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PET fiber fabrics modified with bioactive titanium oxide for bone substitutes

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Abstract A rectangular specimen of polyethylene terephthalate (PET) was soaked in a titania solution composed of titanium isopropoxide, water, ethanol and nitric acid at 25 °C for 1 h. An amorphous titanium oxide was formed uniformly on the surface of PET specimen, but did not form an apatite on its surface in a simulated body fluid (SBF) within 3 d. The PET plate formed with the amorphous titanium oxide was subsequently soaked in water or HCl solutions with different concentrations at 80 °C for different periods of time. The titanium oxide on PET was transformed into nano-sized anatase by the water treatment and into nano-sized brookite by 0.10 M HCl treatment at 80 °C for 8 d. The former did not form the apatite on its surface in SBF within 3 d, whereas the latter formed the apatite uniformly on its surface. Adhesive strength of the titanium oxide and apatite layers to PET plate was increased by pre-treatment of PET with 2 wt% NaOH solution at 40 °C for 2 h. A two-dimensional fabric of PET fibers 24 μm in diameter was subjected to the NaOH pre-treatment at 40 °C, titania solution treatment at 25 °C and subsequent 0.10 M HCl treatment at 80 °C. Thus treated PET fabric formed the apatite uniformly on surfaces of individual fibers constituting the fabric in SBF within 3 d. Two or three dimensional PET fabrics modified with the nano-sized brookite on surfaces of the individual fibers constituting the fabric by the present method are believed to be useful as flexible bone substitutes, since they could be integrated with living bone through the apatite formed on their constituent fibers.

Introduction

Ceramics such as $Na_2O–CaO–SiO_2–P_2O_5$ glasses [1], glass-ceramics with precipitated nano-sized apatite ($Ca_{10}(PO_4)(O, F_2)$) and wollastonite ($CaSiO_3$) in a $MgO–CaO–SiO_2$ glassy matrix [2], sintered hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$) [3], and sintered β-tricalcium phosphate ($Ca_3P_2O_8$) [4] have been found to bond to living bone. Recently, metals such as titanium metal and its alloys [5] and tantalum metal [6] have been found to bond to living bone after being exposed to a NaOH solution and heat treatments. These materials are called bioactive materials, and being used clinically as important bone substitutes. However, they have much higher elastic moduli than human bone and cannot be easily deformed. In such case, the surrounding bone is liable to be resorbed, since the stress is mainly borne by these materials, but not by the surrounding bones. Therefore, the contemporary desire is to develop bioactive materials with low elastic moduli.

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In order to obtain a bioactive material with a lower elastic modulus, Bonfield et al. early prepared a composite of hydroxyapatite granules with polyethylene [7, 8]. This composite is already used clinically as an artificial middle ear bone etc. However, this composite loses deformability, when the hydroxyapatite content exceeds 40 vol%. When the hydroxyapatite content is limited to less than 40 vol%, the composite can not show high bioactivity [9, 10]. Recently, a composite of bioactive titania nano-sized particles with high-density polyethylene was newly developed [11–14]. It was reported that the resultant composite showed apatite-forming ability in SBF, and its mechanical properties such as bending yield strength and Young's modulus were 65 MPa and 10 GPa, respectively [14].

Highly bioactive flexible materials with low elastic moduli could be also obtained if organic fibers were fabricated into two or three-dimensional structure containing interconnected pores of various sizes within them and modified with a bioactive phase on their surfaces. Such materials are expected to be useful as bone substitutes, as they can be deformed into various shapes and, in the body, bonelike apatite deposits on the constituent fibers to make hybrids with living bone.

We previously briefly showed that organic polymers including poly(ethylene terephthalate) (PET) are uniformly surface-modified with bioactive titanium oxide when dipped into a titanium alkoxide solution and subsequently soaked in a hot HCl solution [15]. In the previous study, however, only the results under one experimental condition were reported. In this study, conditions of treatments with titanium oxide solution and HCl solution were systematically changed for PET and apatite forming ability in SBF of the titanium oxide layer formed on PET was discussed in terms of its structure. The optimum conditions for surface modification were applied to a PET fabric.

Materials and methods

Preparation of PET specimens

The optimum conditions for surface modification were first examined by using PET plates and then applied to fabrics of PET fibers. Rectangular PET 10 × 10 × 2 mm plates and 10 × 10 mm PET fabric sheets consisting of 24 μm diameter fibers were supplied by Unitika Ltd (Osaka, Japan). The PET plates were abraded with #400 SiC sandpaper. The particle size of SiC was ranged from 40 to 60 μm. All specimens were ultrasonically washed with 2-propanol for 30 min and then dried.

Surface modification with titanium oxide

Pre-treatment of specimens

Some specimens were soaked in a 2 wt% NaOH aqueous solution (Nacalai Tesque, Inc., Kyoto, Japan) at room temperature for 1 h in an ultrasonic bath, then at 40 °C for 2 h with shaking at 120 strokes min^{-1}, then washed with ultrapure water and dried.

Preparation of titanate solution

Titanium isopropoxide ($Ti(OiC_3H_7)_4$), ethyl alcohol (C_2H_5OH), and nitric acid (60 mass% HNO_3) (Nacalai Tesque, Inc., Kyoto, Japan) were mixed with ultrapure water and stirred at 0 °C for 10 min, to give a titanate solution (solution A) with molar ratios of $Ti(OiC_3H_7)_4$:H_2O:HNO_3:C_2H_5OH of 1.0:1.0:0.1:18.5. To obtain thicker titanium oxide layers, a titanate solution (solution B) with molar ratios of $Ti(OiC_3H_7)_4$:H_2O:HNO_3:C_2H_5OH of 1.0:1.0:0.1:9.25 was also prepared. In addition, a diluted titanate solution (solution C) with molar ratios of $Ti(OiC_3H_7)_4$:H_2O:HNO_3:C_2H_5OH of 1.0:1.0:0.1:37.0 was prepared to obtain thinner oxide layers. Solution A was typically used, unless otherwise stated. Table 1 listed the compositions of the titania solutions used in this study.

Formation of titanium oxide on specimens

PET plate and fabric specimens were placed in 7.0 g of the titanate solution at 25 °C for 24 h, then drawn up at a rate of 1 cm min^{-1}, and dried at 80 °C for 24 h. This treatment was performed once, unless otherwise stated. To obtain thicker titanium oxide layers, this process was repeated three or 25 times, with drying at 80 °C for 10 min between soakings.

Post-treatment of specimens

PET specimens with titanium oxide formed on their surfaces were soaked in 7.0 g of ultrapure water or 0.10, 0.30 or 0.50 M HCl solutions (Nacalai Tesque, Inc., Kyoto,

Table 1 Compositions of titanate solutions used in this study

Notation	Composition/molar ratio			
	$Ti(OiC_3H_7)$	H_2O	HNO_3	C_2H_5OH
Solution A	1.0	1.0	0.1	18.5
Solution B	1.0	1.0	0.1	9.25
Solution C	1.0	1.0	0.1	37.0

Japan) at 80 °C for periods ranging from 12 h to 8 d, then washed with ultrapure water and dried.

Evaluation of bioactivity

It has been shown for various ceramics and metals [16] that materials that form bonelike apatite on their surfaces in simulated body fluid (SBF) [17] with ion concentrations nearly equal to those of human blood plasma will form apatite in the living body and bond to living bone through that apatite layer. Based on these findings, the bone-bonding ability, i.e., bioactivity, of the PET specimens modified with titanium oxide was evaluated by examining their apatite-forming ability in SBF.

SBF with ion concentrations of Na^+ 142.0, K^+ 5.0, Mg^{2+} 1.5, Ca^{2+} 2.5, Cl^- 147.8, HCO_3^- 4.2, HPO_4^{2-} 1.0, and SO_4^{2-} 0.5 mM were prepared by dissolving reagent-grade NaCl, $NaHCO_3$, KCl, $K_2HPO_4 \cdot 3H_2O$, $MgCl_2 \cdot 6H_2O$, $CaCl_2$, and Na_2SO_4 (Nacali Tesque, Inc., Kyoto, Japan) in ultrapure water, and buffering to pH 7.40 with tris(hydroxymethyl) aminomethane ($(CH_2OH)_3CNH_2$) and 1.00 M aqueous HCl (Nacali Tesque, Inc., Kyoto, Japan) at 36.5 °C. PET specimens modified with titanium oxide were soaked in 30 ml of SBF at 36.5 °C for 3 d, washed with ultrapure water, and then dried at room temperature.

Surface characterization

The structures of the surfaces of the PET specimens subjected to the treatments described above were examined by thin-film X-ray diffraction (TF-XRD, RINT2500, Rigaku Co., Tokyo, Japan) with CuKα radiation, with the incident beam set at 1° against the specimen surface. Specimens were also examined using field emission scanning electron microscope (FE-SEM, JSM-6700F, JEOL Ltd, Tokyo, Japan). Substances scratched from the surfaces of the treated PET specimens were examined by powder X-ray diffraction (P-XRD, RINT2500, Rigaku Co., Tokyo, Japan) and high-resolution transmission electron microscopy (HR-TEM, JEM4010, JEOL Ltd, Tokyo, Japan).

Measurement of the adhesion of the surface layer

The adhesion of the titanium oxide and apatite layers formed on the PET plates in SBF for 3 d was examined qualitatively by detaching these layers using Scotch® tape. The thickness of apatite layer was roughly estimated at about 5 μm. In addition, PET plates with titanium oxide and apatite formed on their surfaces in SBF for 6 d were bonded to a stainless steel jig 10 × 10 mm^2 in area with a rapid-type Araldite® glue (Huntsman Advanced Materials, Everberg, Belgium). The thickness of apatite layer was roughly estimated at about 10 μm. A tensile load was applied normal to the PET plates with an Instron-type testing machine (DSS500, Shimadzu Co., Kyoto, Japan) at a crosshead speed of 0.5 mm min^{-1} until fracture occurred. For each type of PET plate, 10–12 specimens were used and the mean and standard deviation of the adhesive strength were calculated from the fracture load and surface area.

Results and discussion

Figures 1 and 2 show TF-XRD patterns and FE-SEM pictures of the surfaces of PET plates with titanium oxide formed on their surfaces, and subsequently subjected to no aqueous treatment, water treatment or HCl treatment at different concentrations at 80 °C for 8 d, and then soaked in SBF for 3 d. It can be seen from Figs. 1 and 2 that, in SBF, apatite does not deposit on the surface of PET plates with the as-formed titanium oxide on their surface, even after subsequent treatment with hot water. However, nano-sized bonelike apatite was deposited entirely over the surface after specimens had been treated with 0.10 M hot HCl solution. The PET plates with titanium oxide formed on their surfaces and subsequently treated with the hot HCl solutions at concentrations higher than 0.30 M also did not have apatite deposits on their surfaces after soaking in SBF. This might be attributed to dissolution of the titanium oxide in the higher concentration hot HCl solutions, as the solutions became turbid during the treatments.

Figures 3 and 4 show TF-XRD patterns and FE-SEM pictures of the surfaces of the PET plates with titanium oxide formed on their surfaces, subjected to 0.10 M HCl treatment at 80 °C for different periods and then soaked in SBF for 3 d. It can be seen from Figs. 3 and 4 that apatite is deposited only sparsely on the surface of the TiO_2–coated

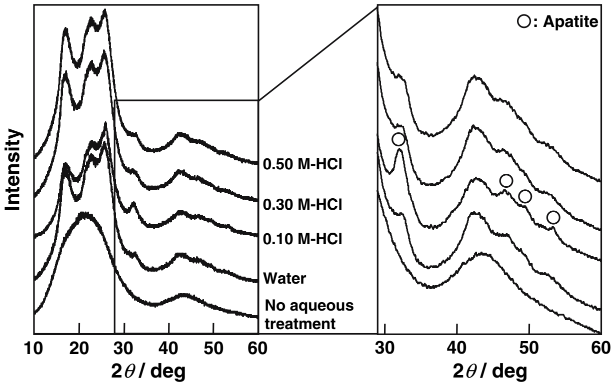


Fig. 1 TF-XRD patterns of the surfaces of PET plates with titanium oxide formed on their surfaces, subjected to no aqueous treatment, water treatment or HCl treatments at different concentrations at 80 °C for 8 d, and then soaked in SBF for 3 d

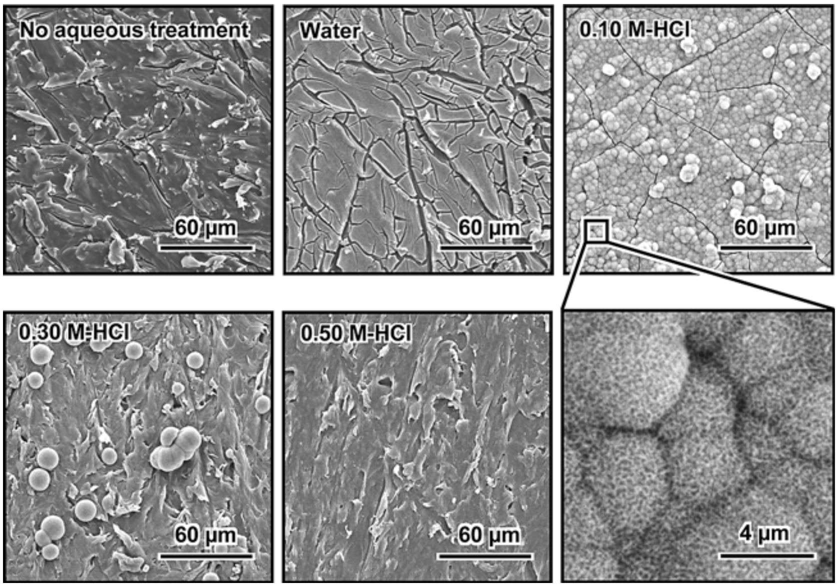


Fig. 2 FE-SEM pictures of the surfaces of PET plates with titanium oxide formed on their surfaces, subjected to no aqueous treatment, water treatment or HCl treatments at different concentrations at 80 °C for 8 d, and then soaked in SBF for 3 d

PET plates that had been subjected to the HCl treatment for 12 h, but that apatite deposits entirely cover the plates subjected to HCl treatment for periods longer than 1 d.

From these findings, we concluded that post-treatment with 0.1 M HCl solution at 80 °C for periods longer than 1 d is essential for apatite to be deposited on PET plates with titanium oxide formed on their surface when soaked in SBF.

Figure 5 shows P-XRD patterns of substances scratched from the surfaces of PET plates that had thicker titanium oxide layers formed on their surfaces by being dipped into titania solution B 25 times and subsequently subjected to no aqueous treatment, or water or 0.10 M HCl treatments for 80 °C for 8 d. It can be seen from Fig. 5 that the titanium oxide precipitate formed on the PET plates with no

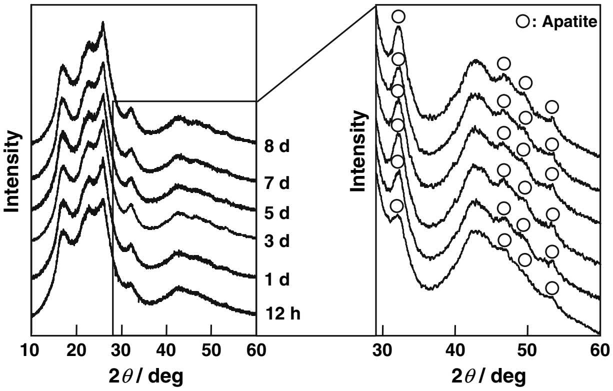


Fig. 3 TF-XRD patterns of surfaces of PET plates with titanium oxide formed on their surfaces, subjected to 0.10 M HCl treatment at 80 °C for different periods, and then soaked in SBF for 3 d

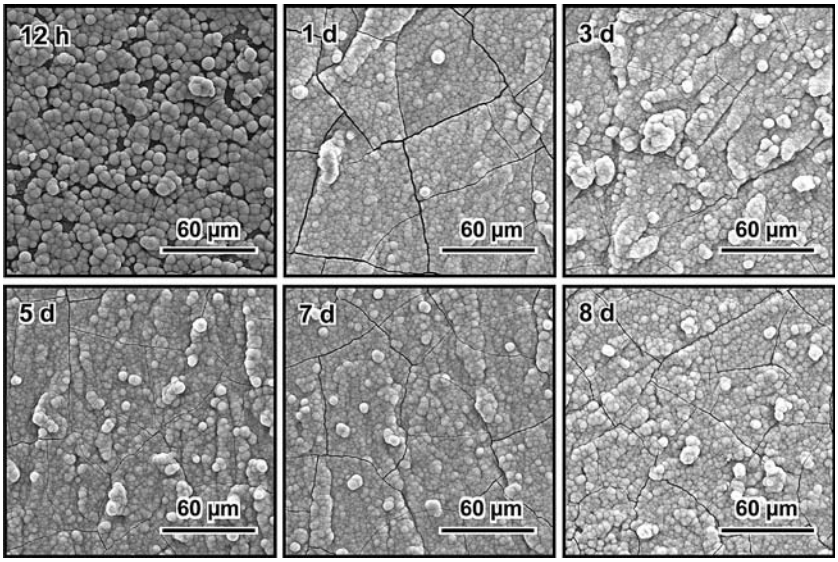
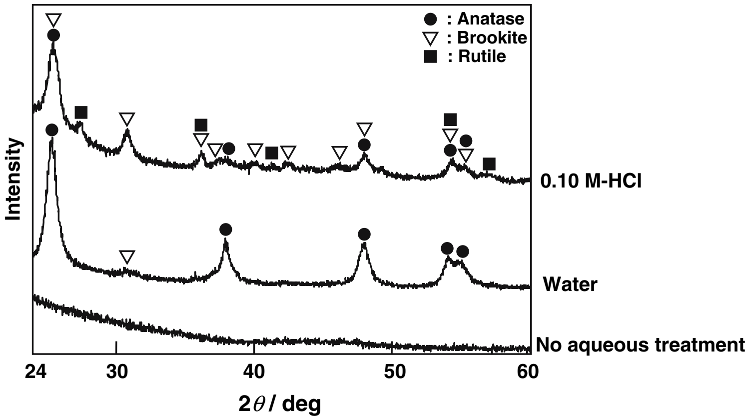


Fig. 4 FE-SEM pictures of the surfaces of PET plates with titanium oxide formed on their surfaces, subjected to 0.10 M HCl treatment at 80 °C for different periods, and then soaked in SBF for 3 d

Fig. 5 P-XRD patterns of the substances scratched from the surfaces of PET plates with thick titanium oxide layers formed on their surfaces and subjected to no aqueous treatment, or water or 0.10 M HCl treatments at 80 °C for 8 d



post-treatment has an amorphous structure. With the water post-treatment, the precipitate is crystalline anatase, and with the 0.10 M HCl post-treatment, brookite accompanied by a small amount of anatase and rutile.

Figure 6 shows the P-XRD patterns of substances scratched from the surfaces of PET plates with thick titanium oxide layers formed on their surfaces and subjected to 0.10 M HCl post-treatment at 80 °C for different periods. It can be seen from Fig. 6 that following the 0.10 M HCl post-treatment, the titanium oxide precipitates as brookite accompanied by a small amount of the anatase and rutile.

Figure 7 shows FE-SEM pictures of the surfaces of PET plates with a less thick titanium oxide layer formed on their surfaces by dipping into titanate solution A three times, and subsequently subjected to no aqueous treatment, or water or 0.10 M HCl treatments at 80 °C for 8 d. It can be seen from Fig. 7 that the titanium oxide has a smooth surface with no post-treatment, a slightly roughened surface with quite a few larger particles following the water post-treatment, and a markedly roughened surface with a 10–100 nm microstructure following the HCl post-treatment. The larger particles formed by the water post-treatment might be anatase and/or brookite crystals, since P-XRD peaks of anatase and brookite were observed after the water post-treatment (See Fig. 5).

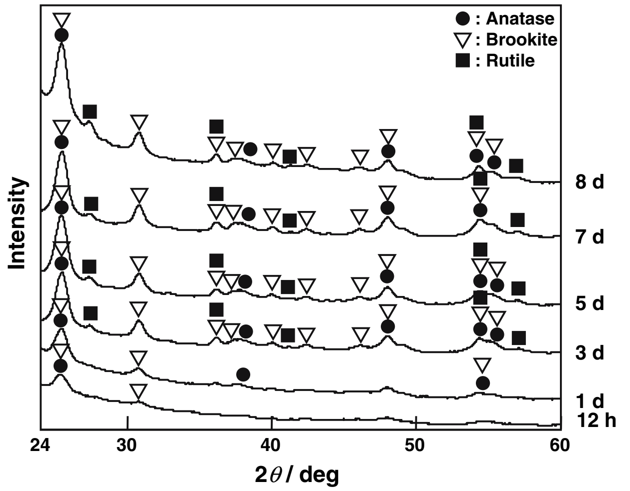


Fig. 6 P-XRD patterns of substances scratched from the surfaces of PET plates with thick titanium oxide layers formed on their surfaces and subjected to 0.10 M HCl treatments at 80 °C for different periods

Figures 8 and 9 show HR-TEM pictures and electron diffraction patterns of substances scratched from the surface of PET plates with the thicker titanium oxide layers formed on their surfaces and subjected to water or 0.10 M HCl post-treatment at 80 °C for 8 d, respectively. It can be seen from Figs. 8 and 9 that the titanium oxide layer precipitates are crystalline anatase 10–20 nm in size after the water treatment and brookite and/or anatase and rutile 10–100 nm in size after the HCl treatment. It can be concluded from these findings that the crystalline 10–100 nm brookite precipitated in the titanium oxide by the 0.10 M HCl post-treatment induces apatite formation in SBF.

Figure 10 shows FE-SEM pictures of the surfaces of PET plates with and without NaOH pre-treatment, with titanium oxide formed on their surfaces, then subjected to 0.10 M HCl post-treatment at 80 °C for 8 d, soaked in SBF for 3 d to deposit apatite, and then subjected to the detaching test with Scotch® tape. It can be seen from Fig. 10 that in the detaching test the apatite was partly peeled from the PET plate without NaOH pre-treatment, whereas it was not peeled off from the PET plate with NaOH pre-treatment, and took glue from the Scotch® tape. This indicates that adhesive between apatite and PET plate was increased by the NaOH pre-treatment.

Figure 11 shows the adhesive strengths of the surface layers of the PET plates with and without NaOH pre-treatment, with titanium oxide formed on their surfaces, then subjected to 0.10 M HCl post-treatment at 80 °C for 8 d, soaked in SBF for 6 d to deposit apatite. It can be seen from Fig. 11 that NaOH pre-treatment gives slightly higher adhesive strength to the surface layer, which might be

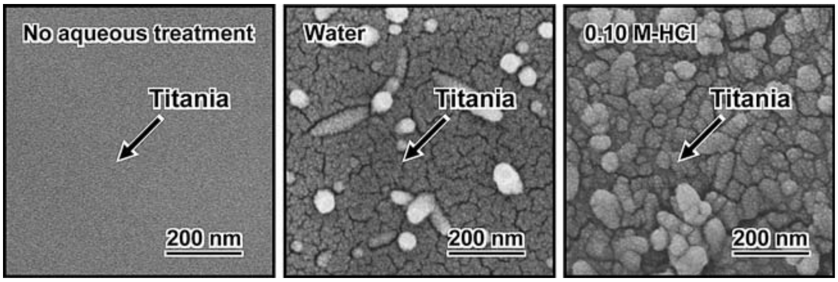


Fig. 7 FE-SEM pictures of surfaces of PET plates with titanium oxide formed on their surfaces and subjected to no aqueous treatment, or water or 0.10 M HCl treatments at 80 °C for 8 d

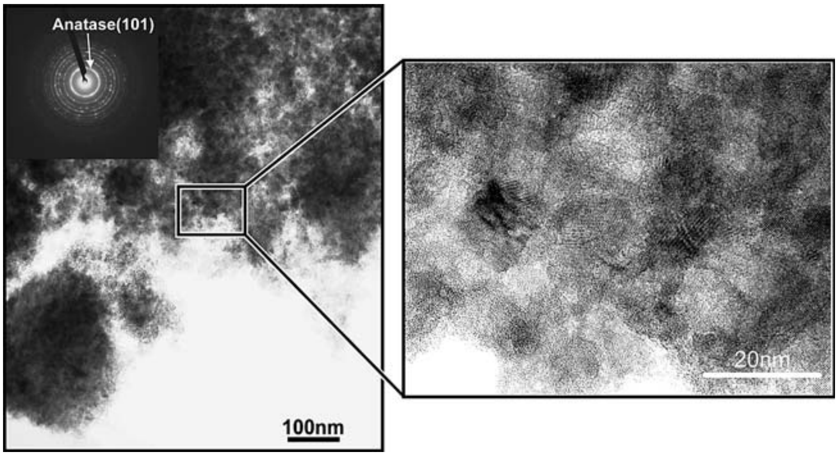


Fig. 8 HR-TEM picture and electron diffraction pattern of substance scratched from the surface of PET plate with a thick titanium oxide layer formed on its surface and subjected to water treatment at 80 °C for 8 d

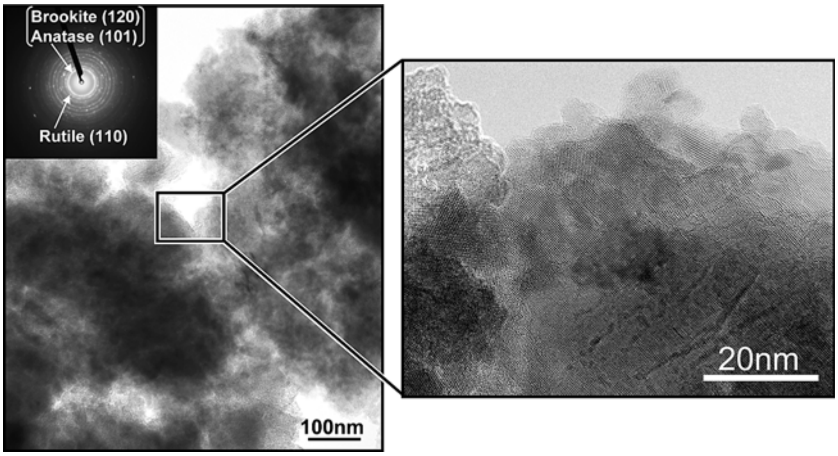


Fig. 9 HR-TEM picture and electron diffraction pattern of substance scratched from the surface of PET plate with a thick titanium oxide layer formed on its surface and subjected to 0.10 M HCl treatment at 80 °C for 8 d

attributed to the formation of chemical bonds between Ti–OH groups of the titanium oxide and C–OH groups formed on the PET surface by saponification of the ester in PET by the NaOH pre-treatment.

Figure 12 shows FE-SEM pictures of a PET fabric subjected to NaOH pre-treatment, with titanium oxide formed on their surfaces and subjected to 0.10 M HCl post-treatment at 80 °C for 8 d, and then soaked in SBF for 3 d. The treatments with NaOH, titania, and HCl solutions were conducted in an ultrasonic bath at room temperature for only the first 1 h, and then conducted under the conditions described in the Experimental section for the remaining periods. It can be seen from Fig. 12 that PET fabric subjected to the treatments described above has nano-sized bonelike apatite uniformly precipitated on the surfaces of the individual fibers constituting the fabric within 3 d of soaking in SBF. Thus, surface-modified PET fabric had apatite uniformly formed on its constituent fibers with soaking in SBF, even after being wound around a stainless steel rod 3 mm in diameter. This means that the bioactive titanium oxide layer is not peeled from the surfaces of the fibers even when the fabric is sharply bent.

In addition, when the titanium oxide on the surface of the PET fabric was modified by using solution C, the

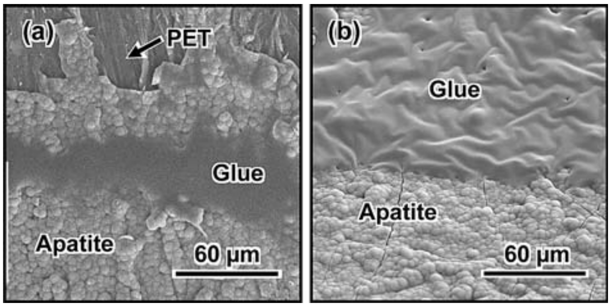


Fig. 10 FE-SEM pictures of the surfaces of PET plates without (**a**) and with (**b**) NaOH pre-treatment, with titanium oxide formed on their surfaces, subjected to 0.10 M HCl post-treatment at 80 °C for 8 d, soaked in SBF for 3 d to deposit apatite, and then subjected to detaching tests with Scotch® tape

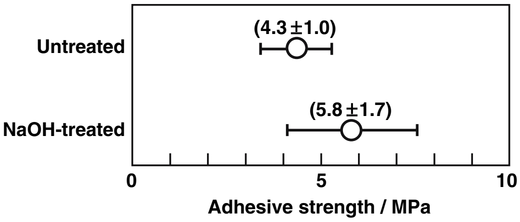


Fig. 11 Adhesive strengths of the surface layers of PET plates with and without NaOH pre-treatment

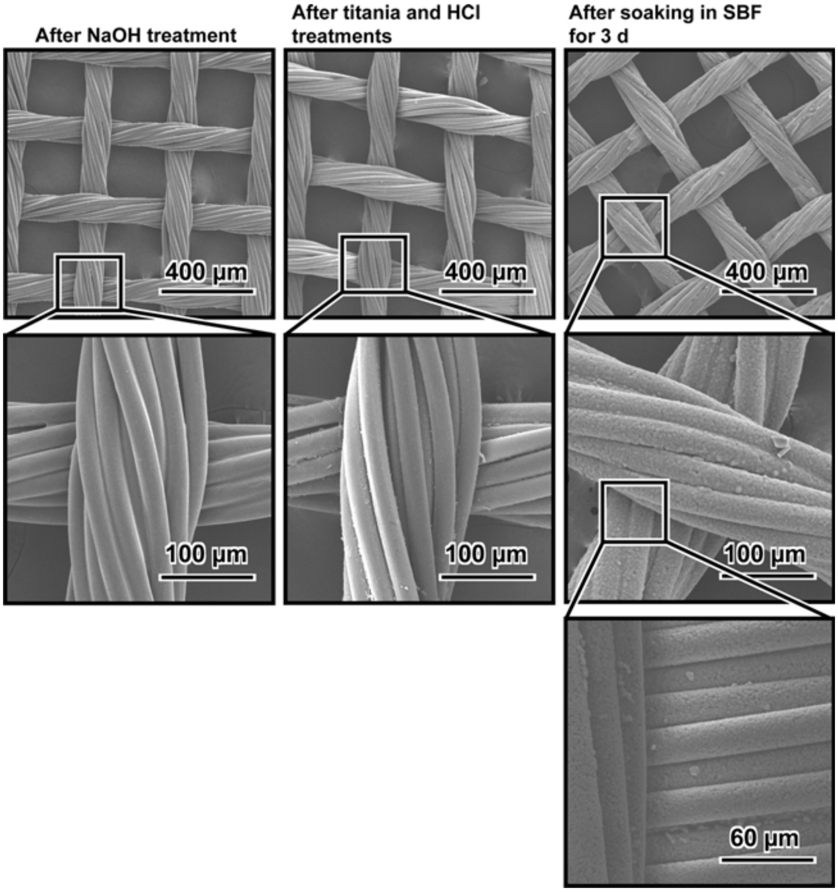
apatite formed uniformly on the constituent fibers of the resultant product with soaking in SBF (data were not shown). This means that a thin titanium oxide layer is effective in inducing PET bioactivity.

PET fibers exhibit high tensile strength and are stable in the body environment for long periods [18]. PET fiber fabric is already clinically used for artificial ligaments [19, 20]. Two or three-dimensional fabrics of PET fibers, with interconnecting pores of various sizes within them, modified with bioactive titanium oxide on their surfaces by the methods described here are anticipated to be useful as flexible prostheses for bone, as bonelike apatite might form on the constituent fibers in the living body.

Conclusions

This study demonstrates that PET fibers can be modified with a bioactive titanium oxide by being dipped into a titania solution and subsequently treated with a hot HCl solution. Nano-sized brookite, which is responsible for the bioactivity, is precipitated in the titanium oxide by the HCl treatment. Adhesion of the titanium oxide to PET is improved by pre-treatment of the PET with a NaOH solution. Two or three-dimensional fabrics of these PET fibers, with

Fig. 12 FE-SEM pictures of PET fabrics subjected to NaOH pre-treatment, titania and HCl treatments and soaking in SBF for 3 d



interconnecting pores of various sizes within them, modified with bioactive titanium oxide on their surfaces are anticipated to be useful as flexible bone substitutes.

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