Chemical surface treatment of silicone for inducing its bioactivity

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It has been confirmed that the apatite nucleation is induced by silanol (Si–OH) groups formed on the surfaces of materials and/or silicate ions adsorbed on them.It was previously shown that apatite nuclei are formed on organic polymers when the polymers are placed on CaO, SiO_2-based glass particles soaked in a simulated body fluid (SBF) with ion concentrations nearly equal to those of human blood plasma, and that they grow spontaneously to form a dense and uniform apatite layer together with high adhesive strength to the substrates when the polymers are soaked in another solution with ion concentrations 1.5 times the SBF. In the present study, silanol groups bonded covalently to the surface of the silicone substrate were formed and its apatite-forming ability was examined. When silicone substrates were treated with 5 or 10 M NaOH with pH 7.25 at 36.5 °C for more than 3 h, silanol groups were formed on the surfaces of the substrates. When thus NaOH-treated substrates were soaked in 1.5SBF at 36.5 °C, a bone-like apatite was formed on the substrates in a short period.

1. Introduction

It has been indicated that the essential requirement for artificial materials to bond to living bone is the formation of a bioactive bone-like apatite layer on their surfaces in the living body [1, 2]. So far, some ceramics such as Bioglass®, sintered hydroxyapatite, apatite- and wollastonite-containing glass-ceramic (A–W), and so on, have been found to bond to living bone through the bone-like apatite layer [3]. It has been confirmed that the apatite nucleation is induced by silanol (Si–OH) groups [4] formed on the surfaces of materials and/or some silicate ions [5] adsorbed on them.

On the basis of these findings, a biomimetic process for coating the bone-like apatite layer on organic polymers has been developed by the present authors [6, 7]. This process includes two steps. Apatite nuclei are formed on organic polymers when the polymers are placed on CaO, SiO_2-based glass particles soaked in a simulated body fluid (SBF) with ion concentrations nearly equal to those of human blood plasma (first step). The formed apatite nuclei grow spontaneously to form a dense and uniform bone-like apatite layer when the polymers are soaked in another solution (1.5SBF) with ion concentrations 1.5 times the SBF (second step). The polymers coated with the bone-like apatite by this process have great potential as bone-repairing materials, because they can exhibit not only high bioactivity but also mechanical properties analogous to natural bone [6, 7].

The adhesive strength of the apatite layer about 10 μm thick to the polymer substrates reached about 10 MPa maximum, when the substrates were pretreated with O_2 glow-discharge [8]. The increase in the adhesive strength by the glow-discharge pretreatment is ascribed to the formation of the polar groups, such as carbonyl and carboxyl, on the polymer surfaces. These polar groups may form a fairly strong bond with the calcium ion of the apatite.

Such a high strength, however, is not retained in living body for a long period, because the adhesion of the silicate ions which are dissolved from the glass particles and adsorbed on the substrates is not stable. In the present study, silicone substrates were treated with alkaline solution in order to produce silanol groups covalently bonded to the polymer, and their apatite-forming ability was examined in 1.5SBF.

2. Materials and methods

Rectangular silicone gum substrates (KE108, Shinetsu Kagaku Kogyo Co., $15 \times 10 \times 1$ mm^3) were soaked in 2, 5 and 10 M NaOH aqueous solutions at 36.5 °C for various periods, washed with distilled water and dried at room temperature for 24 h. Binding energies of O_{1s}

of NaOH-treated silicone substrates were measured by an X-ray photoelectron spectroscope (XPS; ESCA Model MT5500, ULVAC-PHI Co. Ltd, Chigasaki, Japan) and a Fourier transformed laser Raman spectrometer (System 2000 FT–Raman, Perkin–Elmer Ltd, UK) for examining the formation of silanol groups on the substrates. In the XPS measurements, MgK_α X-ray (1253.6 eV) was used as an excitation source. The photoelectron take-off angle was set at 45°. The measured binding energies were corrected with reference to the binding energy of C_{1s} (284.6 eV) of the hydrocarbon adsorbed on the sample surfaces. For Raman spectroscopy, Nd:YAG laser ($\lambda = 1064$ nm) was used as an excitation source.

The NaOH-treated silicone substrates were soaked in 30 ml 1.5SBF (Na^+ 213.0, K^+ 7.5, Mg^{2+} 2.3, Ca^{2+} 3.8, Cl^- 223.2, HCO_3^- 6.3, HPO_4^{2-} 1.5, SO_4^{2-} 0.8 mM) with pH 7.25 at 36.5 °C for various periods. After soaking in 1.5SBF, surface structural and morphological variations of the specimens were characterized using a thin-film X-ray diffractometer (TF-XRD; thin-film attachment CN2651A1, Rigaku-Denki Co., Tokyo, Japan), a Fourier transformed–infrared (FT–IR) reflection spectrometer (System 2000 FT–IR, Perkin-Elmer Ltd, UK) and a scanning electron microscope (SEM; S-2500CX, Hitachi Co., Tokyo, Japan). In the TF–XRD measurements, the incident beam angle against the specimen was set at 1°. In the FT–IR measurements, the incident beam angle against the reflection beam angle was set at 75°. These geometries enable the detection of only a surface about 1 μm thick. The surfaces of the specimens were coated with a Au–Pd alloy film before SEM observation.

3. Results and discussion

Fig. 1 shows the O_{1s} XPS spectra of the surfaces of silicone substrates treated with 2, 5 and 10 M NaOH for various periods. For all the specimens, the peak ascribed to siloxane (Si–O–Si) bonds, which corresponds to the silicone skeleton, was observed at 532 eV. After 5 and 10 M NaOH treatments for more than 3 h, the peaks which are ascribed to Si–OH and Si–ONa newly appeared at 533 and 531 eV, respectively. It was also found that the amount of Si–OH and Si–ONa formed increased with increasing period of NaOH treatment, although there is little difference in the spectra between 5 and 10 M NaOH treatments. Such changes were not observed for 2 M NaOH treatment for all the specimens. When the substrates were treated with 5 and 10 M NaOH for longer than 3 h, the following chain reaction was assumed to proceed

$$\text{Si–O–Si} + \text{NaOH} \rightarrow \text{Si–OH} + \text{Si–ONa} \quad (1)$$

$$\text{Si–O–Na} + \text{H}_2\text{O} \rightarrow \text{Si–OH} + \text{NaOH} \quad (2)$$

As a result, siloxane bonds near the surfaces of the silicone substrates are cleaved and silanol groups are formed on them. Siloxane bonds in silicone are so strong that Reaction 1 hardly proceeds for 2 M NaOH treatment.

Fig. 2 shows the Raman spectra of the silicone substrates treated with 2, 5 and 10 M NaOH for various periods. A peak was observed at 1080 cm^{-1} for all the NaOH treatments, and it became significantly larger in 5 and 10 M NaOH treatments for longer than 3 h. This peak is assigned to silanol groups bonded to organic groups. For the 2M NaOH treatment, the peak was very small even for 1 d treatment. The results of Raman, as well as those of XPS, indicate that siloxane bonds in the silicone structure were partly broken near its surface by the treatments with concentrated NaOH solution.

Figs 3 and 4 show the TF–XRD patterns of the surfaces of silicone substrates treated with 5 and 10 M NaOH for various periods and subsequently soaked

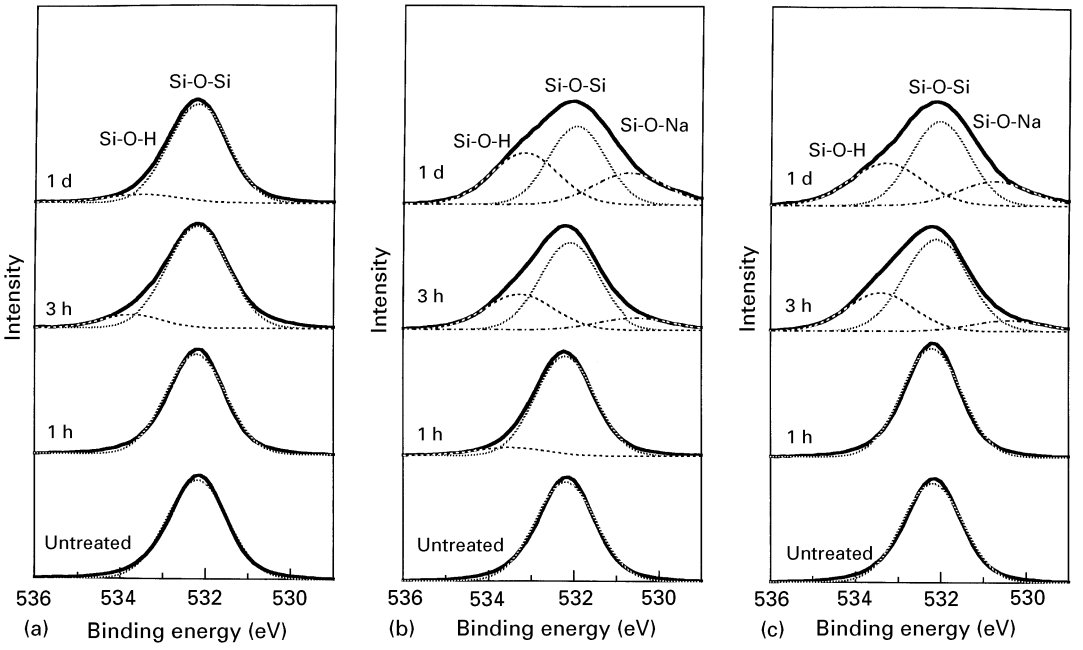

Figure 1 O_{1s} XPS spectra of the surfaces of silicone substrates treated with (a) 2, (b) 5 and (c) 10 M NaOH for various periods. (—) Observed spectra, (----) deconvoluted spectra (left, Si–OH: middle, Si–O–Si; right Si–O–Na).

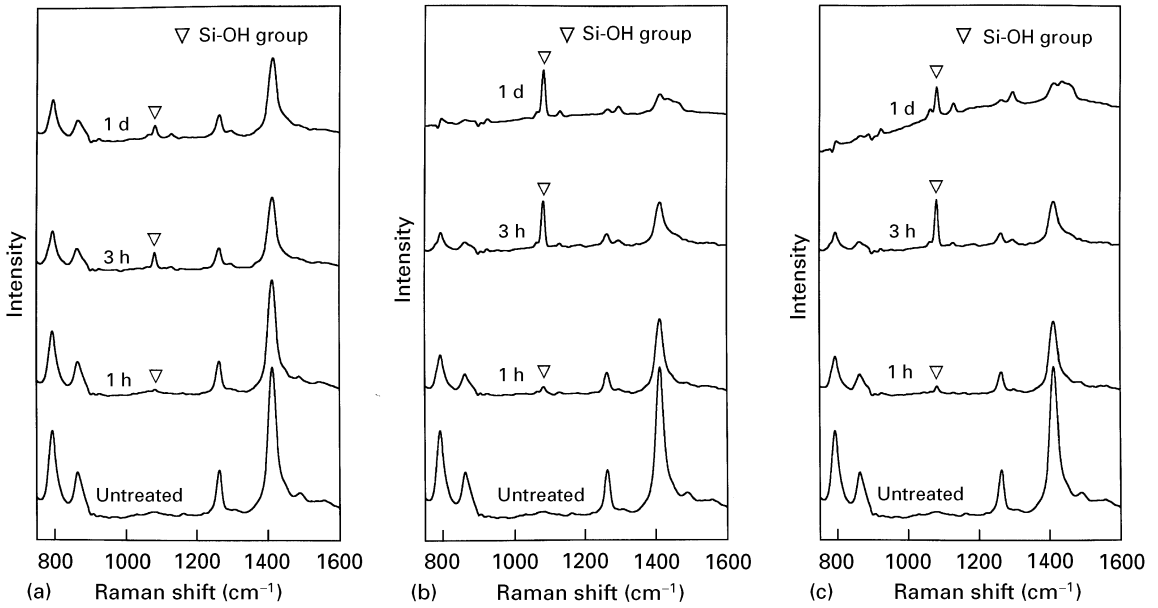

Figure 2 Raman spectra of the surfaces of silicone substrates treated with (a) 2, (b) 5 and (c) 10 M NaOH for various periods.

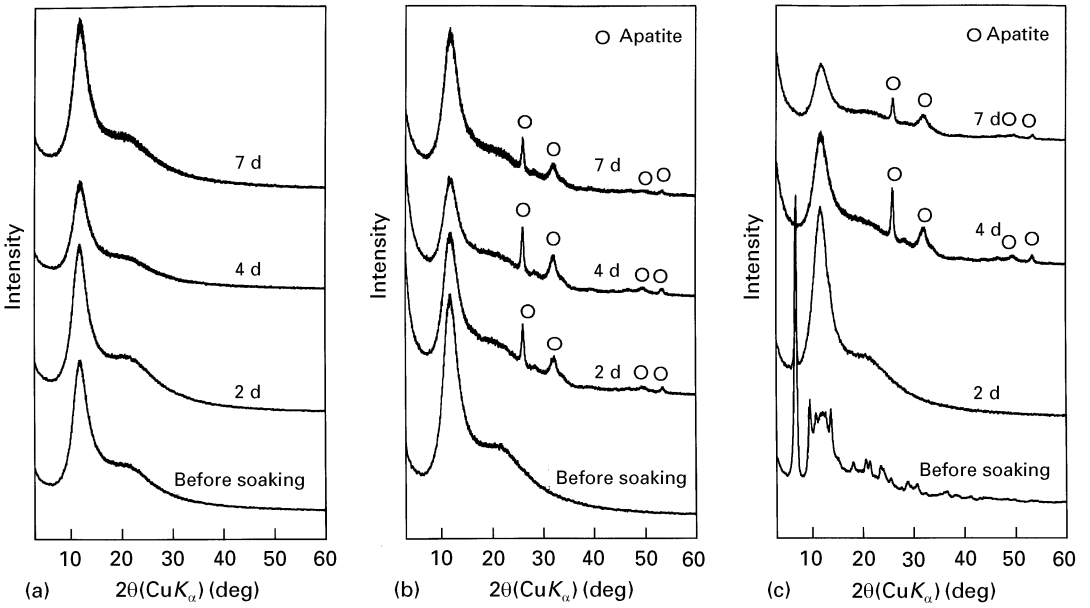

Figure 3 TF–XRD patterns of the surfaces of silicone substrates treated with 5 M NaOH for (a) 1h, (b) 3h and (c) 1d, and subsequently soaked in 1.5SBF for various periods.

in 1.5SBF for various periods, respectively. Figs 5 and 6 show the FT–IR reflection spectra of the surfaces of silicone substrates treated with 5 and 10 M NaOH for various periods and subsequently soaked in 1.5SBF for various periods, respectively. It should be noted that no apatite was formed within 7 d for 2 M NaOH treatment for all the soaking periods. This is due to the absence of little formation of silanol groups on the substrate as described above. For 5 and 10 M NaOH treatments, a bone-like apatite was found to form on the substrates within 2 d for 3 h treatment, and within 4 d for 1 d treatment. These results confirm that silanol groups on the silicone substrates formed by NaOH treatment (see Figs 1 and 2) induce the apatite nucleation in 1.5SBF.

For both 5 and 10 M NaOH treatments, the soaking period in 1.5SBF required for the apatite formation is longer in 1 d treatment than in 3 h treatment. This is explained by assuming that the formed NaOH-treated surface layer was so thick that it could be easily peeled off the substrates during soaking in NaOH solution and/or 1.5SBF for the former. In fact, the Raman peak ascribed to silanol groups is smaller in the former than in the latter for 10 M NaOH treatment (see Fig. 2), indicating peeling off of the surface layer of silicone. Consequently, among the present examined conditions, 5 and 10 M NaOH treatments for 3 h are the most appropriate for rapid apatite formation on the silicone substrates.

Fig. 7 shows scanning electron micrographs of the silicone substrates treated with (a) 2, (b) 5 and (c) 10 M NaOH for 3 h and subsequently soaked in 1.5SBF for 7 d. As shown in the micrographs, a dense apatite layer a few micrometres thick was grown on the

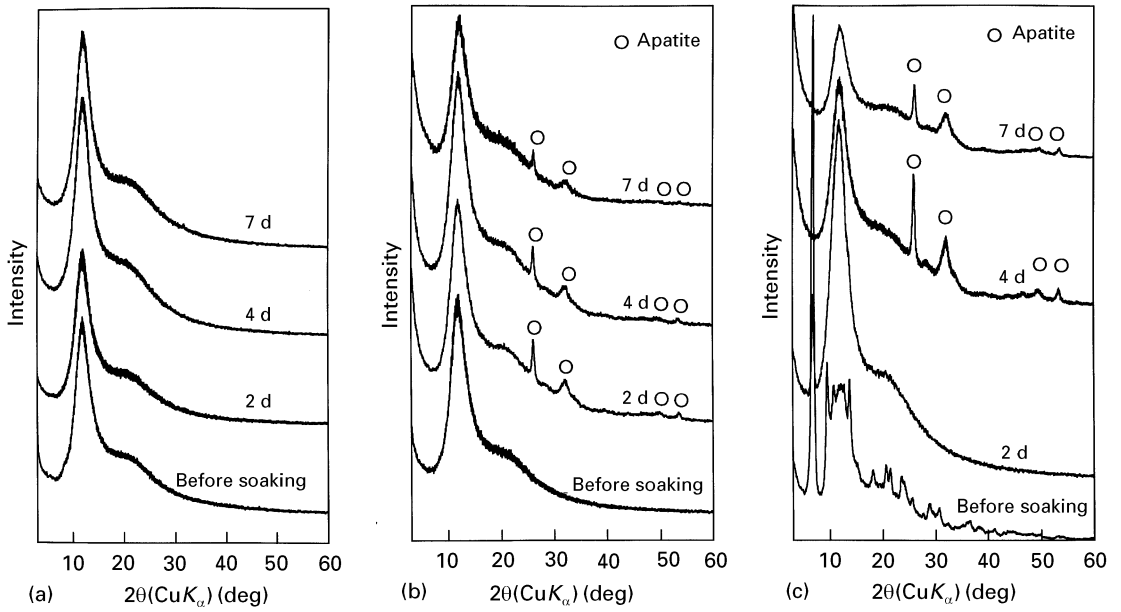

Figure 4 TF–XRD patterns of the surfaces of silicone substrates treated with 10 M NaOH for (a) 1h, (b) 3h and (c) 1d, and subsequently soaked in 1.5SBF for various periods.

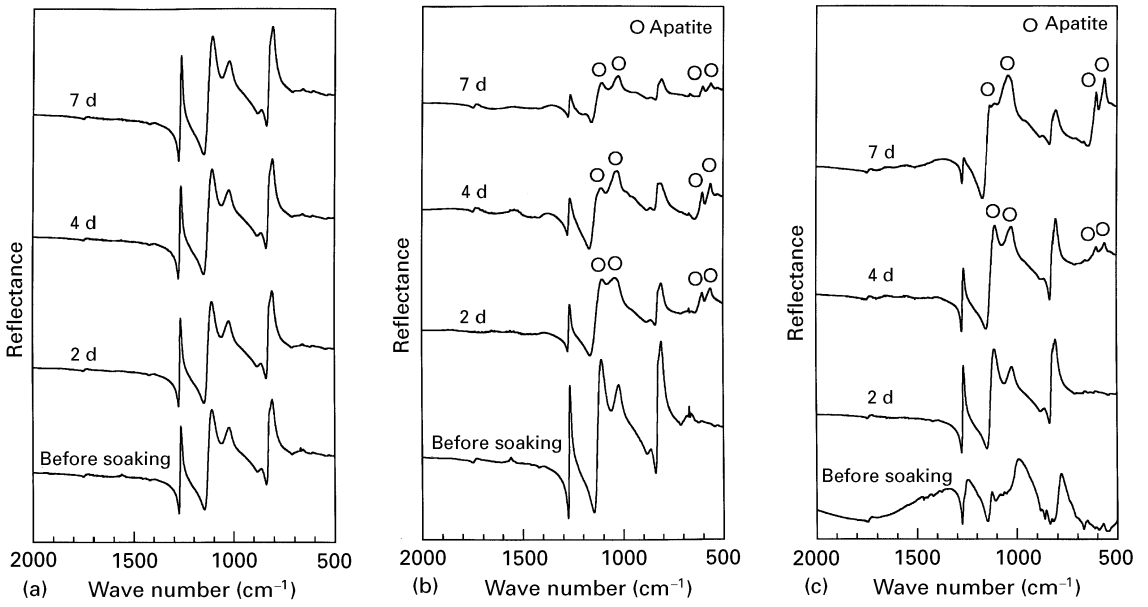

Figure 5 FT–IR reflection spectra of the surfaces of silicone substrates treated with 5 M NaOH for (a) 1h, (b) 3h and (c) 1d, and subsequently soaked in 1.5SBF for various periods.

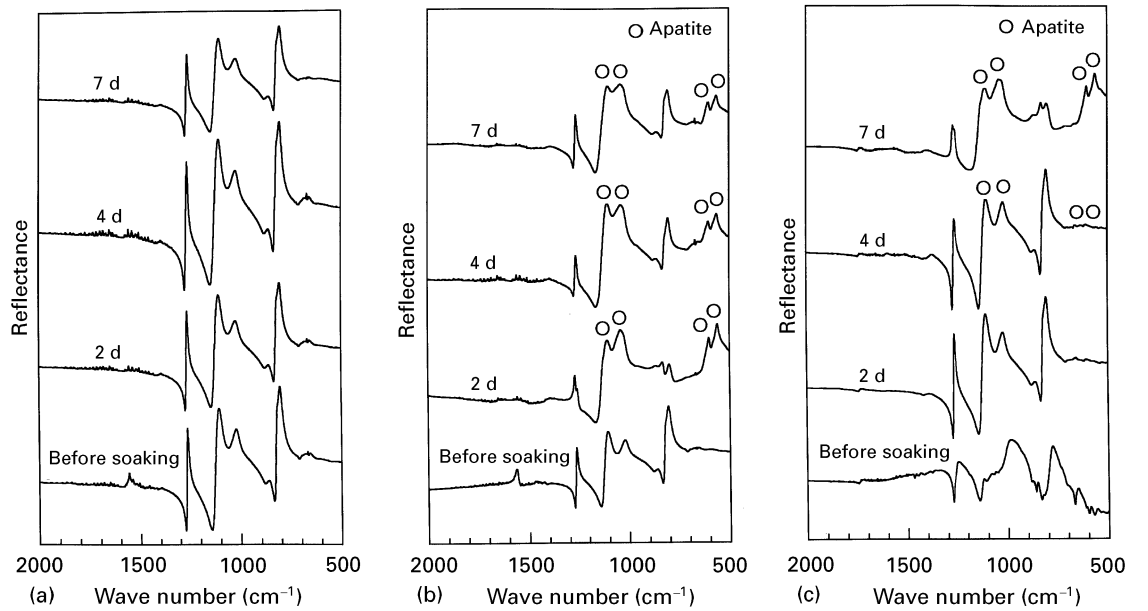

Figure 6 FT–IR reflection spectra of the surfaces of silicone substrates treated with 10 M NaOH for (a) 1h, (b) 3h and (c) 1d, and subsequently soaked in 1.5SBF for various periods.

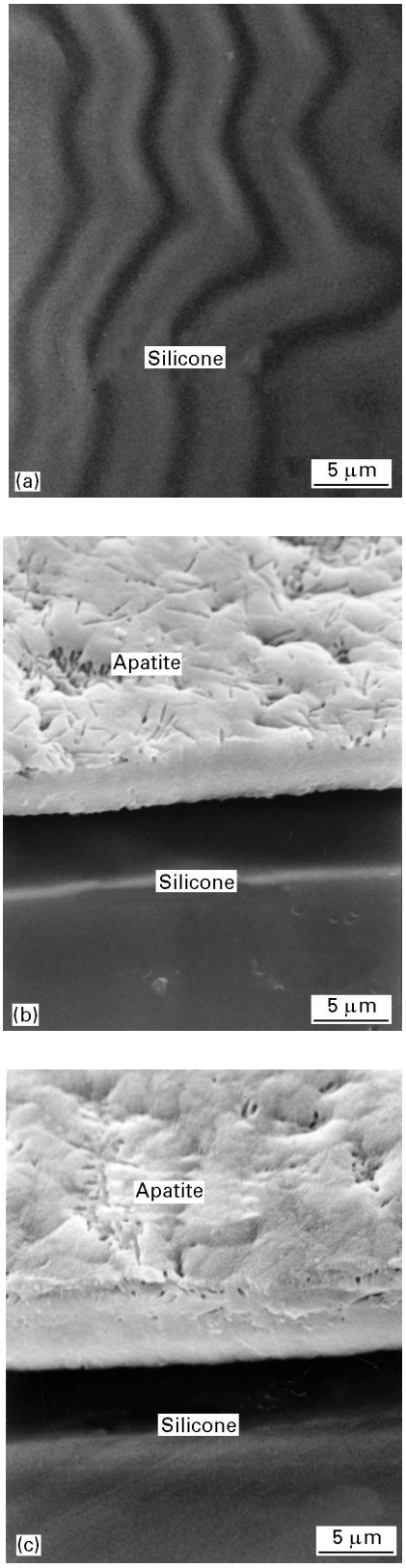

Figure 7 Scanning electron micrographs of the silicone substrates treated with (a) 2, (b) 5 and (c) 10 M NaOH for 3 h and subequently soaked in 1.5SBF for 7 d.

substrates for 5 and 10 M NaOH treatments, whereas no apatite was formed for 2 M NaOH treatment. The similar results were obtained for NaOH treatments for 1 d.

However, it should be noted that the apatite-forming ability of the thus formed silanol groups is assumed to be lower than that of silicate ions dissolved from CaO, SiO_2-based glass particles, because the surfaces of the apatite layer for the former are not so smooth and uniform compared with the latter case [6, 7]. The present work, however, is valuable as the first step in showing that chemical surface treatment can induce the bioactivity of polymers.

4. Conclusion

Siloxane bonds near the surfaces of the silicone substrates were broken and silanol groups were formed on them by the treatments of NaOH solution with concentration above 5 M for longer than 3 h. When thus NaOH-treated substrates were soaked in 1.5SBF with pH 7.25 at 36.5 °C, a bone-like apatite was formed on the substrates in a short period. However, the apatite-forming ability of the thus-formed silanol groups is assumed to be lower than that of silicate ions dissolved from CaO, SiO_2 based glass particles.

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