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Bioactivity and mechanical properties of polydimethylsiloxane (PDMS)–CaO–SiO_2 hybrids with different calcium contents

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Polydimethylsiloxane (PDMS)–CaO–SiO_2 hybrids with starting compositions containing PDMS/($Si(OC_2H_5)_4$ + PDMS) weight ratio = 0.30, $H_2O/Si(OC_2H_5)_4$ molar ratio = 2, and $Ca(NO_3)_2/Si(OC_2H_5)_4$ molar ratios = 0–0.2, were prepared by the sol–gel method. The apatite-forming ability of the hybrids increased with increasing calcium content in the $Ca(NO_3)_2/Si(OC_2H_5)_4$ molar ratio range 0–0.1. The hybrids with a $Ca(NO_3)_2/Si(OC_2H_5)_4$ molar ratio range 0.1–0.2 formed apatite on their surfaces in a simulated body fluid (SBF) within 12 h. The hybrid with a $Ca(NO_3)_2/Si(OC_2H_5)_4$ molar ratio of 0.10 showed an excellent apatite-forming ability in SBF with a low release of silicon into SBF. It also showed mechanical properties analogous to those of human cancellous bones. This hybrid is expected to be useful as a new type of bioactive material.

1. Introduction

Some ceramics, such as Bioglass® [1], sintered hydroxyapatite [2], and glass-ceramic A-W [3], and chemically treated metals, such as titanium [4], titanium alloys [5], and tantalum metal [6], can bond to living bone, i.e. they show bioactivity. However, these materials have higher elastic moduli than human bones, and hence are liable to induce resorption of the surrounding bone due to stress shielding. Therefore, it is desirable to develop new types of bioactive materials with lower elastic moduli. With regard to the development of bioactive materials with lower elastic moduli, Bonfield *et al*. have developed hydroxyapatite–polyethylene composites [7]. However, these composites are brittle when the hydroxyapatite content exceeds 40 vol %. When they contain hydroxyapatite less than 40 vol % for their ductility, they show only low bioactivity [8].

Organically modified sol–gel-derived ceramics are currently attracting much attention because of their unique properties, such as low elastic modulus and deformability. In these hybrid materials, organic components are chemically combined with inorganic components at the molecular level [9–13]. Tsuru *et al*. [14] reported that some polydimethylsiloxane (PDMS)–CaO–SiO_2 hybrids prepared by the sol–gel method form apatite on their surfaces in a simulated body fluid (SBF). This indicates that these hybrids can be bioactive [8, 15]. However, their mechanical properties were not investigated.

Recently, the present authors [16–20] synthesized PDMS–CaO–SiO_2–TiO_2 hybrids using a synthetic method different from that of Tsuru *et al*., and found that these hybrids show an apatite-forming ability and are deformable. We also showed that our method makes it possible to prepare PDMS–CaO–SiO_2 hybrids with a high apatite-forming ability in SBF, with a low release of silicon into SBF. These PDMS–CaO–SiO_2 hybrids also show mechanical properties analogous to those of human cancellous bones [21]. However, the effect of calcium content on the bioactivity and mechanical properties of these hybrids has not been elucidated. The release of calcium ions from these materials would have a large effect on the apatite-forming ability of the hybrid, since it increases the degree of supersaturation with respect to the apatite in the surrounding fluid [22]. In the present study, PDMS–CaO–SiO_2 hybrids with different calcium contents in the starting compositions were prepared, and their corresponding apatite-forming abilities in SBF and their mechanical properties were investigated.

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TABLE I Starting compositions of products with different calcium contents

Product	Composition		
	PDMS/(TEOS + PDMS) (weight ratio)	H_2O/TEOS (molar ratio)	$Ca(NO_3)_2$/TEOS (molar ratio)
Ca0	0.30	2	0
Ca5	0.30	2	0.05
Ca10	0.30	2	0.10
Ca15	0.30	2	0.15
Ca20	0.30	2	0.20

PDMS: Polydimethylsiloxane; TEOS: Tetraethoxysilane.

2. Experimental

2.1. Sample preparation

Polydimethylsiloxane (PDMS, $[-Si(CH_3)_2-O-]_n$, 10 centistokes, molecular weight = 1000, Aldrich Chemical Co., USA), tetraethoxysilane (TEOS, $Si(OC_2H_5)_4$, Nacalai Tesque Inc., Japan), calcium nitrate tetrahydrate ($Ca(NO_3)_2 \cdot 4H_2O$, Nacalai Tesque Inc., Japan), hydrochloric acid (HC1 35 wt %, Nacalai Tesque Inc., Japan), and distilled water were mixed in the ratios presented in Table I to obtain solutions with different calcium contents, using the following procedure. The products with starting compositions containing $Ca(NO_3)_2$/TEOS molar ratios of 0, 0.05, 0.10, 0.15 and 0.20 were denoted as products Ca0, Ca5, Ca10, Ca15 and Ca20, respectively. TEOS was added to a mixture of H_2O, HCl, isopropyl alcohol (IPA, Nacalai Tesque Inc., Japan), and tetrahydrofuran (THF, Nacalai Tesque Inc., Japan). The molar ratios of this mixture were [TEOS/H_2O/HC1/IPA/THF] = [1/1/0.045/0.65/0.49]. The TEOS was pre-hydrolyzed under ambient conditions for 2 h, and then a given mass of PDMS was added. After 15 h, a mixture of $Ca(NO_3)_2 \cdot 4H_2O$, H_2O and IPA, whose molar ratios with respect to TEOS were [TEOS/H_2O/$Ca(NO_3)_2$/IPA] = [1/1/0-0.20/1.82], was added to the former solution. The sol solutions thus obtained were aged under ambient conditions for 1 day in a styrene-acrylonitrile copolymer container covered with a paraffin film having several pinholes. These solutions were then kept in the same film-covered container at 40 °C for 1–2 weeks for gelation. The gels thus obtained were dried at 60 °C for 3 days, and then heated at 150 °C for 1 day.

2.2. Evaluation of bioactivity

The bioactivity of the products was evaluated by examining the apatite formation on their surfaces in 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 [23]. Materials that form apatite on their surfaces in SBF are expected to form apatite *in vivo*, and bond to living bone through the apatite layer [8, 15]. Specimens $10 \times 10 \times 2\,mm^3$ in size were cut from the as-prepared products, and polished with a #400 silicon carbide abrasive paper. They were soaked in 30 ml of SBF at 36.5 °C for various periods up to 14 day, and then removed from SBF, washed with distilled water, and dried at 40 °C.

After the specimens were soaked in SBF, the surfaces of the specimens were analyzed using a thin-film X-ray diffractometer (TF-XRD, RINT-2500, Rigaku Co.,

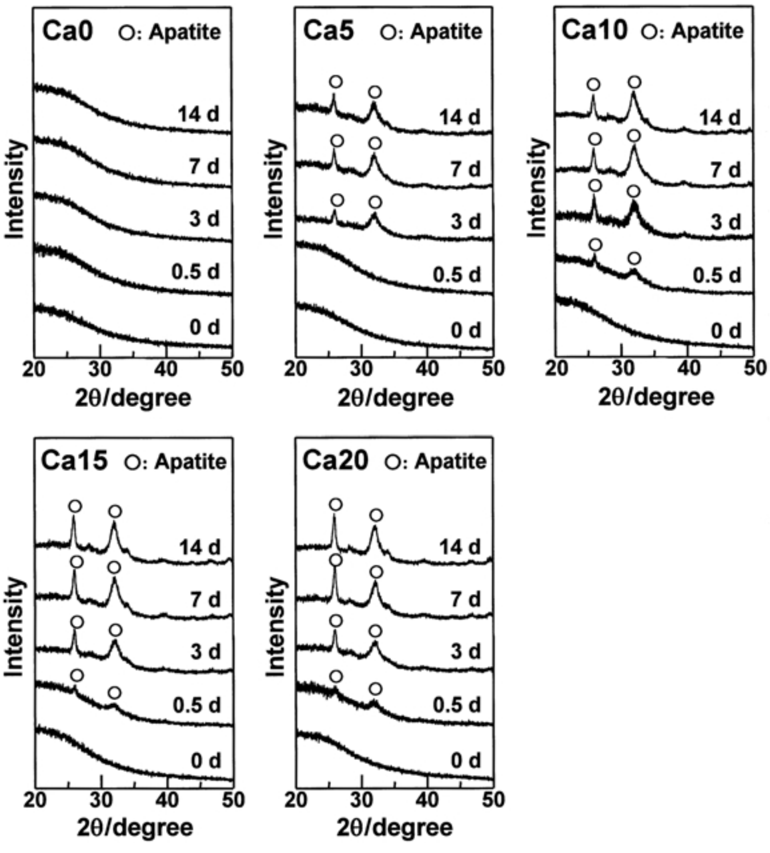

Figure 1 TF-XRD patterns of surfaces of products Ca0, Ca5, Ca10, Ca15 and Ca20 soaked in SBF for various periods.

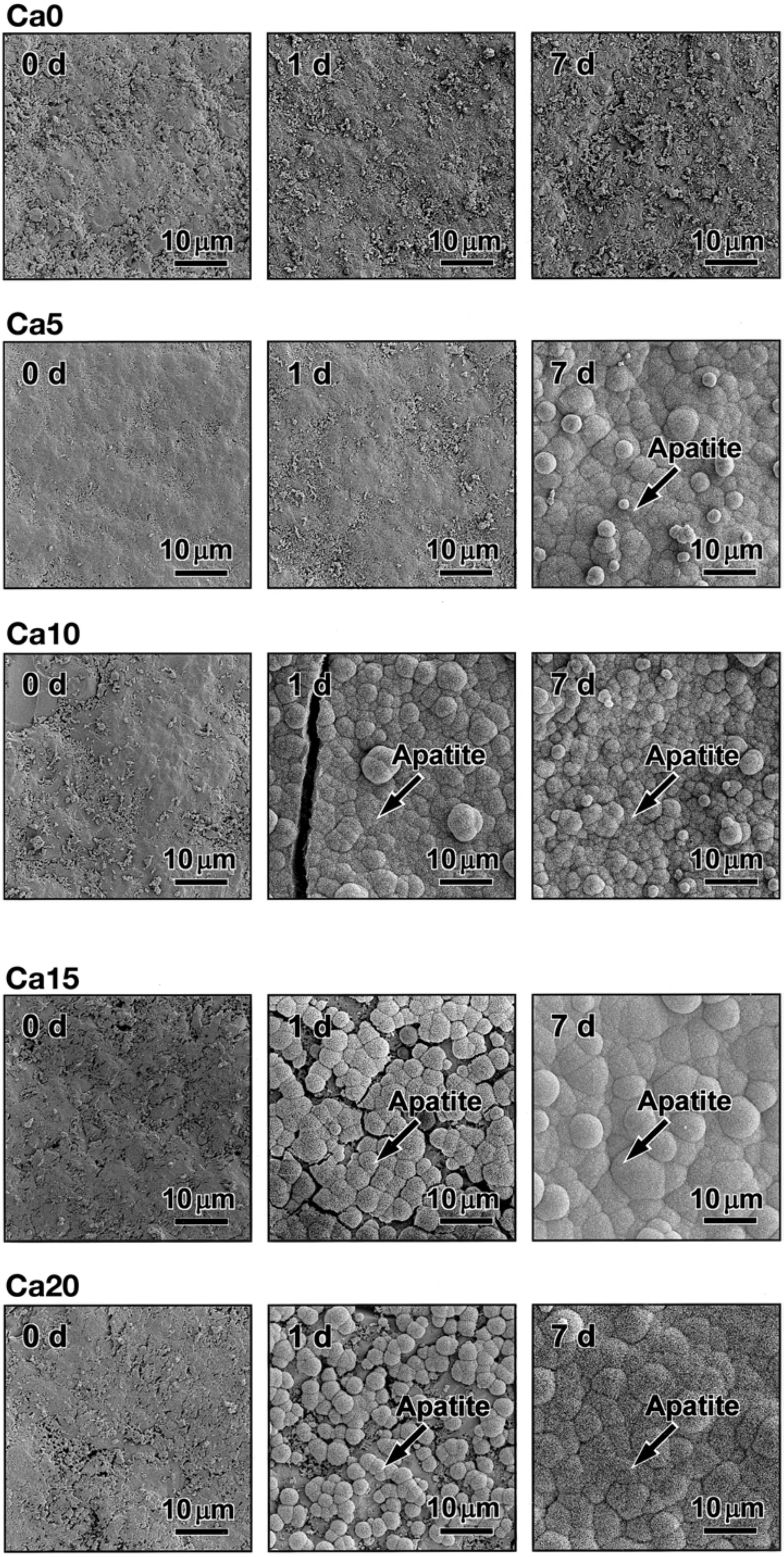

Figure 2 FE-SEM photographs of surfaces of products Ca0, Ca5, Ca10, Ca15 and Ca20 soaked in SBF for various periods.

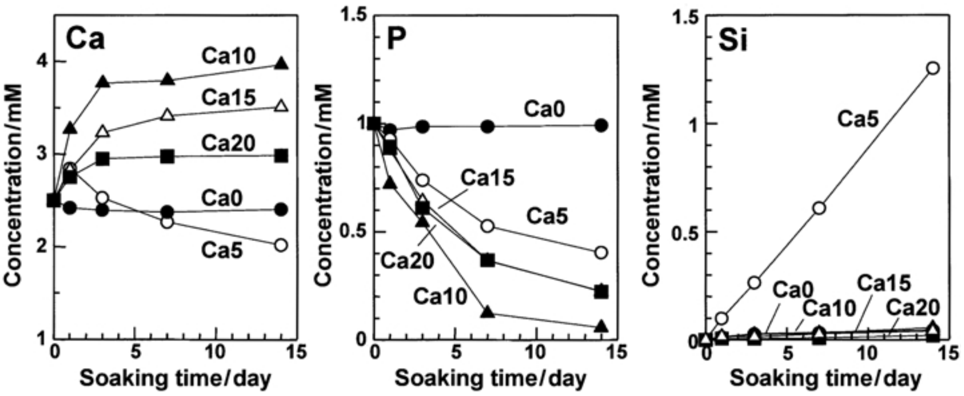

Figure 3 Changes in element concentrations of SBF with soaking of products Ca0, Ca5, Ca10, Ca15 and Ca20.

Japan). In the thin-film X-ray difrractometer, the surfaces of the specimens were fixed at an angle of 1° against the direction of the incident beam. This technique enabled the detection of a surface layer about 1 μm thick. The morphology of the surfaces of the specimens was observed under a field emission scanning electron microscope (FE-SEM, S-4700, Hitachi Ltd., Japan). Changes in the element concentrations of SBF with soaking of the specimens were measured using an inductively coupled plasma (ICP) atomic emission spectroscope (Model SPS1500VR, Seiko Inst. Inc., Japan).

2.3. Measurement of the mechanical properties

Rectangular bar specimens $3 \times 4 \times 30\,\mathrm{mm}^3$ in size were cut from the as-prepared products, and polished with a #2000 silicone carbide abrasive paper. The bending strength was measured using a screw-driven tensile/compression testing machine (Model AGS-10kNG, Shimadzu Co., Japan) with a three-point loading over a 20-mm span. The specimens were loaded in such a way that one $4 \times 30\,\mathrm{mm}^2$ surface was subjected to tensile stress. At least eight specimens for each product were fractured at a crosshead speed of $0.5\,\mathrm{mm\,min}^{-1}$.

3. Results

3.1. Bioactivity

Fig. 1 shows the TF-XRD patterns of the surfaces of the products before and after soaking in SBF for various periods up to 14 days. The induction periods for apatite formation, which were determined by TF-XRD, were 3 days for product Ca5, and 0.5 day for products Ca10, Ca15, and Ca20. Product Ca0, however, did not form apatite on its surface in SBF, even after 14 days.

FE-SEM photographs of the surfaces of the products before and after soaking in SBF for various periods up to 7 days are shown in Fig. 2. It can be seen from these photographs that an apatite layer formed on the surfaces of the products within 7 days for product Ca5, and within 1 day for products Ca10, Ca15, and Ca20. For product Ca0, however, no surface changes were observed, even after soaking for 7 days.

Fig. 3 shows the changes in the element concentrations of SBF with soaking of the products. All products, except for product Ca5, released only a small amount of silicon into SBF, even after soaking for 14 days. All the calcium-containing products released their calcium ions into SBF during the initial stage. The phosphorus concentration decreased with increasing soaking time for the calcium-containing products.

3.2. Mechanical properties

In product Ca0, many cracks developed during gelation at 40 °C, and hence no specimens amenable to mechanical testing were obtained. Fig. 4 shows representative stress–strain curves of the products. The bending strength, strain at failure, and Young's modulus of the products, in comparison with those of the human cancellous bones [24], are shown in Fig. 5. All the examined products showed mechanical properties analogous to those of human cancellous bones (Fig. 5). For products Ca5, Ca10, Ca15 and Ca20, i.e. the products with starting compositions containing $\mathrm{Ca(NO_3)_2/TEOS}$ molar ratios in the range 0.05–0.20, the calcium content showed little effect on the mechanical properties of the products.

4. Discussion

All the calcium-containing products released calcium ions into SBF during the initial stage as shown in Fig. 3,

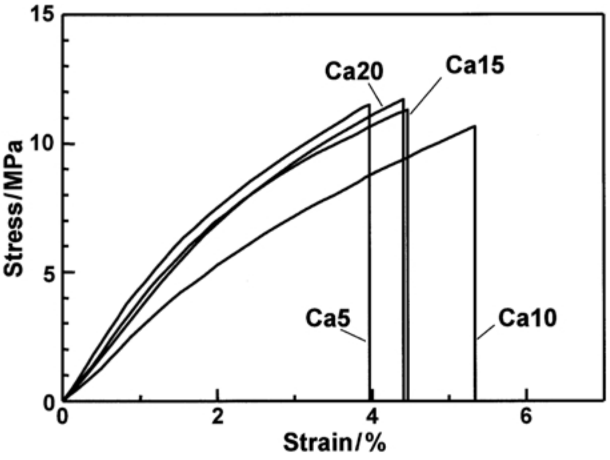

Figure 4 Representative stress-strain curves of products Ca5, Ca10, Ca15 and Ca20 measured by three-point bending test.

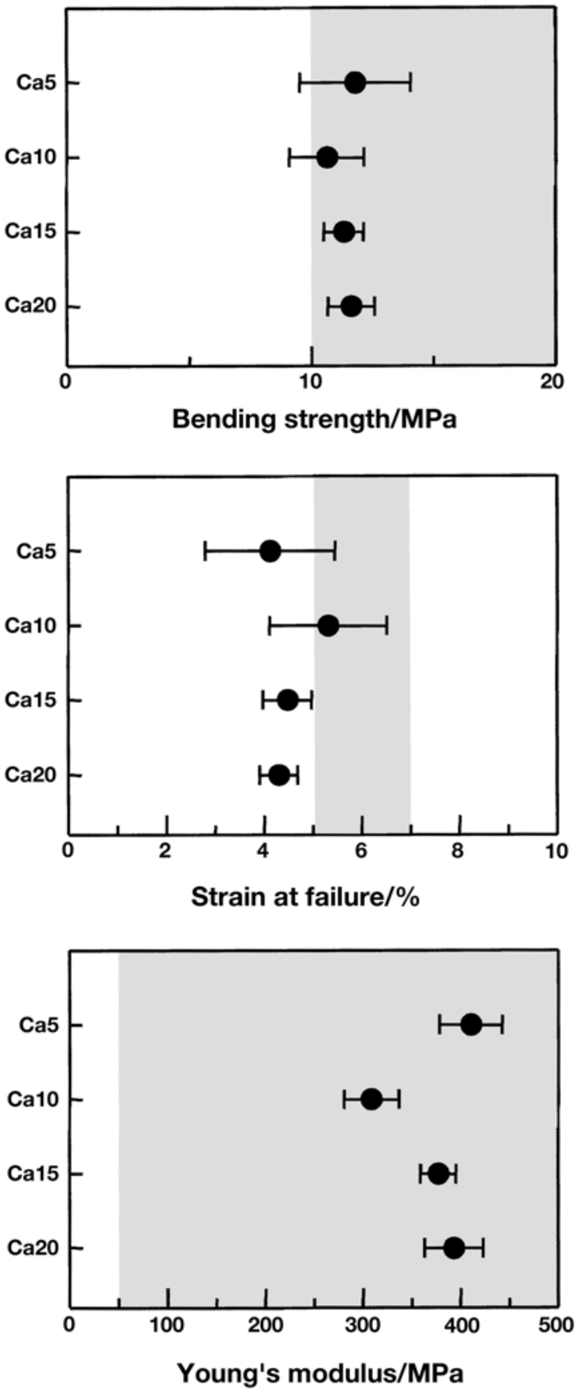

Figure 5 Bending strength, strain at failure and Young's modulus of products Ca5, Ca10, Ca15 and Ca20, in comparison with those of human cancellous bones. (Shaded areas show the range of the values of human cancellous bones [24].)

and formed apatite on their surfaces in SBF within 3 days (Fig. 1). In contrast, the calcium-free product, Ca0, did not form apatite on its surface in SBF, even after soaking for 14 days (Fig. 1), The apatite-forming ability of the products improved with increasing amount of calcium ions released from the products. Therefore, we conclude that the released calcium ions accelerate apatite nucleation. It has been shown that released calcium ions accelerate apatite nucleation by increasing the ionic activity product of apatite [22]. Once the apatite nuclei are formed, they grow spontaneously by consuming calcium and phosphate ions from the surrounding SBF, since SBF is highly supersaturated with respect to apatite.

All the examined products, except for product Ca5, released little silicon into SBF, whereas product Ca5 released more silicon into SBF than the other products. Silicon is the network-forming component in the present products. Therefore, a large amount of released silicon might be attributed to the instability of their network structure. In the point of stability of the products in body environment, the suppression of silicon release is preferable. For product Ca5, its high release of silicon might be due to its unstable network structure that is only a little different from those of the other products.

In product Ca0, many cracks developed during gelation at 40 °C. This may be attributed to the high evaporation rate of the solvents during gelation. In the calcium-containing product, the rapid evaporation of solvents may be suppressed by the additional calcium, and this might be responsible for the crack-free products. All the examined products, except for product Ca0, showed mechanical properties analogous to those of human cancellous bones, not only in their mechanical strength, but also in their elastic moduli and deformability (Figs. 4 and 5). This is attributed to the incorporation of the organic components into their structure. The calcium content, however, showed little effect on their mechanical properties. Their mechanical properties should depend mainly on the network structures of the products. It has been reported that the mechanical properties of the hybrids depend on the ratio of the inorganic to the organic component [17]. It is considered that the formed network structures of the present products were almost same in spite of different calcium contents, because the ratio of inorganic network component (SiO_2) and organic network component (PDMS) was fixed in the products (see Table I). The result of silicon release from the products in Fig. 3 indicates that calcium contents might affect the structures of the products, but the resultant differences in the structures are thought to be too small to affect their mechanical properties.

In conclusion, product Ca10 is expected to be useful as a new type of bioactive material, since it showed an excellent apatite-forming ability in SBF, with a low release of silicon into SBF, as well as showing mechanical properties analogous to those of human cancellous bones.

5. Summary

The hydrolysis and polycondensation of PDMS, TEOS, and calcium nitrate gave hybrids that were large enough for performing mechanical tests when calcium nitrate was added to the starting compositions. The apatite-forming ability of these hybrids in SBF was improved by the addition of calcium. The calcium content showed little effect on the mechanical properties of the hybrids, and all the examined products showed mechanical properties analogous to those of human cancellous bones.

The hybrid with starting composition containing a PDMS/(TEOS + PDMS) weight ratio of 0.30, a $Ca(NO_3)_2/TEOS$ molar ratio of 0.10, and an $H_2O/TEOS$ molar ratio of 2 showed an excellent apatite-forming ability in SBF, with a low release of silicon into SBF, and mechanical properties analogous to those of human cancellous bones. This hybrid is expected to be useful as a new type of bioactive material.

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