Apatite formation on CaO-free polydimethylsiloxane (PDMS)-TiO_2 hybrids

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Polydimethylsiloxane (PDMS)-TiO_2 hybrids with PDMS ($M = 550$)/tetraethylorthotitanate molar ratios at 0.27, 0.68 and 1.35, i.e. Si/Ti atomic ratios at 2, 5 and 10 (hybrids PD2, PD5 and PD10, respectively) were prepared by a sol–gel method. Hybrid PD2 formed many cracks. Hybrids PD5 and PD10 were subjected to hot-water treatment 80 °C for 7 d. Hybrid PD5 produced cracks, whereas hybrid PD10 was crack-free after the hot-water treatment. Hybrid PD10 took a homogeneous amorphous structure before the hot-water treatment, and precipitated anatase particles 10–20 nm in size after the hot-water treatment. Hybrid PD10 did not form apatite on its surface in a simulated body fluid before the hot-water treatment, but formed it after the hot-water treatment. The obtained hybrid showed elastic deformation as large as 200% after the hot-water treatment. This kind of hybrid could be useful as a new type of bone-repairing material.
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1. Introduction

Some ceramics, such as Bioglass® [1], sintered hydroxyapatite [2] and glass–ceramic A–W [3], form bone-like apatite on their surfaces in the living body and bond to living bone through this apatite layer. They are known as bioactive ceramics and are already used clinically as important bone-repairing materials. However, these bioactive ceramics are essentially brittle and hence, can be used only in limited areas. New types of bioactive materials with deformability are desired to be developed. Natural bone is composed of inorganic hydroxyapatite and organic collagen, and hence shows deformability. Bonfield *et al*. developed hydroxyapatite–polyethylene composites [4]. However, these composites lose deformability, when the hydroxyapatite content exceeds 40 vol %. When the hydroxyapatite content is less than 40 vol %, the composite is unable to show high bioactivity [5].

Inorganic–organic hybrids prepared by a sol–gel method are expected to exhibit bioactivity as well as deformability. Recently, the present authors revealed that polydimethylsiloxane (PDMS)–CaO–SiO_2–TiO_2 hybrids prepared by a sol–gel method show apatite-forming ability in a simulated body fluid (SBF) with ion concentrations nearly equal to those of human blood plasma, as well as deformability [6–11]. This indicates the possibility that these deformable hybrids can form apatite on their surfaces even in the living body and bond to living bone through the apatite layer, since the apatite formation on bioactive materials can be reproduced even in SBF [5, 12]. However, it has been found that these CaO-containing hybrids show a decrease in mechanical strength in SBF [13]. On the other hand, CaO-free PDMS–SiO_2–TiO_2 hybrids do not form an apatite layer on their surfaces in SBF [6, 11].

In the present study, preparation of CaO-free PDMS-modified hybrids which can form apatite on their surfaces was attempted. It has been shown that anatase, one of the crystalline phases of TiO_2, is highly effective for apatite formation in the body environment [14]. Hybrids are expected to show high apatite-forming ability even if they contain no CaO when TiO_2 takes an anatase structure in them. In the present study, PDMS–TiO_2 hybrids were prepared by a sol–gel method and subsequently subjected to hot-water treatments. Their apatite-forming ability in SBF and mechanical properties were investigated.

2. Experimental

2.1. Preparation of hybrid

Tetraethylorthotitanate (TEOT, $Ti(OC_2H_5)_4$, Tokyo Kasei Kogyo Co., Ltd., Tokyo, Japan), ethylacetoacetate (EAcAc, Nacalai Tesque Inc., Kyoto, Japan) and ethanol (EtOH, Nacalai Tesque Inc., Kyoto, Japan) were mixed in a TEOT/EAcAc/EtOH = l/2/4 molar ratio and stirred for 30 min under ambient conditions. Polydimethylsiloxane (PDMS, HO–[–$Si(CH_3)_2$–O–]$_n$–

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TABLE I Starting compositions of PDMS–TiO_2 hybrids with different PDMS contents

Notation	Composition (molar ratio)			
	PDMS/TEOT (Si/Ti)	EAcAc/TEOT	H_2O/TEOT	EtOH/TEOT
PD2	0.27 (2)	2	2	8
PD5	0.68 (5)	2	2	8
PD10	1.35 (10)	2	2	8

PDMS – Polydimethylsiloxane, HO–[–$Si(CH_3)_2$–O–]$_n$–H, $M = 550$; TEOT – Tetraethylorthotitanate, $Ti(OC_2H_5)_4$; EAcAc – Ethylacetoacetate, $CH_3COCH_2COOC_2H_5$; EtOH – Ethanol, C_2H_5OH

H, 550 in molecular weight, Aldrich Chemical Co., Milwaukee, USA), whose amount is given in Table I, was then added to the mixture. After a further 30 min, the mixture of ultra-pure water and remaining EtOH was added, and a solution whose composition is given in Table I was obtained. After stirring for 30 min, the solution was poured into a cylindrical Teflon® container 75 mm in diameter and 20 mm in depth covered with aluminum foil with a single pinhole, and kept at 70 °C for 2 d, 100 °C for 2 d and finally 150 °C for 3 d.

2.2. Hot-water treatment of hybrid

Specimens 1–2 mm × 10 mm × 10 mm in size were cut from the as-prepared hybrids and polished with #400 silicon carbide abrasive paper. They were soaked in 10 ml of ultra-pure water at 60 or 80 °C. After various periods, they were removed from the hot water, washed with ultra-pure water and then dried at room temperature.

2.3. Soaking in SBF

Specimens, as-prepared and subjected to the hot water treatments, of 1–2 mm × 10 mm × 10 mm in size were soaked in 30 ml of SBF with pH 7.40 and ion concentrations (Na^+ 142.0, K^+ 5.0, Ca^{2+} 2.5, Mg^{2+} 1.5, Cl^- 148.8, HCO_3^- 4.2, HPO_4^{2-} 1.0, SO_4^{2-} 0.5 mM) nearly equal to those of human blood plasma [15] at 36.5 °C. After 7 d, the specimens were removed from SBF, washed with ultra-pure water and then dried at room temperature.

2.4. Analysis of structure

The structure of the hybrids before and after the hot-water treatments as well as subsequent soaking in SBF were analyzed by thin-film X-ray diffractometry (TF-XRD, RINT-2500, Rigaku Co., Tokyo, Japan), transmission electron microscopy (TEM, JEM-2000FXIII, JEOL Co., Tokyo, Japan) and field emission scanning electron microscopy (FE-SEM, S-4700, Hitachi Ltd., Tokyo, Japan). During TF-XRD, the surfaces of the specimens were fixed at an angle of 1° against the direction of the incident beam. During TEM observations, the specimens were pulverized with an agate mortar, and the particles obtained were dispersed in ethanol and attached to a poly(vinyl formal) film supported by a 200-mesh copper grid.

2.5. Evaluation of mechanical properties

As-prepared specimens were abraded with #2000 silicon carbide abrasive paper. Dumbbell-type specimens were then stamped out using a cutting die and subsequently subjected to the hot-water treatment at 80 °C for 7 d. The tensile mechanical properties of the specimens before and after the hot-water treatment were measured using an Instron-type testing machine (DSS-500, Shimadzu Co., Kyoto, Japan). The gage length was 15 mm and the crosshead speed was 2 mm min^{-1}.

3. Results

3.1. Structure of hybrid

Hybrid PD2 showed many cracks. Bubble- and crack-free transparent hybrids approximately 75 mm in diameter and 1–2 mm in thickness whose colors were brown were obtained for compositions PD5 and PD10. Fig. 1 shows the TF-XRD patterns of the as-prepared hybrids PD5 and PD10. Only two halos around 12° and 22° in 2θ were observed for both hybrids PD5 and PD10. This indicates that these as-prepared hybrids are amorphous.

Hybrid PD5 formed many cracks by the hot-water treatments, whereas hybrid PD10 was crack-free even after the hot-water treatments, although its transparency was a little reduced.

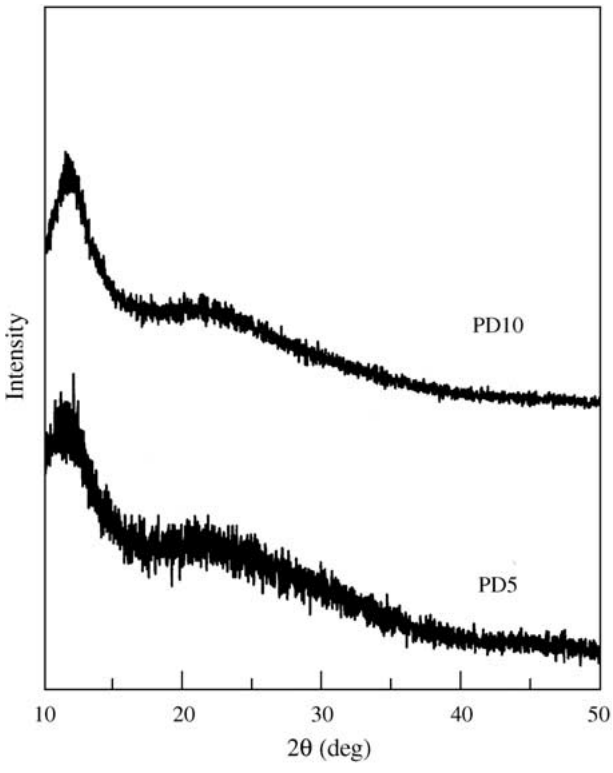

Figure 1 TF-XRD patterns of surfaces of as-prepared hybrids PD5 and PD10.

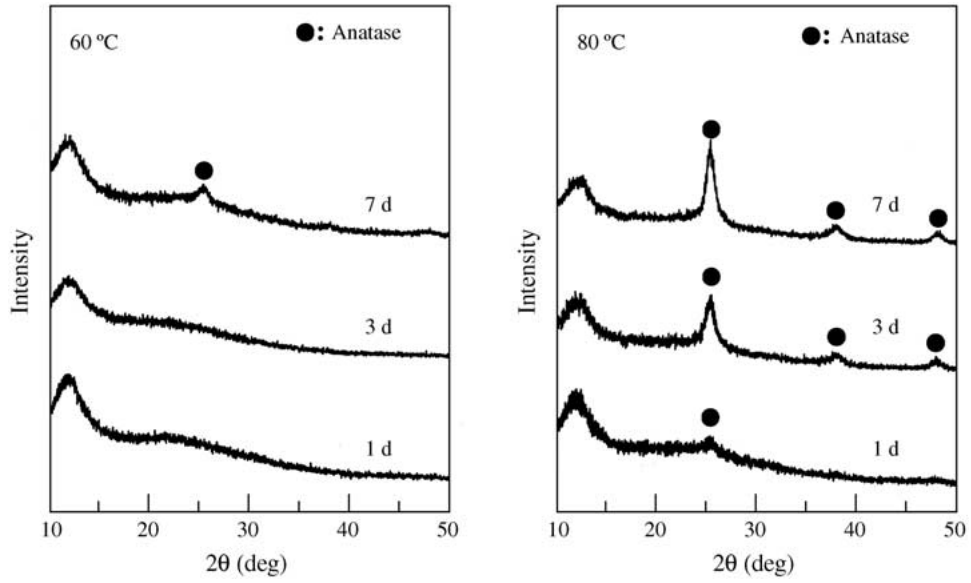

Figure 2 TF-XRD patterns of surfaces of hybrid PD10 treated with hot water at 60 °C or 80 °C for various periods.

Fig. 2 shows the TF-XRD patterns of hybrid PD10 subjected to the hot-water treatment at 60 °C or 80 °C for various periods. Anatase peaks were observed for hybrid PD10 treated with the hot water at 60 °C within 7 d and at 80 °C within 1 d. The peak intensities of anatase increased with increasing hot-water treatment period and temperature. Fig. 3 shows the TEM photographs and electron diffraction patterns of hybrid PD10 before and after the hot-water treatment at 80 °C for 7 d. Neither precipitates nor resolvable electron diffraction rings were observed before the hot-water treatment. This indicates that hybrid PD10, before the hot-water treatment, is homogeneous and amorphous, whereas that subjected to the hot-water treatment was observed to precipitate homogeneously distributed particles 10–20 nm in size ascribed to anatase.

3.2. Apatite formation

Fig. 4 shows the TF-XRD patterns of the as-prepared hybrids PD5 and PD10 after soaking in SBF for 7 d. Apatite peaks were observed in neither the as-prepared hybrid PD5 nor PD10. Fig. 5 shows the TF-XRD patterns of hybrid PD10 treated with the hot water at 60 °C or 80 °C for various periods and soaked in SBF for 7 d. Apatite peaks were observed in hybrid PD10 treated with the hot water at 60 °C for 7 d or at 80 °C for longer periods than 1 d. Fig. 6 shows the FE-SEM photographs of the surfaces of hybrid PD10 treated with the hot water at 60 °C or 80 °C for various periods and soaked in SBF for 7 d. Precipitation of apatite was observed on the surfaces of hybrid PD10 and the amount of apatite formed on it increased with increasing hot-water treatment period and temperature.

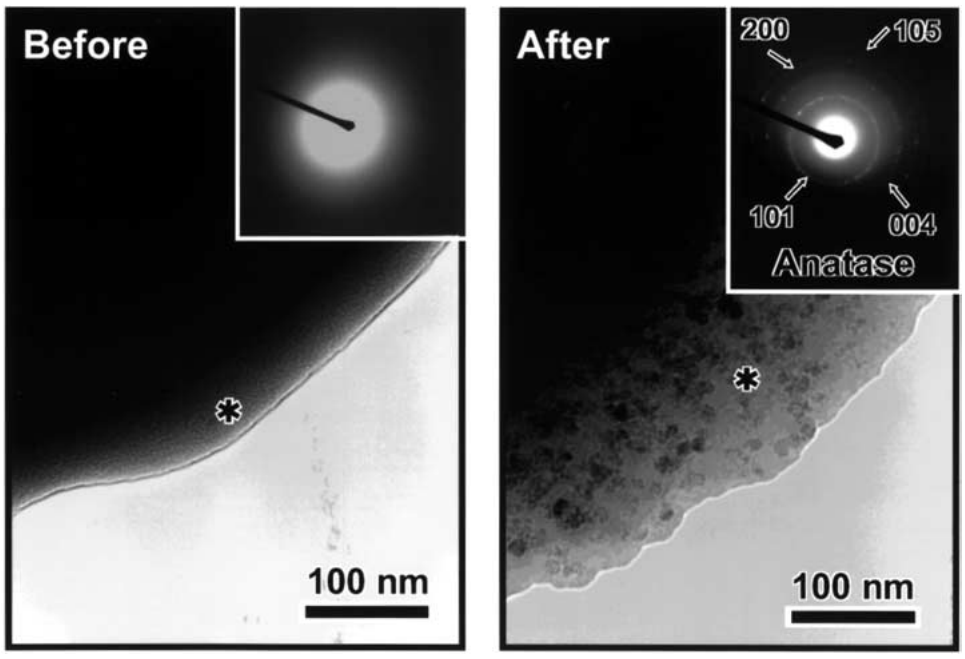

Figure 3 TEM photographs and electron diffraction patterns of hybrid PD10 before and after hot-water treatment at 80 °C for 7 d. (* – Center of electron diffraction.)

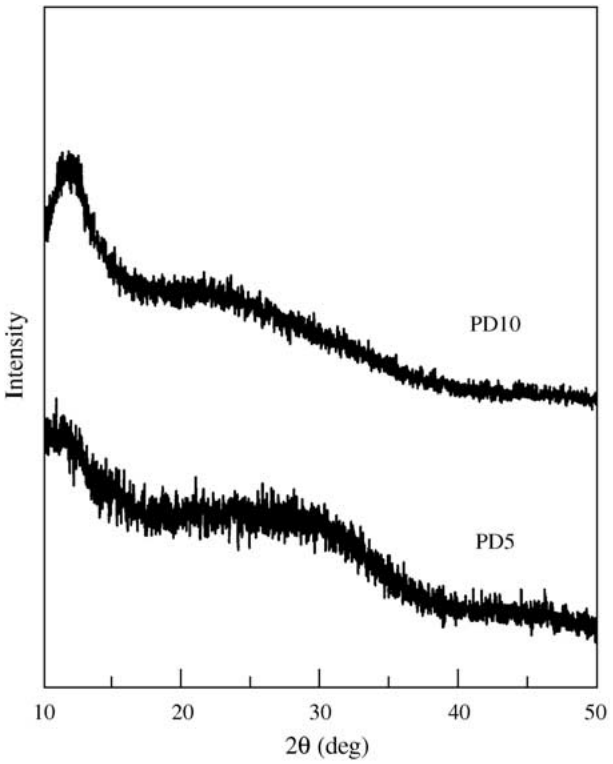

Figure 4 TF-XRD patterns of surfaces of as-prepared hybrids PD5 and PD10 after soaking in SBF for 7 d.

3.3. Mechanical properties

Since only hybrid PD10 showed no crack even after the hot-water treatment and formed apatite on its surface in SBF, only the mechanical properties of hybrid PD10 were examined. Hybrid PD10 showed rubber elasticity both before and after the hot-water treatment. The typical stress–strain curves of the hybrid PD10 before and after the hot-water treatment at 80 °C for 7 d are shown in Fig. 7. The values of tensile strength, strain to failure and Young's modulus of the hybrid PD10 before and after the hot-water treatment at 80 °C for 7 d are shown in Table II. It can be seen from Fig. 7 and Table II that both the tensile strength and Young's modulus decrease, and strain to failure increases by the hot-water treatment. In contrast, the strain energies stored until failure, unaltered. A highly deformable material which can deform as much as 200% before failure is obtained by the present method.

TABLE II Mechanical properties of hybrid PD10 before and after hot-water treatment at 80 °C for 7 d

Specimen	Tensile strength (MPa)	Strain to failure (%)	Young's modulus (Mpa)
Before ($n=5$)	0.91 ± 0.17	77 ± 19	3.4 ± 0.7
After ($n=7$)	0.36 ± 0.05	258 ± 66	0.24 ± 0.03

n – Number of tested specimens.

4. Discussion

Hybrid PD2 formed many cracks during preparation. This is attributed to the insufficient content of the organic component, which gives flexibility and relaxes the stress during gelation and heat treatment. Hybrid PD5 produced many cracks during the hot-water treatment. This might be attributed to large structural rearrangement of the hybrid to allow precipitation of anatase during the hot-water treatment since hybrid PD5 contains large amounts of titania.

Hybrid PD10 took a homogeneous amorphous structure before the hot-water treatment, and homogeneously precipitated anatase particles 10–20 nm in size when hot-water treated (see Fig. 3). The decrease in transparency of the hybrid by the hot-water treatment may be due to the scattering of visible light by these precipitated anatase particles.

Titania may be segregated from the PDMS–TiO_2 homogeneous amorphous phase and crystallize as anatase in nanometer size during the hot-water treatment through the hydrolysis of Si–O–Ti bonds. Precipitation of anatase from sol–gel derived TiO_2–SiO_2 films containing poly(ethylene glycol) by the hot-water treatment has been previously reported [16]. The hydrolysis of Si–O–Ti bonds, segregation of TiO_2 and its transformation to anatase increase with increasing hot

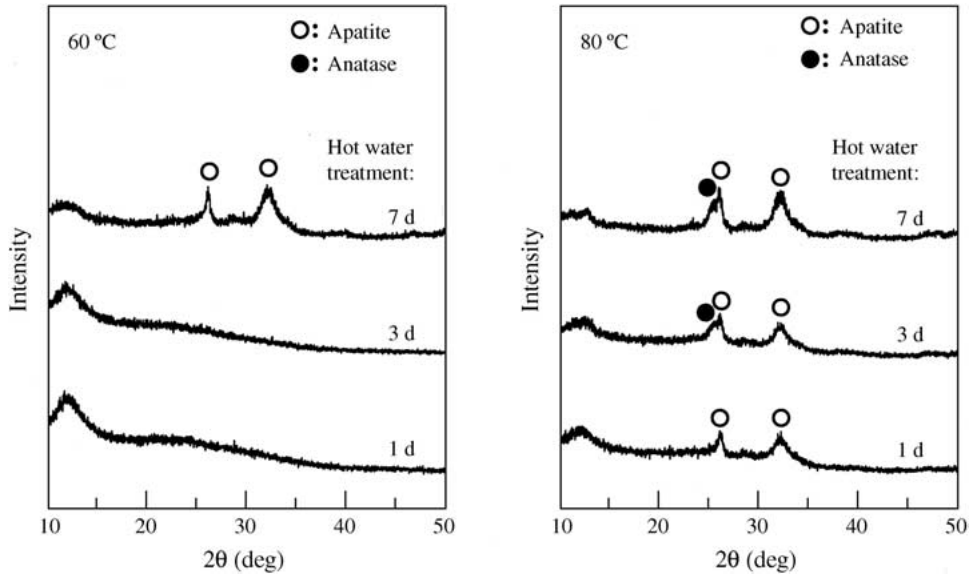

Figure 5 TF-XRD patterns of surfaces of hybrid PD10 treated with hot water at 60 °C or 80 °C for various periods and soaked in SBF for 7 d.

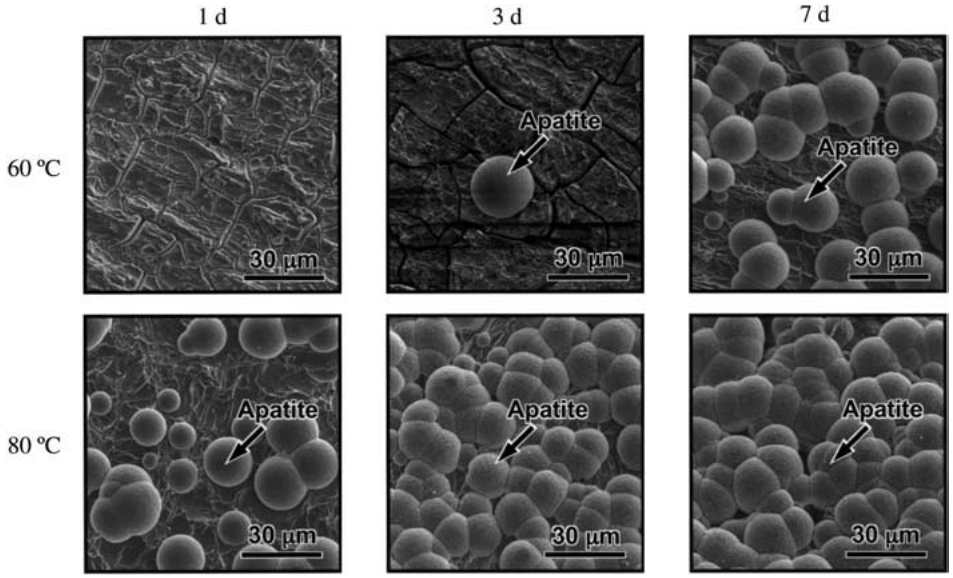

Figure 6 FE-SEM photographs of surfaces of hybrid PD10 treated with hot water at 60 °C or 80 °C for various periods and soaked in SBF for 7 d.

water temperature. As a result, the precipitation of the anatase particles is promoted with increasing temperature of the hot-water treatment.

Hybrids PD5 and PD10 did not form apatite on their surfaces in SBF before the hot water treatment (see Fig. 4), whereas hybrid PD10 treated with hot water formed the apatite on its surface and its amount increased with increasing amounts of anatase precipitated in this hybrid (see Figs. 2, 4, 5 and 6). This indicates that the precipitated anatase induces apatite formation on the surfaces of the hybrids. It has been revealed that the apatite formation on titania depends mainly on its crystalline phase and anatase is more effective for apatite formation than amorphous and rutile-type titania [14]. Hybrid PD10 treated with hot water is expected to form apatite even in the body and bond to living bone through the apatite layer.

Since the environment in hot water is more severe than in the body environment, the unreacted reagents or solvents remaining in the hybrid may be released into hot water causing the resultant hybrid to be nontoxic and stable in the living body at around 36.5 °C.

Both the tensile strength and Young's modulus of hybrid PD10 decreased, and its strain to failure increased after the hot-water treatment (see Fig. 7 and Table II). It

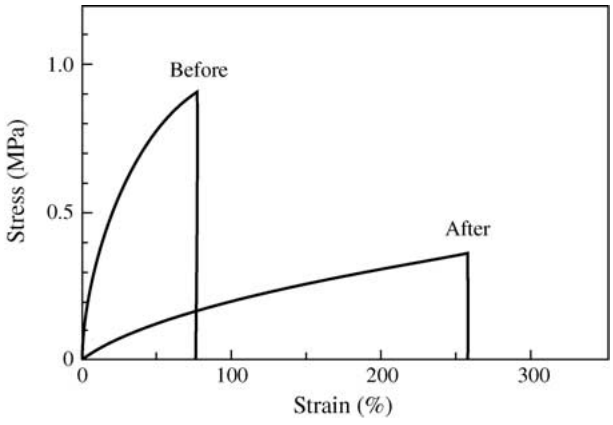

Figure 7 Stress-strain curves of hybrid PD10 before and after hot-water treatment at 80 °C for 7 d.

is considered that the matrix of the hybrid was enriched with PDMS due to the segregation of TiO_2 by the hot-water treatment. Hence, the mechanical properties of the hybrid, subjected to the hot-water treatment, came close to those of matrix rich in PDMS, since the continuous phase predominantly affects the overall mechanical behavior of composite materials. If only the surface structure of the hybrid was changed by the hot-water treatment, the mechanical properties of the hybrid should not change remarkably by the hot-water treatment. However, in practice, the drastic changes in the mechanical properties of the hybrid were observed by the hot-water treatment. This indicates that structural changes of the hybrid by the hot-water treatment occurred not only at the surface but also on the interior of the hybrid. Since the strain energies stored until failure were insignificantly altered, by the hot-water treatment may indicate that the rearrangement of the hybrid by the hot-water treatment does not cause deterioration of the hybrid.

A highly deformable PDMS–TiO_2 hybrid with apatite-forming ability was obtained by the present method. Besides deformability, the rubbery elasticity of the hybrid would also be an advantage, because the hybrid can return to its original shape even after gross deformation. Although the obtained material itself shows low mechanical strength for practical use as a bone-repairing material, this kind of material could be useful as a bone-repairing material, if reinforced with materials possessing high mechanical strength.

5. Summary

A highly deformable PDMS–TiO_2 hybrid with apatite-forming ability can be obtained by hydrolysis and polycondensation of PDMS and titanium ethoxide and then subsequent hot-water treatment to precipitate anatase nano particles. It is expected that this hybrid will be useful as a new type of bioactive bone-repairing material.

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