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Ultrasonic Implantation of Bioactive Glass Particles into Poly(methyl methacrylate) Substrates

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Poly(methyl methacrylate) substrates were immersed in suspensions containing bioactive $50CaO \cdot 50SiO_2$ (mol%) glass particles (45 μm in diameter) and a 6:4 (volume fraction) mixture of ethanol and THF, and an ultrasonic energy was applied to the system. A layer of glass particles was implanted and covered more than 50% of the substrate surface. Thin film X-ray diffraction patterns and FT-IR reflection spectra indicated deposition of apatite on the glass-implanted substrates after they were soaked for 12 h in a simulated body fluid similar in apatite-deposition ability to the human blood plasma. Flake-like apatite crystallites formed on the substrate soaked in SBF for 3 days.

1. INTRODUCTION

A group of materials that form a direct bond to living bones[1] are called bioactive. It is essential that they can deposit a layer of bone-like apatite. A few series of glasses and glass ceramics have exhibited bioactivity, such as Ceravital® [2], Cerabone® A-W[3], and several glasses containing CaO and SiO_2 including Bioglass® [4]. However, almost all of metals, ceramics and organic polymers cannot form such bonds, and they are sometimes called biocompatible as far as they are allowed in human or mammals' bodies with forming a fibrous capsule around them. Poly(methyl methacrylate), denoted as PMMA, is one of the most important polymers that are used in medical care. It is thus significant if one could provide PMMA with bioactivity.

One of the present authors used an ultrasonic energy to stimulate kinetic movements of glass or ceramic powders in suspensions and induced bombarding a substrate immersed in them[5]. Such ultrasonic treatment may easily implant glass particles into any organic polymers when they are immersed in a suspension of a solvent capable of swelling the polymers. In this respect the treatment is denoted as ultrasonic implantation. Then it is expectable that the ultrasonic implantation of bioactive powders provides polymers with bioactivity. The present paper describes the ultrasonic implantation into PMMA of a $50CaO \cdot 50SiO_2$ (mol%) glass whose bioactivity was already confirmed[6], and confirmation of the bioactivity of the glass-implanted PMMA substrate.

2. EXPERIMENTAL

One of the bioactive glasses of a composition $50CaO \cdot 50SiO_2$ (mol%) was prepared by melting at 1600°C a mixture of $CaCO_3$ and SiO_2 in a platinum crucible placed in a $MoSi_2$-heated furnace and quenching the melt between two sheets of steel. The quenched glass was annealed and pulverized with a zirconia ball mill to less than 45 μm in diameter. Several mixtures of ethanol and tetrahydrofurane (THF) in various fractions (volume %) were prepared and tried as suspension media to find an appropriate mixing ratio. A sheet of PMMA (Sumitomo Chemical

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Co., Ltd.) was cut into pieces with 15×10×2 mm in size. Each piece was immersed in a suspension containing up to 1 g of the glass powder dispersed in 20 or 40 ml of ethanol-THF solutions that were held in a 50 ml glass bottle. The bottle was then immersed in an ultrasonic water bath (Iuchi Co., Pasolina USC1, 65W) and was ultrasonically stimulated for 20 min. The temperature of the water rose from 20°C to 40°C.

A simulated body fluid (SBF) that contained inorganic components similar in concentration to the human blood plasma[7] (Table 1) was prepared after the procedure described elsewhere[8], and pH was adjusted to 7.25 by 50 mM (=10^{-3} mol/dm^3) tris(hydroxymethyl)aminomethane and 45 mM hydrochloric acid solutions. The fluid contained no living cells or organic substances. It is already confirmed that SBF produces a bone-like apatite layer that would form *in vivo* on the bioactive materials[9]. The pieces of PMMA implanted with the glass particles were immersed in SBF held in 50 ml polyethylene bottles whose temperature was kept at 36.5°C. After soaking up to 7 days the PMMA substrates were studied on their surface structure with FT-IR reflection spectrometry and thin-film X-ray diffractometry. The IR reflection spectra (75° off-normal) were recorded in a JASCO FT/IR-300 spectrometer at 100 scans and 4 cm^{-1} resolution, using a Spectra Tech attachment Model 501. Thin film X-ray diffraction spectra (CuKα) were taken with a Rigaku RINT 1400 diffractometer operated under 40 kV-200mA acceleration, at the incident angle of 1°. These two techniques give structural information of an only about 1 μmthick surface layer. A scanning electron microscope (SEM, JEOL JSM-6300) equipped with an energy dispersive X-ray spectrometer (Phillips, EDX-4) was used to observe microstructure of the surfaces and cross sections and to examine the element distribution.

Table 1. Conentrations of inorganic ions in simulated body fluid (SBF) and the human blood plasma.

	Concentration (10^{-3} mol/dm^3)	
Ions	SBF	Human body plasma
Na^+	142.0	142.0
K^+	5.0	5.0
Ca^{2+}	2.5	2.5
Mg^{2+}	1.5	1.5
Cl^-	147.8	103.0
HCO_3^-	4.2	27.0
HPO_4^{2-}	1.0	1.0
SO_4^{2-}	0.5	0.5

3. RESULTS AND DISCUSSION

Figure l represents weight changes of the PMMA substrate after the ultrasonic implantation as a function of the ethanol-THF mixing ratio in the suspension medium. The amount of glass suspended was 0, 30, and 500 mg for 20 ml of the ethanol-THF solutions that were held in 30 ml glass bottles. A small weight gain (1 mg) was found irrelevant to the amount of glass until the fraction of THF exceeded 30 vol%. Increase in the THF fraction caused a weight loss of the specimen probably because of chipping the swelled surface due to ultrasonically stimulated glass particles. Note that the suspensions with 30 mg glass powder caused greater weight losses than the 500 mg glass-suspensions and that the latter case gave as much weight loss as the glass-free solutions. This indicated that the implanting rate for the 500 mg-glass suspensions was larger than that for the 30 mg-glass ones. Fig. 2 shows SEM photographs of the cross sections for the specimen that the ultrasonic

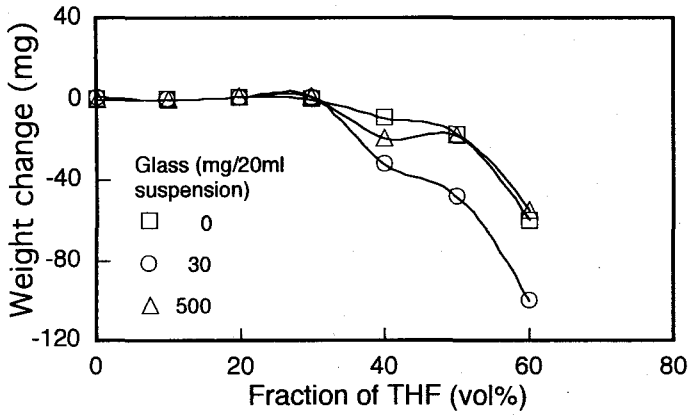

Fig. 1. Weight change of the PMMA substrate after the ultrasonic implantation as a function of the ethanol-THF mixing ratio in the suspension medium.

implantation was applied to with the suspensions where 1000 mg of the glass were dispersed in 40 ml of the ethanol-THF solutions different in mixing ratio. Energy dispersive X-ray analysis of Ca and Si distribution was also carried out along the line indicated in the photographs. After the fraction of THF reached 40 vol%, glass particles implanted were observable on the PMMA surface as well as the strong X-ray signals of Ca and Si. Several layers of glass particles were implanted for the suspension of 60 vol% THF while only a layer was observable for 40 vol%

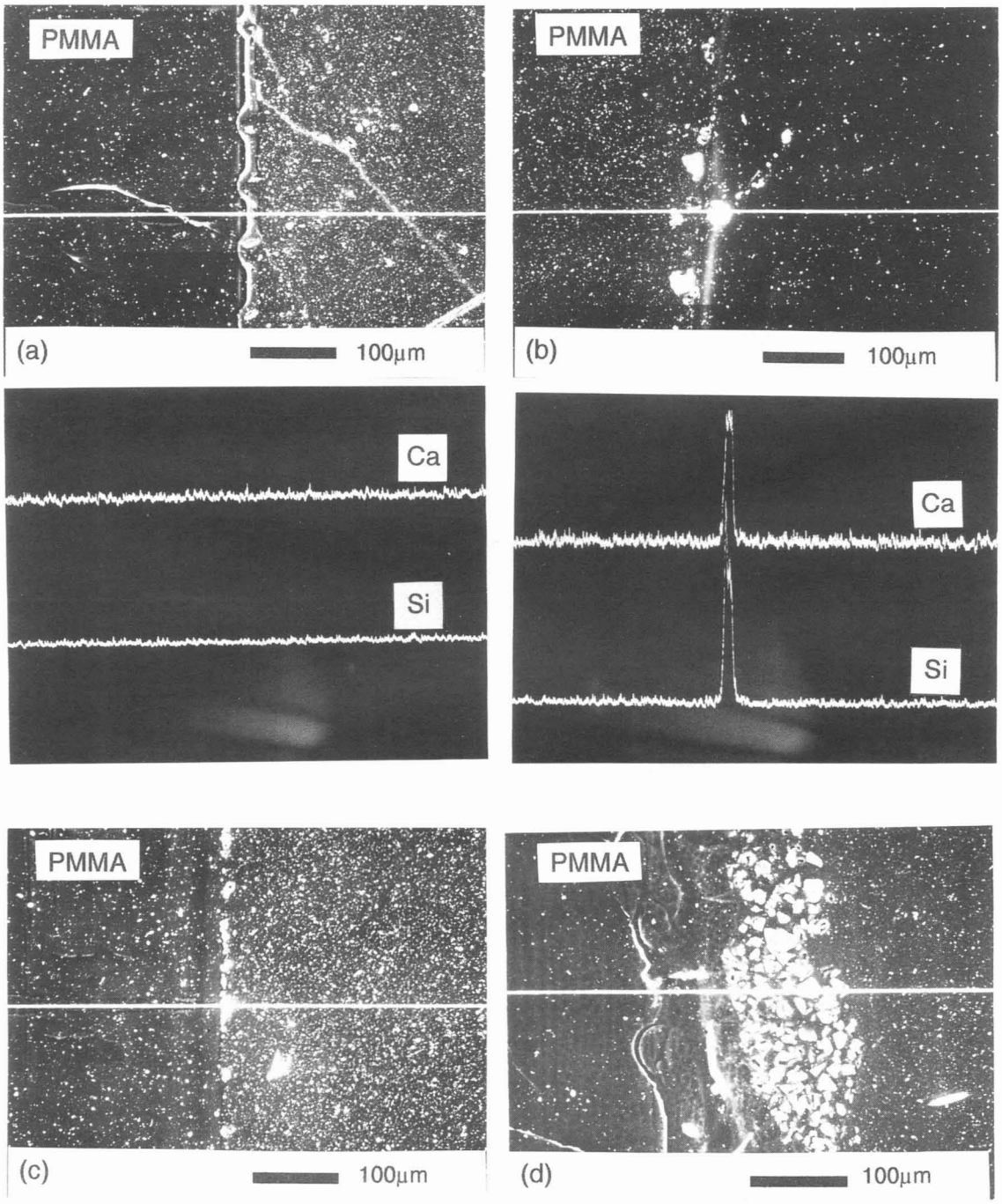

Fig. 2. SEM photographs of cross section of ultrasonically implanted PMMA.1000mg glass/40ml solution. THF:ethanol= (a)7:3, (b) 6:4, (c) 5:5, (d) 4:6., Corresponding Ca and Si distributions after electron probe micro line-analysis are also indicaated.

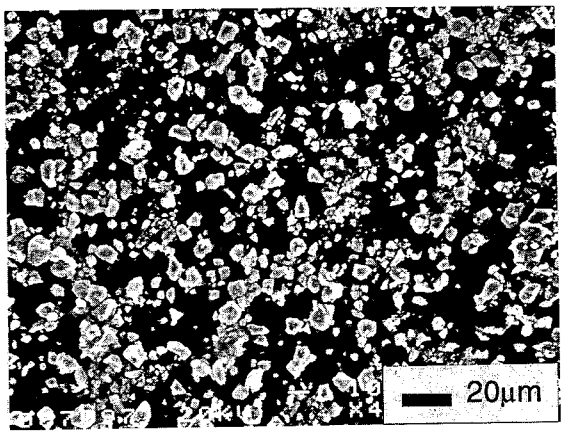

Fig. 3. A SEM photograph of the surface of PMMA after the ultrasonic implantation. 1000mg glass/ 40mL 4THF-6ethanol solution.

THF. From those results a mixture of 6:4 ethanol-THF solution was taken as the suspension medium where the weight/volume ratio of the suspending glass and the media was fixed at 1000 mg-glass/40 ml-solution.

Fig. 3 is a SEM photograph of the surface of a specimen after the ultrasonic implantation, showing that the glass particles implanted homogeneously cover more than 50% of the surface. Fig. 4 shows thin-film X-ray diffraction patterns and FT-IR reflection spectra of the specimen after soaking up to 7 days in SBF. The spectra for a specimen without soaking are denoted as "0h". A broad X-ray diffraction for the 0h specimen near 2θ=30° due to the glass particles and the PMMA substrate grew in only 1 h of soaking in SBF. This suggested some change in surface structure took place on the glass surface at so early a stage of soaking in SBF. The 12 h specimen showed faint X-ray diffraction peaks near 26° and 32° due to the (002) plane and an envelope of (211), (112) and (300) planes of apatite (JCPDS: 9-432), respectively, and they grew to distinct ones in a longer period of soaking. A 1030 cm^{-1} IR reflection peak observed for the 0h specimen was assigned to a Si-O stretching band for the $50CaO{\cdot}50SiO_2$ glass as well as weak 900 and 810 cm^{-1} peaks. A weaker band near 480 cm^{-1} was due to Si-O deformation. After 1 h soaking in SBF several bands newly appeared at about 1240 and 1130 cm^{-1} that were already assigned to a longitudinal optical mode and transverse optical one of Si-O stretching[1-4, 6,8,9] after Almeida et al.[10] For longer soaking periods, 1130 and 1040 cm^{-1} peaks grew in

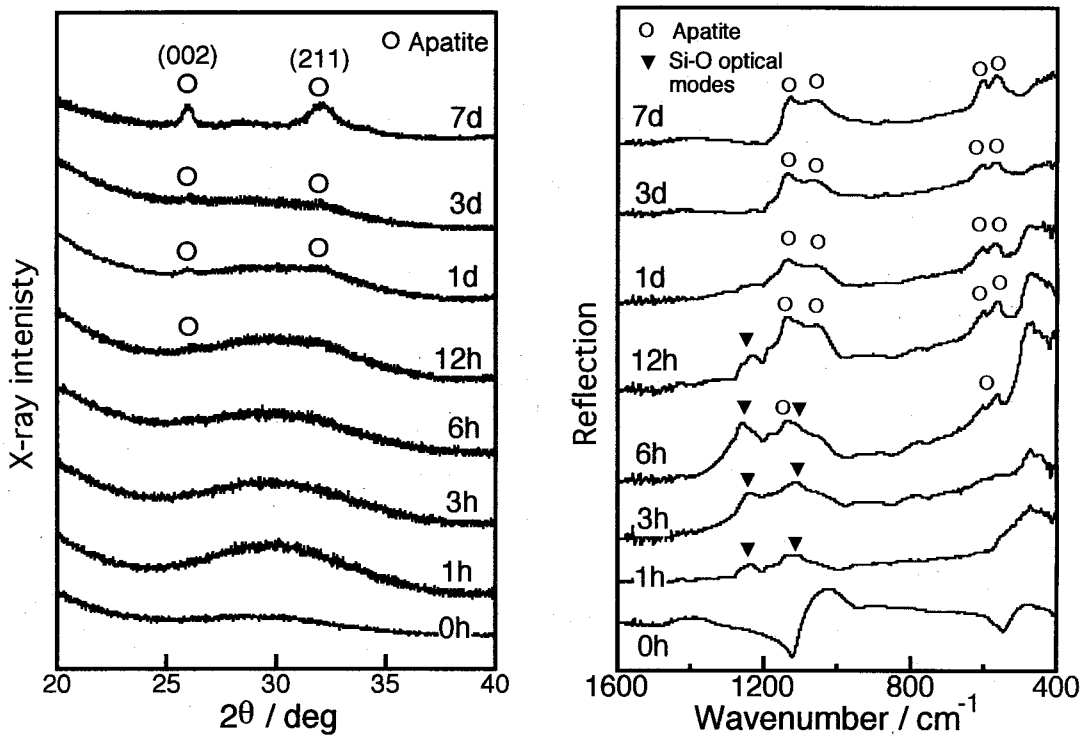

Fig. 4. Thin-film X-ray diffraction patterns (left) and FT-IR reflection spectra(right) of the specimen after ultrasonic implantation (1000 mg glass/40 mL 4THF-6ethanol solution) and soaking up to 7 days in SBF.
O: apatite, ▼ : Si-O optical modes.

intensity whereas the relative intensity of the 1240 and 1180 cm^{-1} bands decreased as well as that of 900-750 cm^{-1} ones until they disappeared after soaking for 7 days. Moreover, the 540 cm^{-1} peak grew and finally split into two peaks at 610 and 570 cm^{-1}. The 1130, 1040, 610 and 570 cm^{-1} peaks were due to apatite[1-3,9]. This supports the previous assignment of the X-ray diffraction near 26° and 32° in Fig. 4.

Fig. 5 shows the SEM photograph of the specimen soaked in SBF for 3 days. Flake-like crystallites composed hemispherical agglomerates <2 μmin diameter to cover the surface of the PMMA substrate. The morphology of the crystallites was the same as apatite crystals found for bulk glasses and glass ceramics[1-4,6,8,9]. Again deposition of apatite was confirmed on the glass-implanted PMMA, and it was concluded that the present ultrasonic implantation was applicable to provide PMMA with bioactivity.

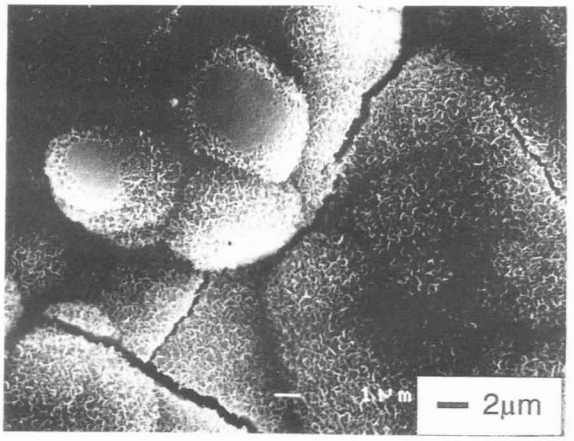

Fig. 5. A SEM photograph of PMMA soaked in SBF for 3 days after ultrasonic implantation (1000 mg glass/40 mL 4THF-6ethanol solution).

4. SUMMARY

Pieces of PMMA were immersed in suspensions that contained particles (45 μm in diameter) of bioactive glass of composition $50CaO \cdot 50SiO_2$ in a 6:4 (volume fraction) mixture of ethanol and THF, and an ultrasonic energy was applied to the system. With a mixture of 40 vol% of THF a layer of glass particles was implanted in the surface of PMMA while several layers were implanted for the 60 vol% THF suspension. A scanning electron micrograph indicated that more than 50% of the surface area were covered with the glass particles when the 40 vol% THF suspension was used for the ultrasonic implantation. The surface structure was examined for the specimen with glass implanted in the 6:4 ethanol-THF suspension after soaking in SBF up to 7 days. Thin film X-ray diffraction patterns indicated trace (002) and (211) peaks of apatite for the specimen soaked for 12 h. They became distinct in a longer period of soaking. FT-IR reflection spectra showed Si-O bands before growth of apatite IR bands. Flake-like crystallites of apatite were observed in SEM photographs for the specimen soaked in SBF for more than 1 day.

5. REFERENCES

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