Basic Properties of Starfish Bone and Its Phase Transformation Reaction in Phosphate Salt Solution

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Introduction: A marine coral, which is porous aragonite-type calcium carbonate, has been received much attention as bone filler by itself in dental and orthopedic fields to reconstruct bone defects [1]. And furthermore, calcium carbonate was also documented to be a precursor material to prepare apatitic bone filler. When the coral calcium carbonate is hydrothermally treated with phosphate salt solution, it transforms into apatite without any structural changes. This is called coralline apatite and widely used as bone substitutes in the United States [2, 3]. Although coralline apatite is one of ideal bone substitutes with similar chemical composition and porous structure to human bone, there are limitations of collection quantity, shape, pore size, etc. Therefore, alternative calcium carbonate source for apatite bone substitute has been awaited in these days. In order to solve these problems, a preparation of artificial calcium carbonate must be one of useful methods. Ishikawa *et al*. previously reported that calcite blocks could be prepared at an ambient condition by exposing calcium hydroxide compacts to carbon dioxide [4, 5]. They also succeeded to prepare calcite porous bodies from calcium hydroxide by reaction sintering method using polyurethane foam as a template [6]. These synthetic calcium carbonates are thought to be promised source materials for apatite. However, it still important to find other calcium carbonate from nature due to its excellent structure. To explore calcium carbonate source from nature, the present study focused on starfish bone because the starfish is constructed from single crystals of porous calcium carbonate combined by some proteins. The chemical and physical properties of calcium carbonate granules from starfish were analyzed and the hydrothermal treatment of the calcium carbonate granules was done to investigate its transformation reaction to apatite. Feasibility of starfish bone to be a porous carbonate apatite bone substitute was studied from the perspective of materials science.

Methods: Patiria Pectinifera, a kind of starfish, was used in this study. In order to remove the inter-granule proteins, the starfish was soaked in 1 M NaOH aqueous solution overnight and rinsed with distilled water. After drying at 60°C, physical and chemical properties of starfish bone granules were analyzed as follows. The structure of the starfish bone granules were observed under a scanning electron microscope (SEM) equipped with an energy dispersive X-ray analyzer (EDX) after Au-Pd sputter coating. Inorganic phase of starfish bone was characterized by X-ray diffractometer (XRD). The starfish bone granules were also dissolved into 1 M HCl aqueous solution and analyzed by atomic absorption flame emission spectrophotometer to calculate their Mg content. For the compositional transformation of starfish bone to carbonate apatite, the hydrothermal treatment was done. Starfish bone granules were immersed in 1 M Na_2HPO_4 aqueous solution in Teflon vessel with stainless-steel jackets, and kept at 200°C for various periods up to 48 hours. After the hydrothermal treatment, the granules were characterized by XRD.

Results: Starfish bone granules were irregular shaped granules with 1-5 mm in size and they had interconnected porous structure with approximately 20 μm of pore size. From the results of compositional analysis based on XRD and EDX, starfish bone was calcium carbonate containing Mg. The content of Mg in starfish bone analyzed by atomic absorption spectroscopy was approximately 3 wt%.

After hydrothermal treatment in phosphate salt aqueous solution, starfish derived calcite was transformed to apatite. The mechanism of this compositional transformation was based on dissolution-precipitation reaction the same as that previous reports about the preparation of carbonate apatite from calcite precursor [6]. Namely, calcite, which is unstable phase thermodynamically in phosphate salt aqueous solution, dissolved and released calcium and carbonate ions into surrounding solution. This resulted in supersaturated environment with respect to apatite and precipitated as apatite involving calcium and phosphate ions.

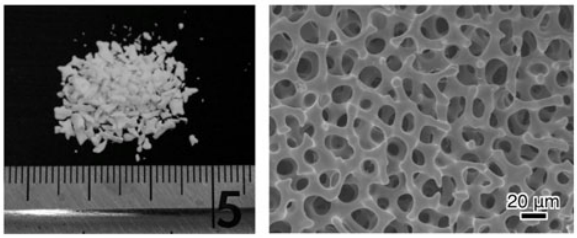

Fig. 1. Morphologies of starfish bone granules. (Left: Macroscopic image; Right: SEM image)

Conclusions: Starfish derived calcium carbonate was Mg containing calcite with fully interconnected porous structure. These calcite porous granules could be transformed to apatite based on dissolution-precipitation process. Therefore, it was concluded that starfish derived calcium carbonate could be a candidate of source material for apatite bone substitute.

References:

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