

Novel Bioceramics of Calcium Phosphates Composed of Rod-shaped Particles

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Abstract: β -Tricalcium phosphate (β - $\text{Ca}_3(\text{PO}_4)_2$; β -TCP) is one of the most biocompatible materials with human bones and teeth. The difference in microstructure has a large effect on the reaction of β -TCP *in vivo*. Therefore micro-pores, as well as macro-pores, must be controlled for porous material design, although the size of micro-pores is too small for cells.

In this paper, porous granules of β -TCP with micro-pores of about 0.1 mm in size were prepared from porous hydroxyapatite ($\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$; HA) granules with calcium deficient composition synthesized by hydrothermal method. The β -TCP granules with about 40 %-60 % porosity were composed of rod-shaped particles of about 10-20 mm in length. Rod-shaped particles were locked together to make micro-pores, and the size of micro-pores formed by tangling of rod-shaped particles was about 0.1-0.5 mm. The particle size, shape, and the micro-pore size were controlled by our unique method.

Key words: calcium phosphate, β -TCP, hydroxyapatite, bioceramics, hydrothermal

Introduction

Porous materials of β -TCP have been known to be osteoconductive and biodegradable¹⁾. In addition, the authors reported that micro-pores of β -TCP with about 0.1-0.5 mm in size were significantly important for bio-resorption in bones²⁾, therefore micro-pores, as well as macro-pores, must be controlled for porous material design, although the size of micro-pores is too small for cells. The present paper deals with the preparation of novel porous β -TCP granules composed of rod-shaped particles with designed microstructure, especially in micro-pores.

Materials and Methods

Powders of α -tricalcium phosphate (α - $\text{Ca}_3(\text{PO}_4)_2$; α -TCP) and gelatin were used as the starting material. The aqueous slurry of α -TCP with gelatin was prepared. The slurry of α -TCP / gelatin was dropped into stirring vegetable oil at 70 °C, and then the oil was cooling down at 4 °C with keeping stirring. These granules were washed with ethanol, and then they were filtered and dried in air. To remove gelatin and to keep the crystal phase of α -TCP, they were heated at 1200 °C for 5 min, and then set in a 105 cm³ autoclave with 10 cm³ of water. The samples were exposed to vapor of water at the temperature from 40-160 °C under saturated vapor pressure for 10 h, and then the samples were heated at 900 °C for 3 h in air for preparation of β -TCP.

The produced phases were identified by powder X-ray diffractometry with graphite-monochromatized CuK α radiation, operating at 40 kV and 20 mA (XRD; Geiger flex 2027, Rigaku, Japan). The samples were dissolved in nitric acid of 0.1 mol.dm⁻³, and then the chemical composition of them was analyzed by inductively coupled plasma spectrometer (ICP-MS; Seiko Instruments, SPQ 9000, Japan). The microstructure of specimens was observed by scanning electron microscope (SEM; JEOL, JSM-T300, Japan). Pore volume and distribution of pore diameter were measured by mercury intrusion porosimetry (MIP; Carlo Elba, Porosimeter 2000, Italy). Specific surface area was measured by using BET method.

Results and Dissociation

The size of spherical particles of α -TCP with gelatin was depended on the stirring rate of vegetable oil and the viscosity of slurry. After heating at 1200 °C in air, porous spherical α -TCP granules were obtained. After hydrothermal treatment, α -TCP was changed into HA composed of rod-shaped crystals³⁾.

HA was formed at the temperatures above 40 °C, and then no phases other than HA were revealed by XRD for the samples treated at the temperatures above 105 °C. The produced HA was not stoichiometric HA, that was calcium deficient HA. In general, chemical formula of calcium deficient HA is described as follows: $\text{Ca}_{10-x}(\text{HPO}_4)_x(\text{PO}_4)_{6-x}(\text{OH})_{2-x}\cdot n\text{H}_2\text{O}$. The authors reported that composition of this apatite could be controlled⁴⁾. The Ca/P ratio of the samples increased from 1.50 to 1.63 with increasing treatment temperature, but the Ca/P ratio of the samples was lower than that of stoichiometric HA (stoichiometric Ca/P=1.67).

Porous HA granules prepared at the temperatures below 80 °C were composed of irregular shaped HA particles. In the contrast, the homogeneous porous structure was observed for the samples treated at the temperatures above 105 °C. Porous HA granules prepared by hydrothermal treatment at 105 °C were composed of rod-shaped crystals elongated along the *c*-axis⁵⁾. The HA crystals were about 5 mm in length at 105 °C, about 10 mm at 120 °C and about 10-20 mm at 160 °C. Rod-shaped crystals were locked together to make micro-pores. The diameter of micro-pore was 0.1-0.5 mm in size. The porosity and the size of micro-pore increased slightly with increasing temperature of the hydrothermal treatment.

Calcium deficient HA tends to decompose easily into tricalcium phosphates by heating in comparison with stoichiometric HA⁶⁾. Thus, porous granules of β -TCP were obtained from the porous granules of calcium deficient HA with Ca/P ratio of 1.50 by heating them at 900 °C for 3 h in air. The β -TCP granules with about 40-60 % porosity had almost the same micro-structure in comparison with the HA granules before heating. The β -TCP granules were composed of rod-shaped particles with about 10-20 mm in length (Fig.1), and it had almost same porosity as the samples before heating. Specific surface area of β -TCP granules prepared

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hydrothermal treatment at 160 °C and then sintering at 900 °C was about $7 \text{ m}^2 \cdot \text{g}^{-1}$ by BET measurement. The mean diameter of micro-pore of β -TCP granules was slight larger than that of HA granules, the value was about 0.2 mm in size. The granules of β -TCP were harder than HA because of sintering which made bonding among particles.

Porous β -TCP with much amount of micro-pores prepared in this study should be more bio-degradable than the conventional materials. These porous granules must be suitable for the bone graft material and the scaffold of cultured bone. It is considered that the implant *in vivo* is probably first coated with plasma proteins and blood coagulation materials before cells adhesion take place, therefore micro-pores must effect the osteointegration process because such pores are similar in size to that of proteins. The micro-pores must make the protein adhesion to this materials surface⁷⁾.

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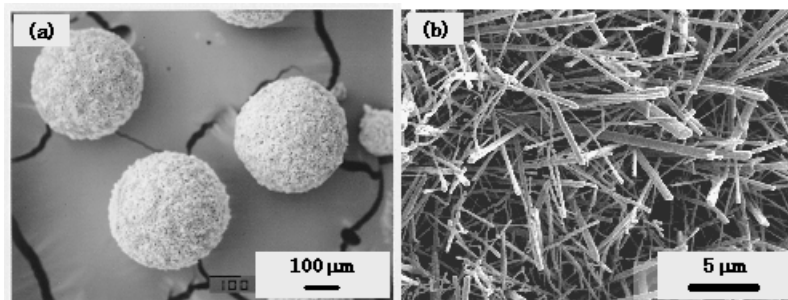


Fig.1 SEM image of β -TCP granules composed of rod-shaped particles, (a) x100 and (b) x3,000.