

Effect of Silane-Coupling Treatment on Thermal Decomposition of Octacalcium Phosphate[†]

by

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Octacalcium phosphate (OCP) has a unique layered structure. The layered structure is feasible for novel organic-inorganic hybrids. We treated OCP powder with a silane-coupling agent, vinyltrimethoxysilane (VS), and examined its thermal properties. The VS was not incorporated in the hydrated layer of OCP but reacted only with the surface. The non-treated OCP (Pure-OCP) and treated OCP (OCP-VS) showed the almost same dehydration behavior when they were examined by thermogravimetry and differential thermal analysis. However, the different behavior in 010 diffraction peaks was observed in X-ray diffraction patterns when they were heated at 150°C. The treatment with VS retarded the decomposition of the layered structure of OCP. Some of the VS molecules in OCP-VS might have undergone the condensation reaction among the silanol groups in VS. Due to this VS network on the surface of OCP, the framework of the layer of OCP becomes stable. When Pure-OCP and OCP-VS heated at 150°C were aged under ambient conditions for 1 week, rehydration occurred in both samples. The VS introduced on OCP may provide a novel organic modification of OCP.

Key words : Octacalcium phosphate, Layered structure, Thermal decomposition, Silane-coupling treatment, Dehydration

1 INTRODUCTION

Calcium phosphates are used as bone substitutes because of its high compatibility with bone tissues as well as adsorbents because of specific adsorption properties against organic substances.¹⁾ There are many types of calcium phosphates,²⁾ such as hydroxyapatite (HAp, $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$), octacalcium phosphate (OCP, $\text{Ca}_8(\text{HPO}_4)_2(\text{PO}_4)_4 \cdot 5\text{H}_2\text{O}$), tetracalcium phosphate (TTCP, $\text{Ca}_4(\text{PO}_4)_2\text{O}$), tricalcium phosphate (TCP, $\text{Ca}_3(\text{PO}_4)_2$), etc.

OCP is known as a precursor of HAp,^{3), 4)} which is the inorganic component of the human bone and tooth and is used as an important bone-repairing material. OCP has a unique layered structure. The layered structure is feasible for novel organic-inorganic hybrids. It has been reported that OCP can incorporate dicarboxylates into the hydrated layer instead of HPO_4^{2-} ions.⁵⁾⁻⁸⁾ In the present study, organic modification of OCP was attempted by the reaction with a silane-coupling agent. Furuzono *et al.*⁹⁾ reported the organic modification of HAp with a silane-coupling agent in order to provide the bonding-ability to a silicone substrate. However, the modification of OCP with silane-coupling agents has not been reported. If some functional groups can be introduced to OCP by silane-coupling treatments, we can combine various organic molecules on OCP or achieve the strong bonding of OCP to organic substrates when OCP is used as a filler of a composite material. In the present study, we treated the OCP powder with a silane-coupling agent, vinyltrimethoxysilane (VS), and examined their properties.

2 MATERIALS AND METHODS

2.1 Preparation of pure OCP

OCP was prepared as follows. The 11.5g of 85 mass% phosphoric acid (H_3PO_4) solution and 13.3g of calcium carbonate (CaCO_3) (Nacalai Tesque Inc., Japan) were added to 1 dm³ of ultrapure water in a glass beaker to obtain Ca/P mole ratio of 1.33. The resultant suspension was stirred at 60°C for 6 hours. The precipitate was collected by filtration and dried at 60°C. Pure OCP was obtained. Hereafter, this OCP is named Pure-OCP.

2.2 Silane-coupling treatment

0.6g of vinyltrimethoxysilane (VS, $(\text{CH}_2 = \text{CHSi}(\text{OCH}_3)_3)$, Chisso Co., Japan) was dissolved in 20ml of 2mass% of acetic acid solution. The slurry containing 3g of Pure-OCP in 30ml of ultrapure water was added to the above solution. The amount of VS is enough to cover whole the surface of OCP. The obtained suspension was stirred at 80°C for 8 hours. The precipitate was collected by filtration and dried at 60°C. The obtained sample is named OCP-VS.

2.3 Characterization of samples

The samples were dissolved in a nitric acid solution and their compositions were examined by inductively coupled plasma atomic emission spectroscopy (ICP, Optima 2000DV, PerkinElmer Japan Co., Japan). Their thermal properties were examined by thermogravimetry and differential thermal analysis (TG-DTA, TG-DTA2020S, MAC Science Co., Ltd., Japan). Their structures were examined by powder X-ray diffraction (XRD, RINT2200V/PC-LR, Rigaku Co., Japan).

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2.4 Rehydration of dehydrated samples

The samples Pure-OCP and OCP-VS were dehydrated at 150°C for 3 hours. The dehydrated samples were aged under ambient conditions in order to examine the rehydration behavior. The structures of the samples before and after aging were examined by XRD.

3 RESULTS

Table 1 shows the compositions of the samples Pure-OCP and OCP-VS. The compositions of both Pure-OCP and OCP-VS had similar Ca/P mole ratio to stoichiometric OCP (1.33). The OCP-VS contained small amount of silicon and this indicates that VS was incorporated in the samples.

Figure 1 shows the TG-DTA curves of the samples Pure-OCP and OCP-VS. Both the samples showed endothermic peaks accompanied with weight loss in the ranges 60–80°C and 120–150°C. The former and the latter peaks are attributed to dehydration of the adsorbed water and the water incorporated in hydrated layer of OCP, respectively.¹⁰ No difference in thermal properties was observed between Pure-OCP and OCP-VS.

Figure 2 shows XRD patterns of the samples Pure-OCP and OCP-VS heated at various temperatures for 3 hours.

Table 1 Compositions of samples Pure-OCP and OCP-VS.

Sample	Compositions (mole ratio)	
	Ca / P	Si / P
Pure-OCP	1.35	–
OCP-VS	1.34	0.003

– : not detected

The peaks of the Pure-OCP and OCP-VS before heating were assigned to OCP (JCPDS #26-1056). No difference was observed between Pure-OCP and OCP-VS before heating. No change was observed until 100°C in both samples. When Pure-OCP was heated at 150°C, its 010 diffraction peak was significantly decreased. On the other hand, the 010 diffraction peak of OCP-VS shifted to higher degree. The enlarged patterns of the samples with and without the heat treatment at 150°C are shown in Figure 3. The intensity of the peak at $2\theta = 4.7^\circ$ decreased and a new peak appeared at $2\theta = 5.2^\circ$ in both samples. The intensity of the peak at $2\theta = 5.2^\circ$ in OCP-VS was larger than that in Pure-OCP. The peak at $2\theta = 5.2^\circ$ was assigned to the dehydrated layers. When the samples were heated at 200°C, their XRD patterns were almost same.

Figure 4 shows the XRD patterns of the dehydrated

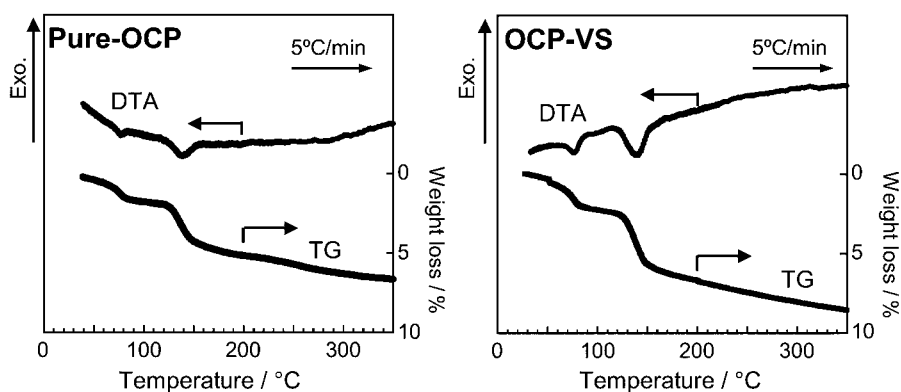


Fig. 1 TG-DTA curves of samples Pure-OCP and OCP-VS.

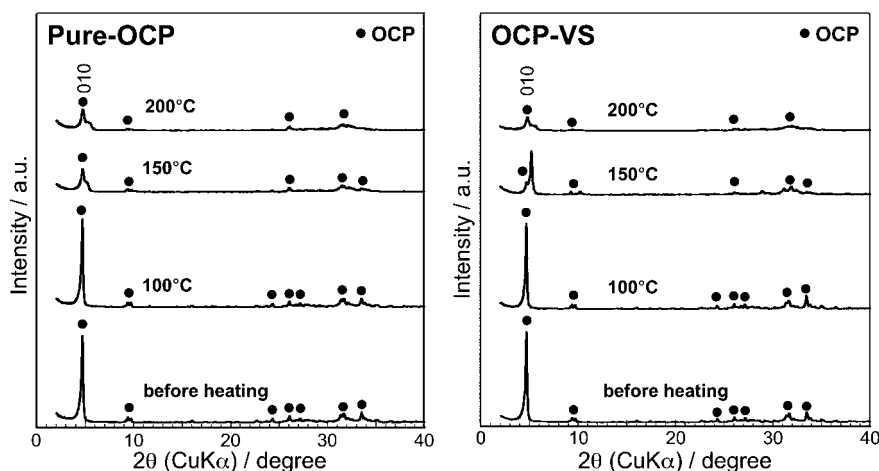


Fig. 2 XRD patterns of the samples Pure-OCP and OCP-VS heated at various temperatures for 3 hours.

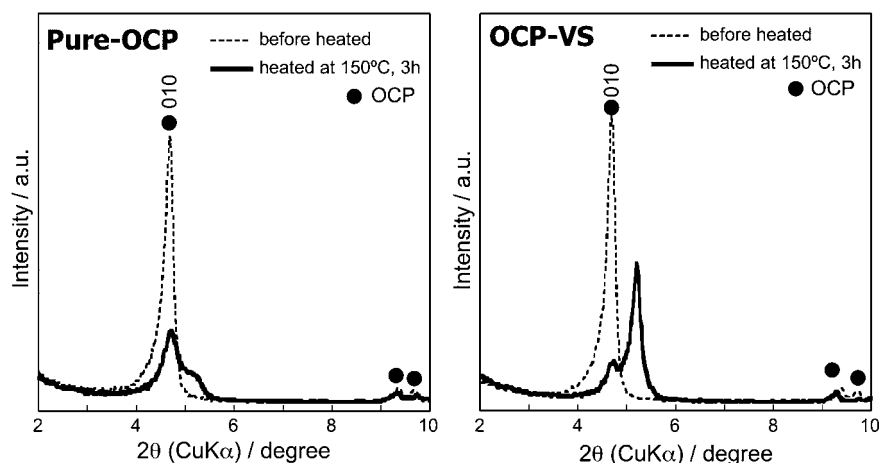


Fig. 3 The enlarged XRD patterns of the samples with and without the heat treatment at 150°C.

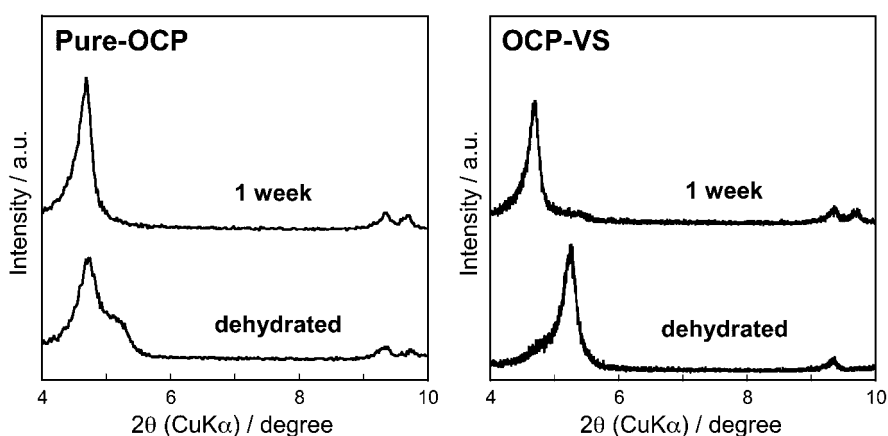


Fig. 4 XRD patterns of the dehydrated samples before and after aging under ambient conditions.

samples before and after aging under ambient conditions. After aging for 1 week, the peak at $2\theta = 5.2^\circ$ disappeared and the intensity of the peak at $2\theta = 4.7^\circ$ increased. Since the peak at $2\theta = 4.7^\circ$ is the original 010 diffraction peak of OCP, the peak shift observed after aging is due to the rehydration phenomena.

4 DISCUSSION

No difference was observed between samples Pure-OCP and OCP-VS in XRD patterns. Monma *et al.*⁵⁾ reported that OCP can incorporate dicarboxylates into the hydrated layer instead of HPO_4^{2-} and this spreads the distance of the hydrated layer. It is speculated that such spread of the hydrated layer occurs if VS is incorporated in the hydrated layer of OCP. However, such shift was not observed in OCP-VS and this would indicate that VS was not incorporated in the hydrated layer of OCP but reacted only with the surface. If VS is incorporated in the hydrated layer, VS can not compensate the charge of HPO_4^{2-} since VS is not an ionic molecule. On the contrary, dicarboxylates incorporated in the hydrated layer compensate the charge of HPO_4^{2-} . Therefore, VS could not be incorporated in the hydrated layer of OCP. Moreover, Monma *et al.* added dicarboxylates during the prepara-

tion of OCP. In the present study, VS reacted not during but after the preparation of OCP. This should also be the reason why VS was not incorporated in the hydrated layer.

The dehydration behaviors of Pure-OCP and OCP-VS were almost same. The adsorbed water was speculated to be removed in the temperature ranges 60–80°C since the XRD patterns did not change until 100°C. The water molecules in the hydrated layers were speculated to be removed in the temperature ranges 120–150°C since the significant changes in the 010 diffraction peak were observed at 150°C. The water molecules in the OCP structure play important roles to stabilize the layer structure and the removal of the water molecules destroys the layer structure. In the case of OCP-VS, the layer structures still remained even after heat treatment at 150°C. These phenomena are explained in the following mechanism: The VS reacted with the surface of OCP, and the OCP is coated with VS in OCP-VS. Some of the VS might trigger the condensation reaction among the silanol groups in VS. Due to this network on the surface of OCP, the framework of the layer of OCP becomes stable and the treatment with VS retards the decomposition of the layered structure of OCP. However, when Pure-OCP and OCP-VS

are heated at 200°C, their XRD patterns were almost same. As the VS layer on OCP is very thin against the OCP body, the retardation effect against the decomposition is not so large. Therefore, the heat treatment at 200°C destroys the layer structure even in the OCP-VS.

When the Pure-OCP and OCP-VS heated at 150°C was aged under ambient conditions for 1 week, rehydration occurred in both samples. The same rehydration phenomena were observed when they were soaked in ultra-pure water (data is not shown). Monma *et al.*¹¹⁾ reported that the rehydration phenomena occurred in Pure-OCP. The present results indicate that even the OCP treated with the silane-coupling agent also shows rehydration phenomena.

The treatment of OCP with VS provided the organic modification of the surface of OCP. The treatment with VS retarded the decomposition of the layered structure of OCP. If we utilize vinyl groups introduced on OCP-VS, we can combine various organic molecules on OCP-VS or achieve high bonding strength of OCP-VS to organic substrate when OCP-VS is used as a filler of a composite material.

5 CONCLUSION

The treatment of OCP with VS provided the organic modification of the surface of OCP. The treatment with VS retarded the decomposition of the layered structure of OCP. The VS introduced on OCP may provide a novel organic modification of OCP.

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