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Effect of Hydroxyapatite on Reaction of Dicalcium Phosphate Dihydrate (DCPD) and Fluoride Ion

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Abstract

DCPD, dicalcium phosphate dihydrate ($CaHPO_4$•$2H_2O$) reacts with fluoride ion in an aqueous solution, and forms fluorapatite (FAp, $Ca_{10}(PO_4)6F_2$). In previous study, we have found that DCPD does not react with fluoride ion directly, but show few hours of induction period by reaction with fluoride. In this study, effect of hydroxyapatite (HA, $Ca_{10}(PO_4)_6(OH)_2$) on the reactivity of DCPD with fluoride ion was investigated. By mixing HA with DCPD, it was appeared that the induction period of the reaction was shortened. Morphology of the obtained FAp was similar to HA paricles. We carried on coating of HA on the DCPD particle by soaking DCPD in simulated body fluid (SBF, Kokubo Solution). By coating HA on DCPD particles, particle morphology of the obtained FAp was consistency to the DCPD particles. These results suggest that the shape and particle size of FAp after reaction of DCPD is controllable by DCPD particle as template, and coating with HA.

Keywords: DCPD; Fluoride; Transform reaction; HA (hydroxyapatite); FAp (Fluorapatite)

Introduction

Calcium hydrogen phosphate dehydrate (DCPD, $CaHPO_4$•$2H_2O$) reacts with fluoride ion in a solution and forms fluorapatite (FAp, $Ca_{10}(PO_4)_6F_2$) [1,2]. This reaction is utilized in the development of dental phosphate cements [3]. We have previously applied the reaction to pre-concentration of fluoride in water [4] and gypsum [5]. In previous study, we have appeared that DCPD does not react with fluoride ion directly, but forms a precursor particle with 20-30 nm on surface of the DCPD particle [6]. The precursor particle formation needs to 2-3 hours, that is one of problems of the DCPD reaction when applying the DCPD reaction to environmental issues, such as water treatment [7]. Hybridization of calcium phosphates is one of the approaches for improvement of the property. Aslanidou et al. [8] carried on the preparation of hybrid of HA/DCPD for controlling dissolution rate and mechanical properties. The present work was an investigation for the effect of hydroxyapatite (HA, $Ca_{10}(PO_4)_6F_2$) on the reaction of DCPD. The HA was mixed with DCPD or coated on the DCPD particle. Simulated body fluid (SBF, Kokubo Solution) [9] was selected for the method of the coating of HA.

Materials and Methods

The DCPD and HA used were a reagent grade (Taihei Chemical Industrial Co., Ltd., Japan). Fluoride solution was obtained by dissolving sodium fluoride (Wako Pure Chemical Co. Ltd., Japan) into pure water. Concentration of fluoride ion was adjusted to 20 mg/L. The SBF was prepared by the following method in the article [10]. Coating of HA on the DCPD particles was carried out by soaking 1 g of the DCPD into 50 mL of the SBF for 1 day.

A 20 mg of DCPD was added in a 20 mL of the fluoride solution in a polycarbonate bottle. The mixture was shaken in the reciprocal shaker (Type MMS-3010, EYELA, Japan) with the incubator (Type FMC-1000, EYELA, Japan) at 25°C for various periods. Shaking speed was fixed to 80 times/min. The fermenter (MBF-250E, EYELA, Japan) was used to observe continuously change of fluoride ion concentration by addition of the DCPD. Two grams of DCPD was added in a 2 L of the fluoride solution in a baffled reactor. Fluoride concentration was monitored by using the ISE (Orion ionplus 9609BN, Thermo Electron Corp., USA) and the ion meter (Orion PCM-700, Thermo Electron Corp., USA).

After the reaction, liquid and solid phase were separated by suction using a 0.45 µm membrane filter. The concentration of fluoride ions in the solution was measured by using the ISE and the ion meter (SevenMulti S40, Mettler Toledo, Switzerland). The crystalline phase of the solid phase was analyzed by the powder X-ray diffraction (Miniflex, Rigaku, Co. Ltd., Tokyo, Japan). The optical microscope (ECLIPSE L100D, Nikon, Japan) or scanning electron microscope (SEM, JSM-6390AX, JEOL, Japan) were also used for microstructure observation of the solid phase.

Results and Discussion

Figure 1 shows continuous change in fluoride concentration in the solution containing DCPD mixed with HA. In case of pure DCPD, fluoride concentration was not changed for 90 minutes. This lag time seems to be time requiring for formation of the precursor particle on the DCPD particles [6]. In this figure, mixing HA with DCPD was disappeared the lag time. Figure 2 shows the lag time in various HA/DCPD ratio. In the figure, there is a threshold value for cutoff the lag time. In this case, optimum HA ratio was more than 30 wt% in the DCPD/HA mixture. On the other hands, pure HA removed fluoride ion slightly.

The morphology of the solid phase after the reaction with fluoride ion was observed by the optical microscope. Figure 3A shows change of morphology of pure DCPD before and after the reaction with fluoride ion. After the reaction, DCPD transformed to FAp. The obtained FAp maintained characteristic plate shape of DCPD particle. However, in case of DCPD/HA mixture (Figure 3B), it was not similar to DCPD but similar to HA. From these results, mixing of HA was applicable to cut off the lag time. Change of the particle shape was different from the case of pure DCPD.

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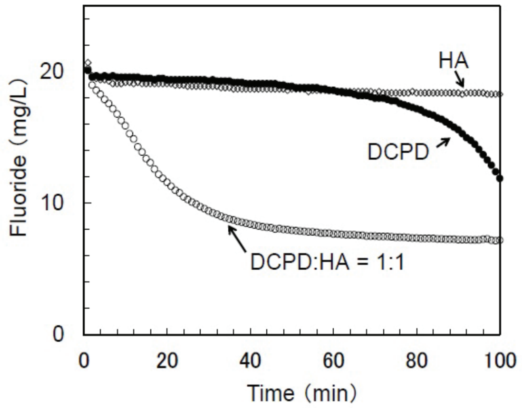

Figure 1: Change in fluoride concentrations in the fluoride solution after adding DCPD, HA, and DCPD/HA mixture.

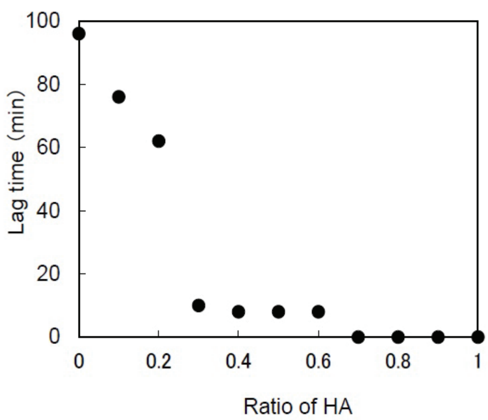

Figure 2: Change in the Lag Time as function of ratio of HA in DCPD/HA mixture.

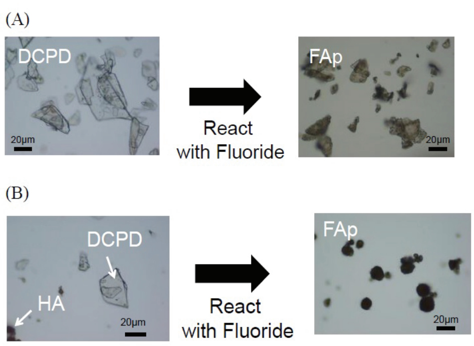

Figure 3: Optical microscope images of particles of (A) DCPD and (B) DCPD/HA mixture before (left) and after (right) reaction with the fluoride solution.

DCPD particle was soaked into SBF. Figure 4 and 5 show SEM photograph and powder X-ray diffraction patterns of DCPD particle before and after soaking into SBF. From Figure 4, it was found that small particles formed on the surface of DCPD. From Figure 5, small peaks of HA were observed. From these results, HA was successfully coated on surface of the DCPD particle. HA-coated DCPD was mixed

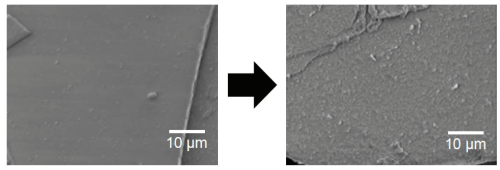

Figure 4: Scanning Electron Microscope (SEM) images of surface of DCPD particle before (left) and after (right) soaking into SBF. DCPD/SBF ratio was 1g to 50 mL, soaking time was 1day.

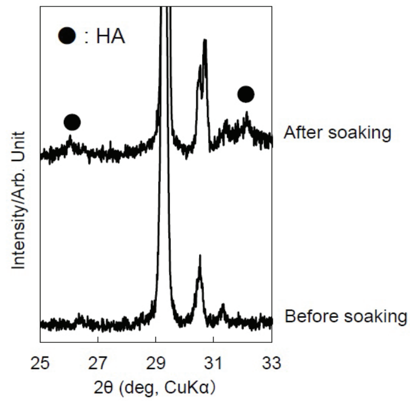

Figure 5: Powder X-ray diffraction patterns of DCPD before and after soaking into SBF. Soaking condition was same to Figure 4.

with fluoride solution. Figure 6 shows the effect of HA coating on DCPD the reactivity with fluoride ion. Figure 6 shows the difference between DCPD and HA-coating DCPD on reactivity with fluoride ion. By coating HA on the DCPD particles, there was no lag time to initiate the reaction. From these results, coating of HA was applicable to cut off the lag time, mixing HA with DCPD alike.

Morphology of HA-coated DCPD was observed by using SEM. Figure 7 shows morphology of DCPD before and after the reaction with fluoride ion. Morphology of the particle was kept after the reaction with fluoride ion. In case of mixing of HA, the characteristic particle morphology (plate shape) of DCPD was disappeared. However, coating of HA was maintained that after reaction with fluoride ion.

From these results, we concluded reaction process of DCPD, as shown in Figure 8. In case of DCPD/HA mixture, HA transformed to FAp in the first stage. After formation of FAp, FAp particle grew by phosphate and calcium ions from DCPD, and fluoride ion in the solution. Therefore, morphology of the obtained FAp was quite different from the shape of DCPD was studied. Coating of HA on DCPD is effective for improving reaction time of fluoride ion and maintains particle morphology of DCPD. We have appeared that morphology of DCPD particle is easily controlled by change of additives such as acetic acid [11]. If we use the characteristic-shaped DCPD and coat them with, the DCPD, in case of HA-coated DCPD, FAp seems to have grown by using calcium and phosphate ion ion, which are originated from DCPD contacted with them, and fluoride ion in the solution. Therefore, the obtained FAp particles had same morphology of initial DCPD particle.

Conclusion

The effect of HA in the reaction of DCPD with fluoride ion will react with fluoride ion in shortly and the obtained FAp was the same

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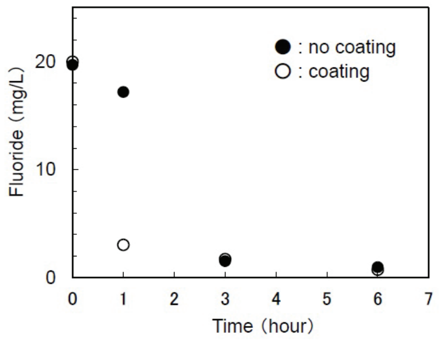

Figure 6: Effect of HA coating by SBF for reaction of DCPD with fluoride ion. Initial fluoride concentration was 20 mg/L, temperature was 25ºC.

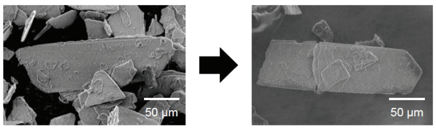

Figure 7: Particle morphology of DCPD coated by HA before (left) and after (right) reaction with a fluoride solution.

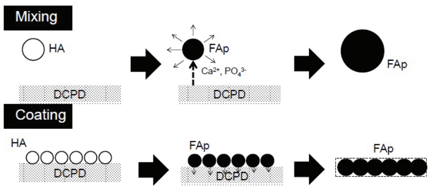

Figure 8: Schematic representation of effect of HA on reaction of DCPD with fluoride ion.

characteristic shape of initial DCPD. This is very useful for application of the reaction of DCPD for environmental issues, such as water treatment. Treatment of fluoride in water by using precipitation of FAp generates a huge amount of sludge containing fine particle of FAp. Separation of the sludge has been one of the problems of water treatment. Using HA-coated DCPD with large size for water treatment seems to improve the reactivity of fluoride and separation of the obtained sludge containing large particle of FAp. Further studies for optimization of the condition of HA coating and application of them to various water treatments are now in progress.

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