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Manufacture and bioactivity of tough hydroxyapatite / nylon hybrid composites

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Abstract—The development of a new type of a hybrid HAP / nylon interpenetrating network composite is described. The key step in the manufacturing process of the hybrid material is the infiltration of melted ε-caprolactam into porous HAP and subsequent *in situ* polymerization. The porous HAP bodies were prepared from HAP powders of several morphologies via sintering processes at various temperatures. The effect of the respective pore characteristics, such as the volume fraction of open porosity and pore size distribution, on the microstructure of HAP/nylon hybrid composites is discussed. The mechanical behavior and some properties of the composites, i.e. fracture energy and *in vitro* bioactivity in simulated body fluid (SBF) are evaluated.

Keywords: Porous hydroxyapatite; sintering; nylon; infiltration; pore characteristics.

1. INTRODUCTION

Hydroxyapatite (HAP) and biocompatible glasses are useful bioceramics, which have been investigated for some decades. Especially, A-W glasses and bioglasses are already clinically applied as bone implantation, due to their superior bioactivity [1]. Contrarily, the usage of HAP ceramics for bone and teeth repairs is limited, because their mechanical properties are poorer than that of human bones, A-W glasses and bioglasses. For medical applications, biomaterials demand both good biocompatibility and mechanical properties over long periods. However, HAP with either a dense or porous microstructure suffers from insufficient fracture toughness and fracture energy (0.5–0.7 $\text{MPa}\,\text{m}^{1/2}$ and 1–2 J/m^2, respectively) [2]. This disadvantage of intrinsic properties hinders certain clinical and orthopedic applications of HAP [3]. Therefore, the development of bulk bioactive ceramics with improved fracture resistance is still needed. As mentioned, the improvement of mechanical

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*To whom correspondence should be addressed. E-mail: pezzotti@ipc.kit.ac.jp properties by the addition of a second phase, such as ceramics or metals whisker or platelet, and at the same time maintaining biocompatibility for clinical applications are the two fundamental issues for HAP-based composites. For example, although HAP coating by plasma spraying processes, etc. on Ti and its alloys or incorporation of metal Ti dispersion into HAP matrix are continually employed, there are still problems of biocompatibility [4, 5]. Furthermore, there have been reports on HAP ceramic composites dispersed with a ceramic phase. For example, it was reported that hot-pressed Al_2O_3-platelet reinforced HAP composites can reach a toughness of 2 MPa $m^{1/2}$ [6]. However, a strong improvement of fracture energy is difficult to achieve by dispersion of a ceramic phase into HAP matrix, because of the intrinsically low fracture toughness and fracture energy of ceramics.

A simple and economical approach to prepare biocompatible hybrid biomaterials is attempted in this paper, which is based on an infiltration process [7, 8]. Especially, polymer infiltration into porous HAP may be advantageous to fabricate high-performance composite biomaterials, because of the variety of polymers available, the low volume fraction of polymer, and their good mechanical properties, like tensile strength and elastic recovery. Here, *in situ* polymerization of ε-caprolactam to form nylon-6 into porous HAP is studied. In this approach, the improvement of fracture properties of HAP is based on the preparation of a porous HAP body, especially designed by the usage of anisotropic morphological HAP powder with high aspect ratio [9]. The first purpose of the present paper is to fabricate porous, structurally optimized HAP sintered bodies, i.e. with high open porosity in order to infiltrate the porous material up to its bulk. The second is to establish an optimized process for infiltration of nylon-6 polymer into this material. This approach implies that the volume fraction of the polymer is low. At this ratio, especially conventional methods like simply mixing HAP and nylon-6 would lead to granulates, rather than to cohesive materials. Finally, mechanical behavior and *in vitro* bioactivity in simulated body fluid (SBF) according to the method by Kokubo *et al.* [10] are evaluated.

2. EXPERIMENTAL PROCEDURE

Three kinds of HAP powder with spherical, ellipsoidal, and whisker-like morphology were used as a starting material. Spherical and ellipsoidal HAP powders were commercially available. Spherical HAP powder, with an average diameter of approximately 18 μm was granulated by spray drying a very fine HAP powder with a particle size of 20 nm. Ellipsoidal HAP had an average diameter of 0.3 μm and a length of 2–3 μm, resulting in an aspect ratio of 6–10. Whisker-like HAP was synthesized through the hydrolysis of tricalcium phosphate in a mixture of H_2O/iso-propanol system [11]. Whisker-like HAP had an aspect ratio of 20–30, an average length of 2–5 μm, and a diameter below 0.1 μm (see Table 1). Porous HAP bodies were prepared from the above three kinds of HAP. The powders were pressed in

Table 1.
Characteristics of hydroxyapatite powders*

	Diameter (μm)	Length (μm)	Aspect ratio	Specific surface area (m^2/g)
Whisker-like HAP	0.05–0.07	2–5	20–30	11
Ellipsoidal HAP	0.3	2–3	5	1.5
Spherical HAP	18	—	1	36

* Hydroxyapitite powders were purchased from Taihei Chemical Co., Nara, Japan.

a stainless-steel die under 5 MPa. These green compacts were sintered by a pressureless sintering method in air atmosphere at 800 to 1000°C and a heating rate of 5°C/min. HAP sintered bodies were cut, and the surfaces were ground by a diamond wheel and polished with diamond pastes. The porosity characteristics, such as pore size distribution, average and median pore-size values, were measured with a mercury porosimeter. Phase identification of samples was done by X-ray diffraction analysis. The microstructures of the sintered bodies were observed with a scanning electron microscope (SEM).

Porous sintered HAP bodies with various volume fractions of porosity were subjected to a vacuum chamber together with an excess amount of ε-caprolactam, 3% water and 2% of 6-aminohexanoic acid as an initiator. While applying a vacuum of 0.1 Pa, the monomer was heated until melting. Within one minute the caprolactam was sucked completely into the capillaries and pores of the sintered body. For polymerization, the chamber was heated up to 200°C for 18 h, while the pressure rose to 3×10^5 Pa. While cooling down the composite material, pressure was released to ambient conditions. Infiltrated samples were wholly covered with nylon-6 polymer. After polymerization, the samples were ground and the extra nylon removed. Samples were cut with a diamond blade and polished with diamond pastes.

Specimens of HAP/nylon hybrid composites for fracture tests were rectangular, with a dimension of $2 \times 3 \times 25$ mm. Fracture energy of the samples was measured with the single edge double-notched beam (SEDNB) method [12]. The notch was cut with a diamond wheel of 0.2 mm in thickness. A straight-through notch with a relative length of $a_0/w = 0.5$ was sharpened to a radius <10 μm. The span was 20 mm in a three-point bending test, while the cross-head speed was 0.1 mm/min. Load–displacement curves were recorded during stable crack propagation. Fractured surfaces of HAP/nylon hybrid composites after fracture tests were observed with a SEM.

3. RESULTS AND DISCUSSION

The relative density of green compacts from any powder was approximately 30–35% before sintering. HAP bodies from spherical powder showed a relative

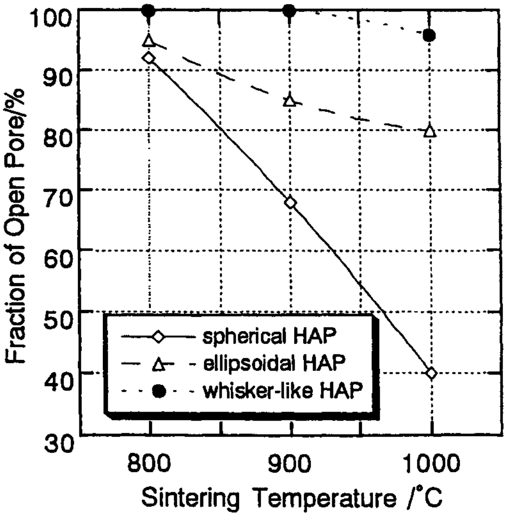

Figure 1. Variation of the fraction of open porosity/total porosity with the sintering temperature for HAP sintered bodies.

density of 40% at 800°C, 50% at 900°C and 58% at 1000°C. On the other hand, sintered HAP bodies from ellipsoidal HAP powder exhibited an almost constant relative density of 40–45% at 800–1000°C and 62% at 1100°C. The sintered bodies from whisker-like HAP powder exhibited a low relative density of 35% at 800–900°C and 40% at 1000°C, respectively. In the case of sintering whisker-like HAP powder, the porosity had the constant value of 35–40% with sintering temperature as well as in the case of sintered bodies from ellipsoidal powder, whereas samples sintered from spherical HAP showed a drastically decrease in porosity with sintering temperatures. These results show that the fraction of relative density and porosity is strongly dependent on the morphology of the respective starting powder. Figure 1 shows the fraction of open porosity/total porosity for all HAP sintered bodies prepared by the pressureless-sintering technique. The samples fabricated from whisker-like HAP powder at 800–1000°C hardly included any closed pores from the mercury porosimeter measurement, independent of sintering temperature. In the case of ellipsoidal powder, HAP bodies showed an open porosity fraction of 95% at 800°C, 85% at 900°C, and 80% at 1000°C. The fractions of open porosity for HAP prepared from spherical powder were approximately 68% at 900°C and 40% at 1000°C. Therefore, sintering of the highly anisotropic starting powder led to HAP bodies with the highest fraction of open porosity. The results of pore size distribution of sintered HAP prepared from three kinds of HAP powders are shown in Fig. 2. The pore size distribution of samples sintered from spherical HAP powder was very broad and below 0.1 μm, as shown in Fig. 2A. All HAP bodies from ellipsoidal HAP powder (Fig. 2B) showed the wide range of 0.1 to 0.5 μm in pore size distribution. These results were independent from sintering temperatures. On the contrary, HAP samples from whisker-like powder

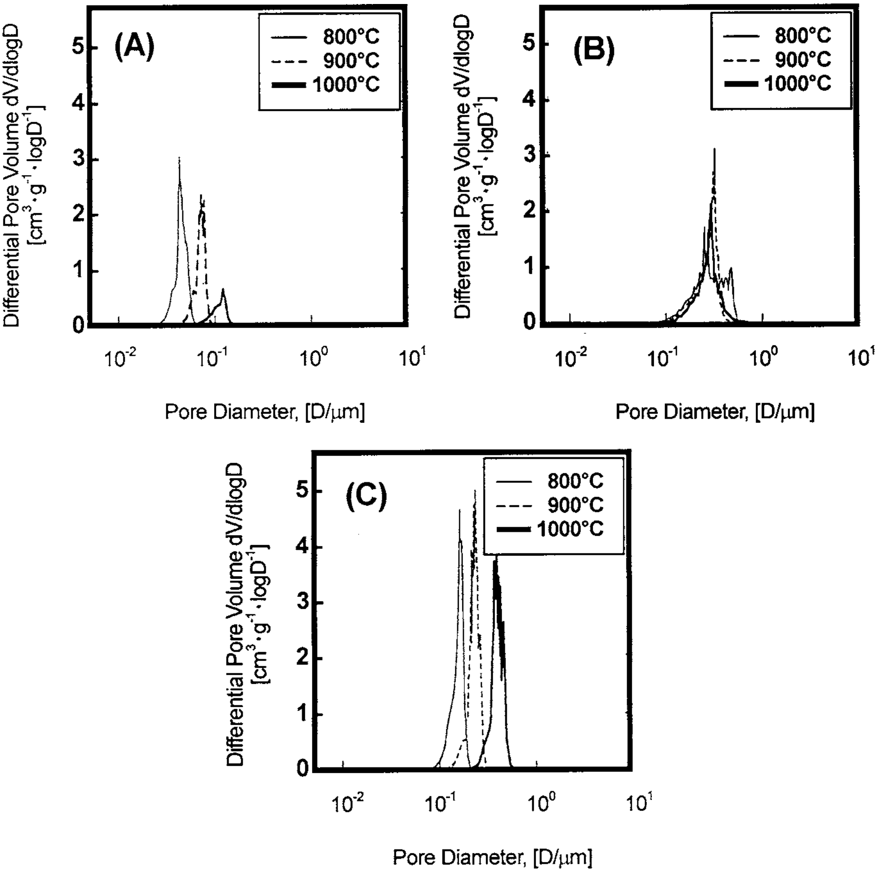

Figure 2. Pore size distributions of sintered HAP prepared from three kinds of HAP powders. (A) spherical HAP, (B) ellipsoidal HAP, (C) whisker-like HAP.

(Fig. 2C) showed a significantly broader distribution of pore size in comparison to HAP from spherical powder. Samples sintered at 800°C revealed pores with a diameter of 0.2 μm. In the case of samples prepared at 900°C, the pore diameter was in the range of 0.2–0.3 μm. At 1000°C, the pore diameter varied from 0.5 to 0.8 μm. Furthermore, it was found that the pore size distribution of HAP samples from whisker-like powder showed a significantly sharp distribution of pore size and possessed very large pore size, mainly in the range of 0.5 to 1 μm, compared to those from other starting powders. These pore characteristics of sintered bodies, fabricated from morphologically different HAP powders, suggest that using anisotropic morphological HAP powder with a high aspect ratio is useful for obtaining a porous HAP structure with a nearly perfect percolation, significantly sharp pore size distribution, and a large pore size. The microstructures of sintered HAP samples were evaluated by the observation of fracture surfaces by SEM. In the microstructure of HAP sintered from spherical powder at 800–900°C, no grain growth occurred during sintering. HAP sintered at 1000°C showed some

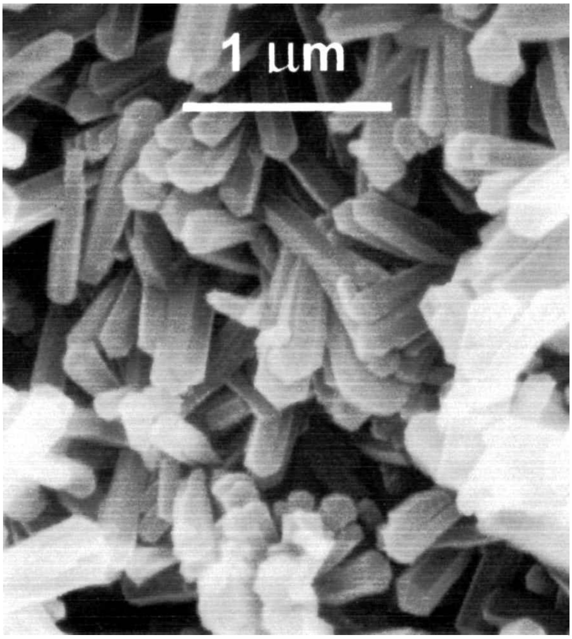

Figure 3. SEM micrograph, indicating grain growth after pressureless sintering of HAP at 1000°C.

grain growth up to approximately 300 nm in the average grain size. Samples fabricated from ellipsoidal HAP powder hardly exhibited significant grain growth and morphology change below 900°C. At 1000°C, a more spherical grain shape was confirmed. On the other hand, HAP treated by pressureless-sintering process at 800–900°C showed a finely whisker-like structure with no grain growth during sintering. At a sintering temperature of 1000°C some grain growth (Fig. 3) and thick whisker were contained, which imply an increase in the diameter of the whisker. Large open pores were clearly observed in a HAP skeleton prepared at 900°C. Infiltration of ε-caprolactam as a nylon precursor was performed into porous HAP bodies, sintered from the ellipsoidal HAP powder at 900 and 1000°C, followed by *in situ* polymerization. Figure 4 shows a typical microstructure of this hybrid composite as observed by SEM. From SEM observation, nylon-6 polymer was homogeneously dispersed inside the porous HAP matrix, although some pores were also observed. The measurement of relative density of these HAP/nylon hybrid composites suggested the presence of residual pores of approximately 5%.

Figure 5 shows the diagram of load (P) and load point displacement (u) for the hybrid nylon-infiltrated [13]. HAP composite, compared with that of monolithic HAP (95% of the relative density). The HAP showed a very brittle fracture behavior and did not show stable crack propagation in bending tests. The area under the load–displacement curve was computed and divided by twice the fracture surface area measured by SEM observation in order to evaluate the value of work of fracture (WOF). Hybrid nylon-infiltrated HAP composites from porous HAP

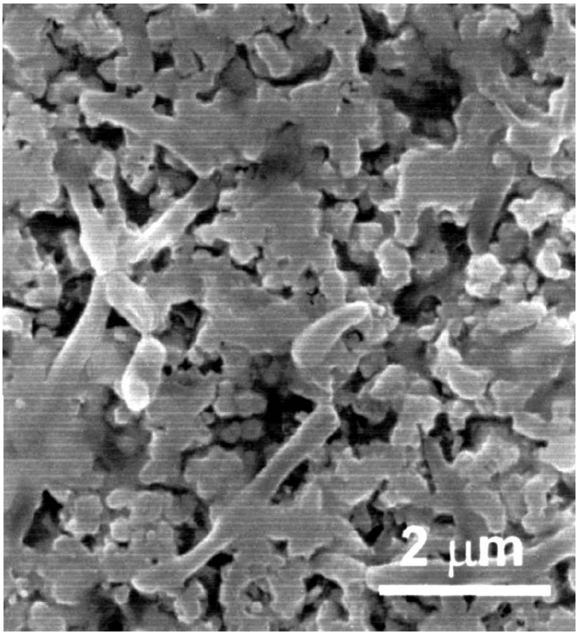

Figure 4. SEM observation of the microstructure of a HAP/nylon*6* hybrid composite: HAP derived from ellipsoidal powder after sintering at 900°C.

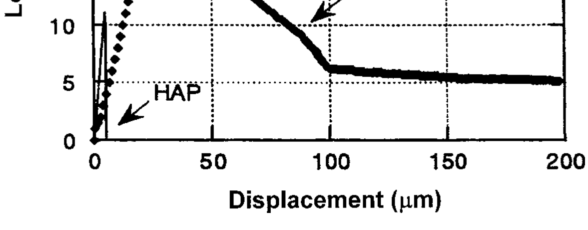

Figure 5. Load–displacement curve for HAP/nylon*6* hybrid composites.

sintered at 900°C and 1000°C exhibited fracture energies of 21 J/m^2 and 29 J/m^2, respectively. By contrast, the fracture energy of dense monolithic HAP was reported to be 1.0 J/m^2 [14]. The value of WOF for the HAP/nylon hybrid composites was significantly high, similar to that measured in earlier studies for bovine femur [15, 16]. This hybrid composite showed a rising R-curve behavior with crack extension, as shown in Fig. 6. The value of K_{I0} for the HAP/nylon hybrid composite ($K_{I0} = 0.9$ MPa m$^{1/2}$) was twice that of HAP ($K_{I0} = 0.4$ MPa m$^{1/2}$), which reached

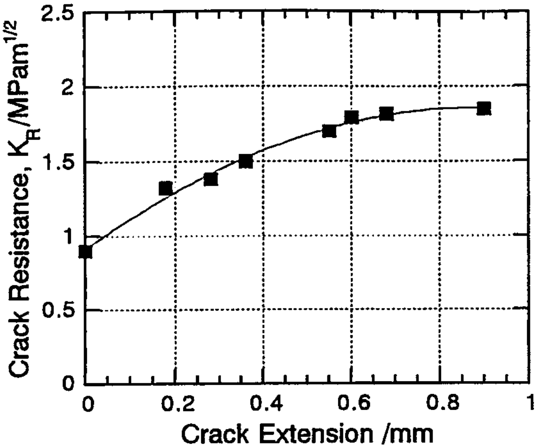

Figure 6. Relation of crack resistance and crack extension for HAP/nylon*6* hybrid composites.

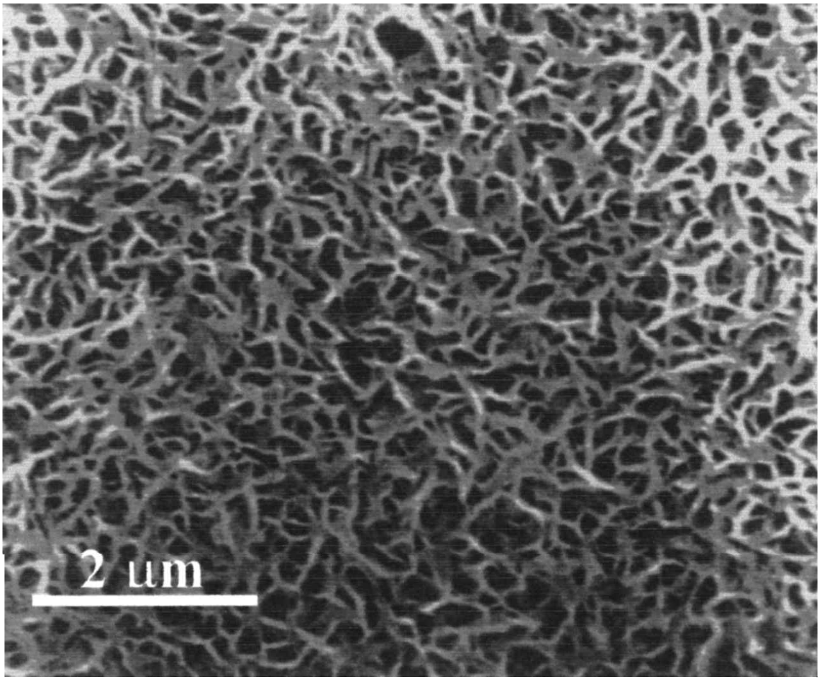

Figure 7. *In vitro* results after immersion in 1.0 SBF solution at 36.5°C for 14 days of a HAP/nylon*6* hybrid. Original HAP bodies were derived from ellipsoidal powder after sintering at 900°C.

a value of 1.85 MPa m$^{1/2}$ after a crack extension of approximately 400 μm in the hybrid composite specimen.

Our pronounced interest in the application of HAP/nylon hybrid composites for medical purposes prompted us to investigate the biocompatibility of these materials. Even though after 1 day in 1.0 SBF solution the anticipated initial fine HAP crystals were not formed on the surface, SEM observation proved that the composite was coated completely with a thick (μm-scale) HAP layer after several days. Figure 7 shows the *in vitro* results of the HAP/nylon hybrid after immersion at 36.5°C for 14 days. This HAP precipitation homogeneously covered the whole surface of the composite. Image processing of SEM micrographs showed that, in a rough approximation, the area fraction of precipitate covers more than 60% of the hybrid sample. This is especially a higher percentage than the HAP surface fraction of the original HAP/nylon-6 composite, where approx. 50% of the surface was covered by nylon-6. Furthermore, the precipitation was composed of a sponge-like structure, according to observation at higher magnification. Therefore, the results of the SBF-test reveal an excellent bioactivity of HAP/nylon hybrid composites.

4. CONCLUSION

Design of pore characteristics of HAP matrix was attempted and a well-developed pore-channel sponge-like structure could be obtained. Then, through *in situ* polymerization of infiltrated ε-caprolactam, a polymeric secondary phase penetrated into pores of HAP. Hybrid HAP/nylon composites could be successfully obtained by this process. These hybrid nylon-infiltrated HAP composites exhibited a fracture energy of 21–29 J/m^2. The *in situ* polymerization processing for infiltration of nylon-6 polymer was found to be a successful technique for the achievement of high fracture energy and fracture toughness, and a promising tool for biomedical applications, according to results of *in vitro* bioactivity in SBF. Furthermore, an optimum choice of the type of polymer infiltrated into the HAP skeleton will provide the fabrication of novel HAP/polymer hybrid composites with tailor-made fracture characteristics in a wide range.

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