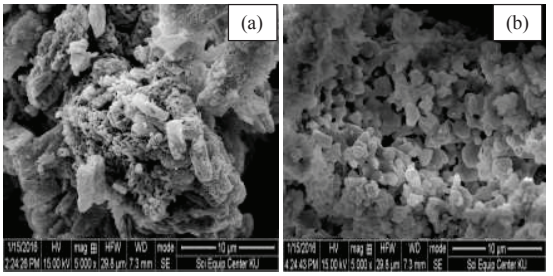


Figure 4. Hydroxyapatite powders at Ca/P ratio = 1.9 produced by (a) solution combustion and (b) solid-state reaction techniques

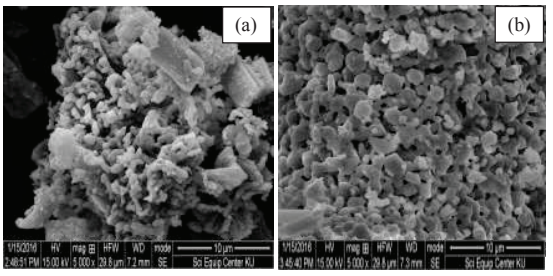


Figure 5. Hydroxyapatite powders at Ca/P ratio = 2.1 produced by (a) solution combustion and (b) solid-state reaction techniques

Table 2. Particle size of hydroxyapatite powders synthesized by solution combustion and by solid-state reaction

	Particle size (μm)
HApCS1.9	0.35±0.06
HApCS2.1	0.51±0.08
HApSS1.9	0.73±0.11
HApSS2.1	0.74±0.13

4. Conclusions

Hydroxyapatite powders were successfully synthesized using solution combustion and solid-state reaction techniques. As a reaction mechanism of solution combustion technique was high temperature exothermic redox chemical between a fuel and an oxidant, that produces flame and heat, results in the capable of producing finer platelet B-type hydroxyapatite powders of higher chemical homogeneity, whereas, powders produced through solid-state reaction, exhibited coarser spherical A-type hydroxyapatite powders of higher crystallinity. Additionally, majority phase HA with minority of CaO and β-TCP powders were successfully synthesized for both technique.

5. Acknowledgements

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