Biomimetic calcium phosphate coating on polyimide films by utilizing surface-selective hydrolysis treatments

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Hydroxyapatite (HAp) coating on commercially available polyimide (PI) films in simulated body fluid (SBF) was examined. Aqueous sodium hydroxide treatment of PI films under proper conditions proceeded surface-selective hydrolysis of PI molecules, which resulted in displaying carboxylic acid groups on the film surfaces. These surface-hydrolyzed PI films had ability to induce deposition of minerals having similar characteristics to that of HAp thereon when incubated in 1.5SBF, a solution having 1.5 times higher inorganic ion concentrations than those of SBF. No deposition was observed for the case of unmodified PI films under the same condition. Additional pretreatments with aqueous calcium chloride for the surface-hydrolyzed PI films realized complete surface coverage on the films by thin mineral layers in 1.5SBF. The present process for PI films is simple and low-cost, and can be widely applicable to other substrates of polymers that can generate carboxylic acid groups by alkaline hydrolysis.

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Technological development for coating of bioceramics such as calcium phosphates on various organic polymer substances is important for providing novel organic–inorganic hybrid materials that can be used in biomedical or biochemical applications. Along this line, simulated body fluid (SBF), has been used to deposit bone-like hydroxyapatite \([\text{HAp, } \text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2]\) on various material surfaces under mild conditions. SBF is a solution that mimics the inorganic ion concentrations of human plasma and has been developed originally by Kokubo’s group for evaluation of apatite forming ability of the specimens under body fluid conditions. In previous studies, SBF, a solution having 1.5 times higher inorganic ion concentrations than those of SBF, has also been used to accelerate HAp deposition. Displaying ionic functional groups such as carboxylic acid groups or sulfuric acid groups was shown to effectively induce the heterogeneous nucleation of HAp on the material surfaces in SBFs. We have also been investigating HAp deposition on various material surfaces in SBFs. Some of these researches include development of simple, low-cost surface modification processes for commonly used polymers that do not have effective functional groups for HAp nucleation. For example, we demonstrated that coating of serum protein layers on polystyrene substrate surfaces is effective to induce HAp deposition in 1.5SBF. Polyimide (PI) is widely used in various industrial fields because of its superior thermal stabilities and mechanical properties. Therefore HAp coating on PI or similar aromatic polyamide substrates has been received attention from the viewpoint of creation of novel hybrid materials having superior physical properties. For example, Miyazaki et al. demonstrated successful HAp deposition on the films of polyamides having carboxylic acid groups in 1.5SBF. Kawai et al. investigated HAp deposition on the films of polyamides having sulfonic acid groups. In this study, we investigated HAp coating on commercially available PI film surfaces in 1.5SBF. We modified PI film surfaces using simple alkaline solution treatments, which generates carboxylic acid groups by imide ring cleavage (Fig. 1). HAp deposition ability of the resulting surface-hydrolyzed PI films was examined by incubation in 1.5SBF. Effect of aqueous calcium chloride treatments on the mineralization behavior was also evaluated.

The experimental procedure of the present study is schematically illustrated in Fig. 1. PI films (Kapton® 100H, 25 µm thickness, Du Pont–Toray Co., Ltd.) were treated with aqueous sodium hydroxide (5 wt%) at room temperature for 10 min. The resulting surface-hydrolyzed PI films were then immersed in 1.5SBF (Na+ 213.0, K+ 7.5, Mg2+ 2.3, Ca2+ 3.8, Cl− 221.7, HCO3− 6.3, HPO42− 1.5, and SO42−, 0.75 mM, pH 7.4; prepared according to Kokubo’s method) and incubated at 36.5°C using a...
surfaces. If microscopic topological changes of PI images of the surface-hydrolyzed PI formation of semispherical deposits consisted of plate-like objects our previous report showing that about 10 min of treatment was treatments (data not shown). These results were well comparable to results in which EDX analysis was not conducted were coated with Pt-Pd using an ion-sputtering device (E-1030; Hitachi Ltd.) with acceleration voltage of 10 kV. Samples for SEM observation con microspheric deposit total-re mineralization behavior. Previous studies showed that such kinds examined effect of aqueous calcium chloride treatments of the samples were conducted using FT-IR spectroscopy (Nicolet 380; Thermo Fisher Scientific Inc.) using a single reflection attenuation total-reflection (ATR) method, static water contact angle (θ) measurements (DM-301, Kyowa Kaimen), scanning electron microscopy (SEM; JSM-7001F, JEOL Co., Ltd.) and energy-dispersive X-ray spectroscopy (EDX; JSM-7001F, JEOL Co., Ltd.) with acceleration voltage of 10 kV. Samples for SEM observations in which EDX analysis was not conducted were coated with Pt-Pd using an ion-sputtering device (E-1030; Hitachi Ltd.) to prevent charge-up.

The average water contact angle of the PI film surfaces was changed from 77 ± 1.8° to 23 ± 1.4° after 10 min of aqueous sodium hydroxide treatments, which showed that the surface became hydrophilic. FT-IR measurements confirmed formation of carboxylic acid groups on the films surfaces after the treatments (data not shown). These results were well comparable to our previous report showing that about 10 min of treatment was sufficient to produce carboxylic acid groups all over the PI film surfaces. If microscopic topological changes of PI film surfaces occurred, resulting rough surfaces might induce HAp deposition in SBFs. SEM observation confirmed that such surface morphological change did not occur by the 10-min of treatments (data not shown). Much longer times of the treatments decomposed macroscopic film morphology.

After incubation in 1.5SBF at 36.5°C for 7 days, deposits were clearly observed, even by naked eyes, on most parts of the surface-hydrolyzed PI films, whereas such deposits were not observed for the case of unmodified PI film surfaces. SEM images of the surface-hydrolyzed PI film surfaces showed formation of semispherical deposits consisted of plate-like objects. The deposits did not cover the film surfaces completely and most of them existed as agglomerates. On the other hand, no such deposits were found for the case of unmodified PI film surfaces [Fig. 2(c)]. FT-IR spectra for the deposits formed on the surface-hydrolyzed PI films surfaces exhibited two intense absorption peaks in the region of about 1150–900 and 650–500 cm⁻¹, which were respectively assignable to v₁(PO₄³⁻) groups and v₄(PO₄³⁻) groups [Fig. 3(a)].²¹⁻²⁵ The shape of the spectra in the region about 1600–1400 cm⁻¹ might indicate the presence of CO₃²⁻, although PI also has peaks in this region.²⁶ EDX spectra of the deposits showed that they contained Ca, P, O, and small amounts of Na and Mg [Fig. 3(b)]. The Ca/P elemental ratio of the deposits appeared smaller than that of stoichiometric HAp (1.67). This might come from the fact that EDX is a semi-quantitative method. Smaller Ca/P ratio and presence of Na and Mg in the EDX spectra are also sometimes seen for HAp deposited from SBFs. Although we have not finished the X-ray diffraction (XRD) studies for the deposits because of technical reasons, these results clearly show that such surface-selective hydrolysis of PI films were effective to deposit apatite-like calcium phosphates thereon. Carboxylic acid groups, having ability to bind calcium ions, displayed on the film surfaces should act as HAp nucleation sites in 1.5SBF. Because homogeneous HAp coating on all over the surface of surface-hydrolyzed PI films was not achieved (Fig. 2), we next examined effect of aqueous calcium chloride treatments of the surface-hydrolyzed PI films before incubation in 1.5SBF on the mineralization behavior. Previous studies showed that such kinds of treatments are effective to enhance HAp deposition on material surfaces in SBFs. The surface-hydrolyzed PI films were treated with aqueous calcium chloride (2.5 M) for 1 h and then incubated in 1.5SBF. SEM results show that deposits were clearly observed after one-day incubation in 1.5SBF for this case [Fig. 4(a)]. Magnified SEM images showed that thin layer of deposits consisted of plate-like objects covered almost all over the film surfaces [Fig. 4(b)]. In addition, granular deposits having micrometer sizes were also formed thereon. FT-IR spectra of these samples were similar to that shown in Fig. 3(a) (data not shown).

These results support that aqueous calcium chloride treatments enhanced formation of apatite-like calcium phosphate layers in 1.5SBF. It is reasonable because calcium ions can bind to carboxylic acid groups on the hydrolyzed PI film surfaces by dry chamber (AS ONE DOV-750A). After an appropriate length of time, the samples were picked up, rinsed with ultrapure water, and dried using gentle nitrogen flushing. In some cases, the PI films were treated with aqueous calcium chloride (2.5 M) for 1 h at room temperature and rinsed using distilled water gently before incubation in 1.5SBF. HAp deposition on unmodified PI films in 1.5SBF was also examined as control. Characterizations of the samples were conducted using FT-IR spectroscopy (Nicolet 380; Thermo Fisher Scientific Inc.) using a single reflection attenuation total-reflection (ATR) method, static water contact angle (θ) measurements (DM-301, Kyowa Kaimen), scanning electron microscopy (SEM; JSM-7001F, JEOL Co., Ltd.) and energy-dispersive X-ray spectroscopy (EDX; JSM-7001F, JEOL Co., Ltd.) with acceleration voltage of 10 kV. Samples for SEM observations in which EDX analysis was not conducted were coated with Pt-Pd using an ion-sputtering device (E-1030; Hitachi Ltd.) to prevent charge-up. The average water contact angle of the PI film surfaces was changed from 77 ± 1.8° to 23 ± 1.4° after 10 min of aqueous sodium hydroxide treatments, which showed that the surface became hydrophilic. FT-IR measurements confirmed formation of carboxylic acid groups on the films surfaces after the treatments (data not shown). 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aqueous calcium chloride treatments, which resulted in increase of local calcium ion concentration on the PI film surface when immersed in 1.5SBF. In this case, initial nucleation sites should increase compared to the case without the treatments. Such a difference probably caused the morphological difference of the deposits between the case with the treatments (thin apatite-like layers covering all over the surface) (Fig. 4) and that without the treatments (semispherical deposits scattered) (Fig. 2). In the case of aqueous calcium chloride-treated samples, additional granular deposits were formed on the sample surfaces. This is probably the result of homoeopitaxial deposition initiated from already-formed thin apatite-like layers. Preliminary cross-sectional SEM observations indicated that the thicknesses of the thin apatite-like layers were about few micrometers. On the other hand, those of the granular deposits, formed on the thin layers, were much thicker (about ten micrometers or so) (data not shown). In the case of HAp deposition on solid substrates in SBFs, such a homoeopitaxial deposition and HAp layer formation triggered by heterogeneous nucleation are competitive, especially for the cases of HAp deposition on solid substrates in SBFs, such as calcium phosphate coatings on polyimide films by utilizing surface-selective hydrolysis treatments.

This study demonstrated that simple alkaline solution treatments were effective to deposit apatite-like calcium phosphates on PI film surfaces in 1.5SBF and aqueous calcium chloride treatments further enhanced nucleation ability of the film surfaces. Detailed characterizations including XRD studies and evaluation of potential applications of the resulting hybrid films have been conducting in our groups, which will be reported in our forthcoming papers. Robustness of the resulting apatite-like layers might be a considerable point in the resulting hybrid materials depending on their applications. The present process is simple, low-cost and can be widely applicable to other kinds of commonly used polymers containing ester, amide, or imide linkages.

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