

Fabrication of calcium-phosphate cements from hydroxyapatite powders surface-modified with various concentrations of sodium inositol hexaphosphate and their material properties

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Introduction

Hydroxyapatite ($\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$; HAp) have been currently used as bioceramics for bone grafting. The HAp is clinically applied as following morphologies: granule, dense ceramic, porous ceramic and cement. Among them, cement has an advantage that can form desired shapes during surgery operation. Generally, apatite cement consist of two kinds of calcium-phosphate powders, acidic dicalcium phosphate dihydrate ($\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$) and basic tetracalcium phosphate ($\text{Ca}_4\text{O}(\text{PO}_4)_2$) [1].

However, the setting reaction based on the above-mentioned acid-base reaction may cause inflammation in surrounding tissues [2]. Thus, we have developed the novel apatite cement without acid-base reactions, "chelate-setting HAp cement" [3, 4]. This cement can be simply fabricated by mixing the HAp powders surface-modified with sodium inositol hexaphosphate (IP6-Na) and distilled water. The handling ability of the cement paste is one of important factors to use in the clinical application, together with mechanical property of set cement paste. Up to now, we enhanced the handling ability and mechanical property of cement by changing the mixing solution. In the present study, we revised the powder preparation process of HAp cement to enhance material properties.

Experimental

Preparation of HAp powder surface-modified with IP6 and their characterization

Commercially-available HAp (HAp-100, Taihei chemical Industrial Co., Ltd., Japan) powders were simultaneously ground and surface-modified using a planetary mill in IP6-Na solution (0, 1000, 5000, 7000, 10000 and 20000 ppm, pH7.3) for 2 h. The slurry after ball-milling was filtrated and freeze-dried for 24h to prepare surface-modified HAp (0-20000-IP6-HAp) powders.

An X-ray diffractometer (XRD) was used to examine the crystalline phase in the surface-modified powders. The morphology of the powders was observed by scanning electron microscopy (SEM). To determine the

particle-size distribution of the powder, a laser particle size analyzer was used. An inductively coupled plasma atomic emission spectrometer (ICP) was used for the measurement of adsorbed amount of IP6 on HAp powder surface. The surface ζ -potential of the powder was examined by the laser-Doppler velocimetry.

Fabrication of IP6-HAp cements and their evaluation

To prepare the IP6-HAp cement paste, the IP6-HAp powder and distilled water were mixed under various ratios of powder and liquid ($P/L=[\text{g/mL}]$). The consistency of the resulting cement paste was evaluated by the following method; a glass plate (120 g) was placed on the cement paste (0.5 mL), and the spread area was measured after 5 min. For measurement of the compressive strength (CS), the resulting cement paste was packed in a cylindrical Teflon mold (6 mm in diameter \times 12 mm of height) and then kept under room temperature for 24 h. The CS test of the cement specimens was performed using a universal testing machine (Autograph AGS-J, SIMAZU CORPORATION, Japan). The Relative density (RD) of cement specimens was calculated from the bulk density divided by the theoretical density of HAp ($3.16 \text{ g}\cdot\text{cm}^{-3}$).

Results and Discussion

Characterization of prepared IP6-HAp powder

All the X-ray diffraction patterns of IP6-HAp powders showed HAp single phase. The morphological observation by SEM revealed that surface-modification of HAp with IP6 inhibited an agglomeration dose-dependently (**Fig. 1**). The median particle size decreased from $7.6 \mu\text{m}$ of 1000-IP6-HAp powder to $4.2 \mu\text{m}$ of 10000-IP6-HAp powder. **Figure 2** shows the relationship between adsorbed amount of IP6 and IP6 concentration (a), together with that between ζ -potential and IP6 concentration (b). With an increment of IP6 concentration, the adsorbed amount of IP6 to HAp powder increased, and ζ -potential decreased. Both parameters reached a plateau in more than 10000 ppm. These results indicate that IP6-Na adsorbed on the surface of HAp powders with

an increase of IP6 concentration and leading to IP6-HAp powder with high negative charge. Gbureck et al. reported that a high value of surface charge improves the dispersion of fine particles as a result of the mutual repulsion of particles [5]. Thus, IP6-HAp powders were well-dispersed with an increment of negative charge.

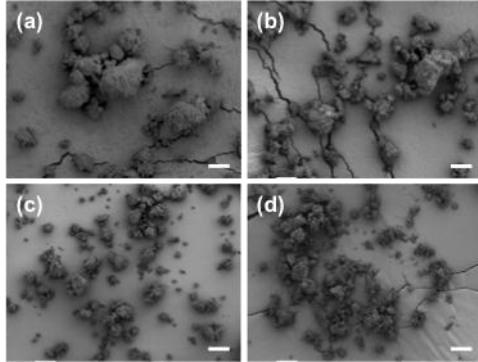


Fig. 1 Morphological observation of IP6-HAp powders
(a) 1000-IP6-HAp, (b) 5000-IP6-HAp, (c) 10000-IP6-HAp and (d) 20000-IP6-HAp. Scale bars indicate 10 µm.

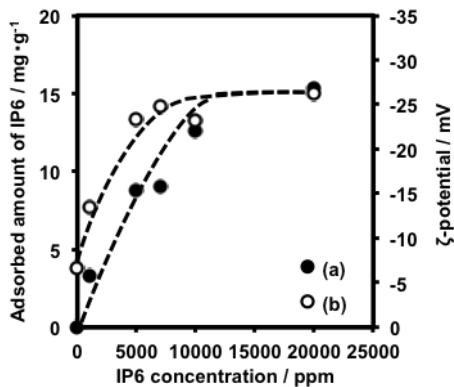


Fig. 2 Relationship between IP6 concentration and adsorbed amount of IP6 (a), together with that between ζ -potential and IP6 concentration

Evaluation of some properties of IP6-HAp cement

The consistency of the cement paste increased with a decrease of P/L ratio in all the cement paste. The P/L ratios of 5000- and 10000-IP6-HAp cement was much larger than 0- and 1000-IP6-HAp cement. These results suggest that an increase of adsorbed amount of IP6 on HAp powder enabled a workable cement paste to be formed with smaller content of mixing solution.

Figure 3 shows the relations between CS of IP6-HAp cements and concentration of IP6. IP6-HAp cements were fabricated with almost the same levels of consistency. The maximum CS was 8.3 ± 1.0 MPa at the ratio of P/L=1/0.60 [g/mL] in the case of 10000-IP6-HAp cement. The CS and RD of 5000- and 10000-IP6-HAp cement specimens were higher than that of 0- and 1000-IP6-HAp cement specimens. These results showed that the consistency of the cement paste reflected the CS and RD of cement

specimens. One of the important factors to control the CS of cement specimen is packing density [6]. Increase of packing density makes it possible to fabricate the cement with higher CS. As above-mentioned, IP6-HAp powder enabled a workable cement paste to be formed at the higher P/L ratio. As a result, packing density in terms of RD and CS of cement specimen increased.

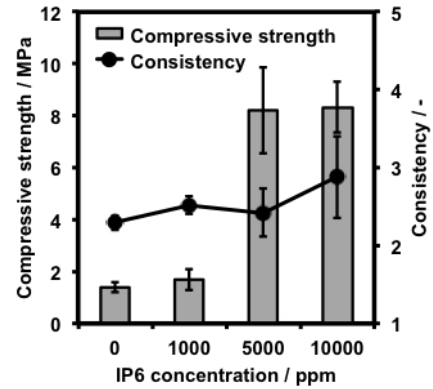


Fig. 3 Relationship between compressive strength of IP6-HAp cements fabricated with almost the same level of consistency and IP6 concentration: 0 ppm (P/L=1/1.2), 1000 ppm (P/L=1/1.2), 5000 ppm (P/L=1/0.5) and 10000 ppm (P/L=1/0.6)

Conclusion

In this study, we investigated the effect of IP6-Na concentration of surface-modification on powder property and mechanical property of HAp cement. The IP6-Na adsorbed on the surface of HAp powders with an increase of IP6 concentration and leading to IP6-HAp powder with high negative charge, which was well-dispersed. The increase of adsorbed amount of IP6 on HAp powder enabled low water content cements to be formed with much higher strength than without IP6-Na.

We conclude that chelate-setting HAp cement might have possibility to apply minimal-invasive treatment as injectable cement by control of IP6-Na concentration.

References

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