

## Hydrothermal Synthesis of Hydroxyapatite – Polymer Composite Materials

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The hydrothermal syntheses of hydroxyapatite and polymer composite materials were studied. The apatite precursor slurry was prepared by agitating a mixture of  $\text{CaCO}_3$  and  $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ , and 3 kinds of polymeric fibers were added. The mixture was treated under hydrothermal conditions at 180 °C for 5 hours. The XRD patterns of the products showed that the products were well-crystallized hydroxyapatite. SEM observations revealed that the thick coatings of hydroxyapatite were formed on the polymer fibers. Spherical apatite particles of sub-micrometer size were observed on the fibers when the pH value was 10 or 6.5. At the pH value of 4, the products on the fibers were rod-like apatite, 20-50  $\mu\text{m}$  long, and seemed to have developed in the same direction.

### 1. Introduction

Research of organic polymer substrates on which calcium phosphate (hydroxyapatite) is induced to form has become active due to the insights such investigations can give into the biomineralization processes in the body. The application of such knowledge may also allow the design of materials which combine strength, elasticity and other remarkable properties. A number of experiments focused on how the concepts of morphogenesis, self-organization and replication are available and could be useful for devising new synthetic strategies. The most common is the phosphate and carbonate salts of calcium that are used in conjunction with organic polymers such as collagen and chitin to give structural support to bones and shells. In these structures, the inorganic crystals are laid down in orderly arrays in association with a matrix of organic macromolecules. The influence of organic macromolecules is important in the regulation of growth of the mineral and in the resulting crystal morphology specificity. The nucleation and growth of inorganic compounds on/in an organized multi-component system can also induce changes in the local structure and phase behavior, such that new morphological patterns develop from existing architectures.

Studies of the stimulation of hydroxyapatite growth on a substrate has employed a number of techniques including a procedure for raising the ionic activity of the hydroxyapatite products in the solution containing the substrate to be coated so

stimulation precipitation and the creation of apatite nucleation sites can occur [1], and the surface modification by surface graft polymerization of a phosphorous-containing monomer inducing the deposition of Ca and  $\text{PO}_4$  ions in the form of a carbonated hydroxyapatite layer firmly bonded with the materials [2]. The surface modification by phosphorylation giving surface sites which have a crystallographic arrangement similar to that of hydroxyapatite so allowing possible epitaxial growth [3]. The authors reported a method for creating favorable local conditions leading to the nucleation and growth of calcium phosphate on cellulose, i.e., chitin [4-7]. This method of phosphorylation and partial hydrolysis of the introduced phosphorous-containing functionalities resulted in hydrolysis products in intimate contact with the substance. Therefore certain functionalities on the substrate should play an important role in inducing the deposition of calcium phosphate from the soaking medium.

In this study, spherical or rod-like apatite crystals formed on 3 kinds of polymeric fibers under hydrothermal condition have been investigated. Characterization tests were carried out using SEM/EDX, TEM, micro-FTIR, XRD, and ICP to determine the presence of calcium phosphate on the polymeric fibers.

### 2. Experimental Methods

**2.1. Apatite-Polymer Composite Preparation** All chemicals used in this study were supplied by Wako Pure Chemical Industries, Ltd., or Katayama

Chemicals and used without further purification. N<sub>2</sub>-purged water obtained from distilled water previously passed through an ion-exchange resin was used in the preparation of all the aqueous solutions. The apatite precursor slurry was prepared as follows; 0.06 mol CaCO<sub>3</sub> and 0.09 mol CaHPO<sub>4</sub>·2H<sub>2</sub>O were agitated in a pot mill using 500 g ZrO<sub>2</sub> balls and 200 ml H<sub>2</sub>O for 24 hours at 50 rpm to yield the apatite precursor slurry. The apatite precursor slurry was diluted, so that the calcium and phosphate ion concentrations are almost the same or twice those of the body fluid. Polymeric fibers were added to the apatite precursor slurry. The 3 kinds of applied polymeric fibers were aromatic polyamide, phenolic resin, and polyvinyl alcohol. The pH value of the solution was adjusted to 10 by NH<sub>4</sub>OH, or at 4 by acetic acid. The mixture was treated in an autoclave with stirring under hydrothermal conditions at 160-200°C for 5 hours to crystallize the apatite.

**2.2. Characterization** The powder X-ray diffraction patterns of the products were recorded using a MAC Science MXP<sup>3</sup> diffractometer with CuK $\alpha$  radiation at 40 kV and 20 mA, and a graphite monochromator. The morphologies of the samples were observed by scanning electron microscopy, and EDX analyses were performed. All micro-FTIR spectra were recorded using samples encased in a transparent KBr pellet. TEM observation of the products were conducted using JEOL, JEM-4000FX at 300 kV. The determination of the Ca and P content of the products were done using an inductively coupled plasma emission spectrometry, a Seiko SPS7000.

### 3. Results and Discussion

Figure 1 shows the XRD patterns of the products hydrothermally treated at various pH value on polymeric fibers. The peaks were very sharp and the d values of these patterns of the products were in good agreement with the JCPDS values of apatite. This indicated that the products were well crystallized apatite independent of the pH value. Figure 1 (c) shows the XRD pattern of the products hydrothermally treated at the pH value of 4. The peak (100), (200), and (300) planes are apparently larger, which indicated the preferential crystal plane of the long axis can be defined as the a-plane. IR spectra of the products hydrothermally synthesized showed that there are adoption peaks of carbonate ions in addition to those of typical apatite and no peaks of other groups such as the methyl group.

These results mean that the products were well crystallized apatite containing carbonate ions.

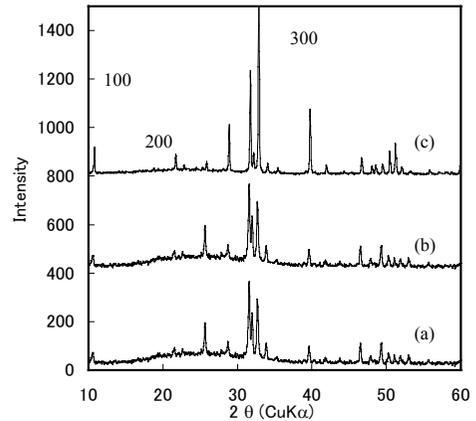


Fig. 1. X-ray diffraction patterns of the products formed by hydrothermal treatment at 180 °C for 5 hours at the pH values of 10 (a), 6.5 (b), and 4 (c).

Figure 2 shows SEM pictures of apatite crystals hydrothermally treated at 180 °C for 5 hours at the pH value of 10 on polymeric fibers. The polymeric fibers are aromatic polyamide (a), polyvinyl alcohol (b), and phenolic resin.(c). The thick coating of hydroxyapatite on the polymer was successfully obtained by hydrothermal treatment. Upon looking at higher magnifications, there is a thick layer over which the spherical apatite particles like petals of sub-micrometers in size is growing all over the polymer. Ioku et al. [8] reported that hydroxyapatite crystals formed under hydrothermal conditions had a rod-like shape around 200 nm long. The petal-like apatite particles may be the aggregates of small crystals. The spherical growth of the calcium phosphate phase is seen scattered over the entire surface of the fibers, but few apatite particles were found on the fibers. The apatite particles seem to be more on the phenolic resin and polyvinyl alcohol fiber compared with those on the aromatic polyamide, which may be due to the hydroxy end radical of the former ones. The hydroxy radical is believed to provide the substrate with an intimate contact with calcium ions. The polymeric fibers of polyvinyl alcohol seem to be stretched and crooked under the hydrothermal condition of 180 °C at a pH value of 10, but the other fibers of the aromatic polyamide and phenolic resin were unchanged in appearance.

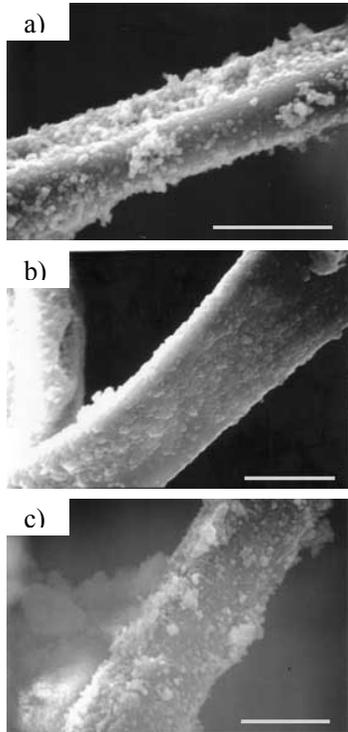


Fig. 2. Scanning electron micrographs of products formed by hydrothermal treatment at 180 °C for 5 hours at pH value of 10 on polymeric fibers of aromatic polyamide (a), polyvinyl alcohol (b), and phenolic resin.(c). Bar is 20  $\mu$ m.

EDX analysis showed that the products were composed of calcium and phosphorous element, and the Ca/P ratio of the hydrothermal synthesized products were larger than 1.67. However, no peaks corresponding to the calcium-containing compounds were found in the X-ray diffraction patterns. Calcium ions infiltrated into the polymeric fibers and may partly combine with the polymer. The ion concentrations of the apatite precursor slurry may influence the amount of the products but the shape of products were the same for the precursor slurry with the same or twice the concentrations of the body fluid.

The pH value of the mixture was adjusted to 6.5. The products formed on the polymeric fibers by hydrothermal treatment were almost the same as the products obtained by hydrothermal treatment at the pH value of 10, and a large amount of spherical

apatite particles was found on the fibers as shown in Figure 3 (a). The appearance of the aromatic polyamide and phenolic resin was unchanged. The polyvinyl alcohol fibers stick to each other and seem to partly melt, but many spherical apatite particles were observed on the polyvinyl alcohol fibers.

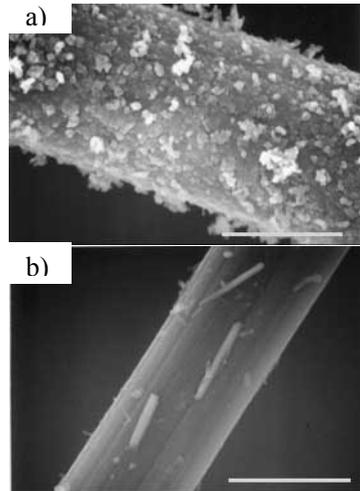


Fig. 3: Scanning electron micrograph of the products formed by hydrothermal treatment at 180 °C for 5 hours on polymeric fibers of the phenolic resin at the pH value of 6.5 (a), and aromatic polyamide at the pH value of 4 (b). Bar is 20  $\mu$ m.

The products obtained under hydrothermal conditions at the pH value of 4 were rod-like crystals about 2-3  $\mu$ m in width and 20-50  $\mu$ m in length. Some crystals adhered to the surface of the polymer as shown in Figure 3 (b). The XRD diffraction patterns showed that the peak (100), (200), and (300) planes of the rod-like products preferentially layered on the substrate were apparently large, so the long axis can be defined as the c-axis. Yoshimura et al. reported the effect of the carbonate group on the morphology change in the hydrothermal treated apatite crystals [9]. In this study, the pH value was adjusted using acetic acid, and the long rod-like apatite crystals were formed by a similar effect. TEM observations showed that the rod-like crystal was composed of many small rods. At high magnification, their tops were seen different in level. They were bundled up in the same direction, and the bundle looks like one rod-like crystal.

The appearance of the aromatic polyamide and phenolic resin was also unchanged after the hydrothermal treatment at 180 °C for 5 hours at the pH value of 4. The polyvinyl alcohol fibers were quite damaged that they could not be recognized.

A number of papers have been published in the area of biomimetic growth or on the in-vitro nucleation of calcium phosphate phase over different substrates. It has been reported that the functionality groups like hydroxy, phosphate, carbonate, or silanol group induced the in-vitro nucleation of the calcium phosphate phase upon immersion in simulated body fluid solutions. In the present case, the deposition of apatite on the polymeric fibers under hydrothermal conditions showed the same behavior as in the case of the above studies. The amount of apatite formed on the substrate may be influenced by the end radicals of the substrate. The forms of apatite crystals on the polymeric substrate also varied by the pH value. Spherical particles and rod-like apatite crystals were formed by the change in the pH value. At the pH value of 4, large rod-like apatite crystals adhered on the polymeric fibers in the same direction. The apatite crystal has a rod-like shape in nature. However, the authors reported that the plate-like apatite crystals were successfully prepared by adding alcohols with 1,2 and 3 hydroxy groups, and amide-containing organic compounds [10,11]. It can be explained that the hydroxy or amide group captured calcium or phosphate ions in the solution by chelation and retarded the supply of calcium or phosphate ions to the apatite nuclei, and the apatite crystals grew under the condition that the calcium or phosphate ions were not sufficiently supplied, therefore, the crystal growth of apatite was inhibited along a particular axis. Here rod-like apatite crystals were formed under hydrothermal condition without such radicals, but at the pH value of 4, large rod-like crystals were formed on the polymeric fibers.

#### 4. Conclusions

A biomimetic growth study of calcium phosphate phase of natural synthetic polymeric materials has been an active area of research with the aim to develop materials with a better elasticity and biocompatibility. This study describes the hydroxyapatite and polymer composite material syntheses under hydrothermal conditions. The apatite precursor slurry was prepared by ball milling, and polymeric fibers were added. The 3 kinds of applied fiber like polymers were the

aromatic polyamide, phenolic resin, and polyvinyl alcohol. The pH value of the mixture was adjusted to 10, 6.5 and 4, and the mixture was treated in an autoclave under hydrothermal conditions at 160-200°C for 5 hours to crystallize the apatite. The XRD patterns of the products hydrothermally treated showed that the products were well-crystallized hydroxyapatite. SEM observations revealed that thick coatings of hydroxyapatite were formed on the polymer fibers. Spherical apatite particles of sub-micrometer size were observed on the fibers when the pH value was 10. When the pH value was adjusted to 6.5, the products on the polymer fibers after hydrothermal treatment were almost the same as the products hydrothermally treated at the pH value of 10. At the pH value of 4, the products on the fibers were rod-like apatite 20-50 μm long and seemed to be in the same direction. The apatite crystals on the polymeric substrate varied in form by the pH value. Here rod-like apatite crystals were formed under hydrothermal conditions without such radicals, but at the pH value of 4, large rod-like crystals were formed on the polymeric fibers.

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