LETTER

Self-Initiated Surface Graft Polymerization of 2-Methacryloyloxyethyl Phosphorylcholine on Poly(ether ether ketone) by Photoirradiation

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ABSTRACT In the present paper, we reported the fabrication of a highly hydrophilic nanometer-scale modified surface on a poly(ether ether ketone) (PEEK) substrate by photoinduced graft polymerization of 2-methacryloyloxyethyl phosphorylcholine (MPC) in the absence of photoinitiators. Photoirradiation results in the generation of semibenzopinacol-containing radicals of benzophenone units in the PEEK molecular structure, which acts as a photoinitiator during graft polymerization. The poly(MPC)-grafted PEEK surface fabricated by a novel and simple polymerization system exhibited unique characteristics such as high wettability and high antiprotein adsorption, which makes it highly suitable for medical applications.

KEYWORDS: poly(ether ether ketone) • phosphorylcholine • surface modification • photopolymerization • wettability • protein adsorption

INTRODUCTION

Poly(aryl ether ketone) (PAEK), including poly(ether ether ketone) (PEEK), is a relatively new family of high-temperature thermoplastic polymers, consisting of an aromatic backbone molecular chain interconnected by ketone and ether functional groups; i.e., a benzophenone (BP) unit is included in its molecular structure. Polyaromatic ketones exhibit enhanced mechanical properties, and their chemical structure is stable at high temperatures, resistant to chemical and radiation damages, and compatible with many reinforcing agents (such as glass and carbon fibers); therefore, they are considered to be promising materials for industrial applications such as aircraft, turbine blades, and electric devices. In the 1990s, the biocompatibility and in vivo stability of various PAEK materials and high-performance engineering polymers were investigated (1). Recently, PEEK has emerged as the leading high-performance thermoplastic candidate for replacing metal implant components, especially in the field of orthopedics and trauma (2). In recent studies, the tribological and bioactive properties of PEEK, which is used as a bearing material and flexible implant in joint arthroplasty, have been investigated (3−5). However, conventional single-component PEEK cannot satisfy these requirements (e.g., wear resistance or fixation with a bone) for the artificial joint (2). Because of interest in further improving implants, the PEEK as biomaterials study has also been focused on the biocompatibility of the polymer, either as a reinforcing agent or as a surface modification (6, 7). Therefore, multicomponent polymer systems have been designed in order to synthesize new multifunctional biomaterials. In order to use PEEK and related composites in novel implant applications, they can be engineered to have a wide range of physical, mechanical, and surface properties.

2-Methacryloyloxyethyl phosphorylcholine (MPC), a methacrylate monomer composed of a phospholipid polar group, which is identical with the neutral phospholipids of cell membranes, is used to synthesize polymer biomaterials having excellent biocompatibility (8−12). MPC polymers, exhibiting a cell membrane like structure, have potential application in various fields such as biology, biomedical science, and surface chemistry because they exhibit several unique properties such as good biocompatibility, high lubricity, low friction, and excellent antiprotein adsorption (8−12).

Surface modification is one of the most important technologies for the preparation of new multifunctional biomaterials. In general, a polymer surface can be modified using the following two methods: (a) surface absorption or reaction with small molecules and (b) grafting of polymeric molecules onto a substrate via a covalent bond. Grafting polymerization is performed most frequently using either of the following methods: (i) surface-initiated graft polymerization termed the "grafting from" method in which the monomers are polymerized from initiators or comonomers and (ii) adsorption of the polymer to the substrate termed the "grafting to"

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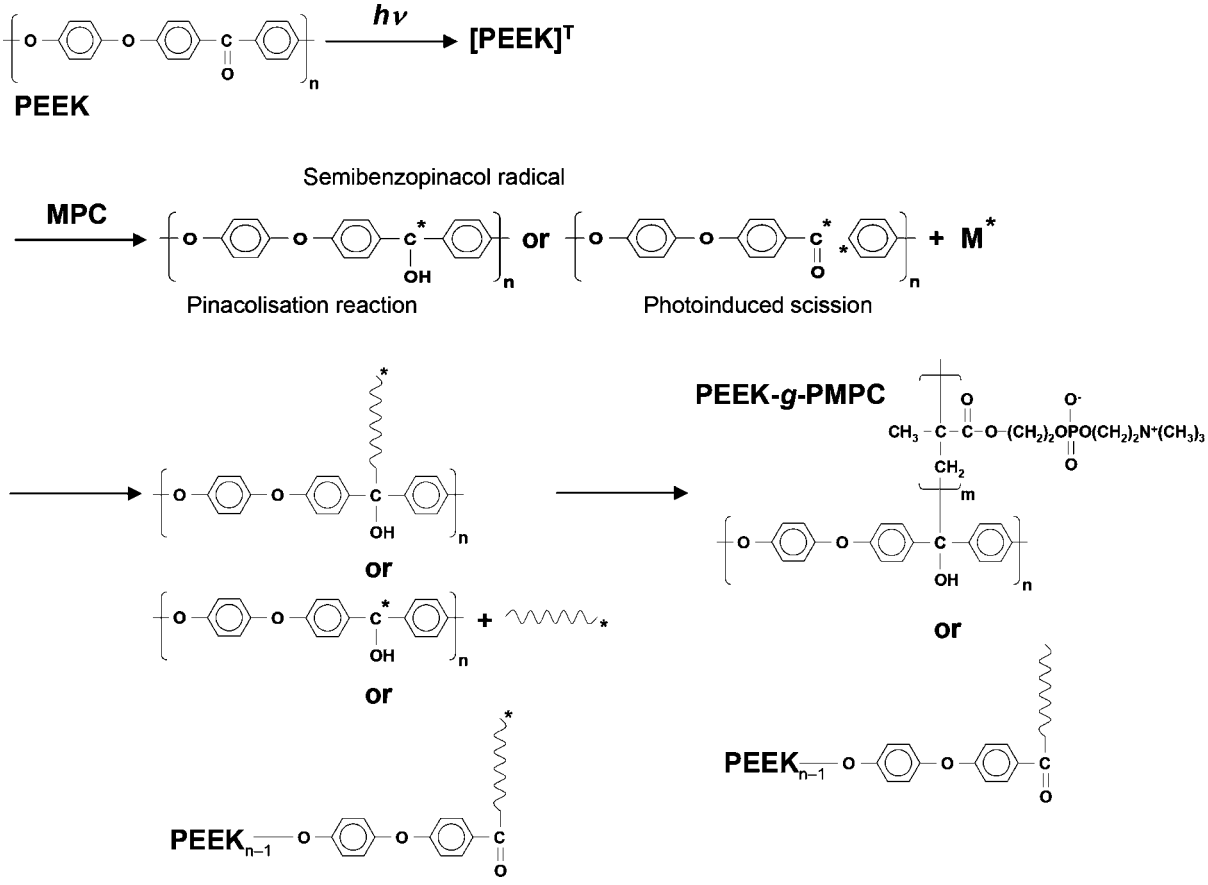

FIGURE 1. Scheme for the preparation of PEEK-*g*-PMPC.

methods such as dipping, cross-linking, or reaction of the end groups of the ready-made polymers with the functional groups of the substrate. The "grafting from" method has an advantage over the "grafting to" method in that it forms a high-density polymer brush interface with a multifunctional polymer; this advantage results in a fruitful function. In previous studies, a multifunctional biomaterial such as poly(MPC) (PMPC) was grafted onto a polyethylene (PE) surface; this was accomplished using photoinduced "grafting from" polymerization in the presence of a conventional BP photoinitiator (13−17). During grafting, the physically adsorbed BP initiators on the PE surface were excited to the triplet-state hydrogen (H) atom from the $-CH_2-$ group of the PE surface; this resulted in the formation of radicals that were capable of inducing surface-initiated graft polymerization, which was conducted under ultraviolet (UV) irradiation.

In this study, we have demonstrated the fabrication of a biocompatible and highly hydrophilic nanometer-scale modified surface by grafting PMPC onto the surface of a self-initiated PEEK using a novel photoinduced "grafting from" polymerization reaction. We hypothesize that photoirradiation results in the generation of semibenzopinacol-containing radicals of the BP units in PEEK, which acts as a photoinitiator during the "grafting from" polymerization. It is well-known that when BP is exposed to photoirradiation such as UV irradiation, a pinacolization reaction is induced; this results in the formation of semibenzopinacol (ketyl) radicals that act as photoinitiators. Our technique enables the direct grafting of PMPC onto the PEEK surface in the absence of a photoinitiator, thereby resulting in the formation of a C−C covalent bond between the PMPC and PEEK substrate. The chemical and physical properties of the PEEK surface were also investigated.

MATERIALS AND METHODS

PMPC Graft Polymerization. The preparation of PMPC-grafted PEEK (PEEK-*g*-PMPC) is schematically illustrated in Figure 1. PEEK specimens were machined from an extruded PEEK (450G; Victrex plc, Thornton-Cleveleys, U.K.) bar stock, which was fabricated without stabilizers and additives. The surfaces of the PEEK specimens were ultrasonically cleaned in ethanol for 20 min and then dried in vacuum. MPC was industrially synthesized using the method reported by Ishihara et al. (8) and supplied by the NOF Corp. (Tokyo, Japan). It was dissolved in degassed water to obtain a 0.5 mol/L aqueous solution; PEEK specimens were immersed in this solution. Photoinduced graft polymerization was carried out at 60 °C for 90 min on the PEEK surface under UV irradiation (UVL-400HA ultrahigh-pressure mercury lamp; Riko-Kagaku Sangyo Co., Ltd., Funabashi, Japan) with an intensity of 5 mW/cm^2; a filter (model D-35; Toshiba Corp., Tokyo, Japan) was used to restrict the passage of UV light to wavelengths of 350 ± 50 nm. After polymerization, the PEEK-*g*-PMPC specimens were removed from the MPC solution, washed with pure water and ethanol to remove nonreacted monomers and nongrafted polymers, and dried at room temperature. As a reference sample, a PEEK-*g*-PMPC with BP was prepared by PMPC grafting with BP precoating. Before PMPC grafting, the PEEK specimens were immersed in an acetone solution containing 10 mg/mL of BP (Wako Pure Chemical Industries, Ltd., Osaka, Japan) for 30 s and then dried in the dark at room temperature in order to remove the acetone. It was reported that the amount of BP adsorbed on the surface was 3.5×10^{-11} mol/cm^2 (9).

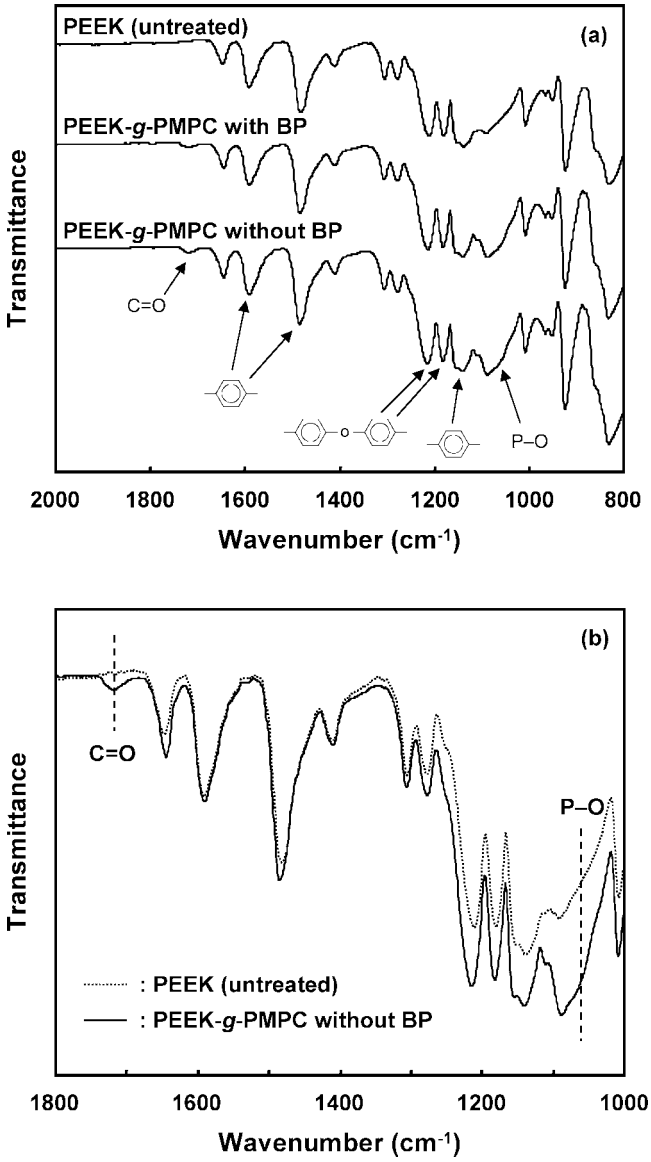

FIGURE 2. FT-IR/ATR spectra of PEEK-*g*-PMPC with/without BP.

Surface Analysis by Fourier Transform Infrared (FT-IR) Spectroscopy, X-ray Photoelectron Spectroscopy (XPS), and Water-Contact Angle Measurement. The functional group vibrations of the PEEK-*g*-PMPC surface that was grafted with/without BP were examined using attenuated total reflection (ATR) by FT-IR spectroscopy. FT-IR/ATR spectra were obtained in 32 scans over a range of 800−2000 cm^{-1} at a resolution of 4.0 cm^{-1} by using an FT-IR analyzer (FT/IR615; Jasco International Co., Ltd., Tokyo, Japan).

The surface elemental contents of the PEEK-*g*-PMPC surface that was grafted with/without BP were analyzed using XPS. XPS spectra were obtained using an XPS spectrophotometer (AXIS Hsi 165; Kratos/Shimadzu Corp., Kyoto, Japan) equipped with a Mg Kα radiation source by applying a voltage of 15 kV at the anode. The takeoff angle of the photoelectrons was maintained at 90°. Each measurement was scanned five times, and five replicate measurements were performed on each sample; their average values were considered for determining the surface elemental contents.

The static water-contact angles of the PEEK-*g*-PMPC surface that was grafted with/without BP were measured with an optical bench-type contact angle goniometer (model DM300; Kyowa Interface Science Co., Ltd., Saitama, Japan) using a sessile drop method. Drops of purified water (1 μL) were deposited on the PEEK-*g*-PMPC surface, and the contact angles were measured directly after 60 s by using a microscope. Subsequently, 15 replicate measurements were performed on each sample, and the average values were taken as the contact angles.

Cross-Sectional Observation of PEEK-*g*-PMPC Using Transmission Electron Microscopy (TEM). The cross section of the PMPC layer fabricated on the PEEK-*g*-PMPC surface that was grafted with/without BP was observed using a transmission electron microscope. First the specimens were embedded in an epoxy resin, stained with a ruthenium oxide vapor at room temperature, and then sliced into ultrathin films (approximately 100 nm thick) using a Leica Ultracut UC microtome (Leica Microsystems, Ltd., Wetzlar, Germany). A JEM-1010 electron microscope (JEOL, Ltd., Tokyo, Japan) was used for TEM observation at an acceleration voltage of 100 kV.

Characterization of Protein Adsorption by a Micro-bicinchoninic Acid (BCA) Method. The amount of protein adsorbed on the untreated PEEK and PMPC layer of the PEEK-*g*-PMPC surface that was grafted with/without BP was measured using the micro-BCA method. Each specimen was immersed in Dulbecco's phosphate-buffered saline (PBS; pH 7.4, ion strength = 0.15 M; Immuno-Biological Laboratories Co., Ltd., Takasaki, Japan) for 1 h to equilibrate the surface modified by the MPC polymer. The specimens were immersed in a bovine serum albumin (BSA; molecular weight = 6.7×10^4; Sigma-Aldrich Corp., MO) solution at 37 °C for 1 h. The protein solution was prepared in a BSA concentration of 4.5 g/L, i.e., 10% of the concentration of human plasma levels. Then, the specimens were rinsed five times with fresh PBS and immersed in a 1 mass % sodium dodecyl sulfate (SDS) aqueous solution and shaken at room temperature for 1 h to completely detach the adsorbed BSA from the PEEK surface. A protein analysis kit (micro-BCA protein assay kit, no. 23235; Thermo Fisher Scientific Inc., IL) based on the BCA method was used to determine the BSA concentration in the SDS solution, and the amount of BSA adsorbed on the PEEK surface was calculated.

Statistical Analysis. The results derived from each measurement were used to determine the water-contact angle, and the amounts of BSA adsorbed were expressed as mean values and standard deviation. The statistical significance ($p < 0.05$) was estimated by the Student's *t* test.

RESULTS AND DISCUSSION

In this study, we investigated the PMPC layer formed on the PEEK surface by photoinduced radical graft polymerization in the absence a photoinitiator. The following methods were employed in our study: (a) grafting from polymerization for the formation of a high-density graft polymer layer, (b) photoinduced polymerization in the absence of photoinitiators, and (c) use of biocompatible hydrophilic macromolecules, which exhibited photoreduction by hydrogen abstraction of a BP unit in PEEK from a hydrogen donor; this induced surface-initiated graft polymerization of the methacrylate-type monomer (i.e., MPC) on the PEEK surface, even in the absence of BP as a photoinitiator. These results are discussed hereafter.

The preparation of the PEEK-*g*-PMPC without BP is schematically illustrated in Figure 1. The present graft polymerization reaction involving free radicals is photoinduced by UV irradiation. Under UV irradiation, a BP unit in PEEK can undergo the following reactions in the aqueous MPC solutions (18−24). The pinacolization reaction (photoreduction by hydrogen abstraction of a BP unit in PEEK) results in the formation of a semibenzopinacol radical (i.e., ketyl radical),

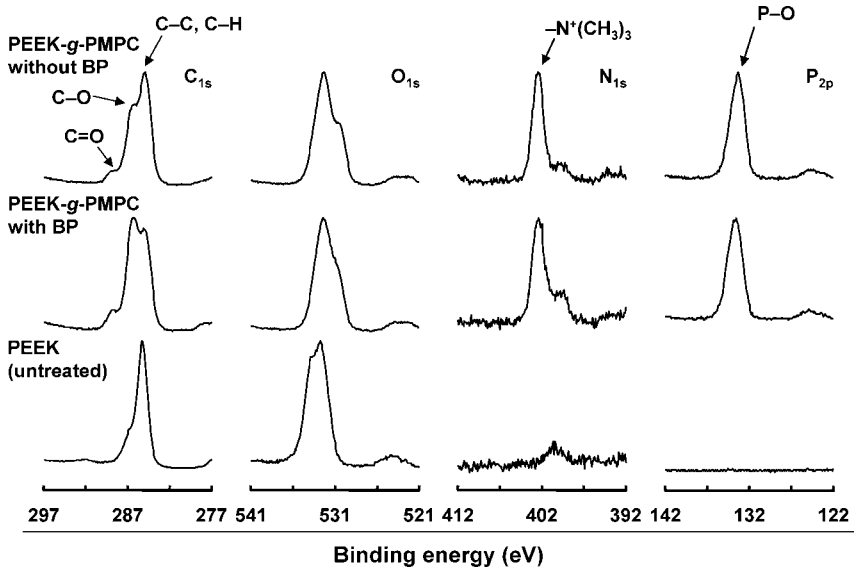

FIGURE 3. XPS spectra of PEEK-*g*-PMPC with/without BP.

Table 1. Surface Elemental Composition ($n = 5$), Static-Water Contact Angle ($n = 15$), and the Amount of BSA Adsorbed ($n = 10$) on PEEK-*g*-PMPC with/without BP

	surface elemental composition (atom %)					
sample	C_{1s}	O_{1s}	N_{1s}	P_{2p}	contact angle (deg)	amount of adsorbed BSA ($\mu g/cm^2$)
PEEK (untreated)	83.2 (0.5)[a]	16.7 (0.5)	0.1 (0.1)	0.0 (0.0)	92.5 (1.9)	0.42 (0.22)
PEEK-*g*-PMPC with BP	64.5 (1.1)	25.2 (0.8)	5.1 (0.2)	5.2 (0.2)	7.1 (1.1)	0.08 (0.08)
PEEK-*g*-PMPC without BP	62.5 (0.6)	27.3 (0.5)	5.1 (0.1)	5.1 (0.1)	6.8 (1.7)	0.08 (0.10)
PMPC[b]	57.9	31.6	5.3	5.3		

[a] The standard deviation is in parentheses. [b] Theoretical elemental composition of PMPC.

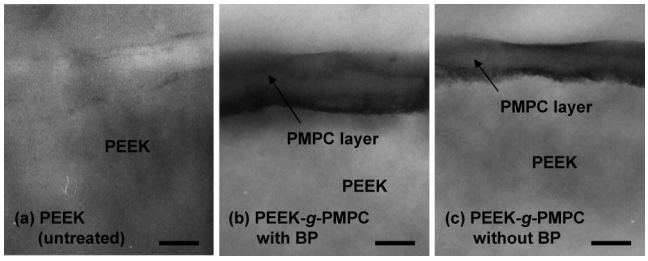

FIGURE 4. Cross-sectional TEM images of PEEK-*g*-PMPC with/without BP. Bar: 100 nm.

which can initiate the "grafting from" polymerization of MPC as the main reaction and the "grafting to" polymerization of MPC (the radical chain end of PMPC couples the semibenzopinacol radical of the PEEK surface) as a subreaction. In addition, a photoscission reaction occurs as a subreaction, which may not need a hydrogen donor. The cleavage reaction induces recombination and the "grafting from" polymerization. When water polymerization is carried out in the presence of a hydrogen donor, a phenol unit may be subsequentially formed due to hydrogen abstraction.

Figure 2 shows the FT-IR/ATR spectra of untreated PEEK and PEEK-*g*-PMPC with/without BP. Absorption peaks were observed at 1600, 1490, 1280, 1190, and 1160 cm^{-1} for both untreated PEEK and PEEK-*g*-PMPC. These peaks are chiefly attributed to the diphenyl ether group, phenyl rings, or aromatic hydrogen atoms in the PEEK substrate (25, 26). However, transmission absorption peaks at 1720 and 1080 cm^{-1} (shoulder peak) were observed only for PEEK-*g*-PMPC (Figure 2b). These peaks corresponded to the carbonyl group (C═O) and the phosphate group (P—O) in the MPC unit (15—17). The FT-IR/ATR spectra showed no clear difference between PEEK-*g*-PMPC with and without BP.

The XPS spectra of the binding energy region of the nitrogen (N) and phosphorus (P) electrons showed peaks for PEEK and PEEK-*g*-PMPC with/without BP, whereas peaks were not observed in the case of untreated PEEK (Figure 3). The peaks at 403 and 134 eV were attributed to the $-N^+(CH_3)_3$ and phosphate groups, respectively. These peaks indicate the presence of phosphorylcholine in the MPC units. After PMPC grafting, the peaks attributed to the MPC unit were clearly observed in both FT-IR/ATR and XPS spectra of PEEK-*g*-PMPC with/without BP. These peaks indicate that PMPC is successfully grafted on the surface of PEEK (15—17).

Table 1 summarizes the surface elemental compositions of the untreated PEEK and PEEK-*g*-PMPC with/without BP. The elemental compositions of N and P in all of PEEK-*g*-PMPC with/without BP were 5.2 and 5.3 atom %, respectively. The elemental composition of the PEEK-*g*-PMPC surface was almost equal to the theoretical elemental composition (atom %; N, 5.3; P, 5.3) of PMPC. These results indicate that the PMPC layer formed on the PEEK substrate covers fully.

Figure 4 shows the cross-sectional TEM images of the untreated PEEK and PEEK-*g*-PMPC with/without BP. In the

cases of PEEK-*g*-PMPC with/without BP, an approximately 100-nm-thick PMPC layer was clearly observed on the surface of the PEEK substrate, and neither crack nor delamination was observed at the PEEK substrate and the interface between the PMPC layer and the PEEK substrate. These results indicate that the PMPC layer formed on the PEEK substrate is uniformly distributed over the substrate and is bound to the substrate by covalent C−C bonds. Because the photoinduced radical graft polymerization proceeds only on the surface of the PEEK substrate, the properties of the substrate remain unchanged. Retention of the properties of the PEEK substrate is very important in clinical use because the biomaterials used in implants act not only as functional materials but also as structural materials in vivo. During the polymerization of PEEK-*g*-PMPC with BP, the pinacolization reaction was photoinduced (UV irradiation) not only by the BP unit in PEEK but also by the BP initiators precoated on the substrate. However, the amount of semibenzopinacol radicals produced from the BP units in PEEK alone would be sufficient to induce surface-initiated graft polymerization, since there is no clear difference in the PMPC layer between the PEEK-*g*-PMPC with and without BP.

Table 1 summarizes the static water-contact angles and the amount of BSA adsorbed on the untreated PEEK and PEEK-*g*-PMPC with/without BP. The static water-contact angle of the untreated PEEK was 92.5°, and it decreased markedly to 7.1° ($p < 0.001$) and 6.8° ($p < 0.001$), respectively, after PMPC grafting was carried out with/without BP. Because MPC is a highly hydrophilic compound, PMPC is water-soluble (8−12). The water wettability of the PEEK-*g*-PMPC surface was considerably greater than that of the untreated PEEK surface because of the presence of a PMPC nanometer-scale layer (Figure 4). The fluid (water) film forming ability of the PEEK-*g*-PMPC surface can be attributed to such a nanometer-scale thin PMPC layer because the outermost PMPC layer determines this ability. The adsorption of the representative plasma protein and BSA on the PEEK-*g*-PMPC surface considerably decreased to 20% ($p < 0.001$) compared to that in the case of the untreated PEEK (0.08 μg/cm^2). It is hypothesized that the mechanism of protein adsorption resistance on the surface modified by the MPC polymer is attributed to the water structure resulting from the interactions between the water molecules and phosphorylcholine groups (27−30). The presence of a large amount of free water around the phosphorylcholine group is responsible for the easy detachment of proteins and the prevention of conformational changes in the adsorbed proteins (29). A decrease in protein adsorption is also considered to be caused by the presence of a hydrated layer around the phosphorylcholine groups (27). These observations are consistent with the results of the static water-contact angle measurements and cross-sectional TEM observations of the PEEK whose surface is modified by PMPC grafting. These results imply that the PEEK-*g*-PMPC surface is biocompatible in terms of tissue and blood compatibility because MPC polymer modified surfaces are known to exhibit in vivo biocompatibility (8−14).

The novel and simple photoinduced graft polymerization in the absence of photoinitiators would be highly suitable for industrial applications (31, 32) as well as the development of medical devices (2−7). The density and thickness of the grafting layer can be controlled by the photoirradiation time and monomer concentration (16, 17). Additional efforts are needed in this aspect. However, the synthesis of a self-initiated biocompatible polymer having unique properties such as antiprotein adsorption and wettability by the photoinduced "grafting-from" polymerization reaction is indeed a novel and simple phenomenon developed in the field of biomaterials science, and the fabrication of the PEEK-*g*-PMPC surface can result in the development of next-generation multifunctional biomaterials.

CONCLUSION

A biocompatible and highly hydrophilic nanometer-scale modified surface was successfully fabricated on the PEEK substrate by the photoinduced graft polymerization of PMPC in the absence of photoinitiators. Because MPC is a highly hydrophilic compound, the water wettability of the PEEK-*g*-PMPC surface was greater than that of the untreated PEEK surface because of the formation of a PMPC nanometer-scale layer. In addition, the amount of BSA adsorbed on the PEEK-*g*-PMPC surface considerably decreased compared to that in the case of untreated PEEK. This novel and simple photoinduced graft polymerization in the absence of photoinitiators is highly suitable in industrial applications, including the development of medical devices.

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