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EFFECT OF PRECURSOR SOLUBILITY ON THE MECHANICAL STRENGTH OF HAP BLOCK

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ABSTRACT

The effect of the solubility of the precursors, alpha tricalcium phosphate (α -TCP) and beta tricalcium phosphate (β -TCP) on the mechanical property of hydroxyapatite (HAp) bone substitute was investigated. Uniaxially pressed compacts starting from these precursors were treated hydrothermally with 1 mol/L of ammonia solution at 200°C for various durations. XRD analysis revealed that α -TCP took 3 hours whereas β -TCP took 240 hours for complete transformation to HAp. The porosity of HAp block obtained from β -TCP was found to be lower than that of HAp block from α -TCP. Diametral tensile strength of HAp block from β -TCP showed a significantly higher value than that of HAp block obtained from α -TCP. It is therefore concluded that solubility of precursor affects the mechanical strength of the HAp block.

INTRODUCTION

Hydroxyapatite (HAp; $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$) have been used clinically to reconstruct bone defects since it shows excellent tissue compatibility and osteoconductivity¹.

Sintering is the most common method in fabricating HAp bone substitute. However, crystallinity of sintered HAp is extremely high¹. HAp in bone shows low crystallinity. Furthermore, it is known that HAp with lower crystallinity shows better osteoconductivity². HAp block with low crystallinity can be fabricated through phase transformation using thermodynamically unstable precursor based on dissolution-precipitation reaction by hydrothermal treatment³. For the dissolution-precipitation reaction, one requirement for the precursor is to have a moderate solubility when compared to the final block product. Due to the instability of the precursor, it is dissolved in aqueous solution and supply ions that are required for the precipitation of the final product³. Precursors with high solubility will dissolve faster while precursor with low solubility will dissolve slower. High solubility of precursor will cause rapid precipitation of crystals and may result in a mismatch crystal arrangement and/or more porosity. In contrast, precursor with low solubility will dissolve slower and thus the precipitated crystals may be arranged closely with less porosity.

The purpose of this study is to evaluate the effect of precursor's solubility on the mechanical property on the HAp block through dissolution-precipitation reaction. For the precursor selection, alpha-tricalcium phosphate (α -TCP; $\alpha\text{-Ca}_3(\text{PO}_4)_2$) and beta-tricalcium phosphate (β -TCP; $\beta\text{-Ca}_3(\text{PO}_4)_2$) were employed as the precursors due to the same chemical composition but of different solubility. α -TCP has been reported to have higher solubility in aqueous solution when compared to β -TCP⁴.

MATERIALS AND METHODS

Preparation of α -TCP and β -TCP blocks

Commercially obtained calcium hydrogen phosphate dihydrate (DCPD; $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$, Wako, Osaka, Japan) and calcium carbonate (Calcite; CaCO_3 , Wako) were mixed with 100 ml of distilled water in 2:1 molar ratio so that the Ca/P molar ratio would be 1.5. The mixing was done using rotary pestle and mortar for 24 hours. After that, the mixture was dried in a 60°C oven (DO-450FA, As One Corp., Osaka, Japan) for 24 hours and then crushed into powder form. The powder was then pressed

uniaxially with an oil press machine (Riken Power, Riken Seiki, Tokyo, Japan) at 5 MPa pressure. The blocks were then sintered at 800°C in a furnace (SBV-1515D, Motoyama, Osaka, Japan) for 12 hours to allow homogenous composition of calcium and phosphate ions. The sintered blocks were then again crushed into powder form followed by grinding in a planetary micro mill (Fritsch, Idar-Oberstein, W. Germany). After grinding, the powder was pressed again with an oil press machine at 5 MPa pressure to obtain a block-type specimen 6 mm in diameter and 3 mm in thickness.

To obtain α -TCP block, the blocks were sintered at 1250°C in a furnace and kept for 4 hours then quenched to room temperature to avoid α to β phase transformation during cooling. To obtain β -TCP block, the blocks were sintered at 1100°C and kept 4 for hours followed by quenching to room temperature. The heating rate used was 10°C/min.

Hydrothermal Treatment

The α -TCP and β -TCP blocks were subjected to hydrothermal treatment with 1 mol/L of ammonia (NH₃; Kanto Chemical Co., INC., Tokyo, Japan) solution. One α - or β -TCP block were immersed in 30 ml of NH₃ solutions and placed in hydrothermal vessel (Shikoku Rika Co. Ltd, Kochi, Japan) which consisted of a Teflon[®] inner vessels with stainless steel jacket. The hydrothermal vessels were kept at 200°C in a drying oven for various durations. After the hydrothermal reaction, the blocks were removed from the solution, washed 20 times with distilled water to remove NH₃ solution and dried at 60°C for 24 hours.

X-Ray Diffraction Analysis

For compositional analysis, the specimens were characterized by powder X-ray diffraction, XRD (D8 Advance A25 Bruker AXS GmbH, Karlsruhe, Germany) using counter-monochromatic CuK α radiation generated at 40 kV and 40 mA.

Porosity Measurement

The bulk density of the α -TCP and β -TCP blocks before and after hydrothermal treatment was calculated based on the weight and volume. To measure the porosity, the relative density of the blocks was calculated based on their bulk densities and theoretical densities of α -TCP (2.86 g/cm³), β -TCP (3.07 g/cm³) and HAp (3.14 g/cm³) as shown in equation 1. The total porosity of the block was then defined as in equation 2. Total porosity was the mean value of at least 6 blocks.

$$\text{Relative density (\%)} = \text{Bulk density} / \text{Theoretical Density} \times 100\% \quad (1)$$

$$\text{Total porosity (\%)} = 100 (\%) - \text{Relative density (\%)} \quad (2)$$

Mechanical Strength Measurement

Mechanical strength of the specimens was evaluated in terms of diametral tensile strength (DTS). The specimens were tested using a universal testing machine (AGS-J, Shimadzu Corporation, Kyoto, Japan) by crushing it at a crosshead speed of 1 mm/min. The DTS values used were average of at least 8 specimens. For statistical analysis, one-way factorial ANOVA and Fisher's PLSD method as a post-hoc test were performed using KalcidaGraph 4.0.

Scanning Electron Microscope

Morphology of the fractured surface was observed using scanning electron microscope, SEM (S-3400N, Hitachi High Technologies Co., Tokyo, Japan) at an accelerating voltage of 10 kV. The fractured surface was coated with gold prior to SEM observation.

RESULTS AND DISCUSSION

Porosity of both α -TCP and β -TCP blocks prepared by sintering methods was approximately 10%. Fortunately, sintering temperature and resulting phase caused almost no effect on the porosity of the precursor. After hydrothermal treatment at 200°C in 1 mol/L NH_3 solution, both α -TCP and β -TCP blocks were transformed to HAP blocks. However, the length of time required for the complete transformation to apatite was different up to the precursors. In other words, the β -TCP block needed longer time, 240 hours, to obtain single phase HAP. In contrast, α -TCP required only 3 hours to obtain single phase HAP.

SEM observation demonstrated different feature after the hydrothermal treatment. Before hydrothermal treatment, both α -TCP and β -TCP block showed smooth surface typical for sintering process. However, needle-like crystals interlocked each other after hydrothermal treatment. It should be noted that the crystals shape and arrangement were different based on the precursors i.e. α -TCP or β -TCP as shown in figure 1. On the surface of HAP block fabricated from α -TCP, many small crystals were formed while the crystals formed were large in the case of β -TCP. It is observed that the HAP crystals from α -TCP were loosely attached with obvious porosity. In contrast, the HAP crystals from β -TCP were arranged closely to each other with no obvious porosity. The difference in crystal morphology is thought to be caused by the effect of precursor solubility. During hydrothermal treatment, dissolution-precipitation reaction would occur and this leads the compositional transformation from TCP to HAP without changing the macroscopic structure. However, rate of dissolution is thought to affect the precipitation process. When α -TCP is used as the precursor, shorter time is required for the solution to reach critical supersaturations with respect to apatite when compared to that of β -TCP since the solubility of α -TCP is higher than β -TCP. Thus, structural mismatch due to the weak interactions between the nuclei might inhibit crystals arrangements and less ordered crystal structures were formed. For β -TCP as the precursor, a more ordered crystals structures were formed since the low solubility creates slower time to reach supersaturations with respect to apatite⁵. This structural mismatch results in the higher amount of porosity in HAP block from α -TCP compared to HAP block from β -TCP.

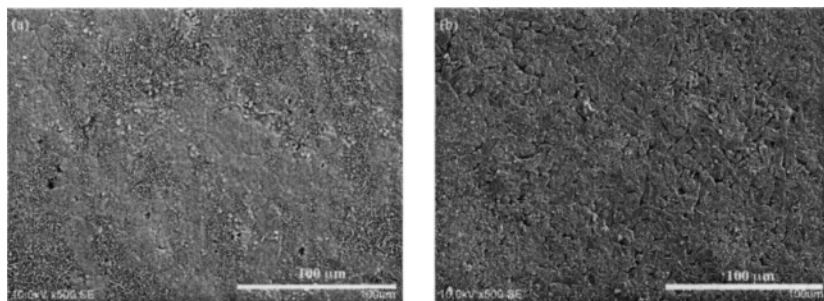


Figure 1. SEM on the surface of (a) HAP from α -TCP (b) HAP from β -TCP

The porosities of HAp block was $17 \pm 0.9\%$ and $14 \pm 0.6\%$ when α -TCP and β -TCP were used as precursors, respectively ($p < 0.05$).

The DTS value of HAp block obtained from β -TCP and α -TCP based on hydrothermal treatment in NH_3 solution at 200°C for 240 hours and 3 hours were 17 ± 2.8 MPa and 11 ± 1.15 MPa, respectively ($p < 0.05$). In other words, HAp block fabricated from β -TCP showed higher DTS value when compared to the value obtained from HAp block fabricated from α -TCP. The high DTS value of HAp block fabricated from β -TCP is thought to be caused by the less porosity. The relationship between the mechanical strength and porosity is well expressed by equation 3.

$$S = S_0 \exp(-bP) \quad (3)$$

where S is the observed mechanical strength of the porous material, S_0 is the ideal mechanical strength when there is no porosity, P is the porosity, and b is the empirical constant. In this equation, it is clear that less pore is the key for higher mechanical strength⁶. Further study is awaited based on the initial findings obtained in this preliminary study.

CONCLUSION

In this study, it was found that β -TCP which has low solubility when compared to α -TCP transformed to HAp with higher mechanical strength. Therefore it is concluded that the selection of precursors with suitable solubility is an important factor in determining the final mechanical property of the HAp bone substitute formed based on dissolution-precipitation reaction.

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