

THE GROWTH OF APATITE CRYSTAL ON PORES POLYGLYCOLIDE MATRIX UNDER THE INFLUENCE OF CARBONATE AND MAGNESIUM

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ABSTRACT

The apatite crystal has been growth on pores polyglycolide through precipitation of supersaturated calcium phosphate carbonate solution. The influence of magnesium on the precipitation was observed. Polyglycolide was prepared by solid state reaction of sodium chloroacetate at 192°C. To obtain pores materials, polyglycolide was pressed into pellet and washed with water to eliminate NaCl, a byproduct of sodium chloroacetate polymerization. Calcium phosphate carbonate solution (calcium: phosphate: carbonate = 0.25 M : 0.25 M: 1 M was precipitated on this pores polyglycolide. Solution with various magnesium concentrations (0, 0.5, 1, 1.5, and 2 M) was added during the precipitation. Samples were characterized by x-ray diffractometer (XRD) and scanning electron microscope (SEM). Most of XRD profiles showed that the samples contained of amorphous and crystalline phase of calcium phosphates as well as polyglycolide .The increase of magnesium ions in solution influenced the crystallization process in which it caused the decrease of amorphouse phase content and eliminated the presence of octa caluim phosphate phase.

Keyword: polyglycolide, apatite crystal

ABSTRAK

Telah ditumbuhkan kristal apatit pada polyglycolide berpori melalui presipitasi larutan kalsium fosfat karbonat yang sangat jenuh. Pengaruh magnesium pada presipitasi juga diamati. Polyglycolide diperoleh dari reaksi zat padat sodium chloroacetate pada suhu 192°C. Untuk mengamati material berpori, polyglycolide dipres dalam bentuk pellet dan dicuci dengan air untuk menghilangkan NaCl sebagai hasil dari polimerisasi sodium chloroacetate. Larutan kalsium fosfat karbonat (kalsium: fosfat: karbonat = 0,25 M : 0.25 M : 1 M) dipresipitasi pada polyglycolide berpori. Larutan dengan variasi konsentrasi magnesium (0; 0,5; 1; 1,5; dan 2 M) ditambahkan selama proses presipitasi. Sampel dikarakterisasi dengan x-ray diffractometer (XRD) dan scanning electron microscope (SEM). Pola XRD menunjukkan bahwa sampel mengandung fase kalsium fosfat amorf dan kristal sebagaimana polyglycolide. Penambahan ion magnesium pada

larutan mempengaruhi proses kristalisasi yang menyebabkan terjadinya pengurangan fase amorf dan menghilangkan kehadiran fase okta kalsium fosfat.

Kata kunci: polyglycolide, kristal apatit

INTRODUCTION

Bone is a natural composite material, composed of about 60 wt% mineral, 30 wt% organic matrix, and 10 wt% water¹. Furthermore as a living tissue, bone consists of about 15 wt% living cells. The bone organic matrix is primarily as type I collagen²., and bone mineral is a mixture of amorphous calcium phosphate and apatite crystals. Besides Ca^{2+} and PO_4^{3-} ions, the bone apatite crystals also consist of other complex and simple ions such as CO_3^{2-} , Mg^{2+} , Na^+ , H^+ , F^+ , and Sr^{2+} ³. These other ions may incorporate and/or substitute Ca^{2+} and PO_4^{3-} ions in lattice producing apatite crystal with various composition and crystallinity.

In this work, to mimic the natural bone as a mixture of polymer, amorphous phase and crystalline phase, synthetic polymer polyglycolide (PGA) was mineralized by precipitating Ca^{2+} , and PO_4^{3-} ions. High concentration of CO_3^{2-} ion was added during precipitation and as well various high concentration of Mg^{2+} ion. It was expected that the CO_3^{2-} and Mg^{2+} ions will interfere the formation of crystal phase and stabilize the amorphous phase. The result was crystal phase in the form of apatite and calcite, while the amorphous phase was might be calcium phosphate and calcite hydrate. From this work, it was illustrated that calcification process takes place with the formation of crystal phase as competition between PO_4^{3-} and CO_3^{2-} ions.

EXPERIMENTAL

The materials used in this work are $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ pro analysis, $\text{NaHPO}_4 \cdot 2\text{H}_2\text{O}$ pro analysis, NaHCO_3 pro analysis, and MgCl_2 pro analysis, and sodium chloroacetate ($\text{C}_2\text{H}_2\text{ClNaO}_2$) pro analysis

Porous PGA is prepared in solid state reaction of sodium chloroacetate. First, sodium chloroacetate was heated up to its polymerization temperature. By using DSC (Differential Scanning Calorimetry) polymerization temperature was found at 192°C. After heating this material was pressed into the form of pellet with the size of 25 mm diameter. To eliminate byproduct NaCl, these pellets were dipped in aquadest several times and then dried by vacuum in 10 minutes. Further a mixture of NaHPO_4 , and NaHCO_3 solution, as well as CaCl_2 solution were given to the pores PGA pellets by titration in turn for 50 times with 5 ml of each titration. Concentration of these ion solutions were selected so that the concentration proportion of calcium, phosphate, and carbonate ions were 0.25 M, 0.25 M, and 1M, for producing sample A. During precipitation, with the same method of titration MgCl_2 solution with various concentrations was added. Variation of magnesium ion

concentration was 0.5 M, 1.0 M, 1.5 M, and 2.0 M and resulting sample A into sample A1, A2, A3, and A4.

X ray diffraction analysis to each samples was carried out by means of Phillips diffractometer with Cu K α radiation ($\lambda = 1.54056 \text{ \AA}$) generated at 40 kV and 10 mA. The measurements were performed with diffraction angle (2θ) in the range of 5° to 80° . Further evaluation of surface morphology to each sample was performed by using JEOL SEM (scanning electron microscope).

RESULTS AND DISCUSSION

In general, X ray diffraction pattern of all samples (Figure 1) consist of continuous curve and discrete lines that represent of amorphous and crystalline phases in the sample. This continuous curve with maximum peak at about $2\theta = 30^\circ$ indicates the existence of amorphous calcium phosphate^{4,5} and might be also calcite hydrate. Discrete lines showed the present of a mixture of calcium phosphate and sodium chloride crystals. Most samples consist of hydroxyapatite (2θ at about 27° , 32° , 44°), apatite carbonate type B (2θ at about 32° , 33° , 48°), calcite (2θ at about 22° , 29° , 43°), sodium chloride (2θ at about 31° , 45° , 56° , 75°), and polyglycolide (2θ at about 21° , 29° , 36° , 39° , 47°). Most of glycolide patterns have wide FWHM that indicated this phase in the form of microcrystalline. It is interesting that only sample A ($\text{Ca}^{2+} : \text{PO}_4^{3-} : \text{CO}_3^{2-} = 0.25 \text{ M} : 0.25 \text{ M} : 1 \text{ M}$) indicates the existence of octa calcium phosphate (2θ at about 16° , 23° , 26°). The addition of magnesium changes the XRD pattern, particularly for apatite crystal. If we consider the peak at $2\theta = 27^\circ$, it appears that the increasing magnesium concentration will reduce the apatite content in the samples. However in the mean time, it will not influence the calcite content.

Polyglyclide is obtained through solid state reaction of halogenoacetate at specific temperature. In this work, it is determined by differential scanning calorimeter which the result is 192°C . It should be noticed that every batch of halogenoacetate, each will have specific polymerisation temperature.

The high amount of carbonate concentration in calcium phosphate solution influences both the formation of calcium phosphate and calcium carbonate crystals. The growth of apatite crystal is preceded by the formation of octa calcium phosphate. The presence of carbonate ions inhibits the first stage of nucleation and the growth of apatite crystals⁶ can be seen from the XRD patterns. Beside that, carbonate also enters into the structure of apatite crystal by replacing phosphate ions to form apatite carbonate type B. On the other hand, the phosphate ions will inhibit the nucleation and the growth of calcite crystals. Phosphate ions will not enter into calcite structure but it will prevent the growth of crystals through adsorption⁷.

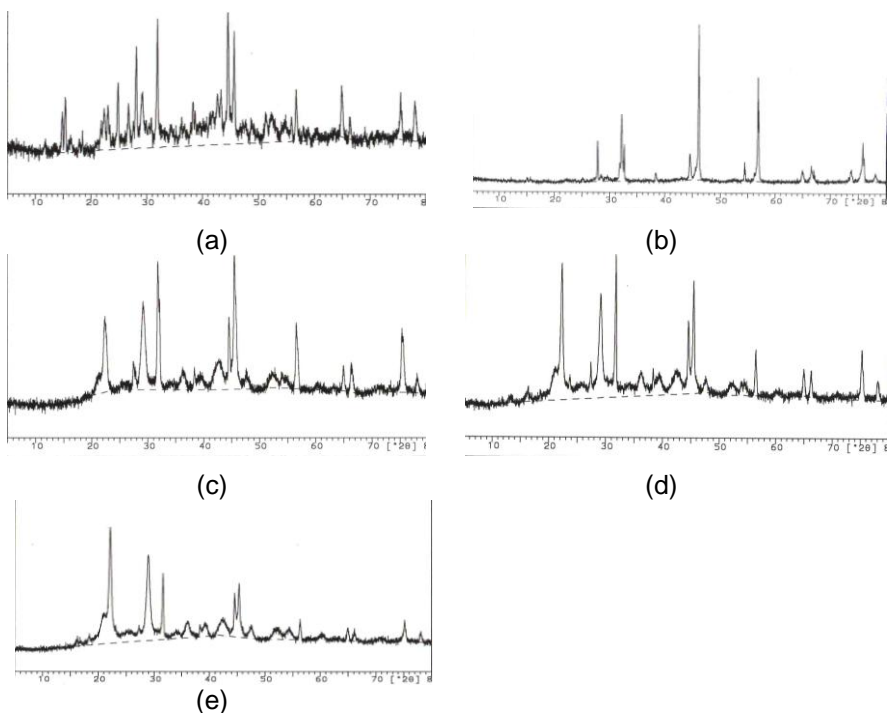


Figure 1 X ray diffraction pattern of samples produced by concentration solution proportion Ca^{2+} , PO_4^{3-} , and CO_3^{2-} ions A) as 0.25 M : 0.25 M : 1.0 M (a) with additional concentration Mg^{2+} ions for A1) 0.5 M (b), : A2) 1.0 M (b), A3) 1.5 M (c), and A4) 2.0 M (d).

Electron micrograph of the porous polyglycolide resulting from solid reaction was shown in Figure 2P. It can be seen that the pore sizes were not homogenous, the pore width was in the range of 0.5 – 1.5 μm . Figure 2A is a micrograph of a sample before the addition of magnesium. The crystalline pattern is clearly seen as rods. There is no significant change on the morphology after the addition of 0.5 M magnesium. The morphological change can be recognized as the magnesium increases to 1.0 M, 1.5 M, and 2.0 M (Figure 2d, 2e, and 2f).

Both XRD and electron micrograph illustrate that apatite formation becomes decrease with the increasing of magnesium content. Magnesium ions may replace calcium ions in apatite structure But, after the crystal is in stable condition, magnesium ions move out from the crystal structure and will have an effect in mismatch for crystalline growth⁸. This mechanism also occurs in calcite.

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