

Impartation of Hydroxyapatite Formation Ability to Ultra-high Molecular Weight Polyethylene by Deposition of Apatite Nuclei

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Abstract: We aimed to impart hydroxyapatite formation ability to ultra-high molecular weight polyethylene (UHMWPE) by deposition of apatite nuclei (ApN) by the following two methods. First method was electrophoretic deposition (EPD). A porous UHMWPE was placed between electrodes in the ApN-dispersed ethanol and constant voltage was applied. By this treatment, the ApN were migrated from anode side surface to the cathode one through the pores by electric field in the pores of the UHMWPE and deposited inside the pores. Second method was direct precipitation (DP) of the ApN. A porous UHMWPE was soaked in a simulated body fluid (1.0SBF) with higher pH than the physiological one and subsequently its temperature was raised. By this treatment, the ApN were precipitated in the pores of the UHMWPE directly in the reaction solution. For both methods, the ApN-deposited UHMWPE showed HAp formation ability not only top surface but also inside the pores near the surface of the porous UHMWPE in 1.0SBF. Although adhesion strength of thus-formed HAp layer was higher in the case of the EPD in comparison with the DP, oxygen plasma treatment before the DP enabled to achieve similar level of the HAp layer adhesion to the EPD.

1. Introduction

In early 1970's, Hench et al. invented the glass materials named Bioglass[®] as world's first materials with spontaneous bone-bonding ability [1]. Since this Hench's work, various types of bioactive ceramics which bonded to living bone spontaneously without use of cements such as sintered hydroxyapatite (HAp) [2], glass ceramic A/W [3], and so on were developed. It was found that these materials formed HAp layer on their surfaces spontaneously and bonded to living bone through this HAp layer in living body [4,5]. In addition, Kokubo et al. found that such HAp formation reaction on the surface of the bioactive ceramics could be well reproduced in a simulated body fluid, which we call it '1.0SBF' hereafter, whose ion concentration is nearly equal to those of human blood plasma [6-8]. However, all the above bioactive materials are ceramics. Hence, the clinical problems derived from their mechanical brittleness have been potentially remained. In order to overcome these problems, development of bioactive metals has been actively studied among many investigators. However, metals have extremely higher Young's modulus in comparison with living bone. Hence, problems of stress shielding have been clinically pointed out [9]. From these findings, it is thought that bioactive organic polymers with both shock resistance and low Young's modulus is effective materials design for clinical use. Among them, poly-L-lactic acid (PLLA)-HAp composite has been already in clinical use as pins and screws for bone fixation [10]. Although the PLLA-HAp composite showed 280 MPa in bending strength, however, it has been reported that its bending strength decreased to 200 MPa after 25 weeks in the phosphate-buffered saline because of its biodegradability. Hence, such-types of composites, that is, bioactive biodegradable polymers, potentially possesses difficulties respect to control of balance between many biological factors such as bioactivity, biodegradation, speed

of surrounding new bone formation, and changes in its mechanical toughness.

Ultra-high molecular weight polyethylene (UHMWPE) is one of the most attractive polymeric biomedical materials with low elastic modulus and high mechanical performance. Moreover, UHMWPE is chemically stable in living body, that is, it does not release harmful metallic ions and its safety to living body is excellent in comparison with metals. In these days, UHMWPE has been widely in clinical use as sliding parts of hip joints and knee joints because of not only the above material properties but also its excellent abrasion resistance respect to ceramics and metals [11]. However, UHMWPE is completely bioinert and cannot bond to living bone directly and spontaneously. If the UHMWPE acquire bioactivity, it is predicted that a range of its clinical application will be largely extended as artificial bone with not only good mechanical performance but also bone-bonding ability.

Thus far, several types of bioactivity treatment processes for polyethylene (PE) have been proposed by some investigators. Among them, physical mixing of PE particles and bioactive ceramics particles are one of the main fabrication techniques to impart bioactivity to PE. For example, HDPE-HAp composite (HAPEXTM) [12], HDPE-Bioglass[®] composite [13], HDPE-glass ceramic A/W composite [14] and HDPE-TiO₂ composite [15] has been proposed as representative candidates. Among them, HAPEXTM has been in clinical use as inner middle ear implant. However, such fabrication process requires excess amounts of ceramic particles for achievement of enough bioactivity because bioactivity of the composite was expressed by only the ceramic particles exposed on its surface. As another types of bioactivity impartation technique, bioactive ceramic coating on organic polymers has been also proposed such as biomimetic solution method [16]. In such ceramic coating techniques, however, it should be potentially paid attention about an interfacial delamination between the

ceramic film and bone tissue when it is implanted in living body for a long time.

In our previous study, we have reported the preparation methodology of bioactive materials by incorporation of apatite nuclei (ApN) to completely bioinert or low bioactive materials [17]. When the substrates with fine pores were soaked in 1.0SBF with higher pH in comparison with physiological one and subsequently its temperature was raised, nucleation of calcium phosphate was promoted, and calcium phosphate fine particles, which we refer as 'apatite nuclei' (ApN), were precipitated in the pores. Thus-treated substrates showed high HAp formation ability regardless of whether the substrate was bioactive or completely bioinert. In fact, we successfully imparted high HAp formation ability to Ti alloys [18], stainless steels (SUS) [19], Co-Cr alloy [20], and polyetheretherketone (PEEK) [21,22] by the above surface modification techniques although these substrates were completely bioinert. In the above case of PEEK, good bone-bonding ability introduced by the ApN was demonstrated in animal test [23].

As one of the other types of fabrication techniques for bioactive materials, in addition, we have studied electrophoretic deposition process (EPD), too. Generally, EPD is attractive method to form ceramic thin films on conductive substrates such as metals. In a biomaterials research field, EPD of HAp particles on metallic implants has been proposed by many investigators to improve bone-bonding ability of the metals such as pure Ti [24], Ti alloys [25] and SUS [26]. Although there were examples of EPD of HAp particles to alumina substrate by coating of conductive carbon on the substrate before the EPD [27], however, EPD was not applicable to insulating substrates such as polymers and ceramics basically. Recently, on the other hand, we have proposed a new type of EPD process respect to insulating substrates. When a porous insulating substrate was placed between electrodes and constant voltage was applied, dispersed ceramic particles were migrated inside the pores by electrical field passing through the pores and deposited inside the porous insulating substrates. Utilizing this knowledge, we electrophoretically deposited bioactive wollastonite (CaSiO_3) particles inside pores of porous alumina and porous UHMWPE [28]. For these materials, HAp formation was induced by the wollastonite inside pores and HAp formation ability was demonstrated in 1.0SBF regardless of the kinds of the substrates. Moreover, thus-formed HAp layer showed high adhesion strength because of mechanical interlocking effect between the HAp in the pores and the porous substrates. Expanding this EPD methodology, in addition, we successfully obtained HAp micropatterns on the porous PTFE film by combination of the EPD of wollastonite and the soak in 1.0SBF [29].

Utilizing our previous knowledge to bioactive materials design for UHMWPE, we aimed to deposit ApN inside the pores of the porous UHMWPE and combine high HAp formation ability of ApN and mechanical performance of UHMWPE in this study. In order to achieve this materials design, we tried two methods for bioactive UHMWPE; EPD of ApN and direct precipitation (DP) of ApN. In the EPD, porous UHMWPE was placed between electrodes in ApN-dispersed ethanol and voltage was applied. By this treatment, we aimed to deposit ApN inside the pores of the UHMWPE electrophoretically. In the DP, porous UHMWPE was soaked

in 1.0SBF adjusted at higher pH than the conventional 1.0SBF and temperature was raised. By this treatment, we aimed to precipitate ApN inside the pores directly in the reaction solution. HAp formation ability was investigated by 1.0SBF soaking test. Then adhesion strength of HAp layer formed in the 1.0SBF were evaluated. In the DP, oxygen plasma treatment as pre-treatment was carried out before the DP and its effect to the adhesion of the HAp layer was also investigated.

2. Materials and Methods

2.1. Materials

Commercially porous UHMWPE with 30% in porosity and 30 μm in average pore size (Nitto Denko, Osaka, Japan) were used as substrates. The substrates were washed in acetone in an ultrasonic cleaner and air-dried.

2.2. Electrophoretic Deposition (EPD) of ApN

Aqueous solution with twice ion concentration in comparison with 1.0SBF shown in Table 1, which we name as '2.0SBF' hereafter, was prepared by dissolving twice amounts of chemical reagents certified in ISO specification 23317 [8] in pure water. The 2.0SBF was adjusted at pH=7.00, 36.5 $^{\circ}\text{C}$ by using 1 M HCl and tris-hydroxymethyl aminomethane ($(\text{CH}_2\text{OH})_3\text{CNH}_2$).

Table 1 Ion concentration of 1.0SBF and 2.0SBF

Ion	1.0SBF	2.0SBF
Na^+	142.0	284.0
K^+	5.0	10.0
Mg^{2+}	1.5	3.0
Ca^{2+}	2.5	5.0
Cl^-	147.8	295.6
HCO_3^-	4.2	8.4
HPO_4^{2-}	1.0	2.0
SO_4^{2-}	0.5	1.0

The 2.0SBF was adjusted at pH=8.20, 36.5 $^{\circ}\text{C}$ by dissolving $(\text{CH}_2\text{OH})_3\text{CNH}_2$ and kept at 36.5 $^{\circ}\text{C}$ for 4 days. By this treatment, ApN were precipitated in the 2.0SBF. Thus-obtained ApN were filtered by suction through a membrane filter, washed with pure water, and air-dried. The ApN were analysed by powder X-ray diffraction instrumentation (XRD; RAD-C, Rigaku, Tokyo, Japan), scanning electron microscope (SEM; SU6600, Hitachi High-Technologies, Osaka, Japan), energy dispersive X-ray analyser (EDX; XFlash[®]5010, Bruker, Germany) and Fourier transform infrared spectrometer (FT-IR; FT-720, Horiba, Kyoto, Japan). The XRD measurements were carried out using Cu-K α radiation at 40 kV, 40 mA of tube voltage and current. The FT-IR measurements were carried out by attenuated total reflection (ATR) method with ZnSe prism.

Fig. 1 shows the schematic illustration of an electrophoretic cell used in this study. The ApN were ultrasonically dispersed in ethanol in 2.5 $\text{g}\cdot\text{dm}^{-3}$ of

concentration. The substrate with $20 \times 20 \times 2 \text{ mm}^3$ in size was placed between gold electrodes (30 mm in interelectrode distance) in the ApN-dispersed ethanol and constant voltage of 100 V, 200 V or 400 V was applied for 30 minutes. By this treatment, EPD of the ApN respect to porous UHMWPE was carried out. After the EPD process, the substrate was washed with ethanol and air-dried. The surfaces of the substrates were analysed by thin film XRD (Rint 2500, Rigaku, Tokyo, Japan) and SEM (ESEM-2700, Nikon, Osaka, Japan). The thin film XRD measurements were carried out using Cu-K α radiation at 50 kV, 300 mA of tube voltage and current.

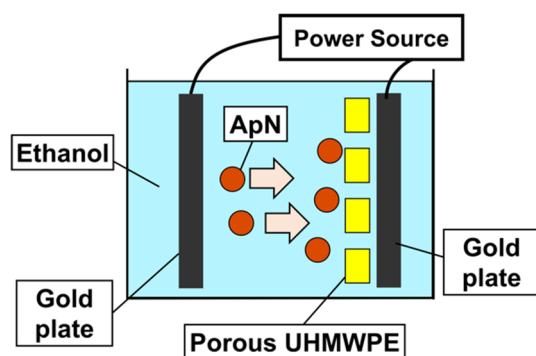


Fig. 1. Schematic illustration of an electrophoretic cell used in this study

2.3. Direct Precipitation (DP) of ApN

The 1.0SBF was prepared by the method certified in ISO specification 23317 [8] and its pH value was adjusted at pH=7.40, 36.5 °C. The pH of thus obtained 1.0SBF was increased to 8.20 at 36.5 °C by dissolving $(\text{CH}_2\text{OH})_3\text{CNH}_2$. This solution is denoted as ‘alkalinized 1.0SBF’, hereafter. The surface of the porous UHMWPE with $15 \times 10 \times 2 \text{ mm}^3$ in size was treated with glow-discharge in oxygen gas atmosphere at $1 \text{ W} \cdot \text{cm}^{-2}$ of plasma density for 30 seconds by using a plasma system (BP-1, Samco, Kyoto, Japan). Then, both the oxygen plasma-treated or the untreated substrates were soaked in the alkalinized 1.0SBF and subsequently the 1.0SBF was kept in an incubator held at 60 °C for 1 day. By this treatment, we aimed to precipitate ApN in the pores of the substrates. Thus-treated substrates were washed with pure water and air-dried. The surfaces of the substrates were analysed by thin film XRD, SEM, and EDX (DX-4, EDAX International, USA).

2.4. Evaluation of HAp Formation Ability

HAp formation ability of each substrate was evaluated by the method certified in ISO specification 23317 [8]. Each substrate was soaked in the 1.0SBF (pH=7.40, 36.5 °C) for 14 days. After the soak in the 1.0SBF, the substrates were washed with pure water and air-dried. The surfaces of the substrates were analysed by thin film XRD, SEM and EDX to check HAp formation on the surface of the substrates. In order to prepare the samples for cross-sectional observation, the substrates were cut with a clean and sharp cutter knife. Thus-obtained cross-sections of the substrates were also analysed by SEM observation and EDX line-scanning.

2.5. Tensile Test

Adhesion strength of the HAp layer formed on the substrates by the soak in the 1.0SBF was measured by a modified ASTM International specification C-633 [30-33]. A couple of stainless jigs were fixed to the surface of each substrate using epoxy-type glue (Araldite®, NICHIBAN, Tokyo, Japan). Tensile load was applied by $1 \text{ mm} \cdot \text{min}^{-1}$ of crosshead speed using universal testing machine (AGS-H Autograph, Shimadzu, Kyoto, Japan) until fracture occurred and maximum stress was measured.

3. Results and Discussion

3.1. EPD of ApN

Fig. 2 shows the results of FT-IR, SEM, EDX and powder XRD of the ApN obtained by keeping the 2.0SBF (pH=8.2, 36.5 °C) at 36.5 °C for 4 days. In the FT-IR, P=O stretching band correspond to phosphate groups were strongly detected around 1000 cm^{-1} . This means that the precipitates were phosphate compounds. In the SEM, precipitates with approximately 200 nm in diameter were observed. In the EDX, peaks of P and Ca were clearly observed. This means that the precipitated ApN were certainly consisted of calcium phosphate. In the EDX, in addition, a peak of Mg was also observed although its intensity was smaller than those of P and Ca. From this result, it is considered that Mg ions contained in 2.0SBF were partly incorporated in the obtained ApN. In the XRD, on the other hand, broad diffraction patterns characteristic to amorphous calcium phosphate (ACP) were observed instead of the crystalline HAp. Such shape of the XRD pattern was quite similar to ACP obtained by sol-gel method reported by Ohta et al. [34]. Taking into consideration the results of FT-IR, SEM, EDX and XRD, hence, it is considered that the obtained ApN were spherical particles mainly consisted of ACP with around 200 nm in diameter.

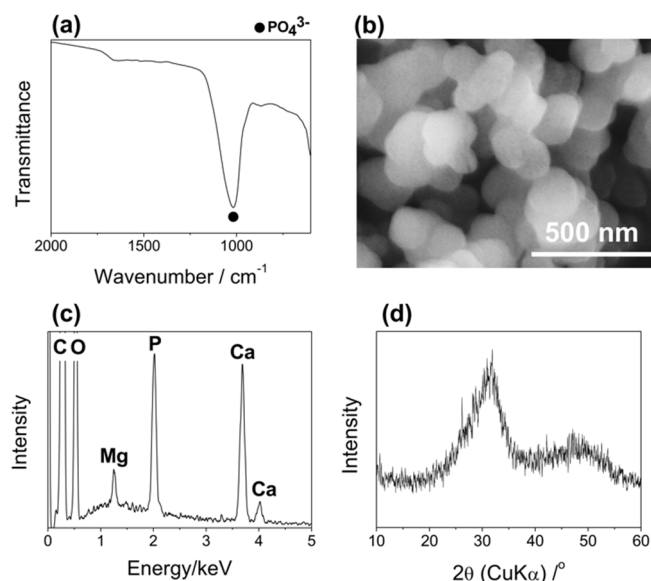


Fig. 2. Results of FT-IR, SEM, EDX and powder XRD of ApN obtained by keeping the 2.0SBF (pH=8.20, 36.5 °C) at 36.5 °C for 4 days

By applying the constant voltage to the electrodes placed in the ApN-dispersed ethanol, the ApN were migrated from anode to cathode. Umegaki et al. reported that HAp particles were migrated from anode to cathode in alcohol [35]. They also proposed that HAp particles were positively charged in alcohol because HAp crystals attached OH groups of alcohol molecules and alkyl groups or hydrogen atoms of the attached alcohol molecules were exposed to the dispersed medium. Although crystallinity of the ApN was largely different from HAp, it is speculated that the ApN was also positively charged in ethanol by similar mechanism.

Fig. 3 shows the SEM images of the surface of the untreated substrate and the anode side surfaces and the cathode ones of the substrates after the EPD at 100 V, 200 V and 400 V of applied voltage. For 100 V, ApN were deposited in the pores on both anode side surface and cathode one. In this experimental system, the ApN should be migrated by the electrical field through the pores. Hence, it was predicted that the ApN were migrated inside the pores at a suitable speed and deposited not only near the surface but also inside the pores where could not be observed by this SEM observation. This point is discussed in 3.3, cross-sectional observation. For 200 V, it was clarified that a huge number of ApN were deposited on the anode side not only in the pores but also the top surface of the substrate. On the cathode side surface, deposition of ApN were slightly observed in the pores of the substrate and it can be seen that numbers of deposited ApN were less than the case of 100 V. Because of higher applied voltage in comparison with 100 V, it is suggested that many ApN clogged up the pores near the anode side surface in early stage of the EPD and numbers of ApN migrated to the cathode side were less than the case of 100 V. For 400 V, ApN were not observed on the anode side surface including in the pores. On the cathode side surface, in contrast, a huge number of ApN were deposited not only in the pores but also the top surface of the substrate similar to the anode side surface in the case of 200 V. It is considered that huge numbers of ApN were passing through the pores almost completely because of the highest applied voltage and the ApN were not remained on the anode side surface. From these findings, it was predicted that 100 V was a suitable applied voltage condition in this experimental system.

Fig. 4 shows the thin film XRD patterns of the anode side surfaces and the cathode ones of the substrates after the EPD at each applied voltage and then soaked in 1.0SBF for 14 days. For the reference, pattern of untreated substrate is also shown. For the untreated substrate, diffraction peaks of PE including those around 30° and 36° corresponded to 210 and 020 in reflection indices were observed. For the cathode side surfaces, all the applied voltage condition showed diffraction peaks of HAp around 26° and 32° . On the anode side surface, the substrate for 400 V did not show such HAp peaks although the substrates for both 100 V and 200 V showed such HAp peaks similar to each cathode side surface. This means that HAp was formed on both surfaces in the 1.0SBF by both 100 V and 200 V condition, and the HAp formation was achieved only on the cathode side surface by the 400 V condition. This result corresponded to the deposition of ApN shown in Fig. 3 except the cathode side at 200 V.

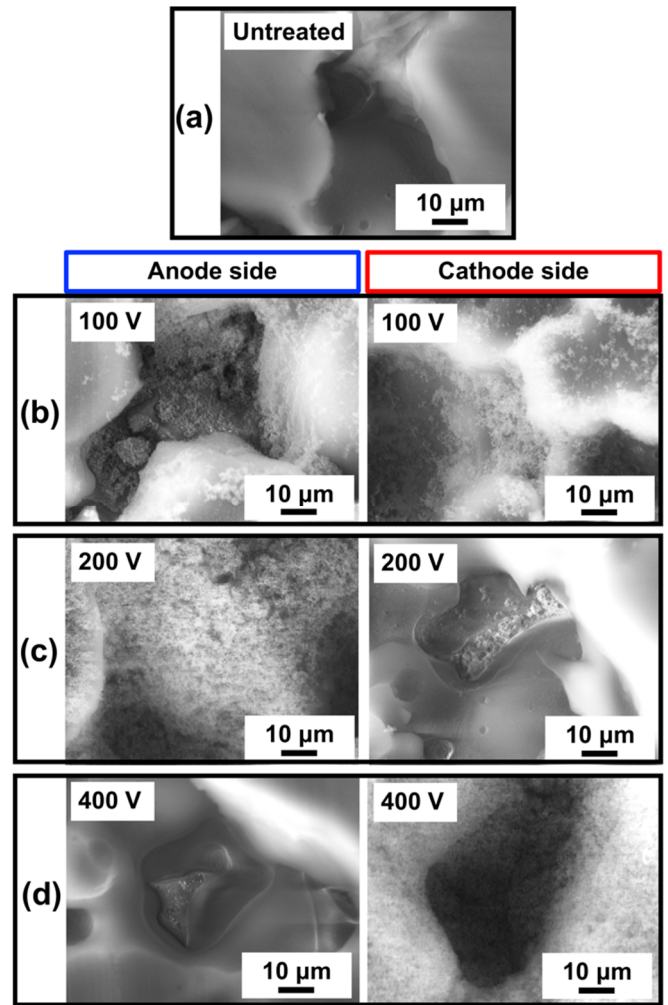


Fig. 3. SEM images of (a) surface of the untreated substrate and anode and cathode side surfaces of the substrates after EPD at (b) 100 V, (c) 200 V and (d) 400 V in applied voltage

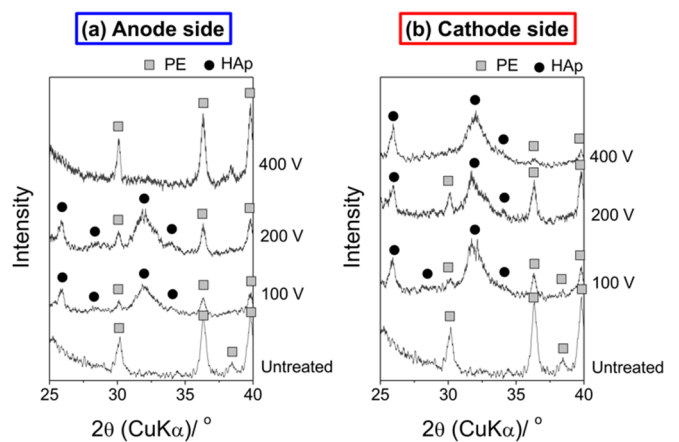


Fig. 4. Thin film XRD patterns of (a) anode side surfaces and (b) cathode side surfaces of substrates after EPD at each applied voltage and then soaked in 1.0SBF for 14 days. For the reference, pattern of untreated substrate is also shown.

Fig. 5 shows the SEM images of the anode side surfaces and the cathode ones of the substrates treated with the EPD at each applied voltage and then soaked in the 1.0SBF for 14 days. For 100 V, both surfaces were completely covered with hemispheric precipitates characteristic to HAp formed in the 1.0SBF. In addition, such HAp formation was observed not only the top surface but also inside the pores, too. For 200 V, anode side surfaces hemispheric HAp was formed both on the entire top surface but also inside the pores similar to the both surfaces for 100 V. On the cathode side surface, however, HAp formation was observed only in the pores. The top surface was not covered with the HAp precipitates and kept smooth morphology. Hence, it is indicated that the HAp formation ability on the cathode side surface was not enough. For 400 V, HAp formation was hardly observed except a part of inside the pores on the anode side surface. On the cathode side surface, on the other hand, HAp fully covered the whole surface and was observed also in the pores similar to the both surfaces for 100 V and the anode side surface for 200 V. These results almost completely corresponded to the deposition of ApN shown in Fig. 3. These results indicate that 100 V was the most suitable condition in this EPD process to impart HAp formation ability to the porous UHMWPE substrate because the HAp formation was observed not only the top surface but also in the pores on the both surfaces. This means that the ApN deposited in the pores induced HAp formation and the HAp grew to the top surface of the substrate in the 1.0SBF similar to the case of the wollastonite-deposited UHMWPE in our previous study [28].

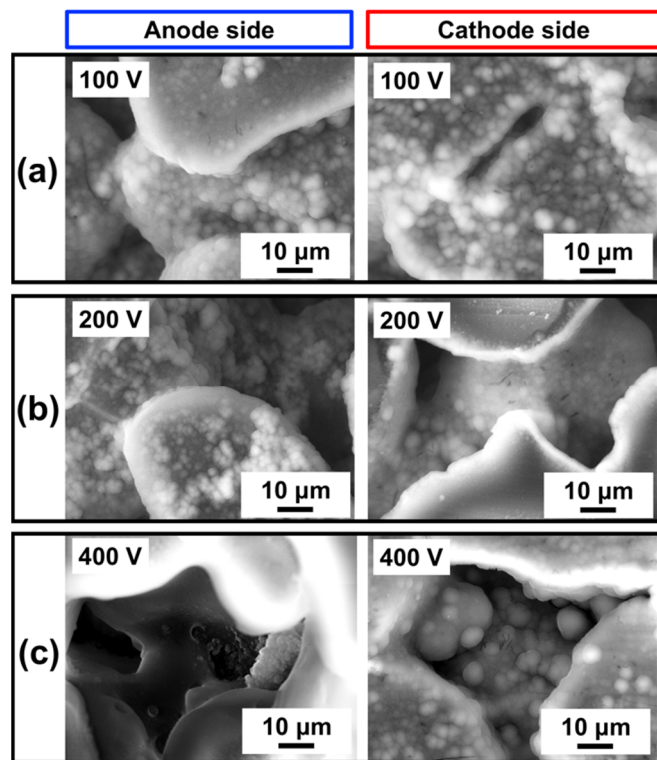


Fig. 5. SEM images of anode and cathode side surfaces of substrates treated with EPD at (a) 100 V, (b) 200 V and (c) 400 V and then soaked in 1.0SBF for 14 days

3.2. DP of ApN

Fig. 6 shows the SEM photographs and EDX spectra of the surfaces of the DP-treated substrates with or without oxygen plasma treatment. After the DP process, a lot of fine precipitates in submicron size were observed both on the top surface and inside the pores in both conditions. In the EDX, peaks of P and Ca were observed on each substrate. This result shows that the ApN were precipitated and kept near the surface of each substrate regardless of presence or absence of the oxygen plasma treatment.

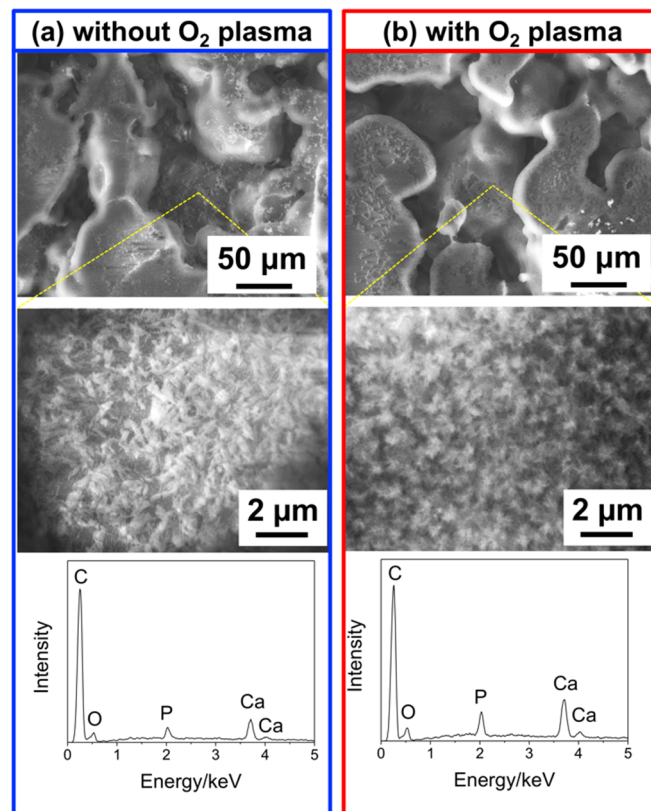


Fig. 6. SEM images and EDX spectra of the surfaces of DP-treated substrates (a) with or (b) without oxygen plasma treatment

Fig. 7 shows the thin film XRD patterns of the DP-treated substrates with or without oxygen treatment and subsequently soaked in 1.0SBF for 14 days. Just after the DP treatment, intensity of diffraction peaks of HAp was extremely small. After the soak in 1.0SBF, in contrast, diffraction peaks of HAp were clearly observed for both conditions. This means that the precipitated ApN induced HAp formation in 1.0SBF and HAp was formed on the surface of the substrate regardless of presence or absence of the oxygen plasma treatment.

Fig. 8 shows the SEM images and the EDX spectra of the surfaces of the DP-treated substrates with or without oxygen plasma treatment after the soak in 1.0SBF for 14 days. For both condition, needle-like crystallites characteristic to HAp formed in the 1.0SBF were observed both on the top

surface and inside the pores. This means that the precipitated ApN induced HAp formation in 1.0SBF and the formed ApN grew and covered the whole surface of the substrates.

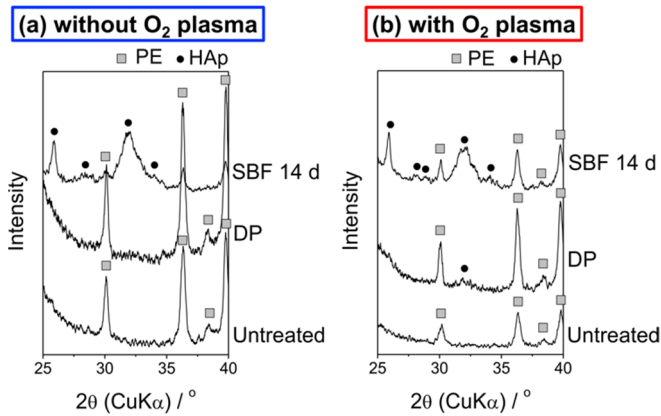


Fig. 7. Thin film XRD patterns of DP-treated substrates (a) with or (b) without oxygen treatment and subsequently soaked in 1.0SBF for 14 days. For the reference, pattern of untreated substrate is also shown.

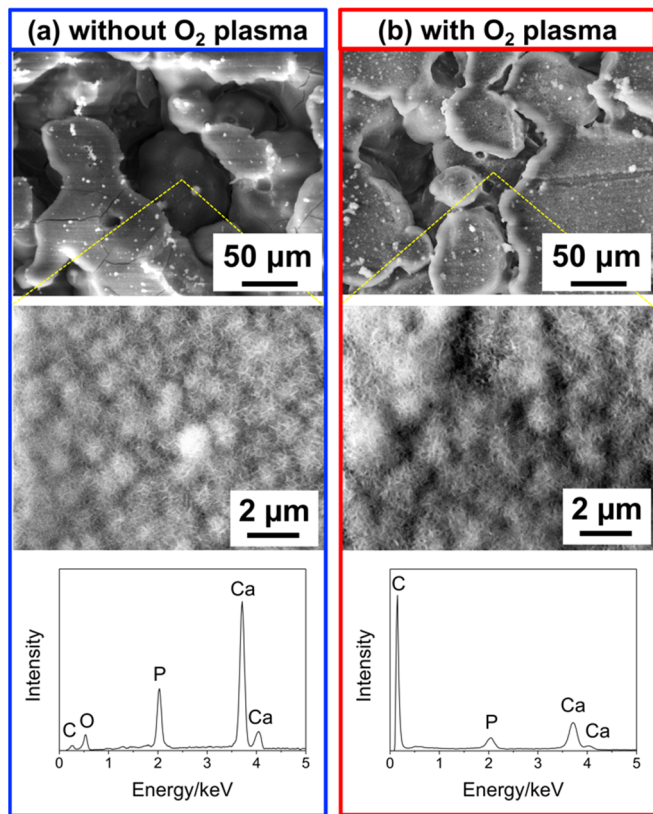


Fig. 8. SEM images and EDX spectra of the surfaces of DP-treated substrates (a) with or (b) without oxygen plasma treatment after the soak in 1.0SBF for 14 days

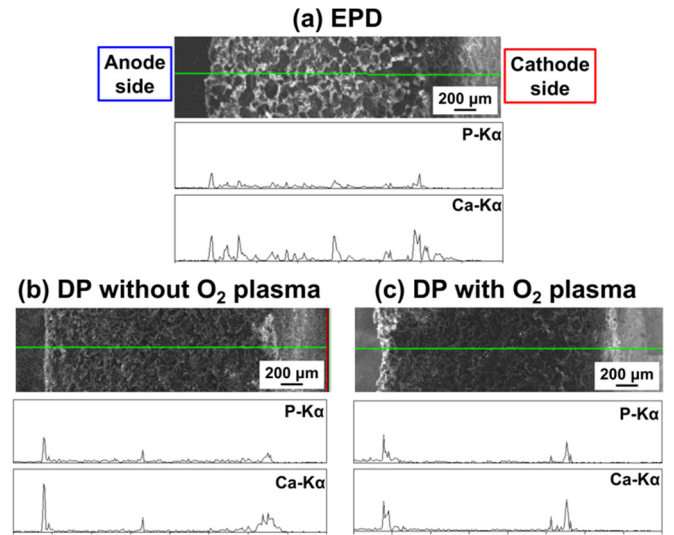


Fig. 9. SEM images and EDX line-scanning profiles of cross-sections of substrates fabricated by (a) EPD, (b) DP without oxygen plasma treatment and (c) DP with oxygen plasma treatment after the soak in 1.0SBF for 14 days

3.3 Cross-sectional Observation after the Soak in 1.0SBF

Fig. 9 shows the SEM images and the EDX line scanning profiles of the cross-sections of each condition after the soak in SBF for 14 days. For EPD, corresponded peaks of P and Ca were detected not only near the both surface but also wide area of inside the substrates. This means that HAp formation was occurred in the pores located both near the surface and inside the substrate by the deposited ApN. It is considered that this is because the ApN were deposited not only near the surface but also inside the porous UHMWPE at the applied constant voltage of 100 V in the EPD process. For DP, corresponded peaks of P and Ca were detected almost only near the surfaces. This means that HAp formation was occurred in the pores located only near the surfaces by the precipitated ApN. It is considered that this is because that the ApN were precipitated in the pores only near the surface of the substrate in the DP process. It was reported that the previously proposed other types of bioactive PE composite such as HApEX™ [13], HDPE-Bioglass® composite [14], HDPE-glass ceramic A/W composite [15] and HDPE-TiO₂ composite [16] also showed HAp formation ability in the physiological 1.0SBF. In a recent decade, in addition, Xu et al. developed bioactive HDPE-HAp-bioactive glass composite [36] and Balakrishnan et al. developed bioactive maleated HDPE compatibilized HDPE-HAp composite [37]. They reported that these HDPE composite showed HAp formation ability within 21 days and 7 days in 1.0SBF, respectively. Jaberzadeh et al. developed bioactive UHMWPE-forsterite composite [38] and reported that precipitation of tiny particles of calcium phosphate were observed on this type of composite after a soak in 1.0SBF for 28 days. As a different type of methodology, Van Vrekhem et al. operated surface modification of UHMWPE with atmospheric pressure plasma jet [39] and reported that this UHMWPE showed partial HAp formation by a soak in

2.0SBF for 14 days after an alternative dipping treatment with Ca and phosphate solutions. It is considered that one of the advantages of our present methodology is a potential to interconnection of living bone inside the pores of the UHMWPE when it is implanted in bone defects as well as good HAp formation ability. From this viewpoint, it is considered that the EPD process is more expected methodology because HAp formation ability was imparted inside the pores from near the surface to inner area of the materials.

3.3. Adhesion Strength of the Formed HAp Layer

Fig. 10 shows the average adhesion strength of the HAp layer on the surface of the substrates formed by the soak in 1.0SBF for 14 days. The average adhesion strength was 6.1 ± 1.6 MPa for anode side surface in EPD, 6.5 ± 1.6 MPa for cathode one, 4.6 ± 0.8 MPa for without oxygen plasma in DP, and 6.9 ± 1.4 MPa for with oxygen plasma in DP. The substrates in EPD and with oxygen plasma in DP showed almost similar values. There was not large difference between the values of the anode side surface and the cathode one in the EPD. The substrate without oxygen plasma treatment showed the lowest average value among these four conditions. It is considered that the EPD enabled the achievement of higher adhesion strength than the DP without oxygen plasma treatment because of the difference of mechanical interlocking effect derived from the growth of the HAp inside the pores. In this tensile test, it is attracted attention that oxygen plasma treatment in the DP achieved comparative level of the adhesion of the formed HAp in comparison with the case of EPD nevertheless HAp was formed only in the pores near the surface of the substrate. It has been reported that oxygen plasma treatment introduced highly polar groups such as carbonyl, ester, hydroxyl and carboxyl ones on various types of organic polymers and such formation of functional groups contributed to improvement of adhesion of the HAp layer formed in the aqueous solution [17]. In the above biomimetic coating of the HAp layer on PE substrate, in fact, it was reported that the adhesion strength of HAp layer improved from 1.9 MPa of average value to 7.5 MPa of maximum value by conducting the oxygen plasma treatment. It is considered that the chemical bonding between the ApN and the UHMWPE or the HAp formed in the 1.0SBF and the UHMWPE might be introduced by the oxygen plasma treatment and this effect improved adhesion strength of the formed HAp layer similar level to the stronger mechanical interlocking effect introduced in the EPD process. It was reported that average adhesion strength of the HAp layer formed on HApEXTM was 2.8 MPa and that of HDPE-glass ceramics A-W composite was approximately 3-4 MPa in most fabrication conditions [33]. Our methods achieved generally higher adhesion strength than those materials. It is considered that the most important reason was stronger mechanical interlocking effect because the HAp could grow inside the pores regardless presence or absence of the oxygen plasma treatment. In addition, it is noteworthy that the flexibility of the porous UHMWPE was maintained through the experiment. This point is also one of the characteristics of this methodology.

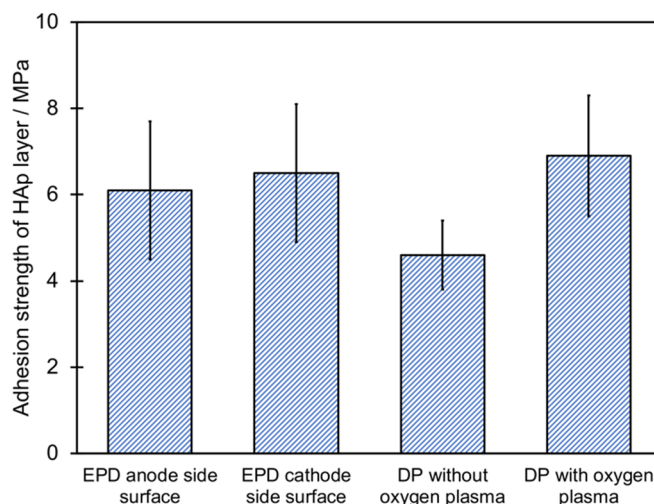


Fig. 10. Average adhesion strength of the HAp layer formed by the soak in 1.0SBF for 14 days on each condition of substrate

4. Conclusion

In order to provide HAp formation ability to porous UHMWPE, ApN were deposited in the pores of the porous UHMWPE. By using EPD of ApN, HAp formation ability was successfully given not only near the surface but also inside the porous structure of the UHMWPE. DP of the ApN was also effective to give HAp formation ability to near the surface of the porous UHMWPE. In the DP, oxygen plasma treatment enabled to enhance adhesion strength of the formed HAp layer and its value was almost similar level in the case of EPD. This methodology will be expected as novel useful processes to give high bioactivity to bioinert UHMWPE with attractive mechanical performance as bone substitutes.

5. References

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