Surface modification of calcium metaphosphate fibers

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β-calcium metaphosphate fibers having high aspect ratios of 10–120 with diameters of 2–10 μm show high strength and good biocompatibility. When the fibers are soaked in simulated body fluid at 37 °C, however, no calcium phosphate phase is newly formed on the fibers. In the present work, by treating the fibers at 70 °C with dilute NaOH aqueous solution, the surface phase was converted successfully into the orthophosphate phase that was in fine sizes and was adhered. After soaking the treated fibers in simulated body fluid at 37 °C for 30 days, a new calcium phosphate phase was precipitated. This was attributed to the surface phase modified using dilute NaOH. The treated fibers are expected to show bone-bonding ability, i.e. bioactivity.

1. Introduction

Calcium phosphate ceramics show high biological compatibility and safety in living tissues [1–4]. In our earlier work, calcium metaphosphate (β-$Ca(PO_3)_2$; denoted by CMP) crystalline fibers were developed [5, 6]. The CMP fibers have high aspect ratios ranging from 10 to 120 with diameters of 2 to 10 μm and are expected to have good biocompatibility. New types of composite materials for biomedical use have been synthesized using the CMP fibers [6–8]. Calcium phosphate ceramics containing CMP fibers with glassy phase as the matrix were prepared by a hot-pressing method; their mechanical properties such as high bending strength of $\approx$ 200 MPa and low elastic modulus of $\approx$ 45 GPa are relatively close to those of natural cortical bone [6, 7]. Porous materials with large porosity of $\approx$ 70% composed of the fibrous CMP skeleton were also successfully prepared by the sintering of the fibers: they differ from conventional porous ceramics in that very large strains of 20–30% are achieved prior to catastrophic failure [6, 8]. These results imply that the CMP fibers are of high-strength and flexibility.

Fibrous materials may be applicable also as fillers for bone repair. When materials with high aspect ratios are implanted in bone tissues, many spaces are formed between them. The fillers would be embedded by the high-convoluted growth of natural bone into the spaces. The CMP fibers may be available for such applications because of their biocompatibility and safety in the living body, to our knowledge by our private communications from animal tests using mice. If the fibers have bone-bonding ability, i.e. bioactivity, they would become possible for use in the application.

It was reported that when some bioactive glasses and ceramics are soaked in simulated body fluid (SBF), which is a tris-buffer solution with inorganic ion concentrations which are adjusted to be almost equal to those of human plasma, a new calcium phosphate phase is formed on their surfaces [9]. No phase is newly formed on the CMP fibers in SBF. In the present work, by modifying the surface of the fibers chemically, we could prepare high-strength fibers with the formation ability of the new calcium phosphate phase on them in SBF.

2. Materials and methods

Detailed preparation procedures of the CMP fibers from previous studies were followed [5–8]. A batch mixture with $45CaO \cdot 55P_2O_5$ (mol %) was prepared using starting materials such as $CaCO_3$ and H_3PO_4 (85% liquid). The mixture was melted in a platinum crucible at 1200 °C for 1 h and then a block of the glass was obtained by casting the melt onto a carbon plate. The glass was heated at 600 °C for 35 h to obtain the crystallized product containing fibrous CMP as a major phase and an ultraphosphate glassy phase as the matrix phase. After the crystallized block was crushed into pieces smaller than several millimeters, they were put into a glass beaker filled with 3 l of distilled water (DW) to dissolve the matrix phases at 70–80 °C. The extracted CMP fibers, which passed through a sieve with 300 μm aperture and were left on a sieve with 106 μm aperture, were gathered.

In the present work, the CMP fibers (10 g) were treated in 230 ml of 0.2 M NaOH aqueous solution for 5 h at 70 °C and subsequently the resulting products were filtrated and subsequently dried at 120 °C.

The fibers were soaked in 50 ml of SBF [9] (Ca^{2+}; 2.5, Mg^{2+}; 1.5, Na^+; 142.0, K^+; 5.0, Cl^-; 148.8, HCO_3^-; 4.2

and HPO_4^{2-}; 1.0 including trishydroxymethylaminomethane; 50 and HCl; 45.0, in mM) for 30 days at 37 °C.

The phases of these fibrous products before and after SBF-soaking were examined by X-ray diffractometry (XRD; Rigaku RAD-B system using Cu$K\alpha$; 40 kV, 20 mA) and laser Raman spectroscopy (JASCO NRS–2000 system using 514.5 nm of Ar-laser). Their morphologies were observed with a scanning electron microscope (SEM; JEOL JSM-6301F) incorporating X-ray microanalysis using energy dispersive spectrometry (EDS; Noran 673B with a Be-window).

3. Results and discussion

Fig. 1 shows SEM photos and Raman spectra of the CMP fibers before and after the NaOH treatment. Numerous grain-shaped products $\approx$ 20 nm in size are seen after the treatment. The surface of the fibers was covered completely with the products. By SEM observation of the face fractured by crushing the treated fibers, the thickness of the product layer was estimated to be 100–200 nm. The Raman spectrum of the original fibers shows peaks due to the PO_3 group [10, 11]. In the spectrum of the treated fibers, peaks at 960 and 1045 cm^{-1} due to the PO_4 group [12] appear. All XRD peaks of the treated fibers were assigned to those of a CMP crystalline phase: the peaks due to the products on the surface were not seen. In the EDS spectrum of the surface of the treated fibers, the peaks of Ca and P were seen. That is, the products consist of a calcium orthophosphate phase with relatively low crystallinity. The surface phase is suggested to be converted successfully into the orthophosphate phase due to the so-called ''dissolution-formation mechanism'': the surface of the CMP fibers is corroded by aqueous NaOH to be dissolved and subsequently the calcium orthophosphate phase with small solubility in alkali solutions is precipitated on the surface of the fibers using Ca^{2+} and HPO_4^{2-} ions dissolved in the solution. The detail elucidation of the mechanism is in progress.

A 0.1 g amount of the treated fibers was put into die of 8 mm diameter and was then pressed uniaxially for 10 min under a pressure of 200 MPa. Such pressing crushes ordinary glass fibers or calcium carbonate whiskers [13]. After removing the load, almost no fibers were found to be broken by SEM observation. It is suggested that the strength of the fibers is not degraded by the NaOH treatment. The high-strength CMP fibers with a calcium orthophosphate layer around their surface can be prepared by the NaOH treatment.

The original CMP fibers and the treated ones were soaked in SBF at 37 °C for 30 days. No products were formed on the original fibers. Fig. 2 shows SEM photos and a Raman spectrum of the NaOH-treated fibers after soaking in SBF. It can be seen that new products are precipitated tightly around the fibers. Intensities of the Raman peaks at 960 and 1045 cm^{-1} due to the PO_4 group are larger in comparison with those before the SBF-soaking as shown in Fig. 1(B-b). An EDS spectrum of the new products on the treated fibers showed that they consist of Ca and P. XRD peaks of the new products after the SBF-soaking did not appear: the newly formed calcium orthophosphate phase would also be low in the crystallinity as well as the layer phase on the treated fibers. The products on the surface of the NaOH-treated fibers may play a role of seeds for formation of the new calcium orthophosphate phase in SBF. This phenomenon may imply a possibility that the treated fibers show bioactivity in the living body. The NaOH-treatment in the present work is expected to be a simple, easy and new method for inducing bioactivity of non-bioactive materials containing calcium phosphates. *In vivo* tests using mice are in progress to clarify the bioactivity of the treated CMP fibers and the results will be reported in the near future.

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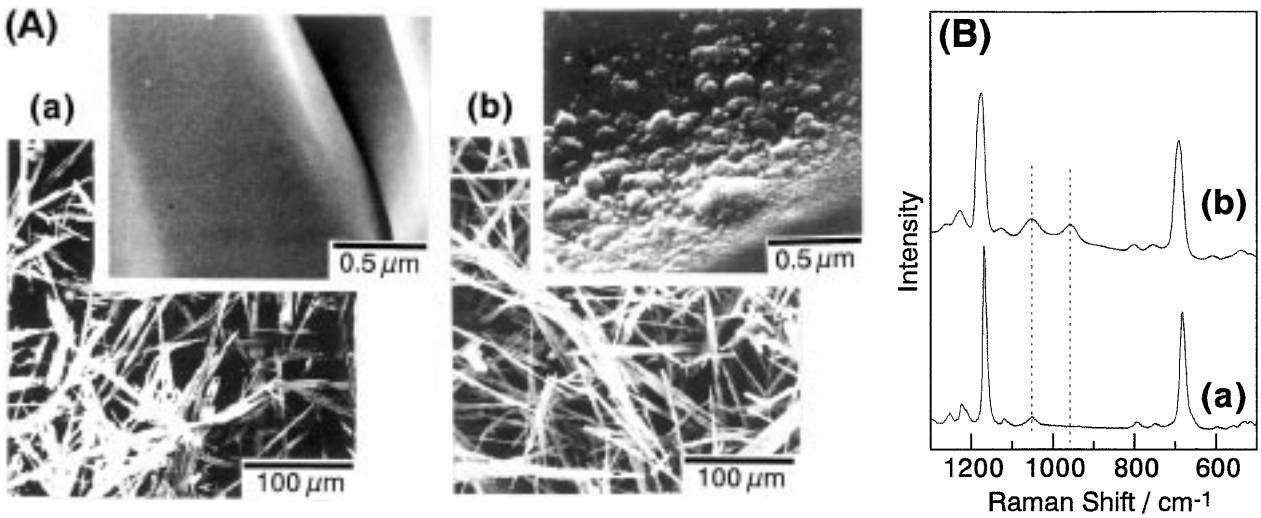

Figure 1 (A) SEM photos and (B) laser Raman spectra of calcium metaphosphate fibers before and after the treatment with 0.2 M NaOH for 5 h at 70 °C. The original fibers (a) and the treated fibers (b).

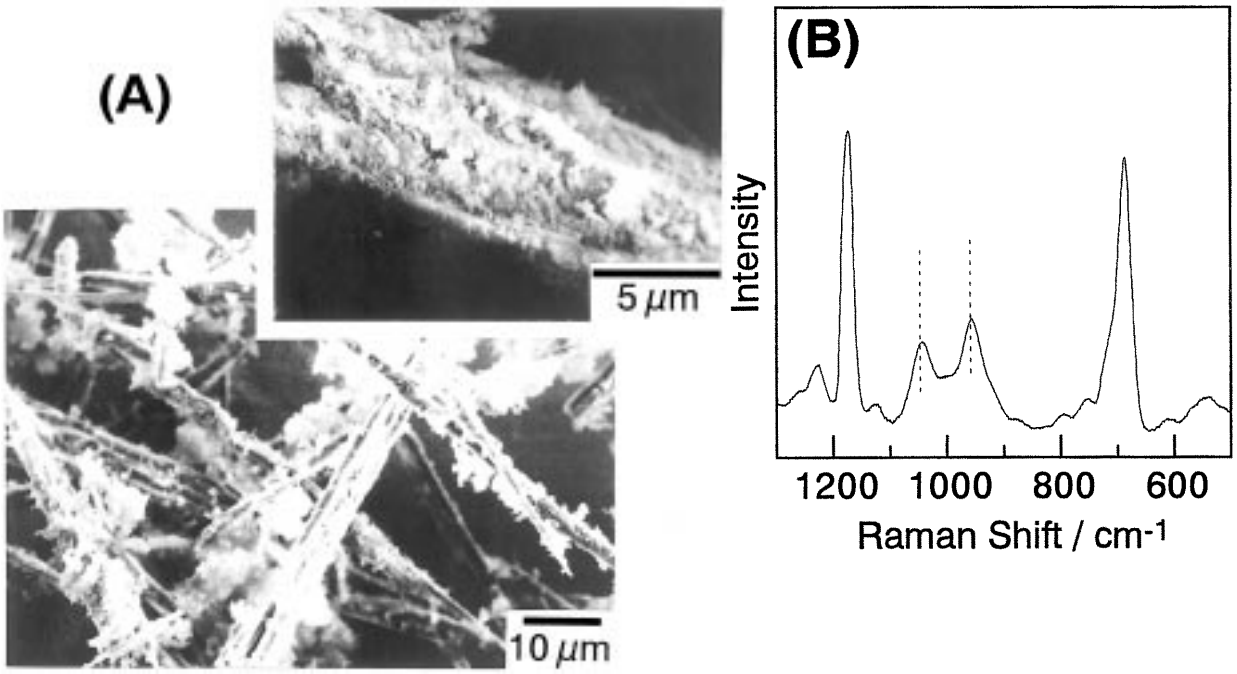

Figure 2 (A) SEM photos and (B) laser Raman spectra of the NaOH-treated fibers after soaking in simulated body fluid for 30 days at 37 °C.

References

1. M. JARCHO, J. F. KAY, K. I. GUMAER, H. P. DROBECK and R. H. DOREMUS, *J. Bioeng.* **1** (1976) 79.
2. L. L. HENCH and J. WILSON, *Science* **226** (1984) 630.
3. R. H. DOREMUS, *J. Mater. Sci.* **27** (1992) 285.
4. T. KITSUGI, T. YAMAMURO, T. NAKAMURA and M. OKA, *Biomaterials* **16** (1995) 1101.
5. T. KASUGA, A. ICHINO and Y. ABE, *J. Ceram. Soc. Japan* **100** (1992) 1088.
6. T. KASUGA, K. TSUJI, Y. OTA, Y. ABE, A. NIIMI and M. UEDA, in ''Proceedings of 8th International Symposium on Ceramics in Medicine, FL, November 1995'', edited by J. Wilson, L.L. Hench and D. Greenspan, (Pergamon, New York, 1995) p. 415.
7. T. KASUGA, Y. OTA, K. TSUJI and Y. ABE, *J. Am. Ceram. Soc.* **79** (1996) 1821.
8. Y. OTA, T. KASUGA and Y. ABE, *ibid.* **80** (1997) 225.
9. T. KOKUBO, *J. Non-Cryst. Solids* **120** (1990) 138.
10. R. K. BROW, D. R. TALLANT, S. T. MYERS and C. C. PHIFER, *ibid.* **191** (1995) 45.
11. J. KOO, B.-S. BAE and H.-K. NA, *ibid.* **212** (1995) 173.
12. K. C. BLASKESLEE, A. ROBERT and A. CONDRATE, *J. Am. Ceram. Soc.* **54** (1971) 559.
13. Y. OTA, S. INUI, T. IWASHITA, T. KASUGA and Y. ABE, *ibid.* **78** (1995) 1983.

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