Rapid formation of hydroxyapatite layer on polyetheretherketone by vacuum ultraviolet irradiation and microwave heating techniques

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Rapid formation of hydroxyapatite [Ca10(PO4)6(OH)2; HAp] layer on the polyetheretherketone (PEEK) substrate was examined by the combined techniques of vacuum ultraviolet (VUV) irradiation and microwave heating. The surface properties of PEEK substrate were modified by the formation of carboxyl group due to the VUV irradiation at room temperature in air, whereas the formation of HAp layer was encouraged by the microwave heating of surface-modified PEEK substrate in the HAp-dissolved solution. The optimization of the fabrication conditions was conducted by checking (i) the distance of VUV lamp to PEEK substrate (1−12 mm) and VUV irradiation time (0−120 min) for the surface modification of PEEK substrate, and (ii) the microwave heating temperatures (100 and 140°C) for the rapid formation of HAp layer on the PEEK substrate. When the PEEK substrate was surface-modified by the VUV irradiation for 120 min with the distance of VUV lamp to PEEK substrate kept being 1 mm, and then was microwave-heated in the HAp-dissolved solution at 140°C for 10 min, the thickness of the HAp layer on the PEEK substrate attained approximately 10 μm.

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1. Introduction

A polyetheretherketone (PEEK), i.e., (O−C6H4−O−C6H4−CO−C6H4)n, is a partially crystalline thermoplastic resin.1) The benzene rings are interconnected by the ketone (C=O) and ether (−O−) functional groups, and the three-dimensional delocalization of orbital electrons, due to the resonance effect, stabilizes the molecular structure.1) Owing to the stabilization of such molecular structure, PEEK possesses the excellent biocompatibility but poor chemical bonding with natural bones.1,2) The tensile strength and Young’s modulus of PEEK substrate are 99.2 MPa and 4.6 GPa,3) respectively, and are close to those of human cortical bone, i.e., approximately 110 MPa4) and 20.7 GPa,5) respectively. Thus the PEEK substrate is a promising material for medical devices, e.g., load-bearing materials or spinal implants.

In order to improve the bio-inertness and enhance the bonding to bone, many researchers investigated the coating of biocompatible inorganic materials (typically, hydroxyapatite [Ca10(PO4)6(OH)2; HAp] on the PEEK substrate.1,5,6) and pointed out the advanced techniques being needed in order to strongly bond the HAp layer to the PEEK substrate.7) Such problem may be based upon the restriction to conduct the post heat treatment, due to the glass transition temperature (Tg) of PEEK being as low as 143°C.1) Taking such restriction of post heat treatment temperature into account, the present authors7) examined the formation conditions of HAp layer on the PEEK substrate at around Tg, i.e., (i) the formation of siliceous film (for assisting the formation of HAp) on the PEEK substrate through the vacuum ultraviolet (VUV) irradiation at the silicon-containing organic precursor, and (ii) the formation of HAp layer through the microwave heating of siliceous-film-coated PEEK substrate in the HAp-dissolved solution.8)9) The advantage of VUV irradiation is to the provision of high photon energy for breaking the single/double bonds of organic compounds with no heat treatment.10)11) On the other hand, the advantage of microwave heating is the provision of high energy-efficient internal energy by the direct coupling of microwave energy with dipoles and/or ions in the reaction system.12) The combined techniques of VUV irradiation with microwave heating, therefore, make the rapid formation of HAp layer on the PEEK substrate possible. The surface modification of polymer substrate through the VUV light is generally conducted in vacuum or nitrogen/argon atmosphere, because the VUV light intensity is significantly attenuated in oxygen atmosphere.13) On the other hand, VUV irradiation in oxygen atmosphere generates the atomic oxygen/ozone, and makes possible to form hydrophilic functional group, typically carboxyl group (COOH),11) on the PEEK substrate. The formation of carboxyl group on the
PEEK substrate may be beneficial not only to change the properties of PEEK from hydrophobic to hydrophilic natures, but also to encourage the formation of HAp in the human bodies. The present paper describes (i) the formation conditions of carboxyl group on the PEEK substrate through the VUV irradiation in air, and (ii) the microwave-heating conditions in HAp-dissolved solution.

2. Experimental procedure

2.1 Preparation of calcium phosphate layer on PEEK substrate

The commercial PEEK substrate (Ketron®1000PEEK, Quadrant Polypenco Japan, Tokyo), which had been cut into a rectangular plate \((30 \times 10 \times 2 \text{ mm}^3)\), was followed by the VUV irradiation for 30–120 min. A xenon excimer lamp (UER 20H-172VB, Ushio, center wavelength: 172 nm, half bandwidth: 14 nm) was used for the VUV irradiation in air. The surface was modified by the VUV irradiation where the distance of VUV lamp to the PEEK substrate was changed from 12 to 1 mm in order to check the degree of surface modification.

The surface-modified PEEK substrate was immersed in HAp-dissolved solution \((15 \text{ cm}^3)\) prepared by the dissolution of commercially available HAp powder \((\text{HAp-100}: \text{Taihei chemical Industrial Co., 1.0 g})\) into the de-ionized water \((1 \text{ dm}^3)\) with bubbling of \(\text{CO}_2\) gas for 1 h. Then it was microwave-heated at 100 or \(140^\circ\text{C}\) for 10 min (output power 150 W, frequency 2450 MHz; Monowave 300, Anton Paar Japan, Tokyo), followed by drying at 70°C for 5 min.

2.2 Evaluation

The phases present were examined using a thin-film X-ray diffractometer \((\text{TF-XRD}; \text{Model New D8 ADVANCE, Bruker AXS, Tokyo})\) with monochromatic CuK\(_\alpha\) radiation generated at 40 kV and 40 mA, and using a Fourier-transform infrared spectrometer \((\text{ATR-FTIR}; \text{Model 8600PC, Shimadzu, Kyoto})\). In order to check the surface properties, the contact angle was measured by putting the droplet \((0.05 \text{ cm}^3)\) on the substrate. The order to check the surface properties, the contact angle was measured by putting the droplet \((0.05 \text{ cm}^3)\) on the substrate. The topographical image on the surface of substrate was observed using an atomic force microscope \((\text{AFM}; \text{Innova, Bruker AXS, Yokohama})\). The microstructural observation was conducted using an atomic force microscope (AFM; Innova, Bruker AXS, Tokyo) with monochromatic CuK\(_\alpha\) diffractometer \((\text{TF-XRD}; \text{Model New D8 ADVANCE, Bruker AXS, Tokyo})\) followed by drying at 70°C for 5 min.

The breaking of bonds and subsequent oxidation to form the calcium and phosphorus contents. The bonding strength of PEEK from hydrophobic to hydrophilic natures, but also to encourage the formation of HAp in the human bodies. The present paper describes (i) the formation conditions of carboxyl group on the PEEK substrate through the VUV irradiation in air, and (ii) the microwave-heating conditions in HAp-dissolved solution.

3. Results and discussion

3.1 Surface modification of PEEK substrate due to VUV irradiation

Firstly, changes in properties of PEEK substrate, due to the VUV irradiation at room temperature for 120 min, were examined on the basis of the characteristic chemical binding of XPS spectra. Typical C(1s) binding energies are shown in Fig. 1, as a function of the distance between VUV lamp and PEEK substrate. XPS spectrum of PEEK substrate with no VUV irradiation showed that the peak of C(1s) binding energy appeared at 284.5 nm [Fig. 1(a)]. When the VUV light was irradiated to the PEEK substrate, the additional peak appeared at 289.0 eV. The peak intensity at 289.0 eV increased with decreasing distance of VUV lamp to the PEEK substrate from 12 to 1 mm [Figs. 1(b)–1(d)].

The peak at 284.5 nm is assigned to the C–C binding, whereas the peak at 289.0 eV indicates the presence of –O–C=O group. This fact demonstrates the formation of carboxyl group on the PEEK substrate. The photon energy of VUV light is as high as 698 kJ mol\(^{-1}\), which enables to break the bonding of C–C \((347.7 \text{ kJ mol}^{-1})\) and C–O \((351.5 \text{ kJ mol}^{-1})\). The active oxygen produced by the irradiation of VUV in air does not degrade the benzene rings within PEEK structure, i.e., \([\text{C}_6\text{H}_4\text{O}–\text{C}_6\text{H}_4\text{O}–\text{C}_6\text{H}_4\text{O}]\) due to the energy insufficient to such degradation, but contributes to breaking the bonds of C–O–C and –C–C=O between benzene rings.

The surface roughness values of the PEEK substrate, as well as typical AFM images, are shown in Fig. 2, as a function of the distance of VUV lamp to PEEK substrate. The arithmetic average of roughness profile \((R_a)\) was evaluated on the basis of following equation:

\[
R_a = \frac{1}{N} \sum_{j=1}^{N} Z_j
\]

where \(N\) represents the number of heights, and \(Z_j\) corresponds to the height of a particular surface “\(j\)”. According to the AFM images, the surfaces of PEEK substrates with and without VUV irradiation were smooth, regardless of the changes in distance of VUV lamp to the PEEK substrate. The checking of surface roughness, \(R_a\), on the basis of AFM images demonstrated that these values were around 10 nm and remained unchanged throughout the VUV irradiation time. Taking the XPS results, i.e., the increased amount of carboxyl group with decreasing the distance of VUV lamp to the PEEK substrate, into account, the surface of the PEEK substrate is found to be modified, regardless of the attenuation of VUV light intensity.

The breaking of bonds and subsequent oxidation to form carboxyl group, must change the surface properties of PEEK substrate from hydrophobic to hydrophilic natures, due to the formation of electrostatic force. The formation of such polar groups are also confirmed by Laurens et al., who reported that...
the oxygen in air contributes to the amorphization and chemical modification on the surface of PEEK substrate. This assumption must also be confirmed by the contact angle of water droplet put on the surface of PEEK substrate. Figure 3 shows the photographs showing the contact angles after the irradiation of VUV light for 0 to 120 min and the distance of lamp to PEEK substrate from 12 to 1 mm. Before the VUV irradiation, the contact angle of the water droplet on the PEEK substrate was 88.8°. The contact angle was reduced from 39.0 to 20.0° with decreasing the distance of the lamp to the PEEK substrate from 12 to 1 mm and with increasing VUV irradiation time from 30 to 120 min.

The contact angle of PEEK substrate (≈88.8°) is consistent to the value reported elsewhere (≈85°). As the AFM results indicate, no significant difference in surface roughness was observed, regardless of the changes in the distance of the lamp to the PEEK substrate and irradiation time. On the basis of the present data, the surface modification conditions can be optimized by the selection of irradiation distance and time being 1 mm and 120 min, respectively.

Figure 4 shows the plots of contact angles of the water droplets on the PEEK substrate against the VUV irradiation time. With increasing irradiation time from 30 to 120 min, the contact angle was reduced from 39.0 to 24.4° at the distance of VUV lamp to the PEEK substrate being 12 mm [Fig. 4(a)], from 37.4 to 20.2° at the distance of VUV lamp to the PEEK substrate being 3 mm [Fig. 4(b)], and from 26.4 to 20.0° at the distance of lamp to the PEEK substrate being 1 mm [Fig. 4(c)].

As the data on the XPS spectra indicate, the electrostatic force between carboxyl group and water contributes to reducing the contact angle. The lower contact angle indicates the higher amount of carboxyl group.

3.2 Formation of HAp layer on PEEK substrate
Since the surface modification of PEEK substrate was conducted by the VUV irradiation, the formation conditions of the HAp layer on the PEEK substrate were examined by the microwave heating of surface-modified PEEK substrate immersed in the HAp-dissolved solution. Firstly, the typical heating curves of surface-modified PEEK substrate from room temperature up to 100 and 140°C are shown in Fig. 5. The temperature increased rapidly and attained 100 and 140°C within 120 s, respectively. It should be noted that the microwave heating is beneficial to heat the surface-modified PEEK substrate above 100°C and reached to the desired temperatures only within 120 s (=2 min).

Due to the microwave heating of the surface-modified PEEK substrate immersed in the HAp-dissolved solution, the precipitates covered the PEEK substrate. Increases in mass of the VUV-irradiated PEEK substrate after the microwave heating are shown in Fig. 6, together with typical FE-SEM micrographs. The noted mass increase was found not only with increasing microwave heating temperature from 100 to 140°C (e.g., 27.8 to 40.2 ×10^-2% at the distance of 1 mm) but also with reducing the distance of lamp to the PEEK substrate from 12 to 1 mm (e.g., 27.0 to 40.2 ×10^-5% at the microwave heating temperature of 140°C).

The amount of precipitate increases with decreasing distance of lamp to the PEEK substrate. Regarding this phenomenon, the contact angle is reduced (i.e., the hydrophilic nature is enhanced) with reducing the distance from lamp to the PEEK substrate, indicating the amount of carboxyl group being enhanced by the VUV irradiation. The larger amount of carboxyl group seems to
encourage the precipitation of calcium phosphate (i.e., the precursor of HAp), due to the electrostatic force between carboxyl group and calcium/hydrogen phosphates ions.

After the microwave heating of VUV-irradiated PEEK substrates immersed in the HAp-dissolved solution at 100 and 140°C for 10 min, the crystalline phases were examined using the TF-XRD. Typical TF-XRD patterns of the PEEK substrate microwave-heated at 140°C for 10 min are shown in Fig. 7, together with FE-SEM micrographs. Only HAp was detected from the XRD pattern. On the other hand, FE-SEM micrograph showed that the plate-like particles with the sizes of 0.5 × 0.2 μm were adhered to one another to form the flower-like agglomerates with diameters of 1 to 3 μm.

The formation of flower-like agglomerates has been reported and discussed by several researchers. The probable mechanisms reported so far are the formation of flower-like agglomerates, due to (i) dissolution–precipitation mechanism of self-assembled plate-like particles and (ii) chemical routes via some precursors, such as amorphous calcium phosphate (ACP), calcium hydrogen phosphate dihydrate (CaHPO₄·2H₂O), and octacalcium phosphate pentahydrate [Ca₈H₂(PO₄)₆·5H₂O]. These plate-like particles appear to take shapes which grow up to be radial from the centers of flower-like agglomerates. Such appearance seems to be formed as the results of not only the bonding of HAp particles with positive charge (a/b planes) to the carboxyl groups on the PEEK substrate, but also the crystal growth due to the operation of dissolution–precipitation mechanism.

The phases of HAp were further checked on the basis of the FT-IR spectrum with the results being shown in Fig. 8, together with the cross-section of the HAp layer. Note that the sample powder for measuring FT-IR spectra was scraped up from the HAp-coated PEEK substrate, and that HAp layer was observed from the side section with no mechanical cutting, because such
Due to such dissolution of HAp with CO2 blowing, pH of the solution decreases from 11.6 down to 5.6. The deposit of HAp on the PEEK substrate seems to be accelerated by heating and degassing CO2 from the solution.

The formation mechanism of HAp on the surface of PEEK substrate is illustrated in Fig. 10. When the surface-modified PEEK substrate is microwave-heated in the HAp-dissolved solution, the carboxyl group having negative charge induces the formation of precursor (calcium phosphate) [Fig. 10(a)]. The crystal growth of HAp particles toward plate-like shape may be occurred by the operation of dissolution-precipitation mechanism, and simultaneously agglomerated by the charge imbalance of HAp crystals, i.e., positive charges on a/b planes and negative charges on c plane [Fig. 10(b)]. The electrostatic force enhances not only the bonding of HAp particles to the PEEK substrate due to the presence of carboxyl group but also the agglomeration of HAp particles with charge imbalance, which also relates to the crystal growth of HAp due to the operation of dissolution-precipitation mechanism [Fig. 10(c)].

The amount of HAp precipitate which relates to the thickness of the layer increases with increasing microwave heating temperature from 100 and 140°C (i.e., approximately 8 to 10 μm). This fact demonstrates that the HAp layer is strongly bonded to the PEEK substrate.
phenomenon may be enhanced with the dissolution–precipitation mechanism of HAp, due to the changes in pH value during microwave heating.20)

4. Conclusions
The fabrication conditions of HAp layer on the PEEK substrate were examined by the combined techniques of VUV irradiation and microwave heating. The results obtained were summarized as follows:
(i) The thickness of HAp layer was affected by the distance of VUV lamp to the PEEK substrate (1–12 mm) and VUV irradiation time (0–120 min) for the surface modification of PEEK substrate, and the microwave heating temperature (100 and 140°C for 10 min).
(ii) When the PEEK substrate was surface-modified by the VUV irradiation for 120 min with the distance of VUV lamp to PEEK substrate kept being 1 mm, and then was microwave-heated in the HAp-dissolved solution at 140°C for 10 min (the number of repeated heating operations: 10), the thickness of the HAp layer on the PEEK substrate attained approximately 10 μm. The tape test results demonstrated the strong adhesion of HAp layer to the PEEK substrate.

References