

Surface modification of organic polymers with bioactive titanium oxide without the aid of a silane-coupling agent

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Abstract Polyethylene (PE), polyethylene terephthalate (PET), ethylene-vinyl alcohol copolymer (EVOH), and poly(ϵ -caprolactam) (Nylon 6) were successfully modified with a thin crystalline titanium oxide layer on their surfaces by a simple dipping into a titanium alkoxide solution and a subsequent soak in hot HCl solution, without the aid of a silane-coupling agent. The surface modified polymers formed a bone-like apatite layer in a simulated body fluid (SBF) within a period of 2 days. PE, PET, and Nylon 6 formed an apatite layer faster and had a higher adhesive strength to the apatite. Three-dimensional fabrics with open spaces in various sizes containing such surface modified polymer fibers are expected to be useful as bone substitutes, since they may be able to form apatite on their constituent fibers in the living body, and thus, integrate with living bone.

1 Introduction

Some ceramics, such as Bioglass[®] [1], glass-ceramic A-W [2], sintered hydroxyapatite [3], and β -tricalcium phosphate [4] have been shown to bond to living bone. These materials are currently used as important bone substitutes. Recently, some metals, such as titanium [5, 6] and tantalum [7, 8] have also been shown to bond to living bone when they are subjected to NaOH and heat treatments. These are now being applied to artificial hip joints. All these bioactive ceramics and metals, however, show higher elastic moduli than that of human cortical bone. Some composites of polyethylene (PE) with hydroxyapatite [9], glass-ceramic A-W [10], or titania [11] particles have been developed as bioactive materials with lower elastic moduli. Their bioactivities however, cannot be increased to a higher level, because they depend the fraction of exposed bioactive inorganic particles, and their inorganic particle content is not very high.

It is expected that a highly bioactive flexible material with a low elastic modulus can be obtained if organic fibers can be fabricated into a three-dimensional structure in various sizes, with open spaces, and modified with a bioactive phase on the fiber's surface. The resultant product may be useful as a bone substitute, since it could be integrated with living bone. We have previously shown that polymers such as, polyethylene terephthalate (PET), ethylene-vinyl alcohol copolymer (EVOH), and poly(ϵ -caprolactam) (Nylon 6) can be modified with bioactive titanium oxide on their surfaces when they are treated with a silane-coupling agent, titania solution, and hot HCl solution [12, 13]. However, silane-coupling agents sometimes exhibit cyto-toxicity.

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In this work, surface modification with bioactive titanium oxide was attempted for PE, PET, EVOH, and Nylon 6 without the aid of a silane-coupling agent.

2 Experimental procedure

2.1 Preparation of the polymer samples

Pellets of low-density linear polyethylene ($M_w = 10,000$ D, Toyoboseki, Co. Ltd., Osaka, Japan), PET (Toyoboseki, Co. Ltd., Osaka, Japan), EVOH (Kuraray, Co. Ltd., Kurashiki, Japan) with an ethylene content of 32 mol%, and poly(ϵ -caprolactam) (Scientific Polymer Products, Co. Ltd., Tokyo, Japan) were placed in an aluminum and brass mold, heated to 5 °C above their melting points (180, 270, 210, and 230 °C for PE, PET, EVOH, and Nylon 6, respectively), and then pressed under a pressure of 9 MPa for 10 min. The resultant plates were cut and abraded with a No. 400 diamond pad into $10 \times 10 \times 1$ mm³ pieces, and then, washed with 2-propanol (Nacalai-Tesque, Kyoto, Japan) in an ultrasonic bath for 30 min.

2.2 Modification with titanium oxide

A titania solution comprising of $\text{Ti}(\text{O}-i\text{-C}_3\text{H}_7)_4$, H_2O , $\text{C}_2\text{H}_5\text{OH}$, and HNO_3 in a 1.0:1.0:9.25:0.1 molar ratio was prepared by mixing titanium isopropoxide ($\text{Ti}(\text{O}-i\text{-C}_3\text{H}_7)_4$, Nacalai-Tesque, Inc., Kyoto, Japan), ultra-pure water, ethyl alcohol, and 60 mass% HNO_3 aqueous solution (Nacalai-Tesque, Inc., Kyoto, Japan) at 0 °C. The polymer samples described above were soaked in the titania solution at 25 °C for 24 h, withdrawn from the solution at a rate of 2 cm/min, and then dried in air at 80 °C for 24 h. After drying, the TiO_2 -dipped samples were soaked in a 0.1M-HCl aqueous solution at 80 °C for 8 days. The samples were then removed from the solution, washed with ultra-pure water, and finally dried in air at 40 °C for 24 h.

2.3 Soaking in an SBF

The bioactivity of the titania-modified samples was evaluated by examining their apatite-forming ability in a simulated body fluid (SBF) with ion concentrations ($\text{Na}^+ = 142.0$, $\text{K}^+ = 5.0$, $\text{Mg}^{2+} = 1.5$, $\text{Ca}^{2+} = 2.5$, $\text{Cl}^- = 147.8$, $\text{HCO}_3^- = 4.2$, $\text{HPO}_4^{2-} = 1.0$, $\text{SO}_4^{2-} = 0.5$ mol m⁻³, pH = 7.40) nearly equal to those of human blood plasma [14] at 36.5 °C for a period of 2 and 7 days. It has already been shown that various materials are able to form apatite on their surfaces in

an SBF, and bond to living bone through the apatite layer formed on their surfaces in the living body. Our SBF was prepared by dissolving reagent-grade chemicals (NaCl , NaHCO_3 , KCl , $\text{K}_2\text{HPO}_4 \cdot 3\text{H}_2\text{O}$, $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, CaCl_2 , and Na_2SO_4 (Nacalai-Tesque, Inc., Kyoto, Japan)) in ultra-pure water, and buffering at pH = 7.40 with tris-(hydroxymethyl)-aminomethane ($((\text{CH}_2\text{OH})_3\text{CNH}_2)$) and 0.1 M HCl solution (Nacalai-Tesque, Inc., Kyoto, Japan) at 36.5 °C. The samples were soaked in 30 ml of the SBF. After a given period, they were removed from the SBF solution, washed with ultra-pure water, and then dried in air at 40 °C for 24 h.

2.4 Analysis of the surface of the polymer samples

The surfaces of the polymer samples after treatment with titania and subsequent HCl solution were examined using X-ray photoelectron spectroscopy (XPS, Model ESCA-3200, Shimadzu Ltd. Kyoto, Japan) using the MgK_α line at 1,305.0 eV. The surfaces of the samples before, and after TiO_2 modification and SBF soaking were analyzed using attenuated total reflectance Fourier-transform infrared spectroscopy (ATR-FTIR, Model Magna 860, Thermo-Nicolet Ltd., Yokohama, Japan), thin-film X-ray diffraction (TF-XRD, Model RINT2500, Rigaku Co., Tokyo, Japan) and field-emission scanning electron microscopy (FE-SEM, Model S-4700, Hitachi Ltd., Tokyo, Japan) combined with energy dispersive X-ray spectroscopy (EDX, Model EMAX9000 Horiba Ltd., Kyoto, Japan). The adhesion of the titanium oxide and apatite layers to the polymer substrates was evaluated by detaching them using Scotch[®] tape.

3 Results

Figure 1 shows XPS spectra of the Ti_{2p} line of the surface of a polymer sample treated with the titania and titania-hot HCl solutions. It can be seen from Fig. 1 that the Ti_{2p} peak [15, 16] is clearly observed for the polymers treated with the titania solution, and that the position of the peak shifts to lower binding energies with the subsequent titania-hot HCl treatment.

No change was observed in the ATR-FTIR spectrum for all the examined polymers on treatment with the titania-hot HCl solutions, as shown in Fig. 2. After subsequent soaking in the SBF for periods of 2 and 7 days, an intense peak ascribed to phosphate groups was newly observed around 1,000 cm⁻¹. After soaking

Fig. 1 Ti_{2p} XPS spectra of the surfaces of polymer samples treated with the titania and subsequent hot HCl solutions

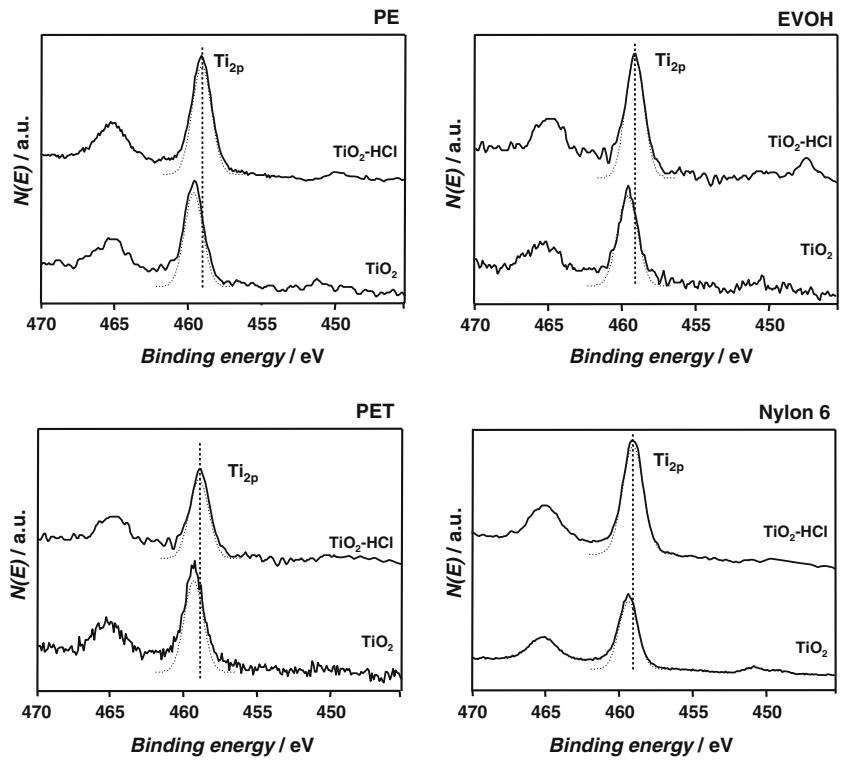
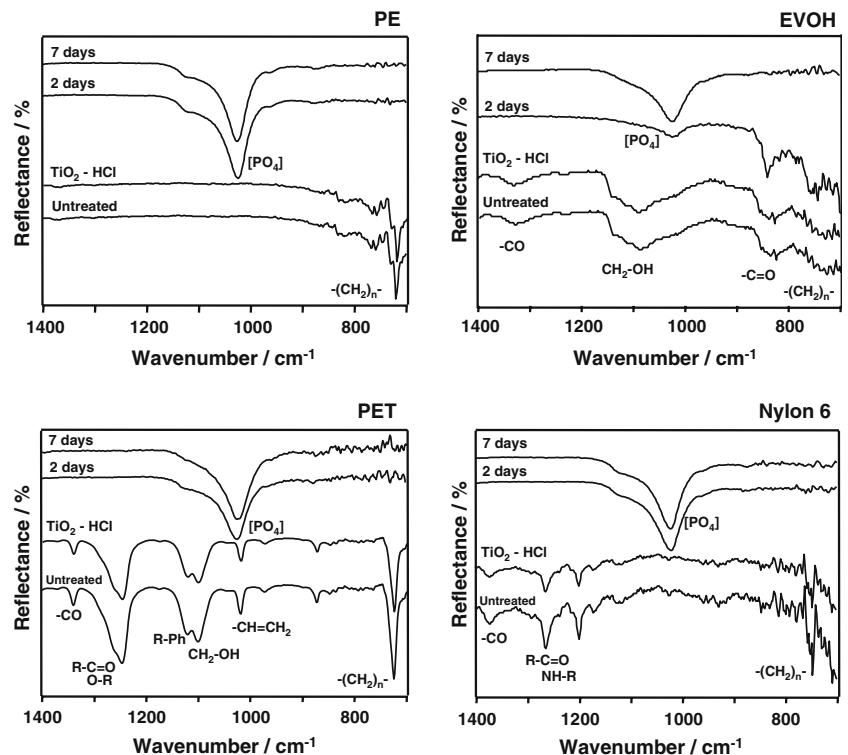


Fig. 2 ATR-FTIR spectra of the surfaces of untreated polymer samples and those treated with the titania-hot HCl solutions and subsequently soaked in the SBF for periods of 2 and 7 days

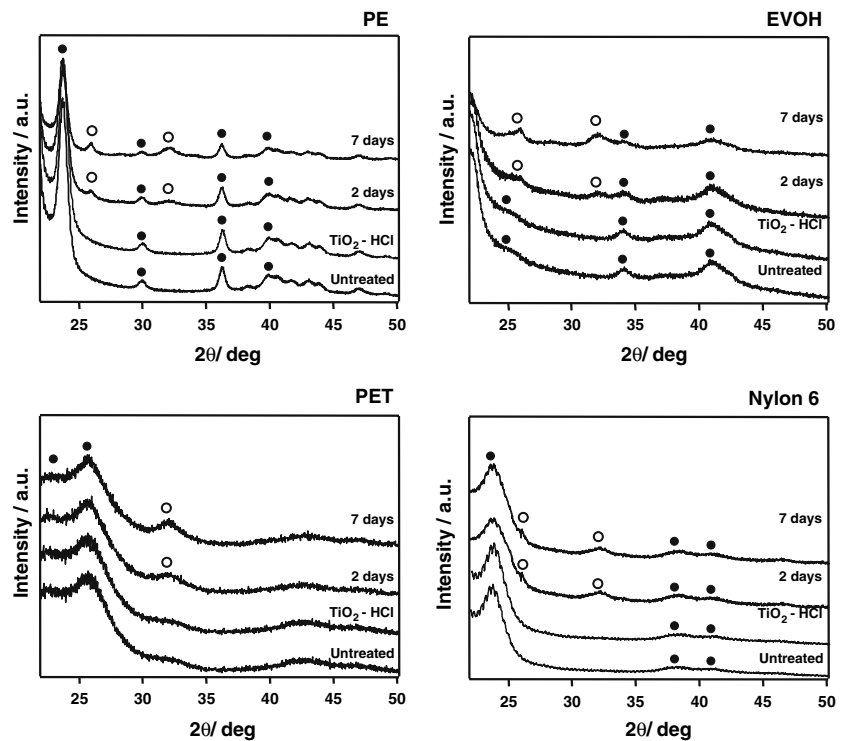


in the SBF for 2 days, the intensity of this peak was higher for PE, PET, and Nylon 6 than in for EVOH.

Figure 3 shows TF-XRD patterns of the surfaces of polymer samples that were untreated and treated with

the titania-hot HCl solutions, which were subsequently soaked in the SBF for periods of 2 and 7 days. No other peaks besides those ascribed to the polymer samples were detected, even after the treatment with the

Fig. 3 TF-XRD patterns of the surfaces of untreated polymer samples and those treated with the titania-hot HCl solutions and subsequently soaked in the SBF for periods of 2 and 7 days (Key: ● = Polymer and ○ = Apatite)



titania-hot HCl solutions, for all the samples examined. After subsequent soaking in the SBF for 2 days, some peaks ascribed to apatite were newly detected, and their intensities increased with increasing soaking period in the SBF.

Figure 4 shows SEM pictures and EDX spectra of the surfaces of untreated polymer samples and those treated with the titania-hot HCl solutions, and subsequently soaked in the SBF for 2 and 7 days. It can be seen from Fig. 4 that all the examined polymers were covered with a thin titanium oxide layer containing nano-sized particles after the titania-hot HCl solutions treatment. The layers on the PE, PET, and Nylon 6 were continuous, but the layer on EVOH exhibited cracks. Thus treated, PE, PET, and Nylon 6 were fully covered with apatite within 2 days in the SBF, whereas EVOH was only partially covered with apatite after 2 days, but was fully covered after 7 days. The apatite formed consisted of nano-sized particles, and contained a small amount of magnesium, similar to normal bone mineral.

Figure 5 shows FE-SEM pictures and EDX spectra of the surfaces of polymer samples formed with an apatite layer on their surfaces that were treated with the titania-hot HCl solutions in an SBF for 7 days, before, and after the detaching test using Scotch[®] tape. The apatite layers formed on the surfaces of PE, PET, and Nylon 6 were not detached by the tape, and removed the glue from the tape, whereas

the apatite layer formed on EVOH was completely detached.

4 Discussion

It can be seen from Figs. 1 and 4 that a thin titanium oxide layer is uniformly formed on the surfaces of all the polymer samples after treatment with the titania and subsequent hot HCl solutions. Figure 1 shows that the titanium oxide layer was structurally transformed by the hot HCl treatment. However, neither the ATR-FTIR spectra in Fig. 2, nor the TF-XRD patterns in Fig. 3, provide any information on this phase transformation, because the thickness of the titanium oxide layer is too thin. The TF-XRD pattern of a thicker titanium oxide layer formed on a silane-coupled EVOH substrate by four repeated titania solution treatments, reported on in a previous paper [12], showed that the as-formed titanium oxide layer is an amorphous phase, and this transforms into a crystalline anatase phase on subsequent hot HCl treatment. In view of this, we propose that the titanium oxide layer formed on all the polymer samples in the titania and HCl solutions in this study assume the crystalline anatase phase. It should be noted here, that the titanium oxide layer was uniformly formed on all the polymers, including PE, without the aid of a silane-coupling agent. This

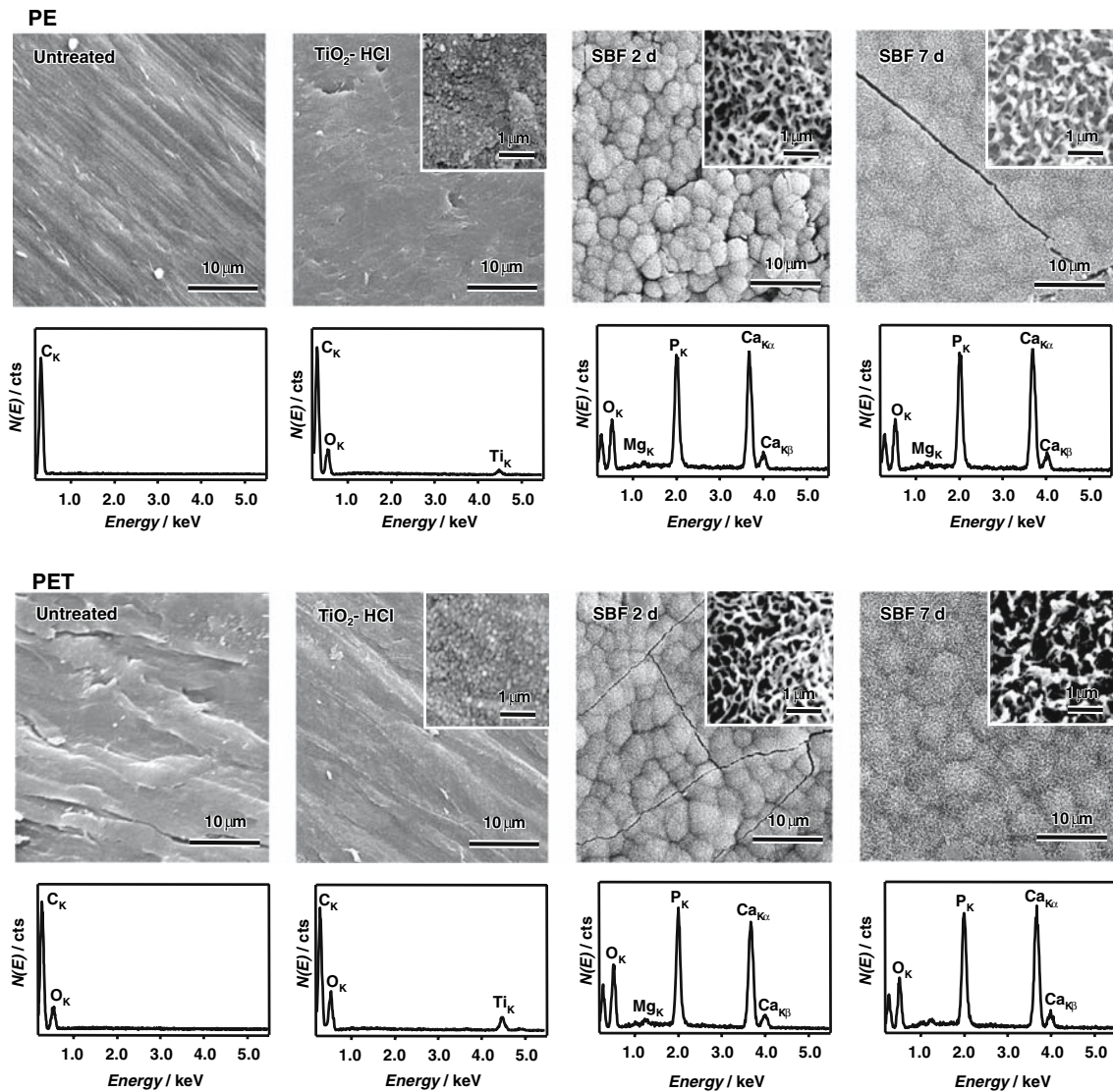


Fig. 4 FE-SEM photographs and EDX spectra of the surfaces of untreated polymer samples and those treated with the titania-hot HCl solutions and subsequently soaked in the SBF for periods of 2 and 7 days

indicates that the titanium isopropoxide ethanol solution containing water and a small volume of nitric acid reacts with the all the polymers to form a chemical bond with the polymers. The thus formed titanium oxide layer was continuous on PE, PET, and Nylon 6, but exhibited cracks on EVOH. These cracks may be the result of too strong a reaction between the titania solution and the EVOH, which could lead to breaks in the chemical bonds near the surface of the polymer.

All the polymer samples examined with a titanium oxide layer on their surfaces induced apatite formation on their surfaces, as shown in Figs. 2, 3, and 4. This is attributed to the catalytic effect of the crystalline anatase phase. It has already been reported that

amorphous titanium oxide does not induce apatite nucleation on its surface in an SBF, but crystalline anatase and rutile can induce apatite nucleation [17]. Among the polymers, EVOH showed a lower apatite-forming ability than PE, PET, and Nylon 6 did, as shown in Fig. 4. The lower apatite-forming ability of EVOH may be attributable to contamination of the titanium oxide layer, which could have been caused by a strong reaction between the titania solution and the substrate. The apatite layer formed was tightly adhered to the PE, PET, and Nylon 6 substrates, whereas it was weakly adhered to the EVOH, as shown in Fig. 5. The lower adhesive strength of the apatite layer to the EVOH substrate may be attributable to the lower adhesive strength of the titanium oxide layer to EVOH,

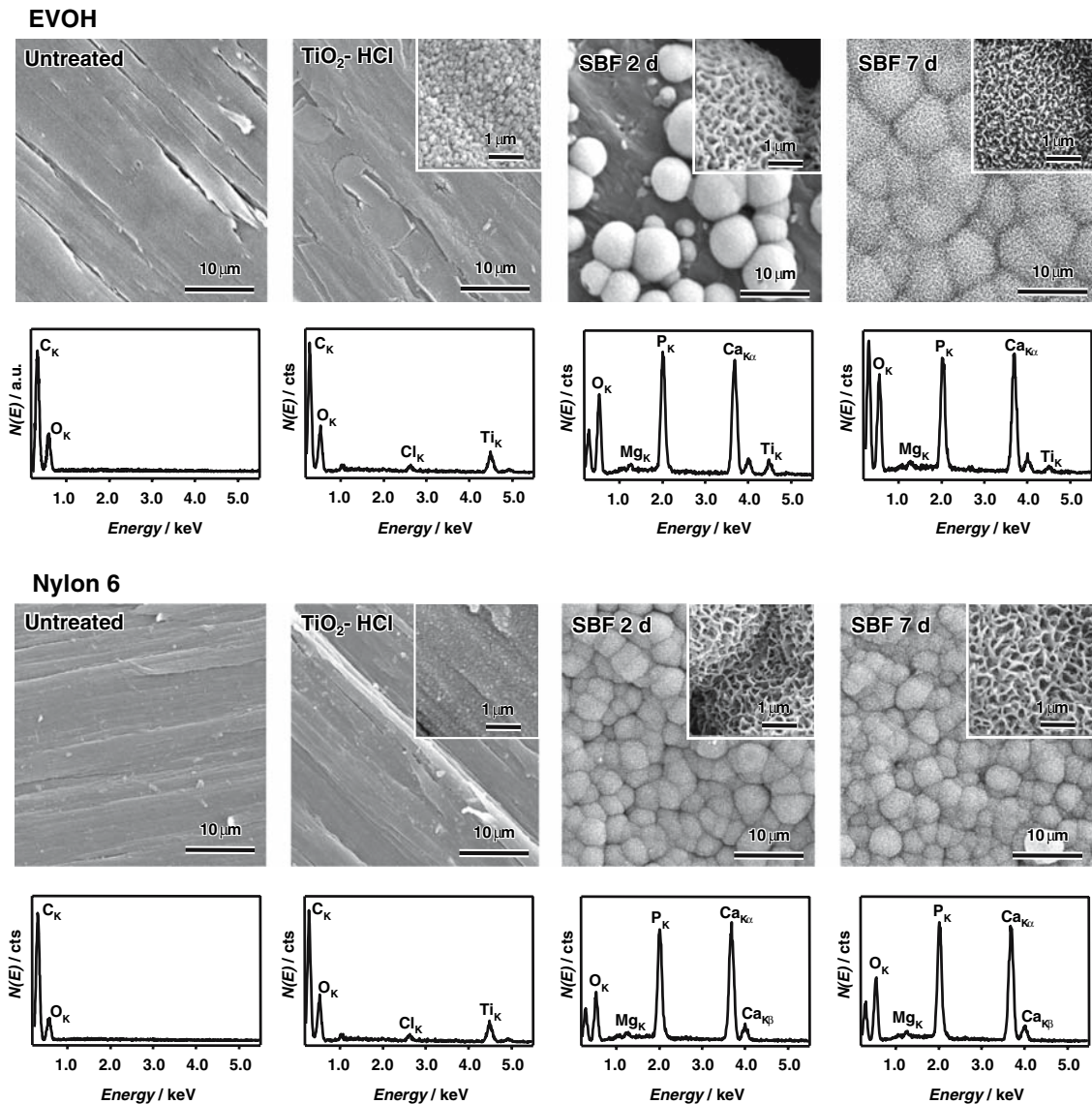


Fig. 4 continued

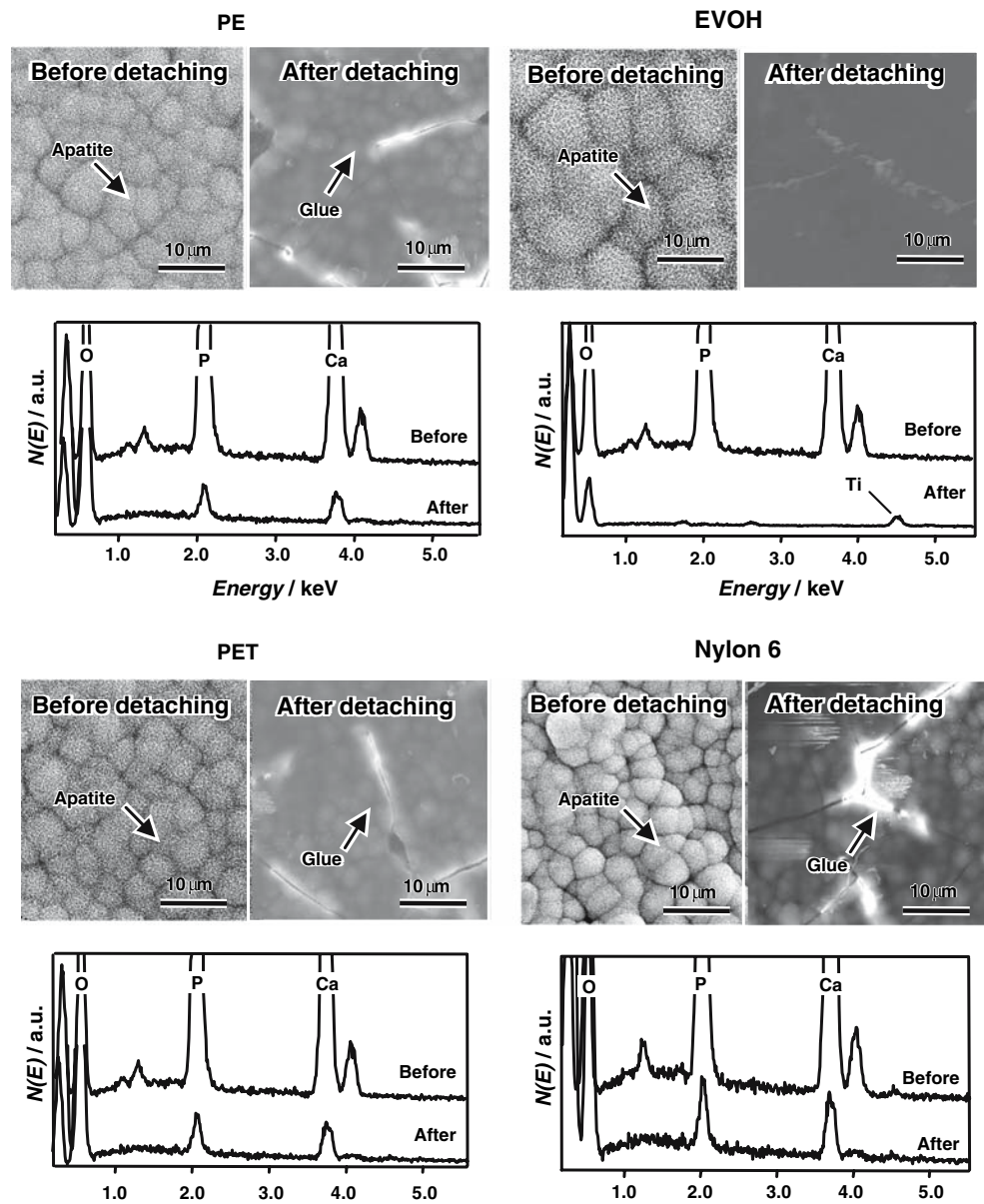
because of the strong reaction of the titania solution with the substrate.

It has been shown that various materials that form apatite on their surfaces in an SBF induce apatite formation in the living body, and bond to living bone through this apatite layer [18]. In view of this, the PE, PET, and Nylon 6 samples modified with a titanium oxide layer using the present method are expected to form a uniform apatite layer in a short period in the living body, and are expected to bond tightly to living bone. Three-dimensional fabrics with open spaces in various sizes composed of these polymer fibers modified with titanium oxide on their surfaces may be useful as bone substitutes, since they may integrate with the surrounding living bone in the living body through the apatite layer formed on the fibers.

5 Conclusions

PE, PET, EVOH, and Nylon 6 were successfully modified with crystalline titanium oxide on their surfaces by simple dipping into a titanium alkoxide alcohol solution with added water and nitric acid, and subsequent soaking in a hot HCl solution, without the aid of a silane-coupling agent. The surface-modified polymers induced apatite formation on their surfaces in an SBF within a period of 2 days. PE, PET, and Nylon 6 formed a full apatite layer in a shorter period, and had a higher adhesive strength to the apatite. Three-dimensional fabrics composed of these polymer fibers are expected to be useful bone substitutes, since they can form an apatite layer on their constituent fibers

Fig. 5 FE-SEM pictures and EDX spectra of the surfaces of polymer samples that formed apatite on their surfaces when treated with the titania-hot HCl solutions in an SBF for a period of 7 days, before, and after the detaching test using Scotch[®] tape



in the living body and bond to bone through the apatite layer.

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