

Synthesis of an Apatite with similar Crystallinity to Bone

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Introduction

The bony defects resulted from the extrinsic or intrinsic causes have been usually restored by autograft or allograft. But in many practical cases, if the autograft or allograft is not available according to the clinical situation, xenograft or polymer bone cements have been used as bone restoration substances. However, many researchers have attempted to develop the better bone restoration substances, for those restoration materials often demonstrate many clinical problems. Ceramics are widely used as implant materials in these days due to their excellent biostabilities and biocompatibilities. More than a decade of investigative researches have shown that calcium phosphate materials are safe and effective for restorative and preservative clinical applications to the bone lesions.

Apatites are main natural inorganic component of the vertebrate hard tissue, comprising 60 to 70 percent of bone and 98 percent of teeth in volume. From the early 1970s many researchers have studied the chemical synthesis of the apatites, and various methods of artificial synthesis of them have been reported. Their physical properties are controllable by varying the synthesis environment.

Hydroxyapatite (HAp), a calcium phosphate ceramic, is a well - known artificial bone restoration material that is already applied in practice due to its outstanding biocompatibility. The synthetic hydroxyapatites are devoid of local or systemic toxicity, produce no inflammation or foreign body reactions, integrate chemically with natural bone, induce no alterations to the normal bone metabolism. But it requires extensive time to acquire sufficient bond between the implanted HAp and the surrounding bone tissue. Brittleness is also a commonly facing disadvantage as it can not resist against the physiological and functional load as the general ceramic's physical characteristics. Otherwise, tricalcium phosphate (TCP) had been researched and recommended to clinical applications, for implanted TCP is resorbed and replaced by the regenerating natural bone. But, not only it demonstrates critically weak compressive

strength, but also phosphate often accumulates in the near lymph nodes and it leads to clinical complications.

The most important aspect to be considered about the HAp and TCP is that these are not or less exist in the natural bone. Crystal structure of HAp and TCP is differ from natural bone apatite, for about 80% of that is consisted of carbonate apatite in physiological condition.

In this study, the authors have investigated to synthesize an inorganic substance that reveals similar crystallinity to the natural bone.

Materials and Methods

0.12M ammonium dihydrogenphosphate solution and 0.06M ammonium carbonate solution was mixed to 1:1 ratio in volume. 0.2M calcium acetate monohydrate solution and the firstly mixed solution were delivered to 1.3M ammonium acetate solution that is stirred at 260 rpm by a digital stirrer (SS-11-D, YJ Precision System, Korea) in a mantle heater (CB105, Misung Scientific Co., Korea) at 98, 80, 60, 58, 56 °C. The precipitates were dried at 60 °C and finally obtained carbonate apatite powders.

The apatite powders were uniformly mixed with hydrogen peroxide solution to 88 : 12 ratio in volume by a digital stirrer at 120 rpm to produce pastes. The pastes were poured into an order made teflon mold of 5 mm x 3 mm \varnothing and produced porous apatite rods. The rods were dried at 530 °C for 2 min and increased temperature to 700 °C by increasing 20 °C per min in vacuum at 70 cmHg. After releasing vacuum at 700 °C, the rods were sintered at 700, 800, 900, 1000 and 1200 °C for 2 min by a sintering machine (Alphplus, Jelrus Co., U.S.A.).

Each 1 mg of the obtained apatite powders were mixed with 300 mg of bromide kalium and pellete specimens were produced. The peaks at 800 - 1600 cm^{-1} wave length, the range that reveals the C=O bond and PO, were investigated by an infrared spectrophotometer (Perkin-Elmer 225 Grating Infrared Spectrophotometer, U.S.A.).

To investigate the variation of apatite crystallinities, X-ray diffraction patterns at (002), (211), (112), and (300) in range between 20° and 40° of 2θ by an X-ray diffractometer (Rigaku Denki, Japan). Obtained intensity data were compared to that of the natural bone.

Results and Discussion

The apatite synthesis process used in this study was modified from the method reported by Napper and Smythe, and Okazaki.^{1,2} The obtained amounts of apatite made of 250 ml of 0.2 M calcium acetate, each 125 ml of 0.06 M ammonium carbonate and 0.12 M ammonium dihydrophosphate, and 500 ml of 1.3 M ammonium acetate solutions were investigated according to the synthesis temperature. By increasing synthesis temperature, the precipitate amounts increased. Similar result to this study was reported by Okazaki who noted that the amount of calcium and phosphate in apatite decreases as the synthesis temperature decreases.²

The mixing amount of the hydroxyperoxide was concerned to the volume of organics in the natural bone,^{3,4} for pores would remained in the rod after sintering process. Compressive strength of the rods were investigated after sintering at various temperatures. Though the specimen sintered at 800 °C revealed the highest strength, it was not significant to the others. This result seems to be related to that as increasing the synthesis temperature, the highly fused grain occurs and the hardness increases. But brittleness also increases and results no significant differences in compressive strength.^{5,6}

On infrared spectrums of 1410 and 1460 cm⁻¹ wave lengths, the intensity increases as carbonate concentration increases with concerning to the CO₃²⁻ ions, and intensity at 960 cm⁻¹ that concerns to PO₄³⁻ decreases as the carbonate concentration increases. And as the carbonate concentration increases, calcium content is not remarkably decreases but phosphohate content is significantly decreased.²

Table 1. Acquired amounts of the carbonate apatite with varying synthesis temperatures (n = 10 / group)

Temperature (°C)	Amounts (mg)
98	1456.5 (+ - 9.2)
80	1360.1 (+ - 11.7)
60	1206.6 (+ - 8.8)
58	1160.3 (+ - 13.2)
56	1103.6 (+ - 9.8)

In this study, the varying synthesis temperature resulted that increased temperature reduces carbonate content and decreased temperature reduces calcium and phosphate contents. This result is related to that the lower synthesis temperature produces the less apatite precipitation.

In X-ray diffraction analysis, the carbonate apatite synthesized at 58°C demonstrated very similar crystallinity to the natural bone.

Conclusions

To produce an inorganic substance that obtains similar crystallinity to the natural bone, carbonate apatites were synthesized, and the follows were concluded.

1. The higher the synthesis temperature, the more precipitate are produced but less carbonate apatite.
2. Carbonate apatite synthesized at 58°C demonstrated very similar crystallinity to the natural bone.

Acknowledgment

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References

1. Napper D.H. and Smythe B.M.: J Dent Res, 45: 1775 -1783, 1966
2. Okazaki M., et al. : Caries Res, 15:477-483, 1981
3. Leeson T.S. and Leeson C.R.: Histology, p110 - 133, WB Saunders Co., Philadelphia, 1970
4. White R.A., Weber J.N. and White E.W.: Science, 176:922-924, 1972
5. Li P., et al.: Biomaterials, 14:963-968, 1993
6. Ishikawa K., et al.: Dent Mat J, 9:58-59, 1990

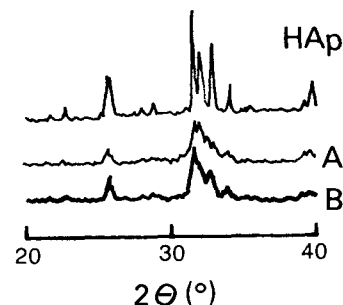


Fig. 1 X-ray diffraction patterns
A: Natural bone
B: Carbonate apatite synthesized at 58°C