

Preparation of Calcium Phosphate Fibers for Applications to Biomedical Fields

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生体用リン酸カルシウムファイバーの調製

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High-strength β -calcium metaphosphate fibers for new applications to biomedical fields were successfully extracted from crystallized products of calcium ultraphosphate glasses by leaching with a dilute NaOH aqueous solution. The crystalline β -Ca(PO₃)₂ fibers obtained have high aspect ratios ranging from 30 to 120 with diameters of 1 to 5 μ m.

Key-words : Fibers, Calcium metaphosphate, Glass-ceramics, Biomaterials

High-strength and high-toughness biomaterials with low elastic modulus have been required for wide applications. In general, the mechanical properties of ceramic or polymer materials are effectively improved by introducing some fibers into the bulk materials. The fibers for toughening biomaterials should be mechanically strong, biocompatible and not toxic. We have been reported on calcium phosphate glasses and glass-ceramics for biomedical applications.¹⁾⁻⁵⁾ It has been reported that Ca(PO₃)₂ glass is nontoxic.¹⁾ The unidirectionally crystallized glass-ceramic having fiber-reinforced composite structure was successfully produced by reheating a calcium metaphosphate glass rod under a temperature gradient around the glass transition temperature.^{2),3)} This glass-ceramic composed of crystalline β -Ca(PO₃)₂ fibers with ca. 1 μ m diameter exhibits extremely high bending strength of 400-600 MPa and low Young's modulus of 70-120 GPa. This result implies that the β -Ca(PO₃)₂ fibers are of high-strength and flexibility. In addition, this glass-ceramic exhibits good biocompatibility.^{4),5)} Therefore, it is expected that this fiber can be used for new composite-biomaterials. In the present work we prepared the fibers by leaching the matrix phases from the glass-ceramics.

Griffith found that a melt in the Na₂O-CaO-P₂O₅ system is an advantageous medium for the long polyphosphate fibers to be grown.⁶⁾ The obtained fibers consist of an asbestiform NaCa(PO₃)₃ crystal.^{7),8)} It is pointed out, however, that straight Ca(PO₃)₂ fibers with high aspect ratios are better for reinforcement than NaCa(PO₃)₃ fibers which show fibrilla-

tion.⁸⁾ Long β -Ca(PO₃)₂ fibers can be prepared by reheating CaO-P₂O₅ glasses. Calcium phosphate glasses around the metaphosphate composition crystallize even at temperatures below the glass transition temperature (T_g). The crystal growth rate is extraordinarily high owing to "stress-induced crystallization",⁹⁾ while the nucleation rate is low around T_g .

Glass-ceramics converted from the calcium ultraphosphate glasses, of which molar ratio of CaO/P₂O₅ is slightly less than unity, consist of crystals such as β -Ca(PO₃)₂, Ca₂P₆O₁₇, and an ultraphosphate glassy phase.³⁾ The ultraphosphate phases are much poorer in chemical durability than fibrous β -Ca(PO₃)₂ crystals. Therefore, β -Ca(PO₃)₂ fibers will be able to be released preferentially from the matrix phase by aqueous leaching.

A batch mixture with CaO/P₂O₅=0.85 in molar ratio was prepared by using raw materials such as Ca(H₂PO₄)₂·H₂O and H₃PO₄. The mixture was melted in a platinum crucible at 1250°C for 2 h. The melt was poured onto a carbon plate and cooled to a room temperature. The resultant glass was reheated at 600°C for 48 h for the crystallization. The crystallized glass block was crushed into powder below 850 μ m using an alumina mortar. Distilled water (DW) or aqueous solutions of 0.1-0.5 N NaOH were used as leaching solutions to extract β -Ca(PO₃)₂ fibers. The 10 g of pulverised crystallized glass powder was put into a teflon container filled with 200 ml of the leaching solutions. They were stirred at 60-70°C for 4-72 h. The resultant products were filtrated and dried at 150°C in air.

Figure 1 shows change in pH values and the concentration of ions in the solution as a function of leaching time, where concentrations of Ca²⁺, P⁵⁺ and Na⁺ ions were determined by an inductively coupled plasma atomic emission spectroscopic method. The pH value decreased rapidly at the initial stage of leaching, which was caused by dissolution of phosphate ions from ultraphosphate glassy and crystalline phases. The Na⁺ ion concentration remained unchanged during the treatment; no precipitates containing Na⁺ ions were formed. X-ray diffraction analysis revealed that, after the treatment in 0.5 N

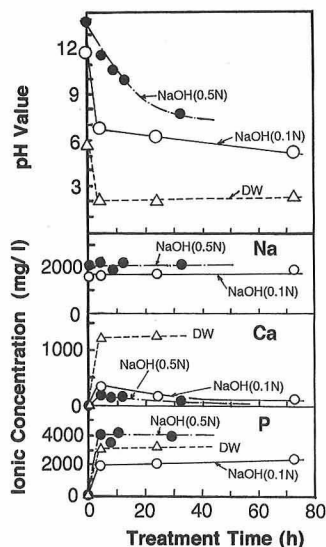


Fig. 1. Ionic concentrations and pH values in the solutions. DW: Treatment in distilled water. NaOH(0.1 N): Treatment in 0.1 N NaOH aqueous solution, NaOH(0.5 N): Treatment in 0.5 N NaOH aqueous solution.

NaOH solution for 32 h, the crystallized glass was completely dissolved out, resulting in the precipitation of hydroxyapatite. After the treatments in H₂O and 0.1 N NaOH solution, new precipitates were not detected. However, the changes in ion concentrations of the solutions imply the formation of a small amount of calcium phosphate compounds such as CaHPO₄ and hydroxyapatite.

Figures 2 and 3 show SEM photographs and X-ray diffraction patterns of the fibers, respectively. The fibers are straight in shape. The fibers obtained by the DW-treatment (denoted as Fiber-A) are larger in diameter compared to those by NaOH-treatment (denoted as Fiber-B). X-ray diffraction analysis showed that a small amount of Ca₂P₆O₁₇ crystals exist in Fiber-A; some fibrous crystals of β-Ca(PO₃)₂ are not released completely from the matrix phases. On the other hand, as shown in Figs. 2 and 3, Fiber-B is more successfully extracted from the matrix phases in comparison with Fiber-A. Fiber-B is of 1–5 μm diameter with high aspect ratios of 30–120.

It is expected that the fibers are available to bioabsorbable carriers which stabilize bone morphogenetic proteins or medicaments for treatments and to fillers for biomedical cushions such as a periodontal substitute. We have already fabricated the fiber-composite materials with porosity. These materials will be reported in a near future.

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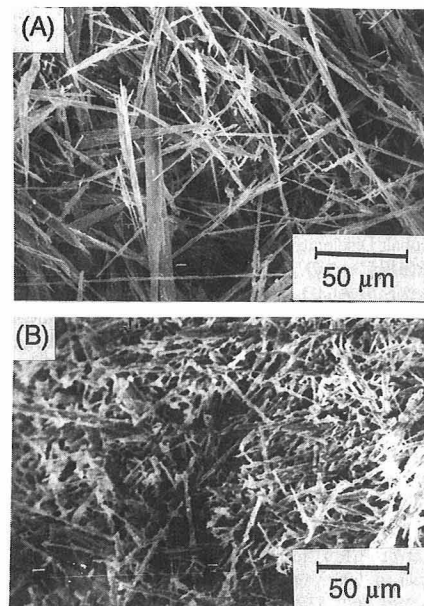


Fig. 2. SEM photographs of calcium phosphate fibers. (A) Fibers obtained by treatment in distilled water for 72 h, (B) Fibers obtained by treatment in 0.1 N NaOH aqueous solution for 72 h.

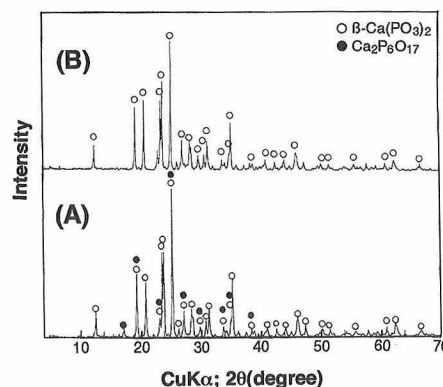


Fig. 3. X-ray diffraction patterns of the fibers. (A) Fibers obtained by treatment in distilled water for 72 h, (B) Fibers obtained by treatment in 0.1 N NaOH aqueous solution for 72 h.

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