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Compressive creep behavior of silane treated TiO_2/high-density polyethylene

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Abstract In biomaterial silane treated TiO_2/high-density polyethylene(silane–TiO_2/HDPE), silane connection structurally corresponds to acid phosphoprotein bond, which connects the noncalcified collagen fibril bands and the adjacent apatite crystals in natural bones. In order to explore the function and variation process of acid phosphoprotein under loading in natural bones, the microscopic variation mechanism of silane connection in silane–TiO_2/HDPE was investigated through the compressive creep tests in air and saline solution. Through the analysis of creep rate curves under different stress loads, different creep mechanisms were proposed, in which silane connection plays a very important role. Through SEM observation of sample surfaces and the creep tests in saline solution, the important role of silane connection in creep process was further proved. That is, silane connection can not only support the loading stress but also hinder the failure process under loading effectively.

Introduction

Designing an ideal bone graft that emulates natural bone's own structure is the common design strategy for bone biomaterial development. It is well known that natural bones mainly consist of noncalcified collagen fibril bands and the adjacent apatite crystals, between which acid phosphoprotein bonds connect them. Therefore, the composites of inorganic fillers and organic matrix sound a good choice for the design of bone biomaterials.

Based on this idea, a composite of hydroxyapatite particles with high-density polyethylene (HAPEX) was developed by Bonfield in the early 1980s [1]. However, the fracture toughness and elastic modulus of HAPEX are lower than those of heavy load bearing bones. Compared with hydroxyapatite, TiO_2 has higher elastic modulus, so Kokubo et al. [2] developed biomaterial of TiO_2/HDPE with high bioactivity. The bending strength and Young's modulus were found to vary from almost 28 to 54 MPa and 1.4 to 7.6 GPa, respectively, depending on the TiO_2 content. To improve weak mechanical adhesion at interfaces effectively, a silane coupling agent was used to modify the surface of TiO_2 particles [3]. The silane coupling agent connects TiO_2 and HDPE by formation of chemical bonds at both of its ends, which can improve the mechanical properties greatly. It should be noted that the silane connection between TiO_2 and HDPE structurally corresponds to acid phosphoprotein bonds in natural bones.

The mechanical behavior of bone tissue's ultra- and micro-structure is fundamental to assess macroscopic bone mechanics. It is also true for biomaterials. Ascenzi et al. made their hypothesis that the acid phosphoprotein bonds between the noncalcified collagen fibril bands and the adjacent apatite crystals tend to weaken and eventually break under mechanical loading [4]. However, this hypothesis has not been proved by other research work. Furthermore, whether the corresponding microstructure in synthesized biomaterials experiences the same process is also meaningful problem.

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For polymer composites, creep behavior is very important for practical application. There are some reports on the creep behaviors of polymer composites filled with inorganic particles [5–7]. For example, Yang et al. [8] carried out tensile creep tests on a few polyamide 66 composites filled with different nanoparticles. One of them was a composite with 1 wt% 21 nm TiO_2 particles modified with octylsilane. It was found that the creep resistance of nanocomposites was significantly enhanced by nanoparticles without sacrificing the tensile properties. Lietz et al. [9] investigated the mechanical properties and creep resistance of SBS block copolymers with nanoclay fillers and found that the introduction of dispersed nanoclays induced promising improvements in creep performance. Although surface modifications of nanofillers with organic chemicals are widely used [10–13], the effect of chemical connection between inorganic particle and organic matrix on creep behaviors was seldom found.

In this work, the microscopic variation mechanism of silane connection in silane–TiO_2/HDPE was investigated through compressive creep tests. Through the analysis of creep rate curves, the creep mechanisms were proposed, in which silane connection plays a key role. That is, upon loading silane connection supports load, stretches to relieve load and is finally broken by the concentrated stress.

Experimental procedures

Materials

Silane treated TiO_2/high-density polyethylene (silane–TiO_2/HDPE) composite was fabricated in Japan Fine Ceramics Center. The ratio of TiO_2 to HDPE is 40vol.%, with anatase mean particle size of 535 nm. TiO_2 powder was treated with silane-coupling agent of γ-MPS (γ[-(methacryloxy)propyl]trimethoxysilane) and mixed with HDPE. During the manufacturing process, kneading and compression molding was involved. The detailed manufacturing process was described in literature [3]. By the analysis of FTIR, it was confirmed that the surface of TiO_2 particles was connected with HDPE through formation of Ti–O–Si bonds.

Compressive creep

The specimens of silane–TiO_2/HDPE were cut to cylindrical shape and polished to diameter of 6 mm and height of 12 mm. A servo-hydraulic fatigue machine Model EHF-EB5 (Shimadzu Co. Ltd., Japan) was employed to carry out the tests. In compressive strength tests, the rate of displacement was maintained at 0.033 mm/s. Tests were carried out in air or in saline solution of 0.9% NaCl. The temperature was kept to be 25 °C in the two conditions. The temperature controlling of saline solution was realized by pumping and recycling the saline solution of 25 °C into the test trough during test process.

Morphology observation

For the tested samples, it is somewhat difficult to observe the fracture surfaces because friction of them during compressive process has blurred the fracture information. For explanation of the possible fracture mechanism, the outer side surfaces of tested specimens were observed by scanning electronic microscopy (SEM) Hitachi S-3000N. Prior to observation, the samples were cleaned ultrasonically and dried. Then the outer side surfaces were coated with Au to ensure clear images using Hitachi ion sputter E-1010. The layer thickness of Au coating is about 10 nm.

Results and discussion

Compressive properties

Compressive tests were performed in air and saline solution at room temperature for silane–TiO_2/HDPE. The compressive curves are shown in Fig. 1. The Young's moduli are 2.9 GPa in air and 2.1 GPa in saline solution. Compressive strengths are 71 MPa in air and 63 MPa in saline solution. Obviously, silane–TiO_2/HDPE is susceptible to saline solution, which resulted in lower Young's modulus and compressive strength.

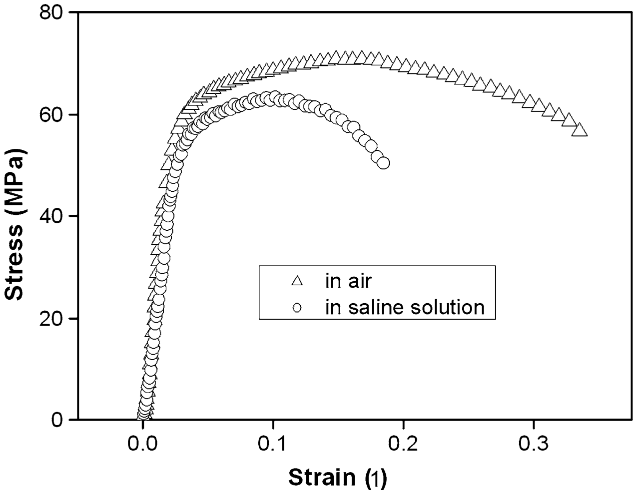

Fig. 1 Compressive stress–strain curves of silane–TiO_2/HDPE at room temperature in different surrounding conditions

Creep characterization

Creep deformability and stress dependence

The experimental curves of creep strain versus log time of silane–TiO_2/HDPE in air are presented in Fig. 2. The curves show that load stress has an important role on the creep behavior of silane–TiO_2/HDPE. With the increase of applied stress, the creep time to rupture becomes shorter and the dimensional deformation becomes larger.

The creep curve in saline solution at 45 MPa is shown in Fig. 3. As a comparison, the creep curve of air sample at the same stress level is also shown in the same figure. Creep life of silane–TiO_2/HDPE in saline solution is shortened greatly compared with that in air, while the creep strain remains almost the same. In other words, saline solution affected creep life greatly but had little influence on the dimensional stability.

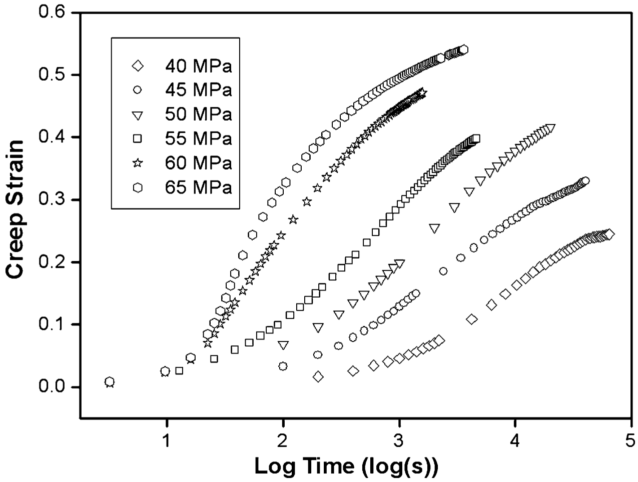

Fig. 2 Experimental creep curves of silane–TiO_2/HDPE in air under different stress levels

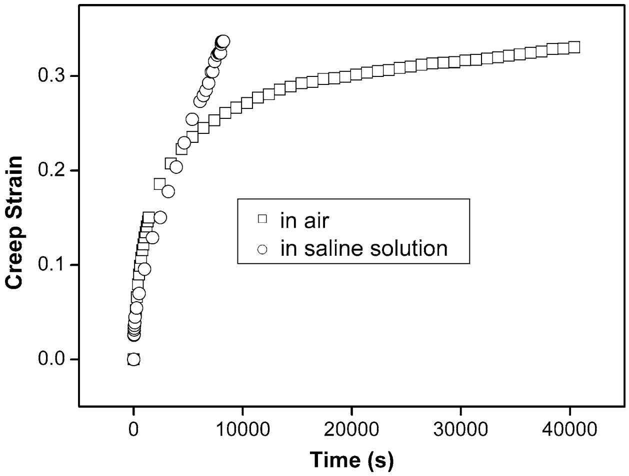

Fig. 3 Experimental creep curves obtained in saline solution and air under 45 MPa

Creep rate

The dimensional stability of materials is also determined by creep rate, which represents the velocity of creep deformation. The creep rate curves versus creep time under different stress levels are shown in Fig. 4. In air, the creep rate curves under stresses lower than 50 MPa all decrease with creep time monotonically. When the stress is higher than 50 MPa, the creep rates remain almost the same at the beginning. For 60 and 65 MPa, after almost 10 s, the creep rates increase sharply and soon come down. That is, all samples tested under different stresses only experienced the first primary creep stage, and did not attain the steady-state in the secondary stage. The creep rate at 45 MPa in saline solution is shown by the dash line. Clearly, the creep rate at the beginning is almost the same as that of 45 MPa in air, but it remains high creep rate for a while, then it decreases quickly and remains almost stable after 100 s. Furthermore, the creep rate at the instant of loading is increased with the load stress level before 50 MPa. After 50 MPa, it remains almost the same.

Outer side surface morphologies

As a comparison, Fig. 5 shows the outer side surface morphology of the original silane–TiO_2/HDPE sample before any test. The surface is very smooth with few exposed TiO_2 particles on it. However, for specimens tested under compressive strength and creep experiments in both air and saline solution, the observation with naked

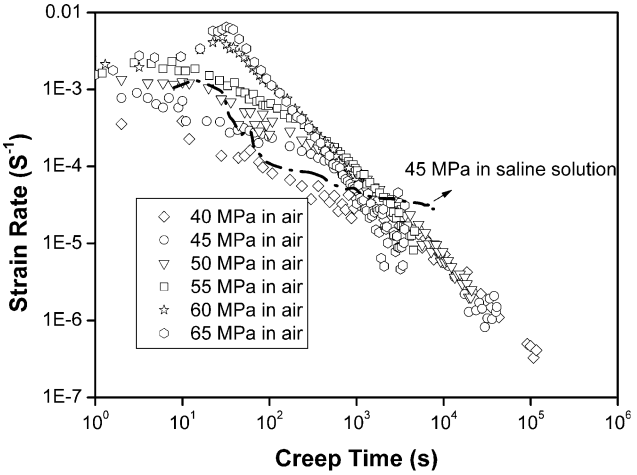

Fig. 4 Creep rate curves versus creep time at different stress levels

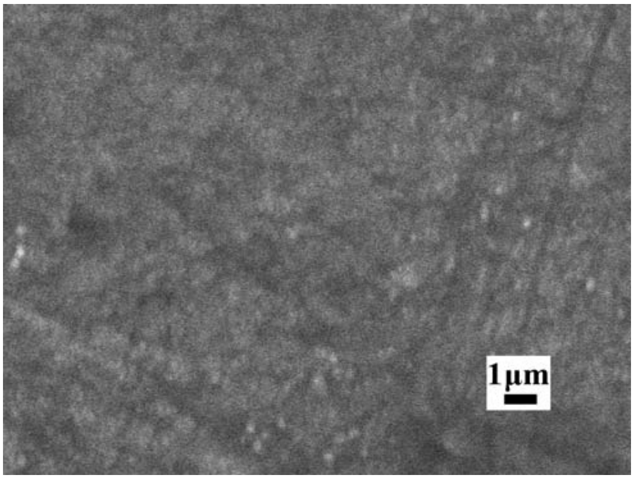

Fig. 5 Morphology of lateral surface of silane–TiO_2/HDPE specimen before any test

eyes and microscope showed that the cylindrical side surfaces (not the rupture surfaces) are covered with cracks and rugged areas, with only some differences in the general width of the cracks and the extent of coarseness between different experimental conditions. The surface coarsenesses of specimens tested in saline solution are severer than those in air. The representative cracks filled with broken crumbs are shown in Fig. 6. The side surface morphologies of the compressive samples are so complicated that only those that can contribute to the explanation of key problems are shown. To offer a clearer demonstration, the morphologies of would-be cracks or just rugged surfaces of high magnification are shown in Fig. 7. Although those samples were ultrasonically cleaned before SEM observation, the roughness and the number of exposed TiO_2 on their surfaces are obviously increased when compared with those of original specimen before any test. It is a common phenomenon for both air and saline solution samples experienced both compressive strength and creep testing. However, in Fig. 7a, deformed HDPE fibrils can be seen (shown by the arrows). These fibrils of HDPE were not found in other samples.

Creep mechanisms in air of silane–TiO_2/HDPE

Guild and Bonfield [14] by computer modeling showed that there are two regions of stress concentrations, one is the pole of the particle and the other is the interface. That is why so much work has been focused on the filler surface modification to reduce the stress concentrations. In silane–TiO_2/HDPE, the introduction of silane connection improved the interfacial compatibility effectively, but the interfacial failure still may be the reason for creep rupture.

Based on the variation of creep rates, creep mechanisms are proposed in Fig. 8. This schematic graph just exhibits a representative micro unit around a TiO_2 particle, which constitutes the whole bulk material. Silane-coupling agent has nine atoms along its main chain with some side chains like methyl, which inevitably resulted in the formation of voids and some unmodified surfaces on TiO_2. In order to squeeze those voids out and condense the material, kneading and compressing were employed during the manufacturing process. Therefore, the structure of this material before any load should be like Fig. 8a, in which the silane chains are entangled and curved on the surface of the particle. Once stress is loaded, the concentrated compressive stress on the interface will destroy the weak mechanical adhesion and be relaxed by stretching the silane chains in the perpendicular direction to the loading axis. Meanwhile the shear stress on the upper and the bottom of the particle surface, which is resulted from the small deformation and reorientation of silane chains, can also stretch other silane chains. The extent of stretching depends on the concentrated stress around the particle. Although under compressive stress the surrounding HDPE has to change in structure to help relieve stress concentrations, compared with silane chains during creep, deformation of HDPE and its effect on creep rate variation is

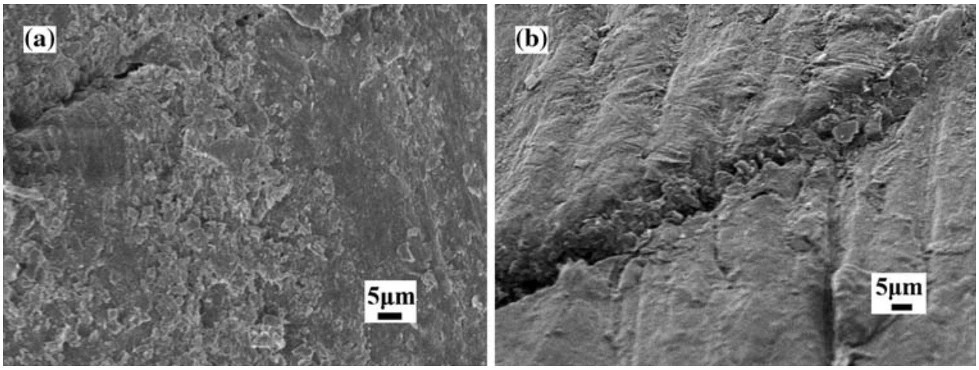

Fig. 6 Morphologies of lateral surfaces of specimens tested in **a** compressive experiment in saline solution; **b** compressive creep experiment in air at 55 MPa

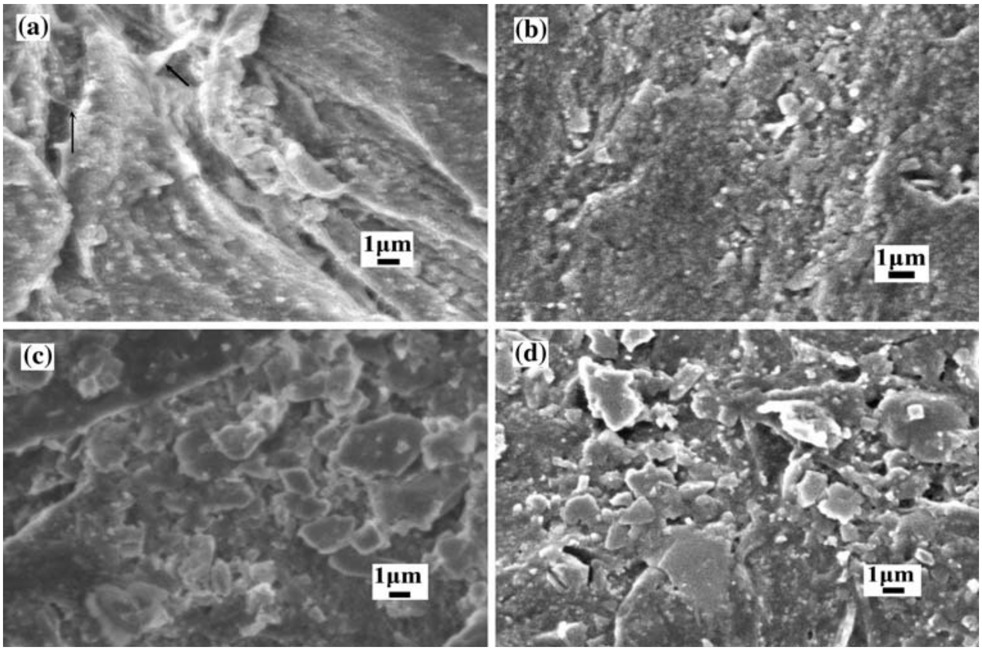

Fig. 7 Morphologies of lateral surfaces of specimens tested in **a** compressive strength experiment in air; **b** creep experiment in air under 55 MPa stress; **c** compressive strength experiment in saline solution; **d** creep experiment in saline solution under 45 MPa stress

negligible. So only the variation of silane chains is discussed here.

Imaginably, the variation extent of the silane chains is dependent on the load stress. From the creep rate curves, it is inferred that at the instant of loading, the loading energy can activate the silane chains even at 40 MPa. Between 40 and 50 MPa, with applied stress increased, the stretching extent is increased gradually without breaking of them (shown in Fig. 8b). Because the stretching process is not restricted within the stress range, the creep rate increases with the load stress at the instant of loading. When the stress reaches around 50 MPa, most of the load-bearing silane chains are stretched to their limitation (Fig. 8c). So at different stresses higher than 50 MPa, the creep rates all remain almost the same at the loading instant.

Accordingly, the destruction at the loading instant on structure is different. Below 50 MPa, the microstructure of silane–TiO_2/HDPE does not suffer obvious destruction. At 50 and 55 MPa, the silane chains are stretched to their limitation and maybe some of them are broken. The process is almost the same as the breakage in human femoral tissue. Acid phosphoprotein bonds connecting the non-calcified collagen fibril bands and the adjacent apatite crystals [4] were hypothesized to tend to weaken and eventually break when subjected to stress. When the stress reaches 60 MPa, most not all of the load-supporting silane chains are destroyed.

Once creep process starts, silane chains experience different process. At stresses lower than 50 MPa, they are pulled more straight gradually, which eventually results in their breakage. At 50 or 55 MPa, they begin to gradually break just after loading. At 60 MPa, although at the instant of loading, some of the silane chains are destroyed (depicted in Fig. 8d), the left still support. However, the left are also broken within short time, which resulted in the softness of bulk material exhibited by the increase of creep rate in Fig. 4. Because severe plastic deformation of composite is usually determined by the slippage between main chains of matrix, the subsequent reorientation hardness of HDPE slows down the creep rate.

Actually, the above discussion was made without considering the practical variation of sample external shape. For polymer composite, when compressed, the central lateral surface will protrude out with the reduction of axial length. With the increase of projection, tensile stress on the lateral surface will come into being and increase gradually. Just like the modeling of Bonfield [14], the tensile stress mainly concentrates on the interfaces between TiO_2 and HDPE and is released by the stretching and destruction of silane chains on the lateral surface of samples. Therefore, the above mentioned load-bearing silane chains at the instant of loading actually are those on the sample lateral surface. The stretching and destruction of silane connection begin from the sample outer surface and propagate gradually from the surface to the inner bulk sample.

The breakage of silane chains on sample surface can undoubtedly result in the initiation and propagation of cracks, which was proved by the morphologies shown in

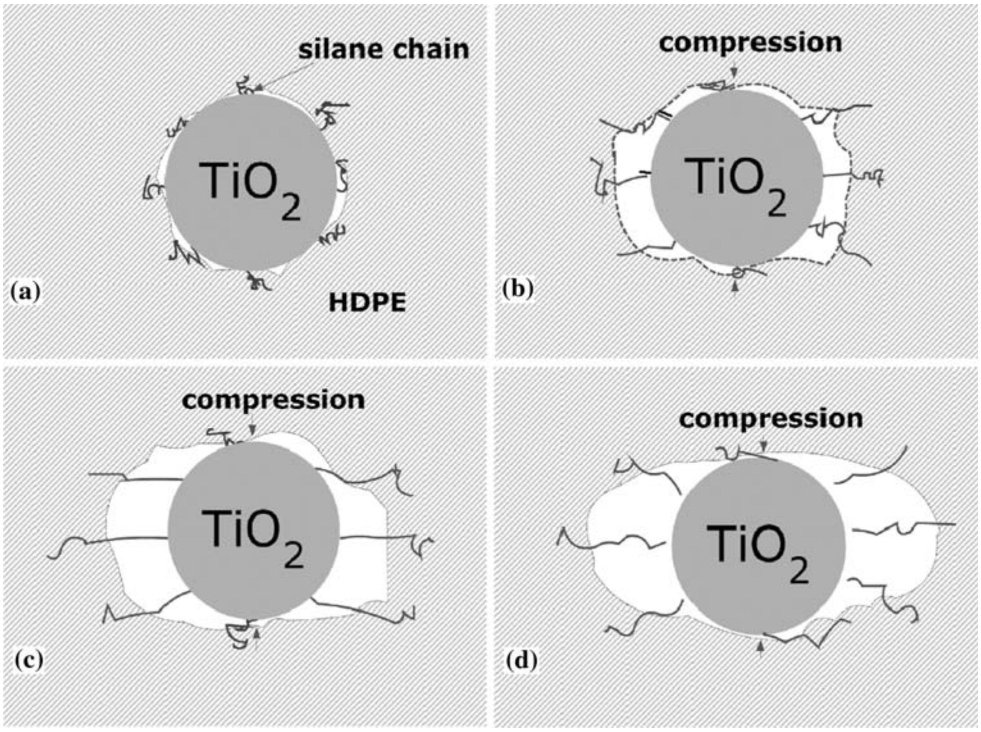

Fig. 8 Schematic graph of compressive creep mechanism **a** without any loading; **b** when load stress lower than 50 MPa; **c** when load stress higher than 50 MPa; **d** almost all the silane chains broken by compressive loading

Fig. 6. From the surface morphologies, the creep failure should be dominated by micorcrack failure mechanism for all the tested samples. Besides the microcrack failure mechanism, ductile failure on HDPE also competes with it, which can be manifested by the coexistence of HDPE fibrils and the exposed TiO_2 in Fig. 7a. Because the creep time to failure in the compressive strength experiment in air was the shortest (about 8 s), it was not enough for the silane connection at the interfaces to react and relieve the loading, so some of the concentrated stress was relieved by the deformation of HDPE directly. When the creep time was enough long or the creep happened in saline solution, interfacial failure mechanism defeated the ductile failure on matrix completely.

Effect of saline solution

It has been proved that biomaterial silane–TiO_2/HDPE is waterproof. When it was placed in saline solution for 2 days without any loading, its weight did not change. It is inferred that the effect of saline solution is synergetic with loading and from sample surface.

The interfacial failures in both air and saline solution are actually microcrack failure process. That is, after the breakage of silane chains at the interfaces, microcracks initiate, propagate, develop into main crack and finally result in the final failure. From the exposed TiO_2 particles in the surface morphology pictures, it is believed that the breakage is from Ti–O–Si bonds. Because of the hydrophilicity of TiO_2 surface, the basis for its bioactivity in biomaterials [15], once stress concentrations on sample surface are enough to break the chemical bond of Ti–O–Si, Ti–OH and Si–OH will form subsequently. In air, the forming process is very slow, while in saline solution, the process is sped up because of the surrounding water. The steric hindrance and repelling force between hydrogen atoms from the introduced –OH in air and the additional hydrostatic force and steric hindrance from water in saline solution all can enhance the stress concentrations in return. Because the tensile stress on lateral surface of samples was increased gradually with creep process, the effect of saline solution on creep rate should be time-dependent. It is very small at creep beginning and becomes gradually remarkable after that, which is the reason for the almost same creep rate at the creep beginning and comparatively higher creep rate after that when compared with the creep rate in air at the same stress level in Fig. 3.

From the creep mechanism at 45 MPa described above, it is known that under compressive load, those load-supporting silane chains stretches to their full length and then are broken gradually. The stretching and breakage of silane chains dominates the whole creep failure process. The sample in saline solution experienced the same failure process as that of air sample at the same stress level only with accelerated speed. Therefore, the total strain at break of sample tested in saline solution is almost the same as that in air at 45 MPa, which is in consistency with the creep mechanisms proposed above.

Conclusions

To explore whether silane chains in silane–TiO_2/HDPE has the same function as phosphoprotein bonds in natural bones, the compressive creep tests of biomaterial silane–TiO_2/HDPE were carried out in both air and saline solution. The intense silane connection played a very important role in the creep process. That is, upon loading, silane chains supported the stress firstly, stretched to relieve the concentrated stress and then were broken. The creep failure process is microcrack initiation mechanism for both air and saline solution samples with only the difference of accelerated failure speed in saline solution. The susceptibility of silane–TiO_2/HDPE to environmental saline solution comes from the hydrophilicity of TiO_2 surface. The time-dependent effect of saline solution on the creep process and almost same total creep strain in saline solution as that of sample tested in air at the same stress level proved the proposed creep mechanisms.

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