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THERMAL EFFECT ON APATITE CRYSTAL SYNTHESIZED FROM EGGSHELL'S CALCIUM

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ABSTRACT

In this study the thermal effect on apatite crystal was observed. Apatite crystal was synthesized by using eggshell as the source of calcium. To obtained calcium powder, chicken eggshell was calcined at 1000°C for 5 hours. Calcium solution was precipitated into diammonium hydrogen phosphate ($(NH_4)_2HPO_4$) solution in nitrogen atmosphere at 37°C to yield apatite. Apatite was further calcined at 800 and 900°C. The apatite was characterized by X-ray Diffractometer (XRD) and Scanning Electron Microscope (SEM). The XRD profiles of uncalcined apatite showed that the samples contained only crystalline phase of hydroxyapatite and a small amount of type B carbonated apatite. Through out the calcination, the carbonate contain is released so that the samples contained of hydroxyapatite only. The degree of crystallinity increases with the raising temperature. The SEM micrograph also shown that the grain size of apatite is bigger as the temperature is increased.

Keyword; thermal effect, apatite crystal, calcination

ABSTRAK

Efek termal pada kristal apatit diamati pada penelitian ini. Kristal apatit disintesis dari cangkang telur sebagai sumber kalsium. Serbuk kalsium diperoleh dari kalsinasi cangkang telur ayam pada suhu 1000 ^oC selama 5 jam. Larutan kalsium dipresipitasi ke dalam larutan diammonium hydrogen phosphate ($(NH_4)_2HPO_4$) dalam atmosfer nitrogen pada suhu 37^oC untuk menghasilkan apatit. Apatit selanjutnya dikalsinasi pada suhu 800 dan 900^oC. Apatit dikarakterisasi menggunakan x-ray diffractometer (XRD) dan scaning electron microscope (SEM). Pola XRD dari apatit yang tidak dikalsinasi menunjukkan bahwa sampel hanya mengandung fase kristal hidroksiapatit dan sedikit apatit karbonat tipe B. Melalui proses kalsinasi, kandungan karbonat hilang sehingga sampel hanya mengandung hidroksiapatit. Derajat kristalinitas meningkat seiring dengan kenaikan temperatur. SEM micrograph menunjukkan bahwa ukuran kristal apatit lebih besar dengan peningkatan temperatur.

Kata kunci: efek termal, kristal apatit, kalsinasi

INTRODUCTION

Calcium phosphate is known as the major compound forming bone mineral. The high demand of calcium phosphate or the bone implant initiates several researchers to conduct observations in order to meet the need[1]. Naturally, calcium phosphate exists in the form of biological apatite. This has a similarity with calcium deficient hydroxyapatite. The deficiency of calcium in natural apatite occurs as the existence of several foreign ions in body plasma. Synthetic hydroxyapatite is known has an ability to form chemical bond with the host hard tissue. Several factors that have an effect on the bioactivity of hydroxyapatite are the starting materials, impurity contents, crystal size, morphology[2]. It is believed that the use of natural raw material will be accepted better by the host hard tissue due to the similarity in the physical and chemical characteristic. Chicken eggshell consist of calcium carbonate up to 94-97% wt. The calcination of chicken eggshell results calcium oxide[3]. In this study, controlled precipitation is performed in order to yield hydroxyapatite. Chicken eggshell is used as the calcium source. To ascertain the termal effect, the samples then calcined at 800 and 900°C.

EXPERIMENTAL

Calcium in this study was obtained from chicken eggshell. It was calcined at 1000°C for 5 hours. Atomic Absorption Spectroscopy (Hitachi Z8230) was performed in order to determine calcium content in calcined eggshell. Apatite was synthesized through stirred precipitation of calcium into diammonium hydrogen phosphtate ($(NH_4)_2HPO_4$) (MERCK). There were three samples which differed in concentration but were similar in calcium to phosphor ratio which was chosen as 1.67 (Table 1). Both atmosphere and temperature were controlled as nitrogenous atmosphere and 37°C. Following the precipitation, aging process was held for 24 hours in room temperature before washed and filtered. Apatite was then dried in furnace (110°C for 3 hours). X-ray diffraction measurement was performed by XRD (PHILIPS APD 3520) while apatite morphology was observed through Scanning Electron Microscope (JEOL JCM-35C). To gain thermal effect on apatite, samples were heated at 800 and 900°C for 5 hours.

Tabel 2 Sample code

Ca/P concentration (M/M)	Temperature (^{0}C)	Sample code
0.01/0.006	110	A1
	800	A2
	900	A3
0.05/0.03	110	B1
	800	B2
	900	B3
0.5/0.3	110	C1
	800	C2
	900	C3

RESULTS AND DISCUSSION

Calcium carbonate in chicken eggshell will transform into calcium oxide when it is heated up to 1000°C. The calcium in calcined eggshell is about 70.86% wt. XRD spectra of sample A, B, and C are given respectively in Figure 1. All samples resemble calcium phosphate character. According to the data given JCPDS, samples consist of non homogenous hydroxyapatite. There are small numbers of carbonated apatite formed in samples. The synthesized results a crystalline calcium phosphate (Table 2). Calcinations leads to higher crystallinity. The SEM micrograph also shown that the grain size of apatite was bigger as the temperature increased.

Tabel 2 Degree of crystallinity

Sample Code	Crytallinity (%)
A1	99,15
A2	99,72
A3	99,74
B1	99,42
B2	99,66
B3	99,73
C1	99,17
C2	99,28
C3	99,42

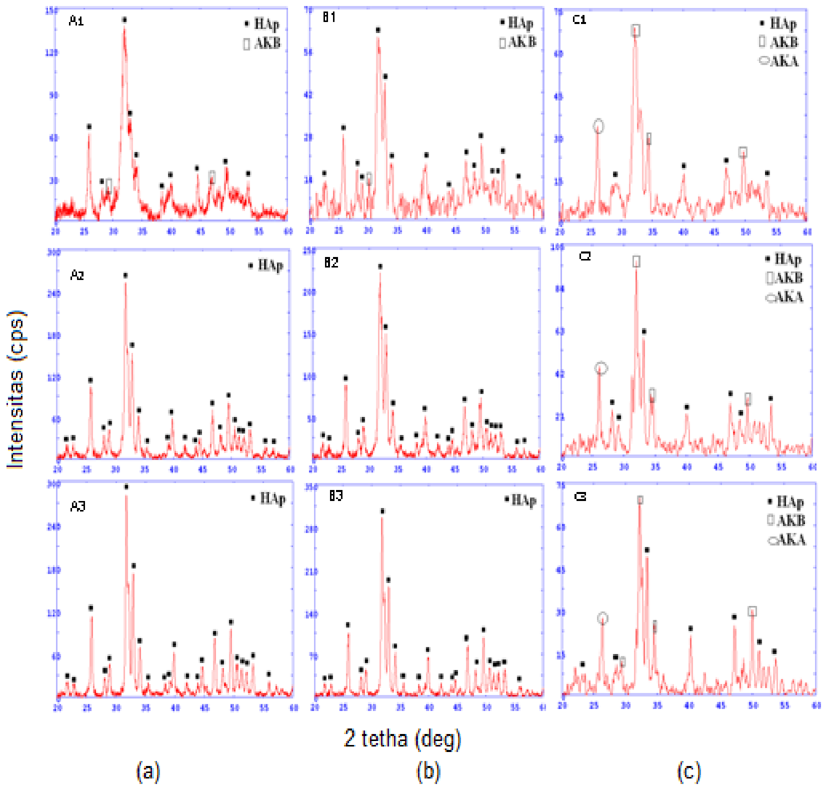

Figure 1 5 XRD spectra of (a) sample A1-A3, (b) sample B1-B3 dan (c) sample C1-C3.

The present study confirms the use of chicken eggshell as a potential source of calcium for synthetic calcium phosphate. The XRD spectra indicate that the samples do not contain calcium oxide that is formed during the calcination of chicken eggshell.The synthesizing results a calcium phosphate in the form of both hydroxyapatite and type B carbonated apatite. However, at higher concentration (Sample C), type A carbonated apatite also appears. Calcination of both sample A and B releases carbonate contain in them so that there are no carbonated apatite in both samples after calcination on 800 and 900°C. Contrary, carbonate still exists in sample C although it has been calcined up to 900°C . This finding therefore gives additional information of previous study which observes that loss of carbonate during heating is time dependent[4]. Although a mixture of β tricalcium phosphate and hydroxyapatite is often prodced by heating non stochiometric hydroxyapatite above 800°C[5], there is disappearance of β tricalcium phosphate in the annealed samples. Therefore, it seems that the carbonate apatite occurs as a minor phase in the samples. Basically, the dissapearance of β tricalcium phosphate will reduce the mechanical strength of the apatite[6].

Thermal effect of apatite can be roughly estimated through the total inverse broadth of a diffraction peak as a size/strain parameter (crystallinity)[7,8]. Heating treatment at 110°C already yields a high cystalline apatite. The broadening peak does not indicate the presence of amorphouse phase but rather the microcystalline. This is supported by the cystallite sizes which are 21.23, 16.73, and 16.69 nm for sample A, B and C, respectively. The crystallite size is obtained from simple Scherrer's formula . The cystallinity tends to increase following the annealing treatment. The sharpening peaks at 2θ around 20-35° indicate this occurance. Although there is an increase if both crystallinity and crystallite size, there is no structural change in lattice as there is no significant peak shiftness.

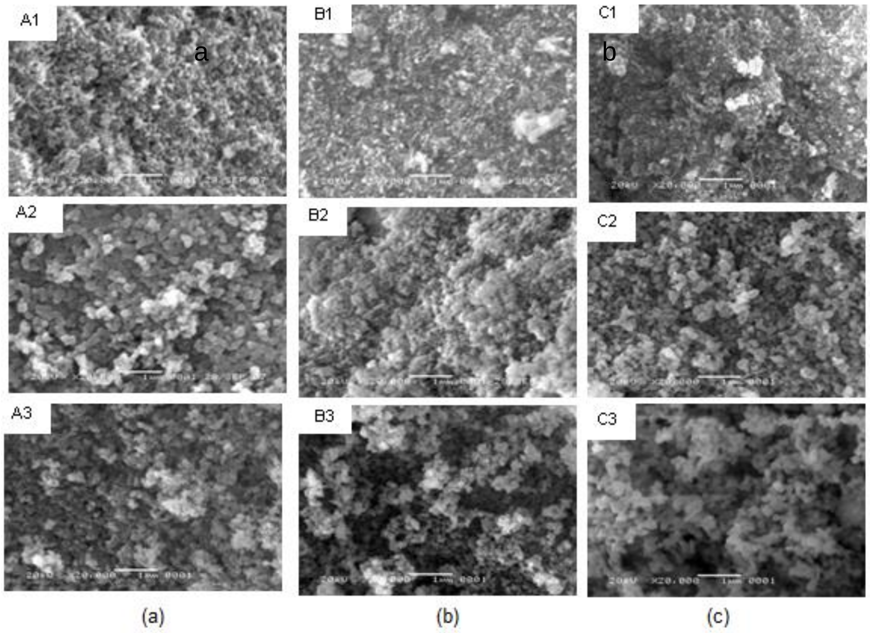

Figure 2 Morphology of (a) sample A1-A3, (b) sample B1-B3 dan (c) sample C1-C3.

CONCLUSION

It is to be hoped that the use of bio-based calcium source will increase the biocomptibility of calcium phosphate. Precipitation of calcium into diamonium hydrogen yields a mixture of hydroxyapatite and carbonated apatite. Carbonate will release during the heating treatment. However, the high concentration of starting materials enables the remaining of carbonate in the sample although it has been annealed up to 1000°C. Thermal stability of samples is indicated by disappearance of the decomposition of hydroxyapatite in to a mixture of hydroxyapatite and β tricalcium phosphate in the annealed samples. The annealing also yields the increasing of both crystallinity and crystallite size.

REFERENCES

1. Kokubo T, Kim HM, Kawashita M. *Biomaterials*. 2003; 24 : 2161-2175.
2. Santos MH, *et al*. *Mater. Res.* 2004; 7: 625-630.
3. Prabakaran K, Balamurugan A, Rajeswari. *Bull. Mater. Sci*. 2005; 28: 115-119.
4. Barralet JE, Best S, Bonfield W. *J. Mater. Sci*. 2000; 11: 719.
5. Barralet JE, Knowles JC, Best S, Bonfield W. *J. Mater. Sci*. 2002; 13: 529-533.
6. Pattanayak, *et al*. *Trends Biomater. Artif. Organs*. 2005; 18: 87-92.
7. Baig AA, *et al*. *Calcif. Tissue Int.* 1999; 64.
8. Doi Y, Moriwaki Y, Aoba T, Takahashi J, Joshin K. *Calcif. Tissue Int.* 1982: 34.