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PHASE IDENTIFICATION OF SYNTHESIZED HYDROXYAPATITE IN DIFFERENT CALCINATION TEMPERATURE

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ABSTRA CT

PHASE IDENTIFICATION OF SYNTHESIZED HYDROXYAPATITE IN DIFFERENT CALCINATION TEMPERATURE. For bone tissue engineering, hydroxyapatite scaffolds for cell growth are attracting due to their bioactivity and similarity to human bone component. The sol-gel route used in previous studies provided high crystalline hydroxyapatite and second phase occurred at higher calcination temperature. The aim of the present research was to synthesize and characterize HA prepared using the wet precipitation method in different calcinations temperature. The synthesis of hydroxyapatite was prepared using calcium and phosphorous precursor. The synthesized hydroxyapatite were then calcined at temperatures up to 900 °C. Rietveld refinement was used to examine the entire XRD patterns and FT-IR measurement was employed to observe the functional group of the synthesized HA. Results showed that HA material with the apatite structure were produced as was analyzed by XRD and Rietveld refinements. Chemical analysis indicated the existence of P-O vibrational modes from phosphate group and O-H from absorbed water confirming the formation of HA. Rietveld analysis revealed the existance of CaO phase at 300 °C, however, it was not observed at higher calcination temperature. The present study indicated that the wet precipitation method has induced the formation of HA without CaO phase at temperature above 300 °C. HA with increased crystallinity were produced in line with the raise in temperature.

Key words : Hydroxyapatite, Calcination, XRD, FT-IR, Sol gel

ABSTRAK

IDENTIFIKASI FASA HIDROKSIAPATIT HASIL SINTESIS PADA BERBAGAI SUHU KALSINASI. Dalam rekayasa jaringan tulang, *scaffolds* hidroksiapatit (HA) untuk pertumbuhan sel merupakan hal yang menarik untuk dikembangkan karena sifat bioaktifitasnya serta kemiripannya dengan komponen tulang manusia. Jalur *Sol Gel* telah dipergunakan dalam penelitian sebelumnya dan menghasilkan tingkat kristalinitas HA yang tinggi serta fasa kedua yang muncul pada suhu yang tinggi. Tujuan dari penelitian ini adalah untuk mensintesis dan mengkarakterisasi HA yang dihasilkan melalui proses presipitasi basah pada berbagai suhu kalsinasi. Sintesis dari HA dilakukan dengan menggunakan kalsium dan fosfor sebagai prekursor. HA yang disintesis kemudian dikalsinasi pada suhu hingga 900 °C. Penghalusan *Rietveld* digunakan untuk mengkaji seluruh data *XRD*. Pengukuran *FT-IR* dipergunakan untuk melihat gugus fungsi dari HA yang dihasilkan. Data menunjukkan bahwa material HA dengan struktur apatit telah dihasilkan dan telah dianalisis dengan *XRD* serta penghalusan *Rietveld*. Analisis kimia mengindikasikan adanya moda vibrasi gugus P-O dari grup fosfat dan gugus O-H dari molekul air yang diserap. Analisis *Rietveld* menunjukkan keberadaan fasa CaO pada 300 °C, namun fasa ini tidak terlihat pada suhu kalsinasi yang lebih tinggi. Penelitian ini telah menunjukkan bahwa metode presipitasi basah telah memungkinkan terbentuknya HA tanpa fasa CaO pada suhu diatas 300 °C. HA dengan tingkat kristalinitas yang lebih tinggi dihasilkan sejalan dengan meningkatnya suhu.

Kata kunci : Hidroksiapatit, Kalsinasi, *XRD, FT-IR, Sol gel*

INTRODUCTION

In the field of dentistry, bone defects frequently result from high energy trauma, infections or from physiological bone resorption which may pose problems when not treated. Being the main mineral component in

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human bone [1], calcium phosphate has been an attracting material for bone replacement [2] or for scaffold in bone tissue engineering [3]. For bone tissue engineering, HA scaffold should degrade that match with the cell growth, whereas the degree of degradation is dependent with the crystallinity of the material.

The most resembling calcium phosphate based bioceramics has been hydroxyapatite. Studies on synthesize of HA include solid state reaction, hydrothermal methods, sol gel route or wet chemical synthesis. The sol gel route have produced HA with high crystallinity and is often associated with CaO phase which was noticed at calcination temperature above 600°C [4]. Synthesis of HA via the wet chemical precipitation route based on the reaction of calcium nitrate and diammonium hydrogen phosphate revealed with $Ca_3(PO4)_2$ at 600 °C [5]. The route based on the reaction of calcium hydroxide and phosphoric acid under slow stirring and with pH 9.5 has produced HA with CaO and $CaCO_3$ phases after heat treatment [6]. The aim of the present study, therefore, was to synthesis HA using the wet chemical precipitation, with vigorous stirring and pH 7 and to identify phases developed during calcination.

EXPERIMENTAL METHOD

The synthesis were carried out by a reaction between $Ca(OH)_2$ (Merck) and H_3PO_4 (85 %, Merck). H_3PO_4 suspension was added in a dropwise manner and in a controlled rate to the $Ca(OH)_2$ suspension, while vigorous stirring being maintained for 24 hours using a magnetic stirrer (Heidolph MR 3001, Germany). At the end of the stirring process, the pH was adjusted until a final natural pH 7 was obtained. The supernatant was then decanted and wet cakes of HA obtained from the precipitant were subjected to filtering. Air drying and repeatedly washing were done, and further drying was conducted at 100 °C. Heat treatment was finally applied at the synthesized HA powder varying from 300 °C to 900 °C at 200 °C intervals with a heating rate of 5 °C/minute.

X-Ray Diffraction (XRD) measurement was performed using Phillips PW-1170 Diffractometer (Cu-Kα = 1.5404Å). Disc samples of different calcination temperature were scanned between 20° and 80° with a stepwise of 0.02°/0.6 Sec. The diffraction data was analysed using RIETAN (Rietveld Analysis) for phase identification for each diffraction pattern obtained at each calcination temperature.

Fourrier Transformed Infra Red (FT-IR) measurement was employed to support the existance of the synthesized HA by observing the functional groups in the chemical state of the materials. FT-IR spectroscopy (Spectrum One, Perkin Elmer, Germany) using KBr pellete technique was conducted in the range of 4000-450 cm^{-1}.

RESULTS AND DISCUSSION

The diffraction patterns from the synthesized HA powder samples are demonstrated in Figure 1. Correspondence with the view, the diffraction patterns are characterized by an intense background that displayed peaks which are typically HA, as expected, and in general are similar with those published in several literatures.

At low temperature, the diffraction peaks are not having good resolution and intensity showing amorphous HA. Broad peaks indicating the amorphous of the natural mateiral. A gradual increase in the intensity with enhanced resolution are observed as the calcination temperature rose. At 900 °C, an abrupt change of the pattern is noticeably with narrow and sharp peaks than others. To achieve satisfactory fits of the difraction patterns, a close inspection at the diffraction pattern is necessary.

Based on the refinements at 300 °C (Figure 2), Rietveld refinements showed good fitting quality with minimum values. The diffraction data observed two phases from the synthesized HA. Minor CaO phase (JCPDS 43-1001) was noticed at around 2θ = 36°-38°. The existance of the second phase was probably because of implying H_3PO_4 solutions with concentration of 85 %. The OH^- ions present in $Ca(OH)_2$ suspension were reacted by the 85 % H_3PO_4 solutions; consequently, remaining calsium stayed in the precipitated HA forming a new phase of calcium oxide (CaO). Previous research

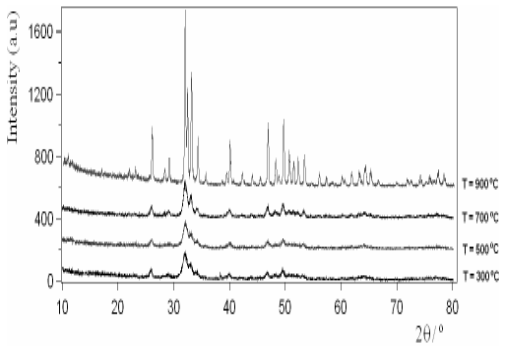

Figure 1. XRD pattern of HA samples calcined at 300-900 °C

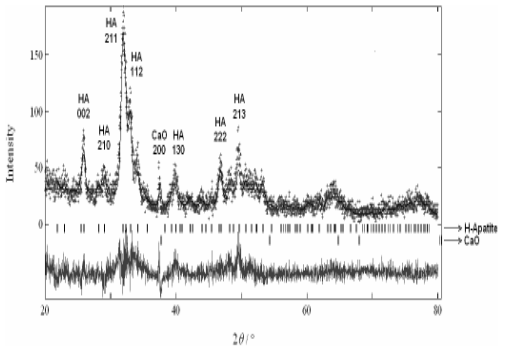

Figure 2. Refinements of the of the synthesized HA calcined at 300 °C

Table 1. Lattice parameters and crystallinity of the synthesized HA with calcinations temperature ranging from 300 °C to 900 °C

Suhu (°C)	300°C	500°C	700°C	900°C
a (Å)	9.4030(2)	9.3976(1)	9.4068(2)	9.4183(2)
b (Å)	9.4030(2)	9.3976(1)	9.4068(2)	9.4183(2)
c (Å)	5.8785(1)	6.8826(9)	6.8768(1)	6.8798(1)
γ	120°	120°	120°	120°
Crystallinity (%)	19.971	22.050	26.641	41.642

reported the existence of second phases, such as CaO, $CaCO_3$ or $Ca_3(PO4)_2$. In the present study, however, CaO phase was noticed only at 300 °C and was not observed at higher calcination temperatures.

Major HA phase, $Ca_{10}(PO_4)_6(OH)_2$, identical to the standard JCPDS 09-0432 for HA, owing a hexagonal crystal structure and described in the space group P 6_3/m (176) with the number of atom per unit cell as $Ca_1 = 4$, $Ca_2 = 6$, P = 6, $O_1 = 6$, $O_2 = 6$, $O_3 = 12$ and H = 2. At further calcination temperatures up to 900 °C, Rietveld refinements also proved the formation of HA with lattice parameters and crystallinity as in Table1.

With respect ro the calcination temperatures, the four lattice parameters displayed evident similarities that point out the analogy between the synthesized HA and the standard HA, having lattice parameters of a = b = 9.432Å , c = 6.881 Å and γ = 120° [7,8]. It seemed that transition of the atoms in the crystals of the synthesized HA approach a perfection of the standard HA unit cell dimension. In addition, this indication can be seen by increased crystallinity (Table 1) and viewed by a better resolution and higher intensities of the crystal planes (Figure 4).

The formation of HA is supported by the FT-IR analysis. The transmittance spectra (Figure 4) showed a characteristic of bio-apatites. Signature bands for HA arise from P-O and O-H bonds for phosphate (PO_4) and OH (hydroxyl) groups respectively.

P-O bonds for PO_4^{3-} ions from PO_4, groups occurred as vibrational modes around 1100 cm^{-1} to 1000 cm^{-1}, 962 cm^{-1} and 473 cm^{-1} due to stretching, and regions at 602 cm^{-1} and 569 cm^{-1} are assigned to stretching and bending. Whereas 633 cm^{-1} region from O-H showed

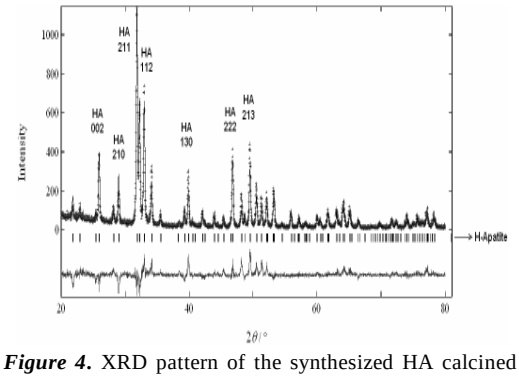

Figure 4. XRD pattern of the synthesized HA calcined at 900 °C

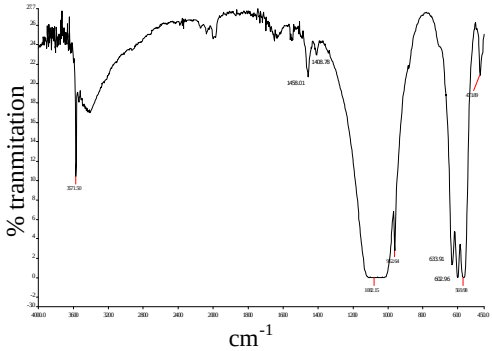

Figure 6. FT-IR spectra of the synthesized HA

absorbed water in HA. Carbonates (CO_3^{2-}) are detected around 1408 cm^{-1} and 1458 cm^{-1}. This was may be due to replacing of some hydroxyl molecules by the carbonates [9]. This situation similarly existed in [10] which is explained as an effect of atmospheric CO_2 uptake by utilizing a reactor without a cover in the experiments. The occurance of carbonates would be an advantage for the use of HA as scaffold for tissue engineering since biological apatites in human bone contain carbonate ions and bonded water. As an addition, these amorphous components in HA would improve the biodegradation of the scaffold [11].

Furthermore, the wet chemical precipitation is a favourable method to some reasons. It produces high percentage of pure product, low working temperature, large amount of HA can be produced at a time, ease in its experiment procedure, and also produce at reasonable cost.

CONCLUSSION

In the present study, HA phase synthesized using the wet chemical precipitation based on the reaction of $Ca(OH)_2$ with H_3PO_4 was identified by XRD measurement, Rietveld refinements and confirmed by the FT-IR analysis. The second phase, CaO, occurred only at 300 °C. The crystal structure is found to be strongly dependent on the calcination temperatures. Further study will be exploring the degradation of the synthesized HA at each calcination temperature that match with the cell growth.

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