JOURNAL OF MATERIALS SCIENCE: MATERIALS IN MEDICINE **9** (1998) 285–290

Apatite–organic polymer composites prepared by a biomimetic process: improvement in adhesion of the apatite layer to the substrate by ultraviolet irradiation

G. J. LIU*, F. MIYAJI, T. KOKUBO, H. TAKADAMA, T. NAKAMURA‡, A. MURAKAMI§
Department of Material Chemistry, Faculty of Engineering, and ‡Department of Orthopaedic Surgery, Faculty of Medicine, Kyoto University, Sakyo-ku, Kyoto 606-01, Japan
§Department of Chemical Engineering, Himeji Institute of Technology, Himeji-Shi, Hyogo 671-22, Japan
E-mail: miyaji@sung7.kuic.kyoto-u.ac.jp

A dense and uniform layer of highly bioactive apatite can be formed in arbitrary thickness on any kind and shape of organic polymer substrates by the following biomimetic process. The substrate is first placed in contact with granular particles of CaO, SiO_2-based glass soaked in a simulated body fluid with ion concentrations nearly equal to those of human blood plasma for forming apatite nuclei, and then soaked in another fluid highly supersaturated with respect to the apatite for making the apatite nuclei grow. In the present study, the polymer substrates were pretreated with ultraviolet (UV) light, and then subjected to the biomimetic process described above. By UV irradiation, the induction period for the apatite nucleation of poly(ethylene terephthalate) (PET), poly-ether sulphone (PESF), polyethylene (PE), poly(methyl methacrylate) (PMMA) and polyamide 6 (N6) substrates were reduced form 24 h to 10 h. The adhesive strengths of the apatite layer to the substrates increased from 2.5–3.2 MPa to 4.5–6.0 MPa for PET, PESF and PMMA, and from about 1.0 MPa to 4.0–6.5 MPa for PE and N6 substrates. These results have been explained by assuming that silicate ions, which induce apatite nucleation, are easily adsorbed on the substrates due to the formation of polar groups, with an improved hydrophilic nature, on the polymer surfaces by UV irradiation.

1. Introduction

When materials are implanted into living bone, their interfacial changes vary with the category of implanted materials. It was found that bioactive glasses, glass-ceramics and ceramics develop a layer of carbonate-containing hydroxyapatite on their surfaces during exposure to body fluids and produce a strong bond with the living bone through the apatite layer [1, 2].

On the basis of the studies on the mechanism for the formation of such a bone-like carbonate apatite layer on the surfaces of CaO, SiO_2-based glasses and glass–ceramics [3, 4], a novel apatite coating method, i.e. a biomimetic process, which enables the formation of a dense and uniform layer of bone-like apatite on various kinds of materials in different shapes, has been developed [5, 6]. In this process, a substrate is set in contact with granular particles of CaO, SiO_2-based glass soaked in a simulated body fluid (SBF) with ion concentrations nearly equal to those of human body plasma at 36.5 °C (first soaking), in order to form apatite nuclei on the substrate opposed to the glass particles. Then the substrate in soaked in another solution with 1.5 times the ion concentrations of SBF at 36.5 °C (second soaking), to induce apatite nuclei growth on the substrate *in situ*.

Organic polymer–apatite composites prepared by this process are believed to be useful for repairing not only hard tissues but also soft ones. The adhesive strength of the apatite layer to the substrate surface formed by this process is, however, not necessarily sufficient for clinical applications [7–9]. It has been reported that some surface modifications of organic polymers with the NaOH solution [10], HCl solution [11] and glow-discharge [12] are effective in improving the adhesion. It is well known that the irradiation of ultraviolet (UV) light with short wavelength (184.9 and 253.7 nm) improves the hydrophilic nature and the adhesive property of the polymer surfaces [13]. In the present study, short wavelength UV irradiation

---

* On leave from Shanghai Institute of Ceramics, Chinese Academy of Sciences, 1295 Ding-Xi Road, Shanghai 200050 People's Republic of China.

0957–4530

was attempted to improve the adhesion to the polymer substrate of the formed apatite layer.

2. Materials and methods

2.1. UV irradiation

Rectangular polymer substrates ($10 \times 10 \times 1\ mm^3$) of poly(ethylene terephthalate) (PET), poly-ether sulphone (PESF), polyethylene (PE), poly(methyl methacrylate) (PMMA), polyamide 6 (N6) and poly(tetra-fluoroethylene) (PTFE) were abraded with #400 diamond paste, washed with ethanol and dried in air. They were irradiated by a UV light ray with main wavelengths of 184.9 and 253.9 nm for different periods in air. The power of the UV lamp and the distance between the light source and the sample were 200 W and 5 cm, respectively.

2.2. Surface characterization

Binding energies of carbon and oxygen in UV-irradiated and unirradiated organic polymer substrates were measured by X-ray photoelectron spectroscopy (XPS) with the ESCA Model MT5500 (ULVAC-PHI Co. Ltd, Chigasaki, Japan). MgK_α X-ray was used as the source. Measured binding energies were corrected by reference to the binding energy of the C_{1s} in the CH_2 group, 284.6 eV. Overlapped peaks in the XPS spectra were separated by the curve-fitting method using a Gaussian profile for the individual peaks.

Contact angles of SBF against the substrates before and after UV irradiation for 3 min were measured. About 1.5 μl drop of SBF was placed on the substrates which were set on the horizontal platform, and the contact angles were obtained geometrically from photographs of the drops.

2.3. Apatite formation on organic polymers

A glass with the nominal composition MgO 4.6, CaO 44.7, SiO_2 34.0, P_2O_5 16.2 and CaF_2 0.5 wt % [14] was used as the CaO, SiO_2-based glass for nucleating the apatite. A mixture of the reagent-grade chemicals of the corresponding composition was melted at 1450 °C for 2 h in a $MoSi_2$ furnace. The melt was poured on to a stainless steel plate and pressed quickly by another plate. The obtained glass plate was pulverized with a planetary-type zirconia ball mill and sieved in order to obtain only particles of 150–300 μm in diameter.

The simulated body fluid (SBF) was prepared by dissolving reagent chemicals of NaCl, $NaHCO_3$, KCl, $K_2HPO_4 \cdot 3H_2O$, $MgCl_2 \cdot 6H_2O$, $CaCl_2$ and Na_2SO_4 in deionized water [15]. The fluid was buffered at pH 7.25 and 36.5 °C with tris(hydroxymethyl)aminomethane and hydrochloric acid. The concentrations of the SBF compared to those of human blood plasma are shown in Table I.

Just after being irradiated by UV light, the organic polymer substrates were set in contact with particles of CaO, SiO_2-based glass soaked in 30 ml SBF at 36.5 °C for various periods in order to form apatite nuclei. Then the substrates were soaked in 30 ml 1.5SBF with 1.5 times the ion concentrations of the SBF solution at 36.5 °C for 6 d in order to induce growth of the nuclei. During this process, 1.5SBF was renewed every 2 d. After these treatments, the substrates were washed gently with distilled water and dried at room temperature.

2.4. Analysis of apatite

The surfaces of the substrates after apatite coating were analysed by thin-film X-ray diffraction with a Rint-1400 (Riguku Co., Tokyo, Japan) and Fourier transform–infrared (FT–IR) reflection spectroscopy with Model FT-IR 5M (Japan Spectroscopic Co. Ltd, Tokyo, Japan) and scanning electron microscopy (SEM) with S-2500CX (Hitachi Co. Ltd, Tokyo, Japan).

2.5. Measurement of adhesive strength

The adhesive strengths of the formed apatite to the substrates were measured by applying a tensile stress to their interfaces by using an Instron-type testing machine (Shimazu Model, Kyoto, Japan) at a cross-head speed of $1\ m\,min^{-1}$, by the same method as that previously reported [6]. Measurements were made for at least five specimens.

3. Results

3.1. XPS analysis

Fig. 1 shows the C_{1s} and O_{1s} XPS spectra of PESF substrate irradiated with UV light for 3 min and unirradiated. The C_{1s} spectrum of the irradiated substrate was deconvoluted into three peaks with binding energies of 284.5, 286.2 and 288.4 eV, which are assigned to carbons in the $-(CH_2)_2-$, $\rightarrow C-O$ or $\rightarrow C-OH$, $>C=O$ or $O-\overset{|}{\underset{|}{C}}-O$ groups, respectively [16, 17]. By UV light irradiation, the peak at 288.4 eV newly appeared and the intensity of the peak at 286.2 eV increased, whereas that of 284.5 eV decreased. This result indicates that the oxidized carbon groups increased in the surface region of the substrates by UV light irradiation. The O_{1s} spectrum of the irradiated substrate was deconvoluted into two peaks with binding energies of 531.7 and 533.4 eV, which are assigned to the oxygens in $-SO_2-OH$, $>SO-OH$ or $>C=O$ groups, and $S-OH$, $\rightarrow C-OH$, $C-O-C=O$ or $HO-C=O$ groups, respectively. By UV light irradiation, the intensity of the peak at

TABLE I Ion concentrations of simulated body fluid (SBF) and human blood plasma

	Ion concentration (m mol)							
	Na^+	K^+	Ca^{2+}	Mg^{2+}	Cl^-	HCO_3^-	HPO_4^{2-}	SO_4^{2-}
SBF	142.0	5.0	2.5	1.5	148.8	4.2	1.0	0.5
Human plasma	142.0	5.0	2.5	1.5	103.0	27.0	1.0	0.5

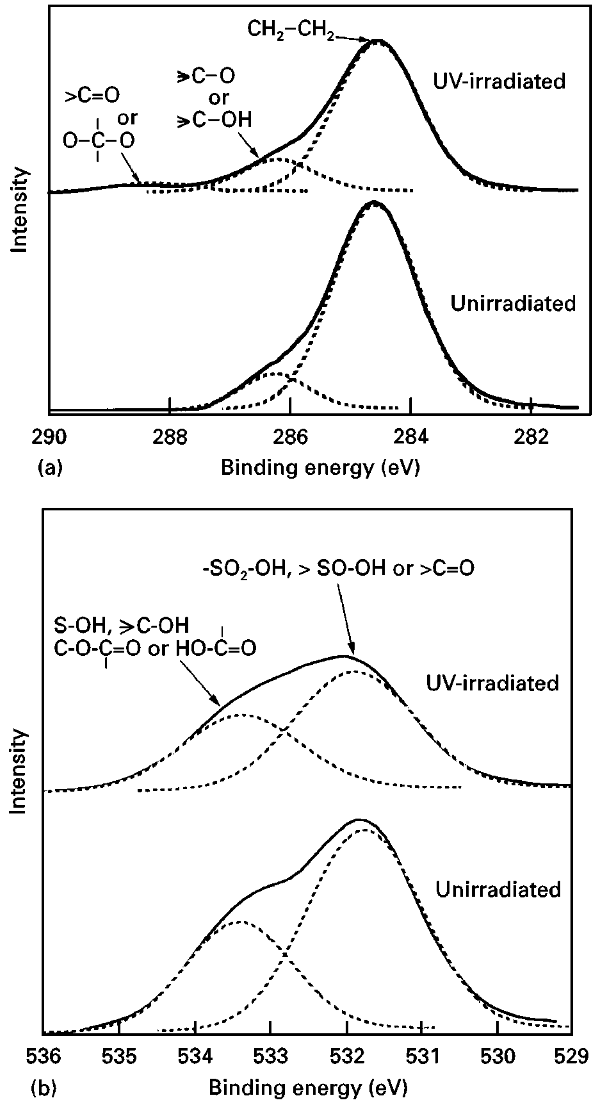

Figure 1 (a) C_{1s} and (b) O_{1s} XPS spectra of PESF substrate surface irradiated by UV light for 3 min and unirradiated.

533.4 eV increased, corresponding to the increase in oxidized carbons. Table II lists the area ratio of peaks ascribed to various functional groups formed on the surfaces of the various organic polymer substrates irradiated by UV light for 3 min and unirradiated. It can be clearly seen from this table that various kinds of oxidized carbon or sulphur groups, such as →C–O, →C–OH, >C=O, O–C–O, or S–OH groups and so on, increased in the surface region of the examined polymer surfaces, except for PTFE, after UV irradiation.

3.2. Wettability

Table III lists the wetting contact angles at room temperature for SBF solution on various polymer substrates irradiated UV light for 3 min and unirradiated. By UV irradiation, the wettability of the polymer surface increased for all the examined polymer substrates to some extent. This is attributed to the increase in hydrophilic groups on the polymer surfaces after UV irradiation.

TABLE II Area ratio of functional groups formed on surfaces of various organic polymer substrates irradiated by UV light for 3 min and unirradiated

C_{1s}

Substrate	CH$_2$–CH$_2$	→C–O C–OH	>C=O O–C–O	O=C–O HO–C=O	F$_2$C–CF$_2$ F$_2$C – CHF	F$_2$C–CH$_2$
Unirradiated						
PET	83	10	0	7	0	0
PESF	88	12	0	0	0	0
PE	100	0	0	0	0	0
PMMA	68	13	4	15	0	0
N6	80	3	17	0	0	0
PTFE	22	0	0	0	72	6
Irradiated						
PET	74	13	2	11	0	0
PESF	80	16	4	0	0	0
PE	95	5	0	0	0	0
PMMA	65	15	3	17	0	0
N6	72	12	16	0	0	0
PTFE	21	0	0	0	72	7

O_{1s}

Substrate	>C=O	→C–OH HO–C=O C–O–C=O	>SO–OH –SO$_2$–OH	S–OH
Unirradiated				
PET	56	44	0	0
PESF	0	0	66	34
PMMA	64	36	0	0
N6	58	42	0	0
Irradiated				
PET	60	40	0	0
PESF	0	0	61	38
PMMA	64	36	0	0
N6	52	48	0	0

3.3. Induction period for apatite nucleation

Figs 2 and 3 show the thin-film X-ray diffraction pattern and FT–IR reflection spectra of the surfaces of PESF substrates irradiated by UV light for 3 min, and then subjected to the first soaking for various periods and to the second soaking for 6 d. It can be seen from the figures that a bone-like apatite is formed on the surfaces of substrates after the second soaking when the substrate is subjected to the first soaking for longer than 6 h. Fig. 4 shows the SEM images of PESF substrates irradiated by UV light for 3 min, and then subjected to the first soaking for several periods and to the second soaking for 6 d. As shown in the scanning electron micrographs, a continuous apatite layer was formed on the substrate subjected to the first soaking for 10 h, although the apatite particles were observed for that for 6 h. Consequently, the induction period for apatite nucleation [6, 10–12] was determined as 10 h for PESF. Similarly, the induction period for apatite nucleation was determined as 10 h for PET, PE,

TABLE III Wetting contact angle, θ, at room temperture for SBF solution on various polymer substrates irradiated by UV light for 3 min and unirradiated

	θ (deg)	
Substrate	Unirradiated	Irradiated
PET	85.37	61.17
PESF	76.22	49.32
PE	98.12	80.86
PMMA	85.58	73.34
N6	62.24	50.38
PTFE	106.43	99.92

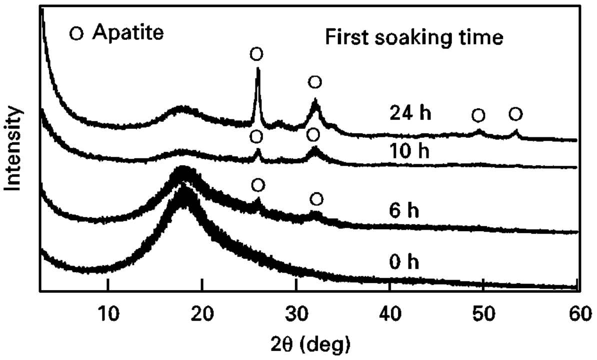

Figure 2 Thin-film X-ray diffraction patterns of the surfaces of PESF substrates irradiated by UV light for 3 min, and then subjected to the first soaking for various periods and to the second soaking for 6 d.

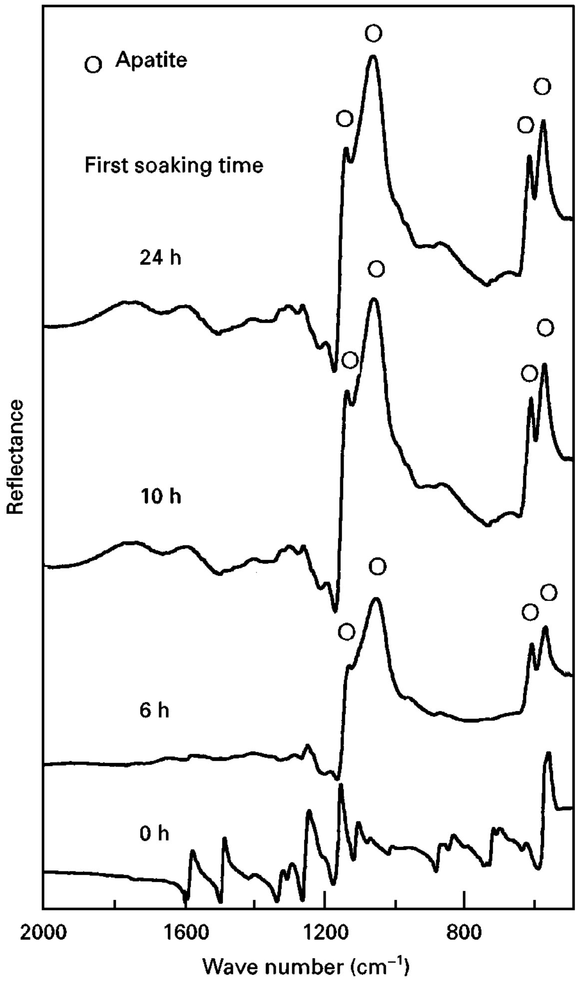

Figure 3 FT–IR reflection spectra of the surfaces of PESF substrates irradiated by UV light for 3 min, and then subjected to the first soaking for various periods and to the second soaking for 6 d.

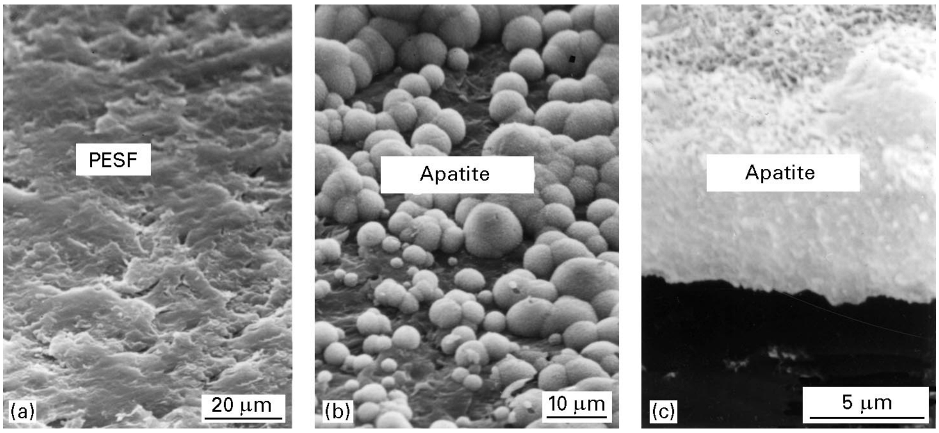

Figure 4 SEM images of PESF substrates irradiated by UV light for 3 min, and then subjected to the first soaking for (a) 0 h, (b) 6 h and (c) 10 h and to the second soaking for 6 d.

PMMA and N6 substrates and as 24 h for PTFE substrate. Because the induction period was 24 h for the untreated original substrates, irrespective of the kind of polymers [6], it is clear that the induction period greatly decreased by UV irradiation except for the PTFE substrate.

3.4. The adhesive strength

The adhesive strengths of the apatite layer to various organic polymer substrates are shown in Fig. 5. For all the polymer substrates except for PTFE, the adhesive strength increases with the UV irradiation time up to 3–5 min: the maximum adhesive strengths (listed in Table IV) reached 4.5–6.0 MPa for PET, PESF and PMMA, and 4.0–6.5 MPa for PE and N6. The adhesive strength, however, decreased by further (> 3–5 min) UV irradiation.

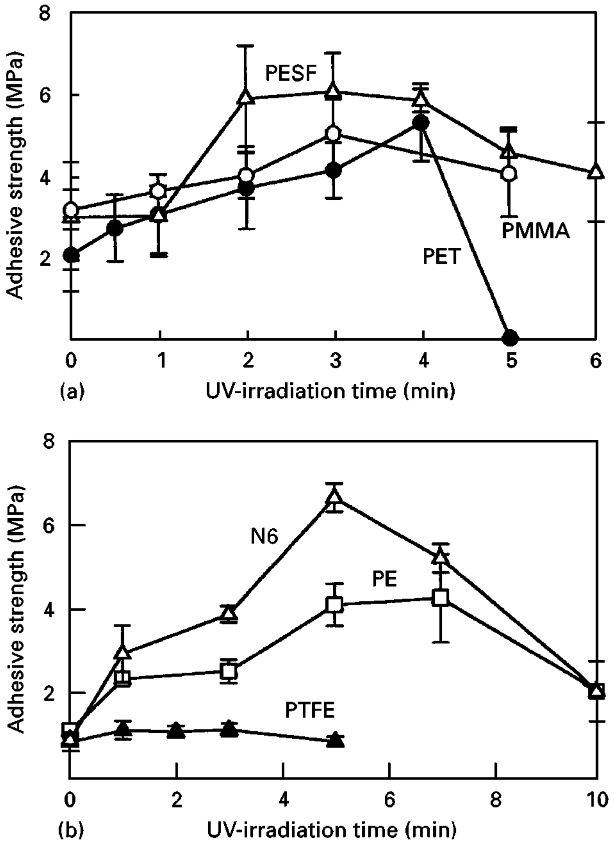

Figure 5 (a, b) Adhesive strengths of the apatite layer to various substrates as a function of UV irradiation time.

TABLE IV Maximum adhesive strength, σ_{max}, and corresponding UV irradiation time of various polymer substrates

Substrate	σ for unirradiated (MPa)	σ_{max} (MPa)	UV irradiation time for σ_{max} (min)
PET	2.13 ± 0.94	5.32 ± 0.94	4
PESF	3.06 ± 1.33	5.93 ± 1.29	2
PE	1.12 ± 0.12	4.12 ± 0.49	5
PMMA	3.23 ± 0.48	5.07 ± 0.84	3
N6	0.91 ± 0.11	6.68 ± 0.34	5
PTFE	0.86 ± 0.22	1.16 ± 0.14	3

4. Discussion

The CaO, SiO_2-based glass used in the first soaking dissolves not only silicate ions, which are adsorbed on the substrates and then induce apatite nucleation [18], but also calcium ions [19], which increase the ionic activity product with respect to apatite in the SBF solution in the narrow gap between the substrate and the glass particles and accelerate apatite nucleation [4, 20]. The present work proved that sufficient apatite nucleation in the first soaking is prerequisite for forming a dense and continuous apatite layer formation, because such a continuous apatite layer was not formed for the first soaking for less than 4 h due to the lack of the number of apatite nuclei.

UV treatment has changed the surface structure and properties of organic polymers by irradiating the light with a short wavelength of 184.9 and 253.7 nm. The energy of the UV light, caused the chemical bonds in the surfaces of organic polymer substrates to break and then to recombine with the oxygens in air. As a result, the surface hydrophilic property was improved due to the formation or increase in the amount of polar groups [20, 21], which were confirmed by XPS and wetting angle measurements (see Tables II and III). This might enhance the adsorption of silicate ions [10–12, 18]. Consequently, a larger number of apatite nuclei are assumed to be formed on the substrates compared with the unirradiated substrates, shortening the apatite induction periods for PET, PESF, PE, PMMA and N6. For PTFE, the induction period did not change due to the absence of the formation of polar groups on the substrates. This is explained by assuming that the fluorine atom in the C–F bond in PTFE is not easily drawn out, even by UV irradiation [13].

The adhesive strengths of apatite layer to the PET, PESF, PMMA, PE, and N6 showed a similar variation with UV irradiation time, except for PTFE. The increase in adhesive strength is closely correlated with the increase in the number of apatite nuclei due to the reduction of the induction period with UV light irradiation, because the adhesive strength is assumed to increase with increasing number of points at which the apatite nuclei are attached to the substrates. Moreover, polar groups, such as carbonyl, ester, carboxyl, hydroxyl and so on, formed by UV irradiation, could enhance the bonding of the apatite layer to the surfaces of the substrates. The decrease in adhesive strength for longer (> 3–5 min) UV irradiation is possibly attributed to the significant destruction of the main chains in the polymer surfaces. For PTFE, the adhesive strength hardly changed even after UV irradiation. This is also ascribed to the lack of formation of polar groups on the substrates [13].

An increase in the adhesive strength due to the increase in the number of polar groups was also observed for organic polymers pretreated with NaOH solution [10], HCl solution [11] and O_2 glow discharge [12]. Of these, the glow discharge was the most effective for improving the adhesive strength of the apatite layer to organic polymer substrates. The effect of the present UV irradiation is not superior to that of the glow discharge, because the former produces fewer polar groups on the polymer surfaces compared with the latter.

5. Conclusion

The effect of UV irradiation of various polymer substrates on the adhesion of apatite formed by a biomimetic process to the substrates, was examined. On UV irradiation, the induction period for apatite nucleation decreased and the adhesion of the apatite layer to the substrates increased for PET, PESF, PMMA, PE and N6, whereas no such improvement was observed for PTFE. These results are explained by assuming that silicate ions, which induce apatite nucleation, are easily adsorbed on the substrates due to the formation of polar groups on the polymer surfaces by UV irradiation.

Acknowledgement

G. J. Liu was partly supported by a foundation from the Chinese Academy of Sciences. This work was supported by Nippon Sheet Glass Foundation for Materials Science and Engineering.

References

1. L. L. HENCH, *J. Am. Ceram. Soc.* **74** (1991) 1487.
2. T. KOKUBO, *J. Ceram. Soc. Jpn* **99** (1991) 965.
3. T. KOKUBO, S. ITO, Z. T. HUANG, T. HAYASHI and S. SAKKA, *J. Biomed. Mater. Res.* **24** (1990) 331.
4. C. OHTSUKI, T. KOKUBO and T. YANAMURO, *J. Non-Cryst. Solids* **143** (1992) 84.
5. Y. ABE, T. KOKUBO and T. YAMAMURO, *J. Mater. Sci. Mater. Med.* **1** (1990) 233.
6. M. TANAHASHI, T. YAO, T. KOKUBO, M. MINODA, T. MIYAMOTO, T. NAKAMURA and T. YAMAMURO, *J. Am. Ceram. Soc.* **77** (1994) 2805.
7. M. TANAHASHI, T. KOKUBO, T. NAKAMURA, Y. KATSURA and M. NAGANO, *Biomaterials* **17** (1996) 47.
8. M. NAGANO, T. NAKAMURA, T. KOKUBO and M. TANAHASHI, *J. Biomed. Mater. Res.* **31** (1996) 487.
9. M. NAGANO, T. NAKAMURA, T. KOKUBO, M. TANAHASHI and M. OGAWA, *Biomaterials* **17** (1996) 1771.
10. M. TANAHASHI, T. YAO, T. KOKUBO, M. MINODA, T. MIYAMOTO, T. NAKAMURA and T. YAMAMURO *J. Appl. Biomater.* **5** (1994) 339.
11. *Idem*, *J. Mater. Sci. Mater. Med.* **6** (1995) 319.
12. *Idem*, *J. Biomed. Mater. Res.* **29** (1995) 349.
13. J.-Y. ZHANG, H. ESROM, U. KOGELSCHATZ and G. EMIG, in "Polymer Surface Modification: Relevance to Adhesion", edited by K. L. Mittal, (VSP, Utrecht, 1996) p. 153.
14. T. KOKUBO, S. ITO, S. SAKKA and T. YAMAMURO, *J. Mater. Sci.* **21** (1986) 536.
15. T. KOKUBO, H. KUSHITANI, S. SAKKA, T. KITSUGI and T. YAMAMURO, *J. Biomed. Mater. Res.* **24** (1990) 721.
16. D. T. CLARK, B. J. CROMARTY and A. DILKS, *J. Polym. Sci. Polym. Chem. Ed* **16** (1978) 3173.
17. J. BREUER, S. METEV and G. SEPOLD, in, "Polymer Surface Modification: Relevance to Adhesion", edited by K. Mittal, (VSP, Utrecht, 1996) p. 185.
18. S. CHO, F. MIYAJI, T. KOKUBO, K. NAKANISNI, N. SOGA and T. NAKAMURA, *J. Biomed. Mater. Res.* **32** (1996) 375.
19. T. KOKUBO, H. KUSHITANI, C. OHTSUKI, S. SAKKA and T. YAMAMURO, *J. Mater. Sci. Mater. Med.* **3** (1992) 79.
20. C. OHTSUKI, T. KOKUBO, K. TAKATSUKA and T. YAMAMURO, *J. Ceram. Soc. Jpn* **99** (1991) 1.
21. D. K. OWENS, *J. Appl. Polym. Sci.* **19** (1975) 3315.

Received 18 December 1996
and accepted 29 July 1997