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Effect of Mixing Temperature on the Synthesis of Hydroxyapatite by Sol-gel Method

TIKA PERMATA SARI, NOVESAR JAMARUN*, SYUKRI, ZEFRI AZHARMAN and ASREGI ASRIL

Department of Chemistry, Andalas University, Padang, West Sumatera
*Corresponding author E-mail: novesar62@yahoo.com

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ABSTRACT

In this work, hydroxyapatite was synthesized from limestone using the sol-gel method. Calcium carbonate ($CaCO_3$) and diammonium hydrogen phosphate ($(NH_4)_2HPO_4$) were used as calcium and phosphate source. The hydroxyapatite was obtained by mixing the precursors at a variaty of temperature 50, 60, 70, 80 and 90°C. The resulting product were characterized by XRD and SEM-EDX. From the XRD data it can be seen that all of the product produced at different mixing temperature is a family hydroxyapatite. The compound prepared at 70°C showed smaller crystal size compared the one synthesized at 50 and 90°C. It also can be seen for SEM picture that the resulty material was agglomerated and spherical shape.

Key word: Hydroxyapatite, Temperature, Sol-Gel, Limestone.

INTRODUCTION

Currently, materials technology have been steadily growing, particularly in biomaterial. Biomaterials is compounds with bioinnert, bioresorbable and bioactive properties and can be implanted into living tissue system or as a substitute for the damaged tissue. [1]There materials are biocampatible in human body and do not have any side effect on human body .

Hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$ has widely been used ini biomedical and dental applications due to its similarity to main mineral component of hard tissue of human body such as bone and dental.[2]In addition, hydroxyapatite can replace toxic ion in human body by its own. Due to its similarity to the mineralized matrix of natural bone (human skeletal system), this inorganic phosphate has been studied extensively for medical application (orthopedics and dentistry) in the form of powders, composites, or prosthetic coatings.[3]

In this research, starting material used to form hydroxyapatite is limestone because its naturally abundant on earth crust. Synthesis of hydroxyapatite can be achieved by several methods such as sol-gel method[4], hidrotermal[5], prescipitated[6], microwave[7], and microemulsi[8]. Among the various methods, which are used in this study is the sol-gel method with several advantages such as increased homogeneity due to atomic level mixing, finer grain microstructure, lower temperature of crystallization, use of little equitment and cost-effectivenes.[9] Precursors used are calcium nitrate ($Ca(NO_3)$) and diammonium hydrogen phosphate ($(NH_4)_2HPO_4$) using NH_4OH as pH regulator.

EXPERIMENTAL

Chemicals and Apparatus

Reagents grade chemicals such as limestone, nitiric acid (HNO_3), ammonium hydroxide (NH_4OH), diammonium hydrogen phosphate ($(NH_4)_2HPO_4$). Apparatus used in this study were thermometers, glassware, magnetic stirre and hot plate, analytical balance, Wattmann (42) filter paper, and pH meter.

Procedure

To synthesize hydroxyapatite powders via sol-gel processing, 5.6 grams of CaO were added to 100 ml of 1 M HNO_3 and stirred (600 rpm, 1 hours , 65°C). Then, they were filtered and resulted $Ca(NO_3)_2$. Stoichiometric ammounts of calcium nitrate ($Ca(NO_3)$) and diammonium hydrogen phosphate were dissolved in two seperate aqueous solotions at room temperature. The pH of mixture was adjusted to 9 in ammonia solution then stirred with temperature variation 50, 60, 70, 80 and 90°C for 5 hour. The formed sol was aging for 1 day to obtain a gel. Then filtered and dried at 105°C for 3 hours and calcined at 600°C for 5 hours. Product were characterized using XRD (Philips X'pert powder) to identify phase composition and crystallinity and SEM for surface morphology and particle size estimation.

RESULTS AND DISCUSSION

X-ray diffraction (XRD)

XRD analysis was conducted to determine whether the hydroxyapatite crystals that are formed were amorphous, crystalline or polycrystalline. Analysis with XRD was depicted in Figure 1 showed for hydroxyapatite synthesized at different temperature.

From figure 1 it can be seen that a sharp peak with high intensity was at an angle = 32.0731 ° and 25.9168 ° in accordance with the standards of the ICSD no.26205 at 50 ° C were confirmed that compound product it was hydroxyapatite with miller indices hkl values (211) and (002). The the highest intensity at 70 °C was 25.8728 ° and 32.2243 ° with miller indices hkl values (211) and (002). It was confirmed that product was hydroxyapatite. XRD was also showed that the obtained hydroxyapatite was formed at 50, 70 and 90°C (amorf phase).

From the XRD spectrum, we knowed the size of crystal by using Scherrer equation, where a sharp peak with narrow peak width indicated that the large crystal size, whereas the width of the peak indicated a small crystal size. By measuring the

Table 1 : Crystal size of hydroxyapatite at 50° C

Line width (FWHM)	2Theta (°)	Crystal Size (nm)	Specific surface area (m^2/g)
0.2558	25.9168	30.72	61.8077
0.8187	32.0731	10.09	188.1798
0.4093	34.0904	20.30	93.5337
0.9210	39.6668	9.17	207.0593
0.7164	46.5840	12.07	157.3102
0.4093	49.5052	21.37	88.8505
0.3582	53.1828	24.80	76.5619

FWHM (Full Width at Maximum Hall) and the Scherrer equation, we can estimate the size of hydroxyapatite crystals. The following table 1 was the size of hydroxyapatite crystal data at temperature 50°C.

From table 1, we know the size of hydroxyapatite crystals were in range 9-30 nm with specific surface area produced ± 61-208 m^2/g. XRD spectrum on hydroxyapatite at 50°C showed the highest intensity were at 2¸ = 25-32 ° angle.

The size of crystals at a temperature 70°C can be seen in the table 2. From the table 2 it could be seen that size of hydroxyapatite crystals were in range 8-11 nm and 91,89 nm at 32.2243°. The specific surface that was produced ± 162-220 m^2/g. XRD spectrum hydroxyapatite at 70°C showed the highest intensity was 25-32°. For the size of the crystals formed was at a temperature of 90°C can be seen in table 3.

From the Table 3, we know the size of hydroxyapatite crystals were in the range 10-37

Table 2 : Crystal size of hydroxyapatite at 70° C

Line width (FWHM)	2Theta (°)	Ukuran kristal (nm)	Specific surface area (m^2/g)
0.9446	25.8728	8.63	220.0155
0.9446	28.7647	8.68	220.7830
0.0900	32.2243	91.89	20.6631
0.9446	39.6516	8.94	212.3863
0.9446	44.0755	9.07	209.3422
0.8659	46.6432	9.99	190.0635
0.9446	49.5696	9.26	205.0468
0.8659	53.3282	11.49	165.2510
0.7872	63.8248	11.89	159.6917
0.8659	72.0091	11.34	167.4368
0.9446	77.8030	10.81	175.6461
0.9446	87.8018	11.67	162.7022

Table 3: Crystal size of hydroxyapatite at 90° C

Line width (FWHM)	2Theta (°)	Ukuran kristal (nm)	Specific surface area (m^2/g)
0.3149	26.1999	25.90	73.2958
0.4723	29.2622	17.39	109.2093
0.3936	31.9897	26.25	72.3409
0.3149	32.4390	26.28	72.2589
0.6298	34.4984	13.21	143.7847
0.7085	40.1119	11.94	159.0429
0.7872	44.1930	10.89	174.2933
0.6298	46.9677	13.76	138.0355
0.3149	49.7569	27.82	68.2706
0.2362	53.4477	37.66	50.4173
0.4723	64.2321	19.86	95.5973
0.9446	72.0305	10.40	182.5917

nm. The specific surface area are ± 50-182 m^2/g. XRD spectrum of hydroxyapatite at 90°C showed the hightest intensity at 2¸ = 26°-32° but, at 90°C, the peak shifted and based on ICSD 26205 standart XRD hydroxyapatite obtained at temperature mixing 50, 70 dan 90° C showed the compound was truly hydroxyapatite. Interestingly , at 70°C of temperature preparation, the size of the crystals were smaller than that the one and as the result is prepared at 50°C and 90°C, they were 8-11 nm.

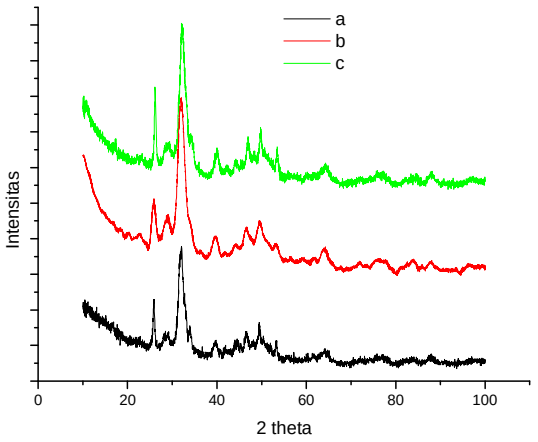


Fig. 1: X-ray diffraction pattern of hydroxyapatite were performed at a temperature of mixing (a). 50 ° C, (b) .70 ° C and (c) .90 ° C

Scanning Electron Microscopy (SEM)

SEM analysis was performed to characterize the surface morphology of the sample. In principle, surface analysis involving surface radiation with enough energy to penetrate and caused some transitions that resulted the emission from beam energy surface.

For SEM characterization, we carried out the formation of hydroxyapatite at 50°C and 70° C. Figure 2 is SEM analysis results for the mixing temperature of 50°C.

From figure 2 it can be seen that for the formation of hydroxyapatite at 50°C, the formed particles are not distributed and homogeneous. In addition, the form of hydroxyapatite compound was less clear.

For SEM results at 70°C was showed in figure 3. From figure 3, can we know that formed hydroxyapatite particle consists of large particles and small particles. The particles that formed were spherical and have aglomeration. There is particles distribution on hydroxyapatite compound. By using SEM-EDS, we could see composition of hydroxyapatite compound. Figure 4 was SEM-EDS analysis result at 70°C.

The table 4 showed composition of hydroxyapatite from EDS analysis.From the EDS

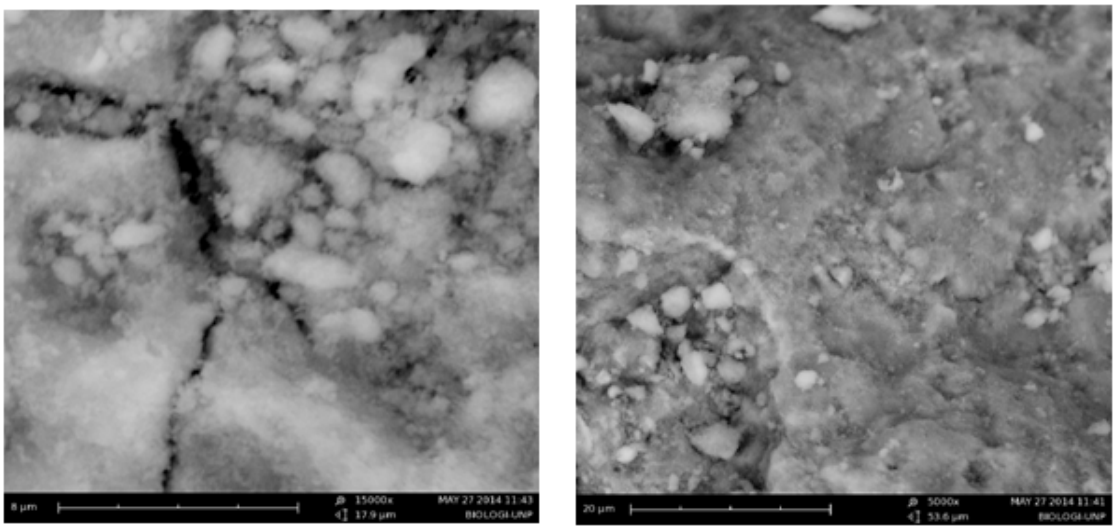
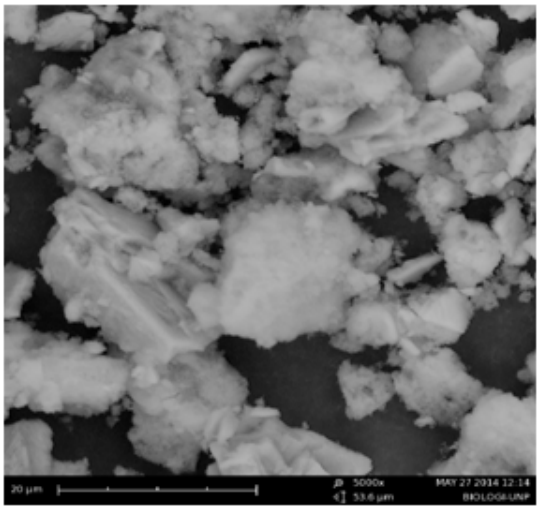


Fig. 2: SEM hydroxyapatite at mixing temperature 50°C (a) 15000x, (b) 5000x.



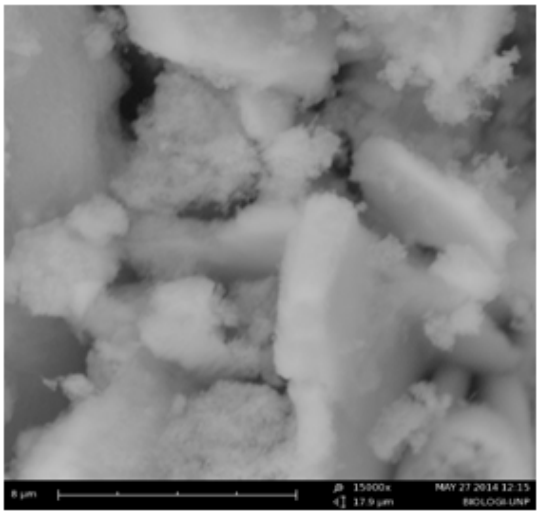
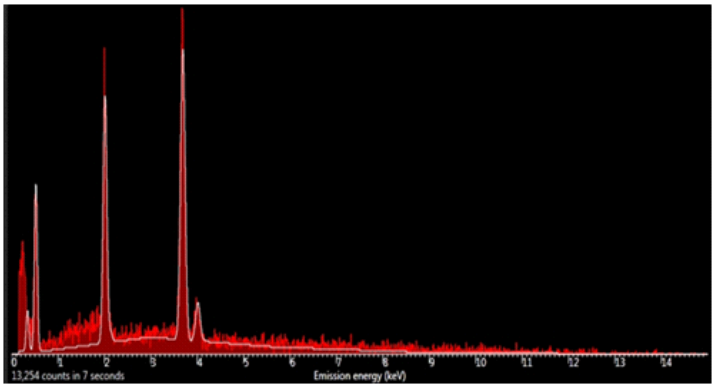


Fig. 3: SEM of hydroxyapatite at the mixing temperature 70°C (a)5000x, (b) 15000x.



Unsur	Persen Komposisi
O	65.2 %
Ca	21.6%
P	13.2%

analysis result, we can conclude that the shape of hydroxyapatite prepared at 50°C was not clear, but at 70°C the hydroxyapatite that formed was spherical shape.

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