

Conversion of sea urchin spines to Mg-substituted tricalcium phosphate for bone implants

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Abstract

The skeleton of sea urchin spines is composed of large single crystals of Mg-rich calcite, which have smooth, continuously curved surfaces and form a three-dimensional fenestrated mineral network. Spines of the echinoids *Heterocentrotus trigonarius* and *Heterocentrotus mammillatus* were converted by the hydrothermal reaction at 180 °C to bioresorbable Mg-substituted tricalcium phosphate (β -TCMP). Due to the presence of Mg in the calcite lattice, conversion to β -TCMP occurs preferentially to hydroxyapatite formation. The converted β -TCMP still maintains the three-dimensional interconnected porous structures of the original spine. The main conversion mechanism is the ion-exchange reaction, although there is also a dissolution–reprecipitation process that forms some calcium phosphate precipitates on the surfaces of the spine network. The average fracture strength of urchin spines and converted spines (β -TCMP) in the compression tests are 42 and 23 MPa, respectively. In vivo studies using a rat model demonstrated new bone growth up to and around the β -TCMP implants after implantation in rat femoral defects for 6 weeks. Some new bone was found to migrate through the spine structural pores, starting from the outside of the implant through the pores at the edge of the implants. These results indicate good bioactivity and osteoconductivity of the porous β -TCMP implants.

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1. Introduction

The regeneration potential of human bone is limited in the cases of repair of large bone defects, such as those associated with comminuted fractures or bone tumor resection. In most cases, autogenous and allogenic bones are used as bone grafts. However, the amount of autogenous and allogenic bones that can be collected is severely limited. Furthermore, there is a risk of donor site morbidity for autografts, and transmission of infection for allografts. Therefore, synthetic bone graft materials, such as calcium phosphate ceramics, cements and different types of

polymers and composites, have been widely developed instead of autografts and allografts [1–5].

Based on observed tissue response, synthetic bone-graft substitutes can be classified into: inert (e.g. alumina, zirconia), bioactive (e.g. hydroxyapatite, bioactive glass) and resorbable substitutes (e.g. tricalcium phosphate, calcium sulfate) [3]. Of these, resorbable bone-graft substitutes are preferred for bone defect filling because they can be replaced by new natural bone after implantation. Beta-tricalcium phosphate ($\text{Ca}_3(\text{PO}_4)_2$, β -TCP) ceramic, as an example, is one of the most used bone substitute materials, due to its good biocompatibility, chemical stability and resorbability in vivo [6–11]. Preparation of pure phase β -TCP in aqueous systems under normal laboratory conditions (i.e. up to 100 °C and at atmospheric pressure) has not been reported. However, preparation of magnesium-

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substituted tricalcium phosphate $((\text{Ca},\text{Mg})_3(\text{PO}_4)_2$, β -TCMP) has been reported by precipitation or hydrolysis methods in solution [12,13]. These results indicate that the presence of Mg stabilizes the β -TCP structure. The incorporation of Mg also increases the transition temperature from β -TCP to α -TCP and decreases the solubility of β -TCP [14]. In addition, the incorporation of Mg in bone substitutes has been reported to promote new bone formation [3]. Porous β -TCMP structures may be ideally suited for bone scaffold structures, allowing both osteoconductivity for bone ingrowth and good resorbability for eventual full replacement by natural bone.

This investigation describes the preparation of porous β -TCMP by hydrothermal conversion of spines of the echinoids *Heterocentrotus mammillatus* and *Heterocentrotus trigonarius*, and their subsequent evaluation for biocompatibility. Hydrothermal conversion of natural calcium carbonate skeletons to hydroxyapatite (HAP) has been reported [15–19]. However, the spines mainly consist of large single crystals of Mg-rich calcite $((\text{Ca},\text{Mg})\text{CO}_3$) [15]. These single crystals usually have smooth, continuously curved surfaces that form a three-dimensional fenestrated mineral network [20]. After the hydrothermal conversion, the product is β -TCMP, rather than HAP, due to the substitution of Mg. The β -TCMP product still maintains the interconnected porous structure of the original spine. Evaluation of the suitability of these converted spines for bio-implant materials was then evaluated in terms of their mechanical properties as well as their biocompatibility via in vivo testing.

2. Materials and methods

2.1. Hydrothermal conversion

The synthesis is a hydrothermal conversion process using as starting materials: diammonium hydrogen phosphate $((\text{NH}_4)_2\text{HPO}_4$, Fisher Scientific) and spines of *H. trigonarius* and *H. mammillatus*, as shown in Fig. 1a. These spines are readily available in large quantities, and sea urchins can be grown in farms to maintain a steady supply of spines due to the ability of these echinoids to regenerate. The spines used here were cut into cylindrical samples

(~ 10 mm diameter \times 6 mm long) (see Fig. 1b), then cleaned with deionized water and placed in an autoclave. The autoclave was filled with a specified concentration of $(\text{NH}_4)_2\text{HPO}_4$ solution, sealed and heated at different temperatures, from 180 to 240 °C, for different period of time. In these experiments, the concentration of $(\text{NH}_4)_2\text{HPO}_4$ solution ranged from 0.1 to 0.2 g ml⁻¹.

2.2. Phase analysis

Sample phases were identified by powder X-ray diffraction (XRD) on a Rigaku Rotaflex X-ray diffractometer using Cu K α radiation ($\lambda = 1.5418$ Å). The diffractometer was operated at 40 kV and 100 mA at a 2θ range of 20–60° with a step size of 0.02°. The lattice constants of the Mg-calcite phase in the XRD pattern were calculated with MDI Jade7 software. Samples for XRD were prepared by grinding the spines with a mortar and pestle, either before or after hydrothermal conversion. By grinding the whole converted spine to homogeneous powder, bulk XRD of the powder can be performed to verify complete conversion of the spines from Mg-substituted calcite to β -TCMP.

2.3. Scanning electron microscopy

The morphology of the structures was studied by scanning electron microscopy (SEM) using a Phillips XL20. The elemental compositions of the products were qualitatively identified by energy dispersive X-ray spectroscopy (EDS) in the SEM. EDS mapping of magnesium, calcium and phosphorous were performed for the tissue samples after 6 weeks' implantation. For EDS mapping, the tissue samples were mounted in epoxy, polished and then coated with carbon for elemental mapping.

2.4. FT-IR analysis

Transmission infrared spectroscopy was performed by the KBr pellet method, using a Fourier transmission infrared spectrometer (FT-IR, Nicolet 550) to determine the various functional groups in the spine and converted spine samples. The specimen powder was ground in an agate mortar and thoroughly mixed with spectroscopic grade

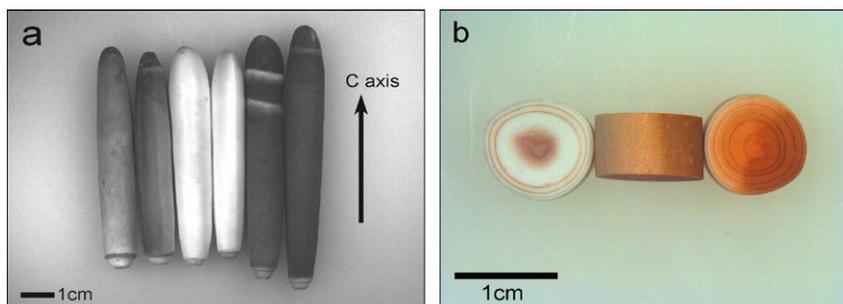


Fig. 1. Optical images of (a) original spines of *H. mammillatus* and *H. trigonarius*, and (b) spine samples for hydrothermal conversion and compression tests.

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