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The Effect of Sintering Parameter on the Properties of Hydroxyapatite from Local Limestone for Bone Implant Application

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Abstract. The damage of bone tissue may cause malfunction of human load-bearing system. To date, hydroxyapatite (HA) is one of the most potential materials to repair bone damages and to restore the load-bearing function. It has been produced from both synthetic chemical and natural resources, including limestone. In this paper, the properties of hydroxyapatite made of $CaCO_3$ from limestone was investigated in a function of sintering time, i.e., 2, 3 and 4 hours, and temperature, i.e., 600, 800 and 1000°C. The preparation of HA included crushing, meshing, grinding and sintering. HA powder was then characterized using X-Ray Diffraction (XRD), Scanning Electron Microscope (SEM) and Energy Dispersive Spectroscopy (EDS). The hardness of compacted hydroxyapatite powder was also characterized using micro-Vickers testing machine. SEM micrograph shows the agglomeration of particle increase in line with sintering temperature. The highest hardness was obtained for hydroxiapatite sample sintered at the highest temperature and for the longest time, while EDS result indicates the highest ratio of calcium and phosphor was 2.33. The percentage of calcium in the observed local HA decreased as the sintering time increased. A comparison of XRD result between the commercially imported and the local HA powder produced in this study shows a similarity pattern, which indicates the potential replacement of the imported HA by our local limestone resources.

INTRODUCTION

Human bone has some functions, such as for mechanical, metabolism, organ protection and hematopoietic support. The damage of bone tissue and structures may cause a function disability thus lead to impaired body function. Hence, the body will undergo the lack of calcium and phosphor, the material to be used for bone implant application should have the main properties such as biocompatibility, nontoxic and bioactive. Bone consists of organic compound (collagen) and inorganic compound (hydroxyapaptite/HA) [1]. Nowadays, patients with bone fracture may undergo an operation and bone reconstruction using a biocompatible material to replace, restore and repair the damages. Calcium phosphate and hydroxyapatite (HA) can be applied as an implantable material for bone healing. In that context, the Calcium to Phosphate (Ca/P) ratio of HA is around 1.67. The structure of HA crystal should also similar with the hydroxyapatite for human and animal bones [1, 2].

Previous studies have investigated the properties of HA from several natural sources, such as animal bones, clamshells, eggshells, coral and natural pumice [2]. One of abundant and available sources for HA production is limestone—which contains mineral to produce Calcium Carbonate (CaCO3) [3]. The properties of limestone-based HA powder are affected by the sintering temperature and time [3]. The mechanical properties of hydroxyapatite may investigated through the tensile test to have Young's modulus, bending strength, fracture toughness number [4], micro hardness and compression [2,5]. An addition of polymer can be used to increase the mechanical and thermal properties of HA [6]. An investigation on the effect of process parameters on the properties of hydroxiapatite made from limestone is still necessary [7].

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In this study, calcium carbonate was extracted from the local limestone resources in order to prepare HA powder. The characteristic and mechanical properties of HA powder made of calcium carbonate from local resources was investigated. Effect of sintering time and temperature on hardness and other properties of HA powder was also investigated. The material characterization covered XRD, SEM and EDS of HA loose powder. Hardness test was using micro-Vickers equipment.

MATERIALS AND METHOD

Calcium Carbonate (CaCO3) was extracted from the local limestone resources in Bandar Lampung, Indonesia and then prepared for the production of hydroxyapatite powder which referred as local HA. The commercial hydroxyapatite is imported as reference materials and referred as imported ones. The other materials to produce local HA are sodium hydrogen phosphate (Na2HPO4.2H2O) obtained from KgaA Germany and demineralised water. The preparation of hydroxyapatite was as follow: firstly, the chunk of limestone was cleaned using demineralised water then dried. The chunk was then manually crushed into the gravel and grinded into particles with mesh of around 250 μm in size for 30 minutes. Afterward, some components were prepared to produce local hydroxyapatite, including calcium carbonate of 5 grams, sodium hydrogen phosphate of 5.34 grams and 10 mL of demineralised water. All components were mixed using ball mill for 2 hours at speed of 300rpm. Subsequently, the compound was oven-dried for 17 hours at temperature of 80°C before sintering process. The variation of sintering temperatures was 600, 800, and 1000°C with variation times of 2, 3 and 4 hours. Finally, the powders were compressed at 5MPa. There were three samples for each variation of sintering temperature and three samples for each variation of sintering time. The characterization of hydroxyapatite loose powder was done using XRD, SEM and EDS. Mechanical property of compacted hydroxyapatite powder was tested using micro Vickers hardness test according to C1327 ASTM Standard.

RESULTS AND DISCUSSION

Figure 1 shows the XRD pattern of CaCO3 from local limestone resources and imported one in which the peak of the pattern shows the similarity between calcium carbonate and calcite of the local resources and the imported material. It shows that the calcium carbonate used in this study is potential as a source to prepare the hydroxyapatite. Table 1 shows the XRD pattern of local hydroxyapatite in compared with the imported one. It is observed that for imported hydroxyapatite, the peak was at 2θ of 31.77° and for local hydroxyapatite, the peak was at 2θ of 31.80°, which is similar. It shows that the local limestone can be considered as calcite resources to produce hydroxyapatite [8,9]. Table 2-4 show the XRD pattern of local hydroxyapatite which was sintered at 600°C for 2, 3 and 4 hours. The 2θ value was also similar, mainly those once sintered for 2 and 3 hours.

Table 5 shows the element composition in limestone loose powders, and Table 6-8 show the element composition of hydroxyapatite loose powders that were sintered at 600°C. Limestone particles contain 36.69% calcium and 34.07 wt% of oxygen. Tables 6-8 show that the calcium percentage decreases in line with the increase in sintering time. The calcium percentages of weight were 38.34 wt%, 33.40 wt%, and 23.75 wt% for sintering time of 2, 3, 4 hours, respectively. The phosphor was 16.49, 23.87 and 20.32 wt% for sintering time of 2, 3 and 4 hours, respectively. The ratios of Ca/P were 2.33, 1.40 and 1.17 for sintering time of 2, 3 and 4 hours, respectively. The amount of oxygen was lowered in hydroxiapatite as compared with one in limestone particles. The amount of oxygen was significantly lower for sintering temperature of 800 and 1000°C. The similar elements composition was identified in other literatures [2].

Figures 2(a) shows the SEM micrograph for limestone particles while Fig. 2(b), (c) and (d) show the SEM micrograph of local hydroxyapatite sintered at 600, 800 and 1000°C. The SEM micrograph shows the agglomeration of particle increases with sintering temperature, as also founded by others [6,9]. Different crystal phases and particle morphology affected the properties of hydroxyapatite. The SEM scanning micrograph shows unstable porous structure of the powder, which is caused by the formation of aggregate of HA particles [10,11].

Table 9 shows the micro Vickers hardness number of compacted hydroxyapatite. The highest hardness number was 27.10 obtained at sintering temperature of 1000°C for 4 hours. The higher the temperature of sintering, the higher the number of particle agglomeration. This agglomeration may increase the density of compacted hydroxyapatite powder when it was pressed for 4 hours.

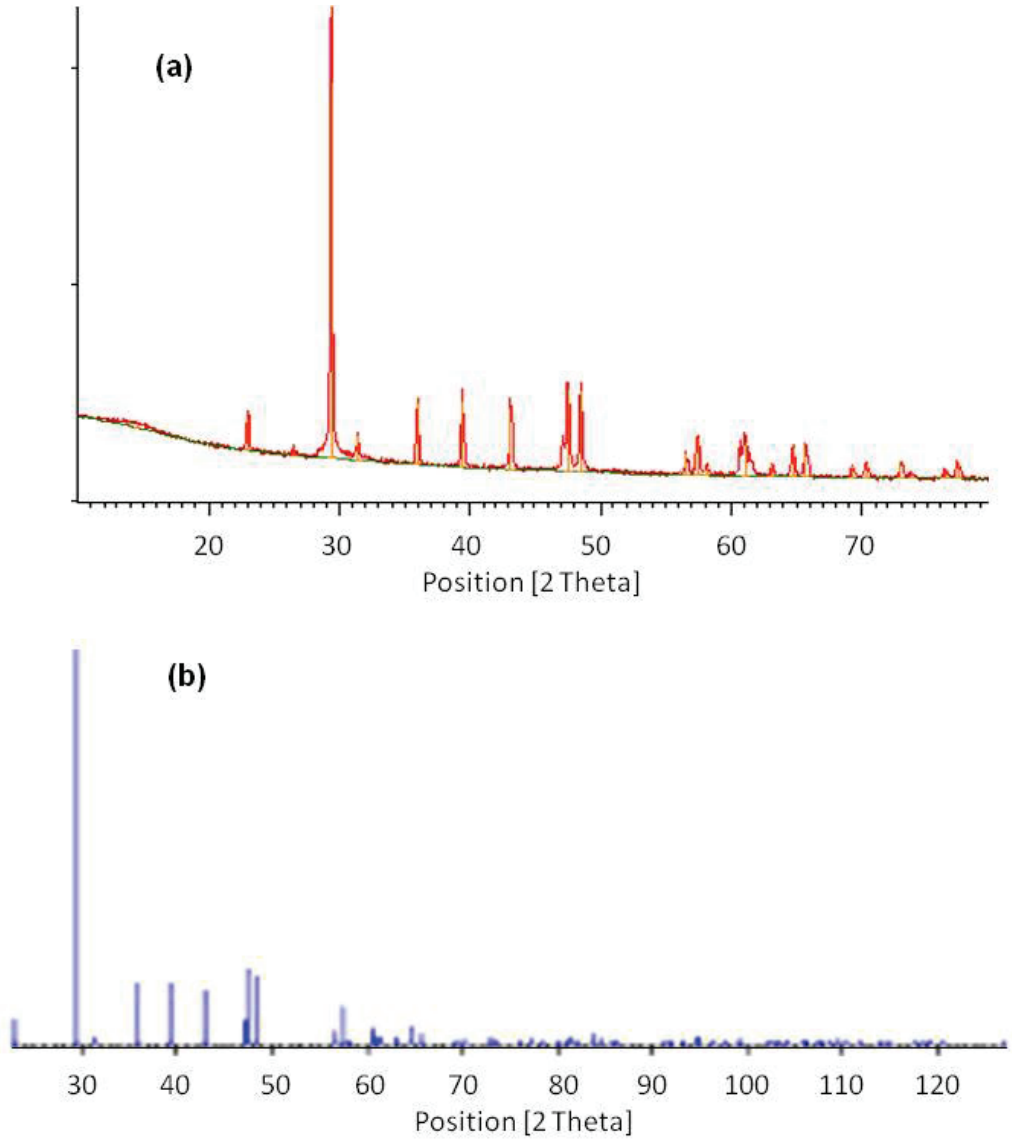

FIGURE 1. XRD pattern of $CaCO_3$ samples prepared from: (a) local resources, and (b) an imported ones.

TABLE 1. XRD pattern of imported and local hydroxyapatite

Imported Hydroxiapatite			**Local Hydroxiapatite**		
2θ	**D(A)**	**Height (%)**	**2θ**	**D(A)**	**Height (%)**
31.77	2.81	100	31.80	2.81	100
32.18	2.78	53	32.24	2.77	57
32.90	2.72	63	32.92	2.72	61
25.86	3.44	35	25.96	3.43	38

TABLE 2. XRD pattern of local hydroxyapatite particle sintered at 600°C for 2 hours

2θ	D(Å)	Height (%)
32.26	2.77	100
33.03	2.71	75
34.14	2.62	32
34.87	2.57	17

TABLE 3. XRD pattern of local hydroxyapatite particle sintered at 600°C for 3 hours

2θ	D(Å)	Height (%)
32.15	2.78	100
33.21	2.69	31
34.00	2.63	82
35.62	2.52	12

TABLE 4. XRD pattern of local hydroxyapatite particle sintered at 600°C for 4 hours

2θ	D(Å)	Height (%)
37.43	2.40	100
38.71	2.32	68
39.68	2.27	15
41.00	2.20	31

TABLE 5. Element composition of limestone particles using EDS

El	AN	Series	unn. C [wt.%]	norm. C [wt.%]	Atom. C [at.%]	Error (1 Sigma) [wt.%]
Ca	20	K-series	34.46	36.69	22.99	1.17
O	8	K-series	32.00	34.07	53.48	4.72
Au	79	M-series	17.99	19.16	2.44	0.75
C	6	K-series	9.47	10.08	21.08	1.75
		Total:	93.92	100.00	100.00	

TABLE 6. Element composition using EDS of local hydroxyapatite sintered at 600°C for 2 hours

El	AN	Series	unn. C [wt.%]	norm. C [wt.%]	Atom. C [at.%]	Error (1 Sigma) [wt.%]
Ca	20	K-series	23.65	38.34	22.13	0.83
O	8	K-series	23.46	38.04	55.00	3.74
P	15	K-series	10.17	16.49	12.32	0.43
C	6	K-series	2.44	3.95	7.61	0.75
Al	13	K-series	1.09	1.76	1.51	0.09
Na	11	K-series	0.87	1.42	1.42	0.10
		Total:	61.68	100.00	100.00	

TABLE 7. Element composition using EDS of local hydroxyapatite sintered at 600°C for 3 hours

El	AN	Series	unn. C [wt.%]	norm. C [wt.%]	Atom. C [at.%]	Error (1 Sigma) [wt.%]
Ca	20	K-series	17.14	33.40	22.26	0.60
Na	11	K-series	14.87	28.98	33.67	0.99
P	15	K-series	12.25	23.87	20.58	0.51
O	8	K-series	6.54	12.75	21.28	1.54
C	6	K-series	0.51	1.00	2.22	0.34
		Total:	51.31	100.00	100.00	

TABLE 8. Element composition using EDS of local hydroxyapatite sintered at 600°C for 4 hours

El	AN	Series	unn. C [wt.%]	norm. C [wt.%]	Atom. C [at.%]	Error (1 Sigma) [wt.%]
Fe	26	K-series	15.29	27.22	15.29	0.72
Ca	20	K-series	13.33	23.75	18.59	0.51
P	15	K-series	11.41	20.32	20.58	0.51
Na	11	K-series	10.11	18.01	24.58	0.76
O	8	K-series	6.00	10.69	20.97	1.42
		Total:	56.15	100.00	100.00	

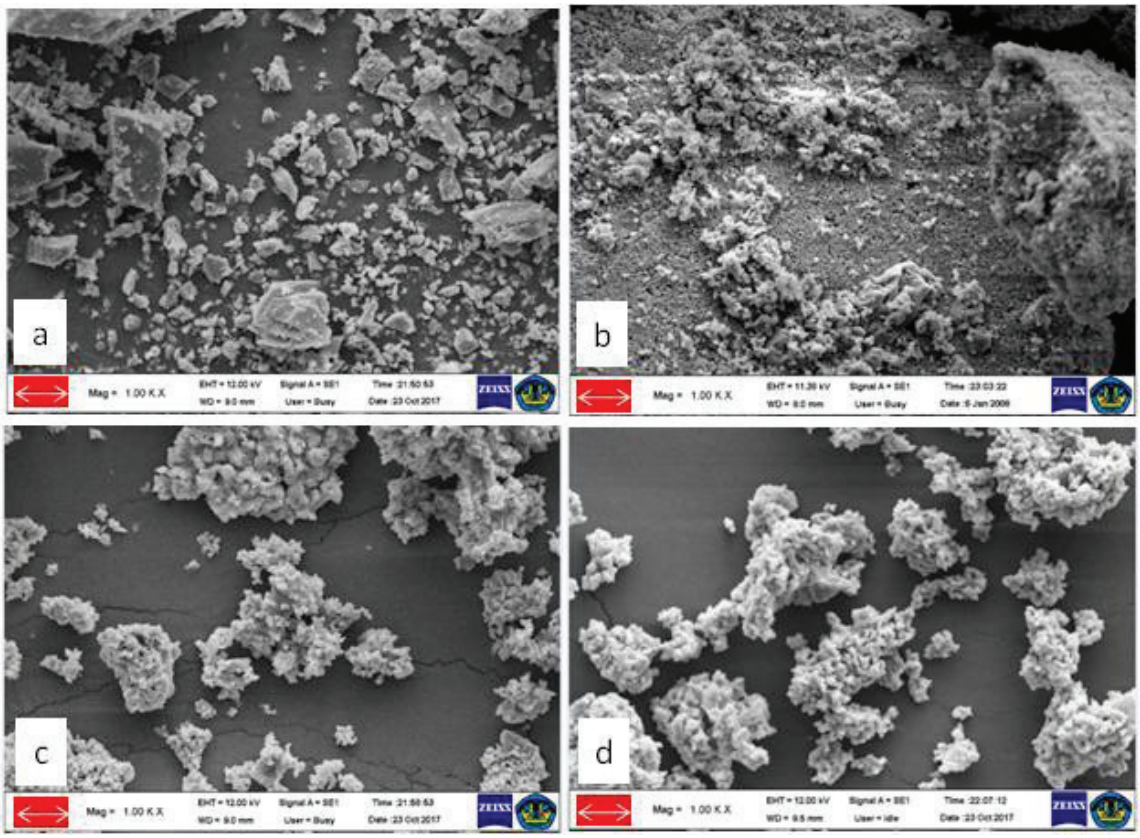

FIGURE 2. SEM micrograph of: (a) limestone particle sintered for 2 hours at 600 °C, and hydroxyapatite loose powder sintered for: (b) 2 hrs at 600°C, (c) 2 hrs at 800°C, and (d) 2 hrs at 1000°C. Red bar is 100µm.

TABLE 9. The micro hardness of compacted hydroxyapatite particles

		Sintering Time (hours)		
		2	**3**	**4**
Sintering temperature (°C)	600	10.6 HV	18.04 HV	18.14 HV
	800	13.0 HV	18.00 HV	14.36 HV
	1000	14.8 HV	15.42 HV	27.10 HV

CONCLUSION

Calcium carbonate was extracted from the local limestone in Lampung province, Indonesia. The hydroxyapatite material was made of calcium carbonate, sodium hydrogen phosphate and demineralised water. The preparation of

hydroxyapatite loose powder was done by grinding, heating and sintering process at temperature of 600, 800, and 1000°C for 2, 3 and 4 hours. This product refers as local HA. The commercially imported HA was used as reference sample. The XRD result shows the peak between local HA and imported one was similar, which indicates that the local resources HA potentially replace the imported HA product that much more expensive. The EDS result also shows that the highest ratio of calcium and phosphor of the local HA was 2.33 while the commercial one was 1.67. The percentage of calcium contents of the local HA decreases in line with the increase in sintering time. The SEM micrograph shows the agglomeration of particle increases in line with the increase in sintering temperature. The HA powder sintered at 1000°C for 4 hours generates the highest hardness number of 27.10 HV.

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