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# THE MICROSTRUCTURES OF HYDROXYAPATITE POWDER FROM PRECIPITATION METHOD IN DIFFERENT SOLUTION

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## ABSTRACT

**THE MICROSTRUCTURES OF HYDROXYAPATITE POWDER FROM PRECIPITATION METHOD IN DIFFERENT SOLUTION**. Biomaterial is conceptually defined as a bioactive material which can undergo chemical reactions in the body only at its surface and the surface reactions lead to bonding of the tissues at the interface. From the requirements point of view, one of the prospective biomaterials is hydroxyapatite sometimes called hydroxylapatite (HA) with a chemical formula of $Ca_{10}(PO_4)_6(OH)_2$. In the present study we used calcium hydroxide and phosphoric acid as the $Ca^{2+}$ and $PO_4^{3-}$ source, while water and synthetic body fluid (SBF) solutions as parameter. Microstructure characterization of the synthesized HA powders was performed using Scanning/Scanning Transmission Electron Microscopy (SEM/STEM) and Fourier Transformed Infra Red (FT-IR) Spectrometry. From the micrographs, it shows that the HA powder from water solution has a rounded shape and the diameter of about 100 nm. The other HA powder using SBF solution shows needle like shape and the elongation is about 50-100 nm. Different powder drying method applied in the HA synthesizing exhibit difference micrographs especially for HA from SBF.

***Key words*** : Hydroxyapatite, Precipitation method, Microstructure, SBF

## ABSTRAK

**STRUKTURMIKRO SERBUK HIDROKSIAPATIT DENGAN METODE PENGENDAPAN DARI PELARUT YANG BERBEDA.** Secara umum biomaterial didefinisikan sebagai material bioakatif yang dapat membuat ikatan kimia dengan tubuh hanya pada permukaan saja dan reaksi permukaan tersebut menyebabkan terjadinya ikatan dengan jaringan pada bagian permukaan saja. Dari persyaratan-persyaratan yang ditetapkan, salah satu biomaterial yang prospektif adalah hidroksiapatit atau hidroksilapatit (HA) dengan rumus kimia $Ca_{10}(PO_4)_6(OH)_2$. Pada penelitian ini, digunakan kalsium hidroksida dan asam fosfat sebagai sumber $Ca^{2+}$dan $PO_4^{3-}$, dengan parameter pelarut yaitu air dan cairan tubuh sintetik *Synthetic Body Fluid* (*SBF*). Serbuk HA lalu diperiksa mikrostrukturnya menggunakan *Scanning/Scanning Transmission Electron Microscope (SEM/STEM)* dan *Fourier Transformed Infra Red (FT-IR) Spectrometry* untuk mengetahui anion/gugus yang ada. Hasil mikrostruktur yang diperoleh menunjukkan bahwa HA dari pelarut air mempunyai bentuk bulat dengan diameter sekitar 100 nm. Sedangkan HA dari pelarut SBF mempunyai bentuk seperti jarum dengan panjang sekitar 50 nm hingga 100 nm. Dengan metoda pengeringan yang berbeda menunjukkan hasil mikrostruktur yang berbeda pula terutama untuk HA dari SBF.

***Kata kunci*** : Hidroksiapatit, Metode pengendapan, Strukturmikro, *SBF*

## INTRODUCTION

Biomaterial is conceptually defined as a bioactive materials which can undergo chemical reactions in the body only at its surface and the surface reactions lead to bonding of the tissues at the interface. From the requirements point of view, one of the prospective biomaterials is hydroxyapatite sometimes called hydroxylapatite (HA) with a chemical formula of $Ca_{10}(PO_4)_6(OH)_2$. Besides having bioactive properties, HA also exhibits bioinert and biocompatibility behavior. In recent years, the application of HA is not only for bone graft but also for eye implantation, maxillofacial or reconstruction and drug carrier.

The undesired properties of HA is its mechanical properties, i.e. it exhibits relative low mechanical strength. Hence, it becomes a handicap for applying HA in higher load bone substitutions. In order to increase this

properties for extended use, there are many promising ways, such as mixing with other materials, coating on bio-inert metallic, or sintering in high temperature to produce more dense materials. To achieve satisfied characteristics of the mixing (as a composite), coated bio-inert metallic, and sintered HA, we have to considered carefully the important role of powder preparation. We have to be able to appropriately control the physicochemical characteristics, such as purity, stoichiometry morphology and crystallinity. To produce HA powder through precipitation method [1-4], we can use different sources of $Ca^{2+}$ and $PO_4^{3-}$.

In the present study, we use calcium hydroxide and phosphoric acid as the $Ca^{2+}$ and $PO_4^{3-}$ source, while water and synthetic body fluid (SBF) solutions as parameter. SBF with ion concentrations similar to those of the inorganic constituents of human blood plasma were able to act as a medium for the development of a poorly crystallized HA similar to bone and simply used as dissolution medium, instead of water [1-4]. Other parameter is powder drying, different method for it by oven and freeze drying were experienced on the synthesized HA. Because the different drying method will lead to different characteristic of powder, especially for non-stoichiometeric HA.

This is in agreement with the characteristics of biological apatites, which are typically non-crystalline and non-stoichiometric. The chemical, structural and morphological properties of synthetic HA can be arranged by varying the method and the conditions of synthesis [5-7]. In this paper, characterization of the microstructure of HA powders synthesized in our laboratory was performed using Scanning/Scanning Transmission Electron Microscopy (SEM/STEM) and Fourier Transformed Infra Red (FT-IR) Spectrometry.

The purpose of this experience is to produce HA powder in different source to validate the HA procedure for product utilization in medical application, for promoting early bone in-growth.

## EXPERIMENTAL METHOD

SBF solutions were prepared by dissolving appropriate quantities of chemical reagents in de-ionized water, following the procedure reported by Elena et al. The pH of the SBF solutions was about 7.4. The nominal concentrations of $HCO_3^{2-}$, $HPO_4^{2-}$, $Ca^{2+}$, $Mg^{2+}$, $Na^+$ and $K^+$ ions were the same of those of human plasma, i.e.: 27.0, 1.0, 2.5, 1.5, 142.0 and 5.0 mM respectively [4,5].

In this experiment, classical neutralization synthesis of hydroxyapatite based on $Ca(OH)_2$ and $H_3PO_4$ was performed using SBF and water. A hundred grams of $Ca(OH)_2$ (Merck 95%) were added to 1000 mL SBF (basic solution), and then was stirred and heated at 40 $^oC$. $H_3PO_4$ (88.8 g) were dissolved in 600 mL SBF (acid solution) and then was dropped (1-2 drops/s) into the basic suspension, taking about 3-4 h. The suspension was kept under stirring and heating to 40 $^oC$ for 2 h, and then left for 24 h without stirring and heating. The precipitate, as the result of the process mentioned before, was separated from the mother liquor by filtration and washed with de-ionized water. After that, the precipitate was heated at 80 $^oC$ in the oven overnight and other in freeze drying, then underwent crushed and sieved.

The as-prepared powders from water medium solution were designated as *HA1-A* and *HA1-B* for oven and freeze drying, while powders from SBF solution as *HA2-A* and *HA2-B*, respectively.

The presence of anions in the HA then was determined using Fourier Transformed Infra Red (FT-IR) and the powder morphologies were evaluated using scanning electron microscopy (SEM). The obtained data then were evaluated altogether and compared with commercial HA (Aldrich).

## RESULTS AND DISCUSSION

The SEM micrographs as shown in Figures 1, 2, 3 and 4 indicated that the primary particles were in nanometer size (about 50-100 nm). The HA powders

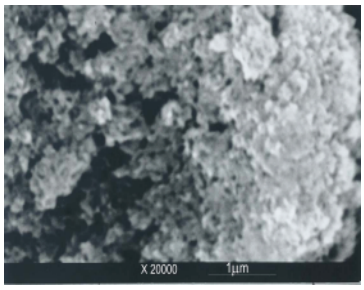


***Figure 1.*** HA1-A (H20-oven) at a magnification of 20,000 times.

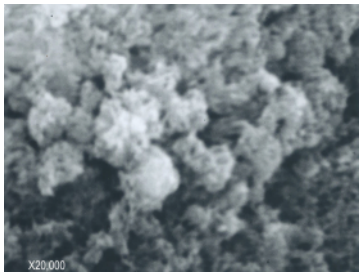


***Figure 2.*** HA1-B (H20-Freeze Drying) at a magnification of 20,000 times.

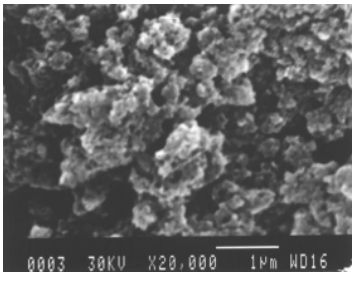


***Figure 3.*** HA2-A (SBF-oven) at a magnification of 20,000 times.

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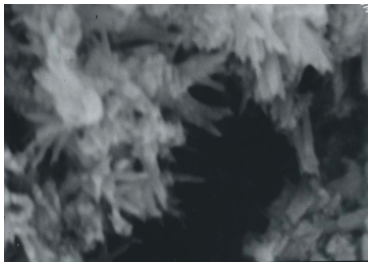


***Figure 4.*** HA2-B (SBF-Freeze Drying) at a magnification of 20,000 times

generated from SBF and water solution showed a needle-like and rounded shape, respectively. Both the nano-sized particle showed high tendency to agglomerate.

The difference of powder shape between generated from SBF and water solution may be caused by the difference of the solution. HA prepared by precipitation in SBF solutions were carbonated (called CHA) and incorporated small amounts of the cations provided by SBF. The presence of carbonated could be in the $PO_4^{3+}$ or $OH^-$ position, and designated as B-CHA and A-CHA, respectively. The cations will affect the orientation of the particle growth due to the change in the bonding. This can be seen from the FT-IR spectrum (Figure 6) which shows the changes in the absorption band and peaks shape.

According to references [5,6,8], the presence of B-CHA cause decreasing in the HA crystallinity and an increase in absorbility in both in-vitro and in-vivo tests, and improving the bio-mimetism of the synthetic HA. Meanwhile, A-CHA indicate lower affinity for the human trabecular osteoblastic cells giving rise to lower cell attachment and collagen production compared with HA. It was demonstrated that the carbonation, in one hand, improved the densification of the hydroxyapatite, and in particular conditions, the densification process could be happened at a temperature of H"350 $^oC$ lower than the usual one (1250 $^oC$). On the other hand, the carbonate-substituted hydroxyapatite should be thermally stable so that it will not decompose into undesirable secondary phases upon calcinations and sintering at high temperatures (i.e. when the goal is to improve densification and the mechanical properties).

Mg ion, which is another constituent of the SBF, was found to substitute for the Ca ions, contributing (as $CO_3^{2-}$ does) to decrease the degree of crystallinity of the hydroxyapatite and to stabilize the carbonate substitution in the lattice [8,9]. Solubility tests [9], demonstrated higher solubility of Mg-substituted HA powder, pointing towards an improved bio-re-absorbability, compared with the stoichiometric HA. Moreover, the presence of $Na^+$ ions substitute the $Ca^{2+}$ position and its affinity might place the OH sites and the P-bonded oxygens close to the $Na^+$ ions, and hence, cause a reduction in the extent of the dehydroxylation at high temperatures. The presence of those ions, such as carbonate and Mg, are also maintained by freeze drying, which it is proven by the shape of the powder. The shape of HA2-B is more elongated that HA2-A meaning that those ions are more stable in freeze drying.

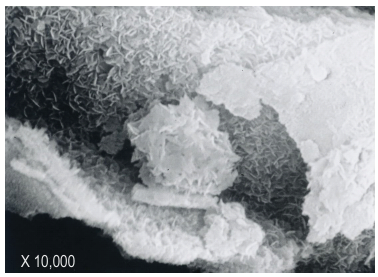
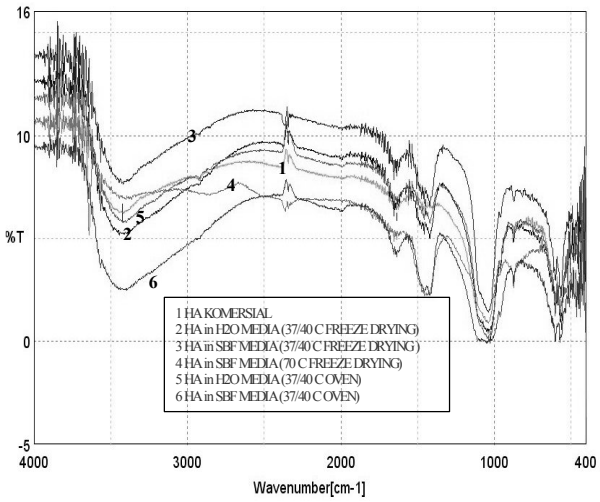



***Figure 5.*** HA Commercial at a magnification of 20,000 times

From the explanation before, it is well known that several factors such as the precursors used, the synthesis process and the precipitation conditions, influence the particle size. Comparing with the micrographs of Figure 1-4, the microstructure of commercial HA (Figure 5) also indicates nano-sized particles, but different in shape and not rather agglomerate. It could be predicted that commercial HA had previously been heat-treated.

Figure 6 and Table 1 show the FTIR spectra and wavelength number of the as-prepared and commercial HA. From the reference [10], we have informed that HA has peaks at about 561, 602, 962 and 1032 $cm^{-1}$ for the phosphate absorption bands. For $OH^-$ anion the peaks will appear at about 3572 $cm^{-1}$, and when there is a carbonate substitution, the peaks will appear at around 875, 1430 and 1450 $cm^{-1}$. The peaks at 875 $cm^{-1}$ and around 1430–1455 $cm^{-1}$ indicates that carbonate ions have substituted phosphate or hydroxide positions in the apatite lattice (B-type or A-type substitution, respectively).




***Gambar 6.*** FT-IR peaks of the as-prepared and commercial HA powders.

On the other side, however, the peaks of the phosphate absorption bands of our HA2-A and HA2-B (as-prepared powder in the SBF solution) indicate wavelengths at around 500, 570, 960, 1040 $cm^{-1}$. These peaks have lower wavelengths as compared to the values reported in the reference [10]. This could be happened due to the presence of $Na^+$, $K^+$ and $Mg^{2+}$ ions that cause the changes in the bonding (depends on the valence difference and ionic strength). Moreover, the as-prepared powders show also carbonate spectra and mainly indicating B-types. The quite shift of $PO_4^{3-}$ absorption band could be caused by the presence of carbonate and ions ($Na^+$, $K^+$ and $Mg^{2+}$) from SBF. The difference in the ionic affinities of $Na^+$, $K^+$ and $Mg^{2+}$ caused stretching and bending to change among $PO_4^{3-}$ ions.

***Tabel 1.*** FT-IR wavelength number of the as-prepared and commercial HA powders.

| Reference [10] | As-prepared | | | | Commercial | Legends |
|---|---|---|---|---|---|---|
| | HA1-A | HA1-B | HA2-A | HA2-B | | |
| 561 | 520 | 480 | Not clear | Not clear | 500 | $PO_4^{-3}$ (v1) |
| 602 | 560 | 560 | 570 | 560 | 580 | $PO_4^{-3}$ (v2) |
| 962 | 960 | 960 | 960 | 960 | 960 | $PO_4^{-3}$ (v3) |
| 1032 | 1020-1030 | 1030 | 1020+100 (wide) | 1040 | 1020 | $PO_4^{-3}$ (v4) |
| 3572 | 3560 | 3560 | 3560 | 3420 | 3560 | $OH^-$ |
| 875 | 870 | 860 | 880 | 860 | 1440 (small peak) | $CO_3^{-2}$ |
| 1430 | 1420 | 1420 | 1420 | 1420 | - | B-CHA |
| 1450 | 1460 | 1460 | 1460 | - | - | A-CHA |
| 1660 | 1660 | 1660 | 1660 | 1640 | 3420 | H20 |
| 3400 | 3400 | 3400 | 3400 | 3400 | | |

The absorption band of $H_2O$ was appear at about 3400 and 1620 $cm^{-1}$, and all of the as-prepared powder indicated these peaks, but commercial HA and HA from oven has slightly lower and shifted peaks as compare with HA from freeze drying. The $OH^-$ absorption bands in the FT-IR spectrum of commercial HA were sharper compared with the as-prepared. In water solution, the carbonate substitution may arise due to the reactive absorption of the atmospheric carbon dioxide during the process. However, the carbonate absorption band did not exist in the commercial HA.

The peaks of commercial HA, shown in Figure 6, explain that the absorption band is nearly to the absorption band of HA1-A, although the $H_2O$ content is less then in HA1-A. Also, the peaks are sharper than the HA1-A. This might be due to the improvement in the degree of crystallinity in the powder after having heat treatment. Based on these conditions, it is assumed that the commercial HA had previously been heat treated or, in other word, it had been dried at the temperature of around 40 °C.

Return to Figures 1 and 3, it is obviously that HA powder generated through oven shows some pores that we assumed came from release of vapour ($H_2O$ or $CO_2$). The presence of pores reduces the density of HA, and will deteriorate its mechanical properties. Moreover, it may also act as the source of cracking during the process to produce a dense HA. The cracks might be useful for enhancing compacting and sintering processing. Additionally, the presence of pores will increase the surface area which will lead to higher absorbability. Based on the above conditions, it can be said that the powder characteristic highly depends on the process parameters. Each characteristic will relate to the purpose of the application. The densification and decomposition behaviour of hydroxyapatites is very variable depending on the powder characteristics. For example, B-CHA, which is easily absorbed by human tissues is good for bone filler. Dense HA is appropriately used for implantation (e.g. eye implantation, bone graft), and HA powder is effectively for bone coating).

## CONCLUSION

From the electron microscopy micrograph shows that all of the as-prepared and commercial HA powder were nano-sized particles and exhibit different shape especially for as-prepared powder because of the influence of ions provided by SBF and for commercial HA, it could be heat treated performed. The powder characteristics are highly depends on the process parameters. Each characteristic will relate to the purpose of the applications

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