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AUTHOR(S):

Fukushima, Keito; Yabutsuka, Takeshi; Takai, Shigeomi; Yao, Takeshi

CITATION:

Fukushima, Keito ...[et al]. INVESTIGATION OF EFFECTIVE PROCEDURES IN FABRICATION OF BIOACTIVE PEEK USING THE FUNCTION OF APATITE NUCLEI. Phosphorus Research Bulletin 2016, 31: 31-37

ISSUE DATE:

2016

URL:

http://hdl.handle.net/2433/269241

Phosphorus Research Bulletin Vol. 31 (2016) pp. 031-037

INVESTIGATION OF EFFECTIVE PROCEDURES IN FABRICATION OF BIOACTIVE PEEK USING THE FUNCTION OF APATITE NUCLEI

Keito Fukushima[1], Takeshi Yabutsuka[1,*], Shigeomi Takai[1], Takeshi Yao[2, 3]
(*Corresponding author: yabutsuka@energy.kyoto-u.ac.jp)

[1] Department of Fundamental Energy Science, Graduate School of Energy Science, Kyoto University, Yoshida-honmachi, Sakyo-ku, Kyoto 606-8501, Japan
[2] National Institute of Technology, Kagawa College, 355 Chokushi-cho, Takamatsu, Kagawa 761-8058, Japan
[3] Institute of Advanced Energy, Kyoto University, Gokasho, Uji, Kyoto 611-0011, Japan

Keywords: Polyether ether ketone (PEEK), Bioactivity, Apatite Nucleus (AN), Implant material

Abstract: We made micropores on the surface of a polyether ether ketone (PEEK) by immersing in sulfuric acid. In order to provide bioactivity to PEEK, we treated the surfaces of the specimens with glow-discharge in O_2 gas atmosphere and precipitated Apatite Nucleus (AN) in the micropores. We evaluated apatite-forming ability of the specimens by using SBF and measured adhesive strength of formed apatite layer. In this study, we researched which treatment is effective to give bioactivity to PEEK.

(Received December 31, 2015; Accepted March 30, 2016)

INTRODUCTION

When either the pH or the temperature of a simulated body fluid (SBF)[1-3] is raised, fine particles of calcium phosphate are precipitated. In our recent studies, we found that these fine particles are very active for forming hydroxyapatite (HAp) in SBF or body fluid, and named this fine particle Apatite Nucleus (AN)[4, 5].

Conventionally, metallic materials or bioceramics have been applied as artificial bone materials. The former metallic materials have much higher elastic moduli than the living bone. When we use the metallic materials as artificial bones, there is a possibility that stress shielding occurs and density of the surrounding living bones decreases[6]. The latter bioceramics have high biocompatibility. However, the range of the acceptable affected parts is limited because they are brittle. In recent years, as a material that might be overcoming all these disadvantages, polyether ether ketone (PEEK) has attracted much attention.

PEEK is one of the most attractive super engineering plastic materials with its high mechanical properties such as excellent fatigue, shock, abrasion and chemical resistance. Moreover, its elastic modulus is more similar to that of cortical bone than those of many metals such as titanium alloys. For these reasons, PEEK is expected to be a candidate for replacing existing implant components[7].

In this study, we investigated the fabrication process of bioactive PEEK using the function of AN in order to find out effective procedure for giving bioactivity to PEEK.

MATERIALS AND METHODS

1) Preparation of SBF

We prepared SBF by dissolving reagent-grade NaCl, $NaHCO_3$, KCl, $K_2HPO_4{\cdot}3H_2O$, $MgCl_2{\cdot}6H_2O$, $CaCl_2$ and Na_2SO_4 in an ultrapure water with the composition as shown in TABLE 1 and buffered at pH 7.40 with tris(hydroxymethyl)aminomethane ($(CH_2OH)_3CNH_2$) and 1 M HCl at 36.5 °C.

TABLE 1 Ion concentrations of human blood plasma and simulated body fluid (SBF).

Ion	Ion concentration / mM	
	SBF	Blood plasma
Na^+	142.0	142.0
K^+	5.0	5.0
Mg^{2+}	2.5	2.5
Ca^{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

2) Preparation of specimens.

a) Micropores formation by sulfuric acid treatment.

We used natural grade PEEK plates (Plaport, Japan) with 15 × 10 × 5 mm^3 in size. We treated the surfaces of the PEEK plates with 98 wt% sulfuric acid (Hayashi Pure Chemical, Japan) at room temperature for around 10 seconds. Then we washed the specimens in distilled water and dried in the air.

b) Glow-discharge treatment.

We treated the surfaces of the specimens with glow-discharge in O_2 gas atmosphere at 200 W for 2 minutes by using a plasma system (Model BP-1, Samco, Japan). We supplied reactive functional groups which have hydrophilic property on the surfaces of organic polymers by this treatment[8].

c) AN treatment.

We increased the pH value of SBF to 8.40 by dissolving $(CH_2OH)_3CNH_2$ at 25.0 °C. In order to precipitate AN in the micropores, we immersed each specimen in this solution and put in an incubator at 70 °C for 24 hours. We denote this treatment as 'AN treatment' hereafter.

In order to examine which combination of above three treatments contributes to the realization of bioactivity, we prepared 8 Groups of controlled specimens as shown in TABLE 2.

TABLE 2 Prepared specimens and their conditions

Group	Sulfuric acid	Glow-discharge	AN
A	○	○	○
B	×	○	○
C	○	×	○
D	○	○	×
E	×	×	○
F	○	×	×
G	×	○	×
H	×	×	×

3) Evaluation of apatite-forming ability.

We evaluated apatite-forming ability of each specimen by immersing in SBF at pH 7.40, 36.5 °C, which method is certified as ISO 23317[9]. Then we analyzed the surfaces of the specimens by thin film X-ray diffraction (TF-XRD; Rint 2500, Rigaku, Japan), scanning electron microscopy (SEM; SU6600, Hitachi High-Technologies, Japan) and energy dispersive X-ray analysis (EDX; XFlash® 5010, Bruker, Germany).

4) Measurement of adhesive strength of apatite layer.

We measured the adhesive strength between PEEK substrate and the apatite layer formed by immersing in SBF for 14 days by a modified ASTM C-633 method[10, 11]. We attached both sides of the specimens to stainless steel jigs (10×10 mm^2) by Araldite® glue and applied tensile load at 1 mm•min^{-1} of a crosshead speed until a fracture occurred with an universal testing machine (Model AGS-H Autograph, Shimadzu, Japan).

RESULTS AND DISCUSSION

1) Apatite forming ability of the samples with the sulfuric acid treatment, the glow-discharge treatment and the AN treatment (Group A).

In FIGURE 1, the SEM picture of the surface of the untreated PEEK is shown. Smooth surface was observed.

In FIGURE 2, the result of EDX of the surface of the untreated PEEK is shown. Peaks of C and O were detected. An Au peak was caused by sputtering for the SEM observation.

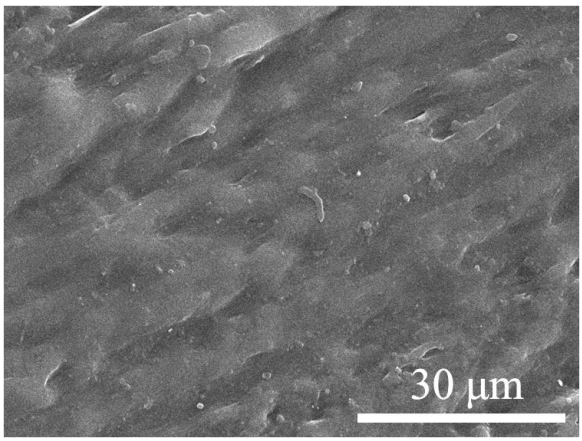

FIGURE 1 SEM picture of the surface of the untreated PEEK.

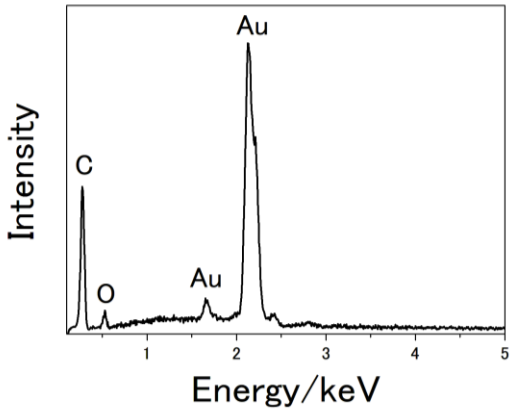

FIGURE 2 Result of EDX of the surface of the untreated PEEK.

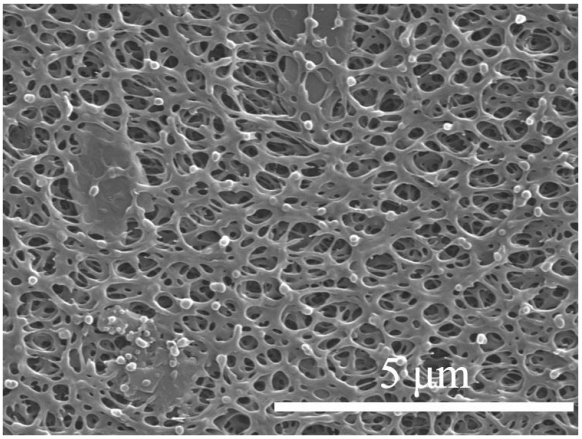

FIGURE 3 SEM picture of the surface of the PEEK after the sulfuric acid treatment.

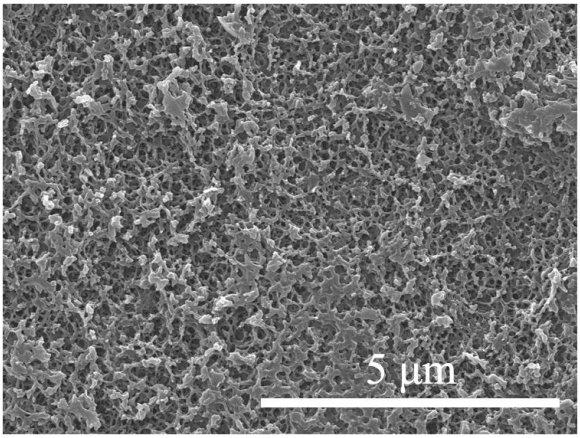

FIGURE 4 SEM picture of the surface of the PEEK after the sulfuric acid treatment and the glow-discharge treatment.

In FIGURE 3, the SEM picture of the surface of the PEEK after the sulfuric acid treatment is shown. Cancellous micropores around 500 nm in size were formed on the surface. The result of EDX of the specimen was almost same as that of the untreated PEEK.

In FIGURE 4, the SEM picture of the surface of the PEEK after the sulfuric acid treatment and the glow-discharge treatment is shown. Surface morphology was changed in comparison with FIGURE 3, after the sulfuric acid treatment. It is suggested that morphological change was occurred by heat during the glow-discharge treatment. The result of EDX of specimen was also almost same as that of the untreated PEEK.

In FIGURE 5 and FIGURE 6, the SEM picture and the result of EDX of the surface of the PEEK after the sulfuric acid treatment, the glow-discharge treatment and the AN treatment are shown. Surface morphology was changed from FIGURE 4, after the sulfuric acid treatment and the glow-discharge treatment. In the EDX, P and Ca were detected. In the SEM, spherical particles, which characterize amorphous calcium phosphate (ACP), observed on the whole surface. It is considered that nucleation was progressed and precipitated AN grew to the ACP particles in the AN treatment.

In FIGURE 7 and FIGURE 8, the SEM picture and the result of EDX of the surface of the PEEK with all treatment after the soak in SBF for 1 d are shown. The whole surface was covered with needle-like crystallites, which characterize bone-like apatite, and peaks of P and Ca were strongly detected. In addition, Na, Mg and Cl were slightly detected. This means that these elements were derived from minerals contained in the bone-like apatite.

In FIGURE 9 and FIGURE 10, the SEM picture and the result of EDX of the surface of the PEEK with all treatment after the soak in SBF for 7 d are shown. It was observed that needle-like crystallites of bone-like apatite grew and peak of C was not detected.

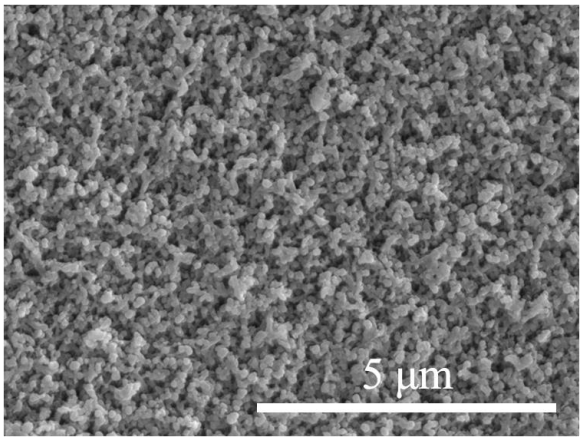

FIGURE 5 SEM picture of the surface of the PEEK after the AN treatment.

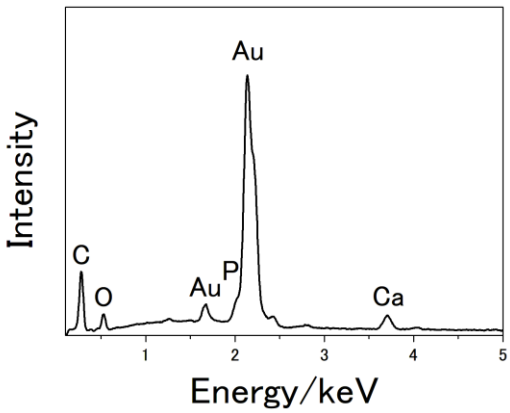

FIGURE 6 Result of EDX of the surface of the PEEK after the AN treatment

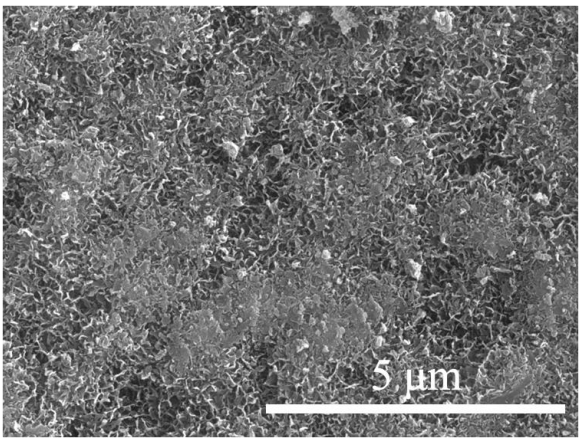

FIGURE 7 SEM picture of the surface of the PEEK with all treatment after the soak in SBF for 1 d.

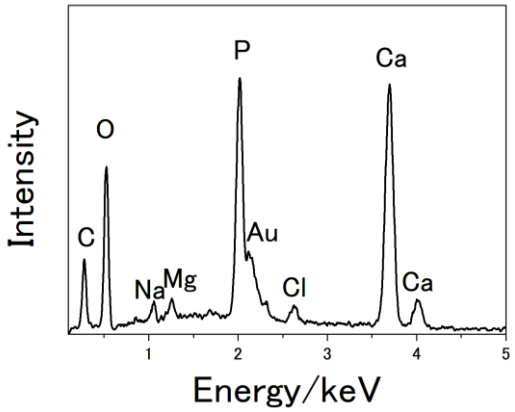

FIGURE 8 Result of EDX of the surface of the PEEK with all treatment after the soak in SBF for 1 d.

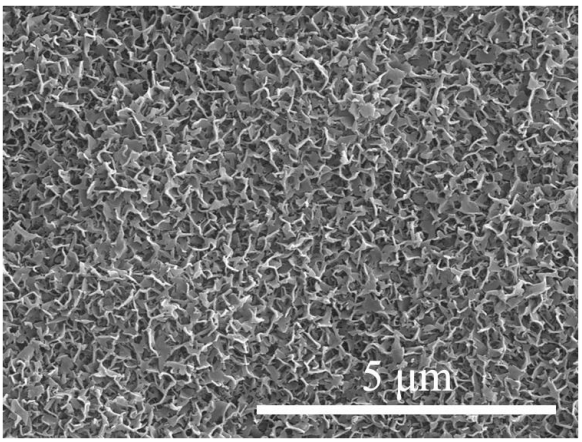

FIGURE 9 SEM picture of the surface of the PEEK with all treatment after the soak in SBF for 7 d.

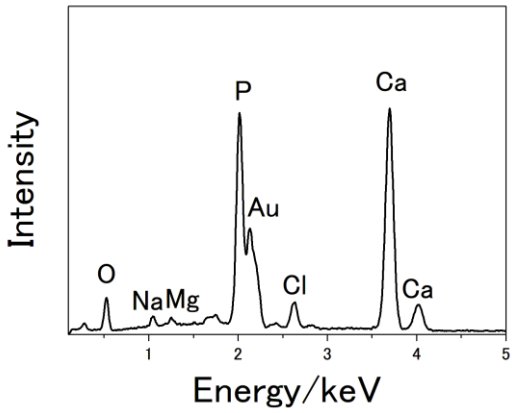

FIGURE 10 Result of EDX of the surface of the PEEK with all treatment after the soak in SBF for 7 d.

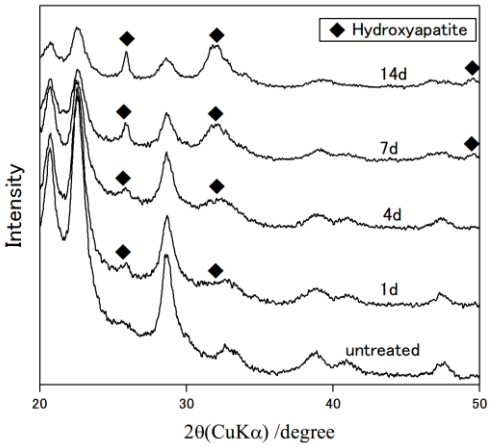

FIGURE 11 TF-XRD profiles of the surface of the PEEK with the AN treatment after the soak in SBF for various periods.

In FIGURE 11, the TF-XRD profiles of the surface of the PEEK with the AN treatment after the soak in SBF for various periods are shown. For the reference, that of the untreated PEEK is also shown. For 1 d, diffraction peaks of apatite were detected. As elapse of immersing time, the intensity of the diffraction peaks became increased and those of PEEK became decreased.

Taking into consideration the results of SEM, EDX and XRD, it is revealed that the bone-like apatite, which was induced by AN precipitated in the micropores, covered the whole surface of the PEEK within 1 d and the apatite layer grew thick as elapse of immersing time.

2) Effects of each treatment on apatite-forming ability and adhesive strength of the apatite layer.

The results of the SBF test and the adhesive strength test for each Group were summarized in TABLE 3. Results of SBF test were assessed by the appearance of the HAp formed on the PEEK surface. In the TABLE, "○" shows that whole surface was covered with HAp within 1 day, "Δ" shows that the surface was partially covered with HAp within 7 days and "×" shows that HAp was not observed on the surface even after 7 days. The adhesive strength test was conducted only if the whole surface of the specimen was covered with the HAp. In the TABLE, "N / A" means that the adhesive strength test was not performed because the entire, or a part of the surface was not covered with the HAp.

TABLE 3 Results of the SBF test and the adhesive strength test for each fabrication condition.

Group	Sulfuric acid	Glow-discharge	AN	HAp formation in SBF	Adhesive strength of HAp layer [MPa]
A	○	○	○	○	6.7 ± 1.5
B	×	○	○	○	2.1 ± 0.8
C	○	×	○	Δ	N / A
D	○	○	×	×	N / A
E	×	×	○	○	0.5 ± 0.4
F	○	×	×	×	N / A
G	×	○	×	×	N / A
H	×	×	×	×	N / A

Effect of AN treatment.

Groups A, B, C, E, with the AN treatment, HAp was formed on their surfaces. Groups D, F, G, H, without the AN treatment, HAp was not observed at all even after 7 days. Therefore, these results revealed that the AN treatment is essential to give the apatite-forming ability to PEEK.

Effect of sulfuric acid treatment.

As shown in FIGURE 3, cancellous micropores were formed by the sulfuric acid treatment. Between Group A and Group B, there was not clear difference in the appearance of the formed HAp layer in the SEM. However, clear differences in the adhesive strength test came out. Group A, with the sulfuric acid treatment, realized almost three times the adhesive strength as compared to Group B, without the sulfuric acid treatment. This is because, the formed HAp behaves as an anchor in the micropores. As a result, strong mechanical interlocking effect was performed.

In FIGURE 12, synthetic image of the SEM picture and the EDX mapping images, the SEM picture and the EDX mapping images of Ca and P on the fractured surface of the PEEK of Group A after the adhesive strength test are shown. In FIGURE 12 (a), area (A) is the place where the jig had been attached and area (B) is the place where the jig had not been attached before the tensile load was applied. In area (A), HAp layer was removed by the adhesive strength test and Ca and P were not detected. In area (B), in contrast, the HAp layer was remaining and Ca and P were strongly detected.

In FIGURE 13, synthetic image of the SEM picture and the EDX mapping images, the SEM picture and the EDX mapping images of Ca and P on the fractured surface of the jig of Group A after the adhesive strength test are shown. HAp was observed and Ca and P were detected on the whole surface.

From these results, it was confirmed that the fracture was occurred between the HAp layer and the PEEK substrate in the adhesive strength test.

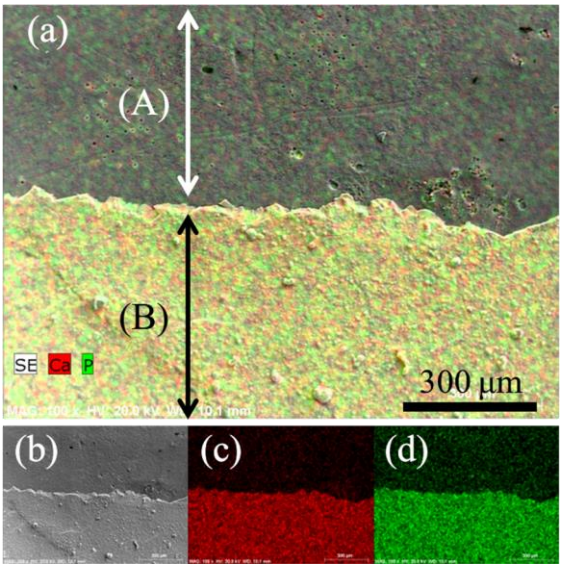

FIGURE 12 (a) Synthetic image of SEM picture and EDX mapping images ((A) Jig had been attached. (B) Jig had not been attached.), (b) SEM picture, (c) EDX mapping image of Ca and (d) EDX mapping image of P on the fractured surface of the PEEK of Group A after the adhesive strength test. Red points indicate Ca and green points indicate P.

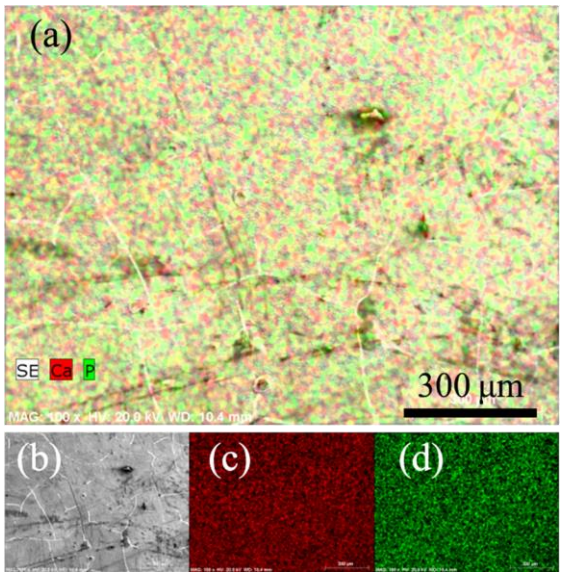

FIGURE 13 (a) Synthetic image of SEM picture and EDX mapping images, (b) SEM picture, (c) EDX mapping image of Ca and (d) EDX mapping image of P on the fractured surface of the jig of Group A after the adhesive strength test. Red points indicate Ca and green points indicate P.

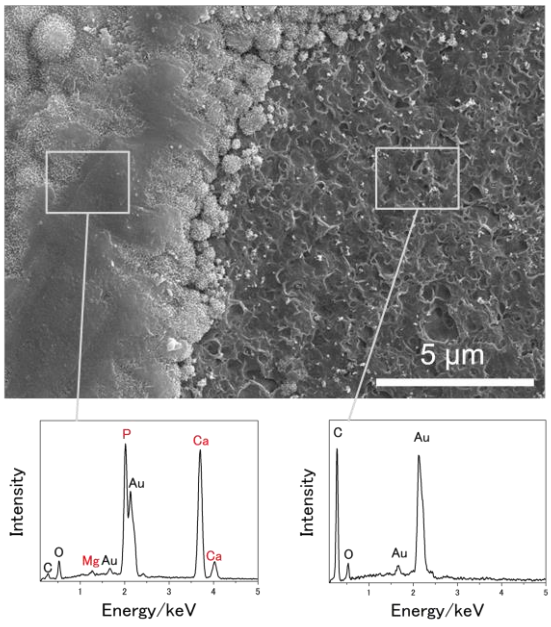

FIGURE 14 SEM picture and Result of EDX s of indicated areas of the surface of the PEEK of Group C after the soak in SBF for 7 d.

Effect of glow-discharge treatment.

Compared with Group A and Group C, Group A was covered whole surface with HAp within 1 day. On the other hand, Group C was partially covered with HAp even after the soak in SBF for 7 days as shown in FIGURE 14. It is suggested that, in order to form the HAp on the entire surfaces of the PEEK specimens which were formed micropores by the sulfuric acid treatment, the glow-discharge treatment is necessary. The adhesive strength of Group C was not measured because HAp formation was not sufficient.

Compared with Group B and Group E, the formed HAp layer of Group E, only with the AN treatment, was peeled easily. This means that the adhesive strength between HAp and PEEK substrate without the glow-discharge treatment was very low. It is suggested that the glow-discharge treatment also contributes to improve the adhesive strength between HAp layer and PEEK substrate. The AN sticks to PEEK substrate more firmly by applying the glow-discharge treatment.

CONCLUSION

Apatite layer was formed on the whole surface of the PEEK by the AN treatment. The specimen which was applied the glow-discharge treatment and the AN treatment was obtained around 2.1 MPa adhesive strength. All the treatments, the sulfuric acid treatment, the glow-discharge treatment and the AN treatment, was applied, adhesive strength rose around 6.7 MPa. The specimen which was applied sulfuric acid treatment and AN treatment ,without glow-discharge treatment, was not covered whole surface.

As a result, in order to give high bioactivity and sufficient adhesive strength, to apply all the treatments is preferable.

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ACKNOWLEDGMENTS

This work was partly supported by Kyoto University Research and Development Program “Ishizue”.