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Morphology Controlled Calcium Orthophosphates Induced by Chemical Additions under Hydrothermal Reaction

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Abstract

Morphology controlled calcium orthophosphates under hydrothermal reaction was achieved using saturated solution of monocalcium phosphate monohydrate (MCPM) as a starting material. MCPM saturated solution was hydrothermally treated at 180°C for 4 and 12 hrs. Citric acid as a chelating agent and a mixed solution of $NaNO_3$ and NaF were individually added into the reactor. The morphologies, phases and microstructures of the obtained products were characterized by optical microscope (OM), X-ray diffraction (XRD) and scanning electron microscope (SEM), respectively. Irregular shape crystals were obtained when a saturated solution of MCPM was autoclaved at 180°C for 4 hrs. Though citric acid was added into the reaction, the irregular shape products were still obtained with a minority of hexagonal plate crystals. As a result, the whiskers were synthesized when the mixed solution of $NaNO_3$ + NaF was added into MCPM saturated solution and treated at 180°C for 12 hrs. Although the reaction time decreased from 12 to 4 hrs, the whisker products were still obtained. Phase analyses clarified by XRD that the whiskers were hydroxyapatite.

Key words : Calcium Phosphate, Hydroxyapatite, Whisker, Hydrothermal

Introduction

Calcium phosphate compounds have been classified by Elliot(1) into two types. One is the calcium orthophosphates which are salts of the tribasic phosphoric acid, thus can form compounds that contain $H_2PO_4^-$, HPO_4^{2-} or PO_4^{3-} ions. The other is pyrophosphates and polyphosphates, which contain P-O-P bonds, e.g. $P_2O_7^{4-}$. The latter is of less importance than the orthophosphates in biological viewpoint. Many attempts have constantly been made to develop the appropriate morphology of these calcium orthophosphates since many of them, e.g. hydroxyapatite (HA), brushite (DCPD), monetite (DCPA), β-tricalcium phosphate (β-TCP), were acceptable as bioactive and biocompatible materials. These attempts include Yoshimura, et al.(2) who obtained HA whiskers from β-TCP with the addition of citric acid under hydrothermal reaction at 200°C, 2 MPa for 1 hr. Suchanek, et al.(3) succeeded in controlling the morphology of HA crystal by adjusting Ca/P molar ratio of the starting solution which was composed of H_3PO_4 and $Ca(OH)_2$ with addition of lactic acid as a chelating agent, and which was subjected to hydrothermal treatment at 200 °C, 2 MPa for 5 hrs. Jinawath, et al.(4-5) had accomplished control of the morphology of various compounds of calcium orthophosphates, e.g. monetite whiskers, HA platelets and HA needles using monocalcium phosphate monohydrate (MCPM) as a starting solution which was hydrothermally treated at 160°C and 200°C for 4 hrs. Moreover, another attempt included transformation of aragonite from coral to the morphology controlled HA under hydrothermal reaction at 160°C with the presence of MCPM, DCPD solutions and H_3PO_4.(6) The Ca/P ratios of starting solution were adjusted by addition of $Ca(OH)_2$(4-6) in order to achieve the desired phases of calcium orthophosphates. It is worth noting that Monma(7) found that HA needle-like shape was promoted to form on titanium substrate with addition of NaF and $NaNO_3$ into MCPM electrolyte. The electrolyte was prepared from saturated MCPM solution and the current density used in the electrodeposition process was

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6+1 mA/cm^2 at 20-90°C. $NaNO_3$ and NaF are less expensive and less economical compared to lactic and citric acids which are well known as chelating agents normally used to control the morphology of various powder materials. It would be interesting to use $NaNO_3$ and NaF as morphology control reagents of calcium orthophosphates in the hydrothermal process. The present work aims at using hydrothermal treatment with the presence of $NaNO_3$ and NaF instead of electrochemical reaction.(7) The results would be clarified as comparative studies between citric acid (normal chelating agent) and sodium salts of NO_3^- and F^-, respectively. The morphology controlled calcium orthophosphates promise to be used not only in the biomedical applications but also in many applications such as reinforcing filler for composites, packing media for column chromatography, and bone bonding bioactive materials.

Materials and Methods

MCPM ($CaH_2PO_4)_2 \cdot H_2O$), the most soluble calcium phosphate salts was prepared as a saturated solution used for starting materials. MCPM (Fluka with purity > 85 %) was dissolved in 500 ml of distilled water and stirred over more than 3 hrs. until the precipitate of MCPM was observed. It was then kept overnight without stirring, then filtered to separate the precipitate and saturated solution. Only saturated solution was used as a starting solution for hydrothermal reaction. The experiments were done in two different chemical additions.

The first route, citric acid (analytical grade (99%), Lancaster synthesis) was diluted to 10% w/v and added into the saturated solution of MCPM. The volume of MCPM was controlled at 10 ml in all batches and the volume of citric acid was varied from 1, 3, 5, and 7 ml.

The second route, 7 grams (0.0824 mol) of NaNO3 (analytical grade (99%), Ajax chemical) and 0.05 gram (0.0012 mol) of NaF (analytical grade (98%), Ajax chemical) were mixed together and dissolved in 50 ml distilled water, then pipetted 1, 3, 5, and 7 ml and individually added to 10 ml MCPM saturated solution. The control group was also done using 10 ml MCPM saturated solution and hydrothermal treated at 180°C for 4 hrs. All conditions were summarized in Table 1.

Table 1. Summarized conditions for all experiments

Sat.MCPM (ml)	Citric acid (ml)	$NaNO_3$+ NaF (ml)	T(°C) / time (hr)
10	1	-	180/12
10	3	-	180/12
10	5	-	180/12
10	7	-	180/12, 180/4
10	-	1	180/12, 180/4
10	-	3	180/12, 180/4
10	-	5	180/12, 180/4
10	-	7	180/12, 180/4
10 (control)	-	-	180/4

Each condition of the starting mixed solutions from route 1 and 2 was transferred into a PTFE bottle and stirred. After well stirring, the bottle was tightly sealed and put in a stainless steel autoclave which was then put in an oven at 180°C for 4 and 12 hrs. After the autoclave cooled down to room temperature, the product was filtered, washed with distilled water, then dried in an oven at 60°C overnight. Phase analyses were clarified by X-ray diffractometer (XRD, Bruker D8-Advance, with Ni filtered CuK_α radiation at 40 kV and 40 mA). Morphologies of the obtained products were characterized by optical microscope (OM, Olympus BX60M microscope) and scanning electron microscope (SEM, JEOL JSM 5410LV) at an operating voltage of 300 kV.

Results and Discussion

Irregular shape crystals were obtained when a saturated solution of MCPM was autoclaved at 180°C for 4 hrs. (control group). Morphologies of the obtained products from the first route with addition of citric acid showed irregular shape crystals with non-uniform size and minority of hexagonal plate crystals as shown in Figure 1. On the other hand, with the morphology of the products from the second route with the presence of $NaNO_3$ + NaF, needle-like particles with a high aspect ratio of 15-20 were observed as shown in Figure 2. From these comparative results, it can be summarized that citric acid did not play a role as a morphology control reagent; the anion of nitrate and fluoride from sodium salts, however, strongly affected the morphology of the obtained crystals. Under hydrothermal reaction at 180°C, citric acid ($C_6H_8O_7$) might decompose (boiling point is 175°C) and it could not act as the chelating agent to control the morphology of the products. Considering the inside of the reactor at such condition, the amounts of vapor phase of citric acid was greater than liquid phase. Thus, citric acid (liquid phase) was not sufficient to act as the chelating agent for Ca^{2+} to form a ring with anions such as $H_2PO_4^-$, HPO_4^{2-}, PO_4^{3-}, and OH^- ions. Finally, irregular shape crystals with minority of hexagonal plate crystals were obtained as obviously shown in Figure.1.

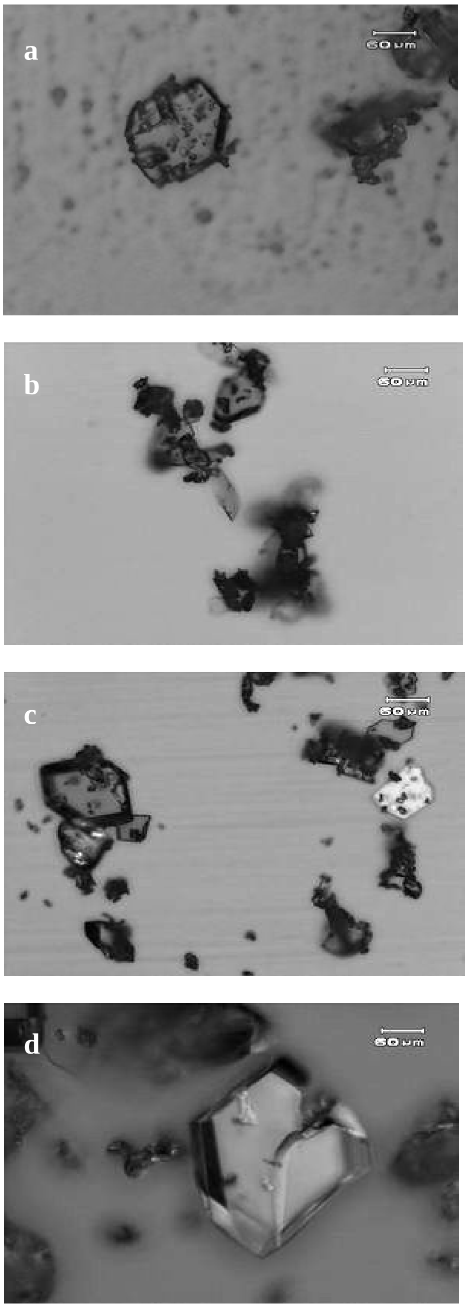

Figure1. Optical micrographs of the obtained products from saturated MCPM with addition of various amounts of citric acid at a) 1ml., b) 3 ml., c) 5 ml, and d) 7 ml. under hydrothermal condition at 180°C for 12 hrs.

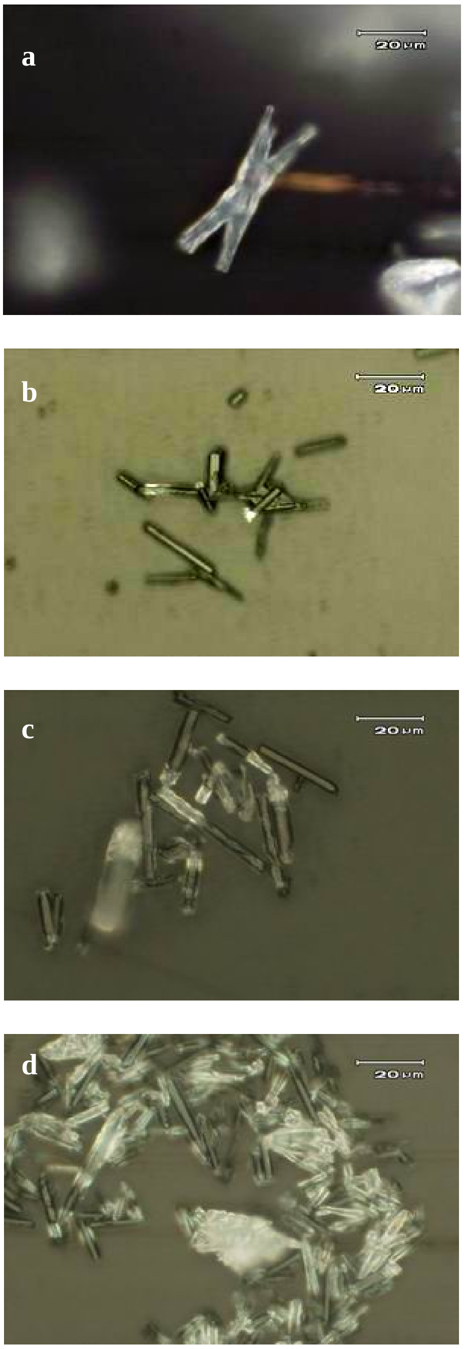

Figure 2. Optical micrographs of the obtained products from saturated MCPM with addition of various amounts of $NaNO_3$+NaF at a) 1ml., b) 3 ml., c) 5 ml. and d) 7ml. under hydrothermal condition at 180°C for 12 hrs.

From Figure 2. it can be concluded that $NaNO_3$ and NaF could promote the morphology control of calcium phosphates during hydrothermal reaction. In the next step, our attempts were to decrease the reaction time from 12 hrs to 4 hrs. The results from optical micrographs indicate that although the reaction time was three times decreased (12 to 4 hrs.) the morphology of the obtained products were still of needle-like shape. SEM micrographs from Figure 3. clearly show that the perfect morphology controlled crystals appeared when $NaNO_3$+NaF 1 ml was added into the saturated MCPM solution. The higher amount of $NaNO_3$ + NaF brought about the imperfect crystal surface as obviously seen in Figure 3c. The incorporation of the adequate amount of fluoride increases in structural stability of hydroxyapatite crystals due to a better fit of the fluoride ion within the imaginary Ca triangles in the apatite structure.(8) The excess fluoride leads to the deviating of crystals from the normal. Phase analyses of the obtained products with the presence of $NaNO_3$ + NaF at the reaction time 4 hrs were selected to be characterized by XRD. The XRD patterns from Figure 4. show that the obtained products with addition of $NaNO_3$ + NaF were the whiskers of single phase hydroxyapatite with 15-25 μm in length and 1-4 μm in width. All peaks in XRD pattern were indexed according to JCPDS No. 72-1243. However, there was a small percent yield of the products when adding of $NaNO_3$ + NaF 1 ml, so it was not sufficient to characterize by XRD powder technique. The best-documented effect of fluoride is that this ion substitutes for a column hydroxyl in the apatite structure(9), giving rise to increase in crystallinity, crystal size(8, 10) and thickness.(10) Hydrothermal treatment at 180°C for 4 hrs of saturated solution MCPM with the presence of $NaNO_3$ and NaF tends to show the equivalent results in needle-like crystal products to that of electrochemical reaction in reference.(7) Moreover, it has been found that the crystallinity and crystal size of hydroxyapatite whiskers from hydrothermal treatment is much higher than that from electrochemical method. The average size of hydroxyapatite whisker obtained from electrochemical method(7) is 3-4 μm in length and 0.5-1 μm in width with an aspect ratio of 3-5. The whisker obtained from hydrothermal reaction is 15-25 μm in length and 1-4 μm in width with an aspect ratio of 15-20.

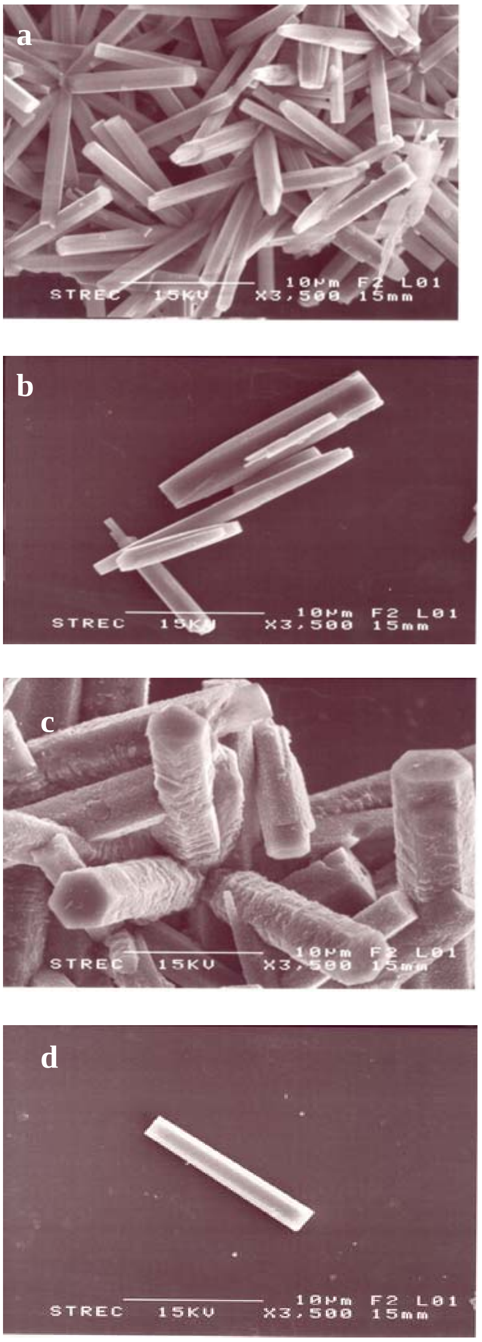

Figure 3. SEM micrographs of the obtained products from saturated MCPM with addition of various amounts of $NaNO_3$ + NaF at a)1ml., b)3 ml., c) 5 ml. and d) 7 ml. under hydrothermal condition at 180°C for 4 hrs.

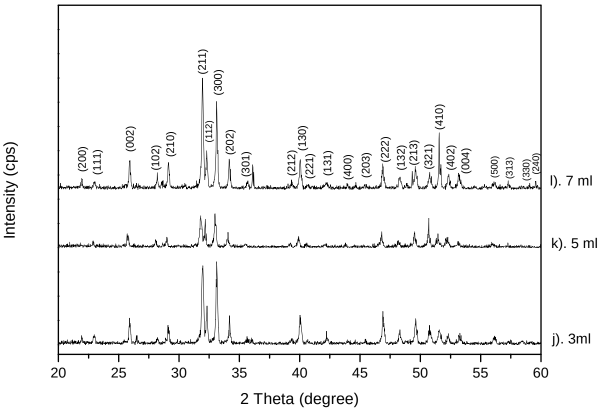

Figure 4. XRD patterns of the obtained products from saturated MCPM with addition of various amounts of $NaNO_3$+NaF at a) 3 ml., b) 5 ml. and c) 7 ml. under hydrothermal condition at 180°C for 4 hrs.

Conclusions

Morphology controlled calcium orthophosphates were successfully obtained from saturated MCPM solution with the presence of $NaNO_3$ and NaF under hydrothermal treatment at 180°C for 4 hrs. The morphologies of the obtained crystals from SEM revealed that the high amounts of $NaNO_3$ + NaF addition would impart the imperfection to the obtained crystals. The most perfect whisker of hydroxyapatite could be synthesized when addition of $NaNO_3$ + NaF was 1 and 3 ml. The average size of hydroxyapatite whiskers is 15-25 μm in length and 1-4 μm in width with an aspect ratio of 15-20. Increasing the amounts of $NaNO_3$ + NaF addition, especially at 5 ml, the surface defect of hydroxyapatite whiskers would appear.

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