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ORIGINAL ARTICLE

Smart PEEK Modified by Self-Initiated Surface Graft Polymerization for Orthopedic Bearings

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Abstract

Poly(ether-ether-ketone) (PEEK)s are a group of polymeric biomaterials with excellent mechanical properties, chemical stability, and nonmagnetism. In the present study, we propose a novel self-initiated surface graft polymerization technique, using which we demonstrate the fabrication of a highly hydrophilic and biocompatible nanometer-scale layer on the surfaces of PEEK and carbon fiber-reinforced PEEK (CFR-PEEK) by the photoinduced graft polymerization of 2-methacryloyloxyethyl phosphorylcholine (MPC) without using any photoinitiators. The thus formed hydrophilic and smooth 100-nm-thick PMPC-grafted layer caused a significant reduction in the sliding friction of the bearing interface because the thin water film and hydrated PMPC layer acted as extremely efficient lubricants (so-called fluid-film lubrication or hydration lubrication). Fluid-film lubrication suppressed the direct contact of the counter-bearing surface with the PEEK substrate and thus reduced the frictional force. A PMPC-grafted layer is therefore expected to significantly increase bearing durability. Furthermore, the PMPC-grafted layer shows unique phenomena, e.g., it prevents damage of the metal counter surface regardless of the carbon fiber content of CFR-PEEK. Smart PEEK using the self-initiated surface graft polymerization of MPC should lead to development of novel orthopedic bearings.

***Keywords**: poly(ether-ether-ketone), 2-methacryloyloxyethyl phosphorylcholine, surface modification, photopolymerization, joint replacement, wear mechanism*

Introduction

In recent years, joint reconstruction surgeries ranging from minor repairs to damaged joints to total hip arthroplasty (THA) have become increasingly important with the increasingly aging population worldwide. THA has emerged as one of the most successful of such surgeries, and it has been demonstrated to dramatically relieve patients' pain and to improve their quality of life. The most popular artificial hip joint is a bearing couple composed of polyethylene (PE, specifically cross-linked PE (CLPE)) and a cobalt–chromium–molybdenum (Co–Cr–Mo) alloy. However, the implantation duration and clinical outcome of THA is significantly limited by the incidence of osteolysis [1]. Osteolysis is triggered by various inflammatory responses to wear particles produced from a PE articular

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surface [2]. These undergo phagocytosis by macrophages, in turn inducing the secretion of bone resorptive cytokines [3]. Although osteolysis is one of the most common reasons for late revision surgery, the major short-term complication is dislocation. As a solution to this problem, a large femoral head increases not only the range of motion prior to the impingement of the femoral stem neck on the liner but also the jump distance. Therefore, larger femoral heads involving a thin acetabular liner have been frequently used in recent times to improve the stability of the bearing surface.

To reduce wear particles, improve stability, and increase the longevity of artificial hip joints, studies have focused on various bearing alternatives and the improvement of bearing materials [4–10]. Recently, studies have shown that poly(ether-ether-ketone) (PEEK) might be useful in reducing wear debris and improving stability. PEEK consists of an aromatic backbone molecular chain interconnected by ketone and ether functional groups (i.e., its molecular structure contains a benzophenone (BP) unit). It is well known that PEEK is chemically inert, insoluble in most conventional solvents, and compatible with several reinforcement agents (such as carbon fibers, i.e., carbon fiber-reinforced PEEK (CFR-PEEK)); furthermore, it exhibits excellent mechanical properties and nonmagnetism. PEEK and CFR-PEEK are therefore considered potential high-performance plastic replacements for conventional implant materials. Consequently, PEEK and/or CFR-PEEK bearing materials are being increasingly utilized in various applications [11, 12]. However, both PEEK and CFR-PEEK do not satisfy certain properties required in an artificial joint, such as low friction, high wear resistance and biocompatibility [11]. CFR-PEEK acetabular cups, e.g., MITCH PCR Cup (Stryker SA, Montreux, Switzerland) [13] and ABG II acetabular liner (Stryker SA) [14, 15], have been clinically used to a limited extent in several hospitals; the available early clinical results support the short-term efficiency of CFR-PEEK but do not yet demonstrate a long-term clinical advantage over other well established orthopedic bearings [12]. In this light, surface modification has emerged as one of the most important techniques for developing new multifunctional biomaterials for joint reconstruction in order to satisfy various requirements.

Herein, we propose a new and safer methodology for constructing a nanometer-scale functional layer on PEEK and CFR-PEEK substrates by the self-initiated photoinduced graft polymerization of functional vinyl compounds at the surface. It is well known that when BP is exposed to photoirradiation such as ultraviolet (UV) irradiation, a pinacolization reaction is induced [8]. This results in the formation of semi-benzopinacol-containing radicals that act as photoinitiators. We therefore focused on the BP units in PEEK and developed a self-initiated surface graft polymerization technique that uses these units [6–8]. The polymerization reaction involving free radicals is photoinduced by UV irradiation. This technique enables the direct formation of a functional polymer layer on the PEEK surface in an aqueous medium without any photoactive low-molecular-weight compounds, making this an easy and human-friendly process. Additionally, we prepared a biocompatible polymer layer, i.e., poly (2-methacryloyloxyethyl phosphorylcholine (MPC)) (PMPC). MPC is a methacrylate monomer bearing a phosphorylcholine group, and it can provide various types of polymers upon copolymerization with other vinyl compounds [16–25]. MPC polymers show great potential for applications in the fields of biomedical science and bioengineering because they possess beneficial properties such as excellent antibiofouling ability and friction suppression. Thus, numerous medical devices, including intravascular stent [24], soft contact lenses [25], artificial heart [19], and artificial hip joint [22, 23] have been developed from MPC polymers and applied clinically. The biomedical efficacy and safety of MPC polymers are therefore well established.

Toward finding a solution, we investigated the surface characteristics of surface modified PEEK and CFR-PEEK samples, including the wettability, lubricity, and wear resistance. Such investigations are of great importance for designing life-long artificial hip joints and for obtaining a better understanding of the limitations resulting from the use of this material. During our studies, we sought answers to two questions: (1) Will the PMPC grafting affect the lubrication characteristics of PEEK and CFR-PEEK surfaces? (2) Will the modifications affect their wear resistances?

Materials and Methods

Self-initiated graft polymerization of MPC

The preparation of PMPC-grafted PEEK is schematically illustrated in Fig. 1. PEEK (450G; Victrex PLC, Thornton-Cleveleys, UK) and CFR-PEEK (Sumiploy CK4600; Sumitomo Chemical Co., Ltd., Tokyo, Japan) specimens were machined from extruded bar stocks, and then finished by surface-polishing. CFR-PEEK was blended with discontinuous polyacrylonitrile (PAN)-based carbon fiber of 30 mass%. The surfaces of the PEEK and CFR-PEEK specimens were ultrasonically cleaned in ethanol for 20 min, and then dried in vacuo. MPC (NOF Corp.; Tokyo, Japan) was dissolved in degassed water to obtain 0.50-mol/L MPC aqueous solution. The PEEK and CFR-PEEK specimens were then immersed in these solutions. Photoinduced

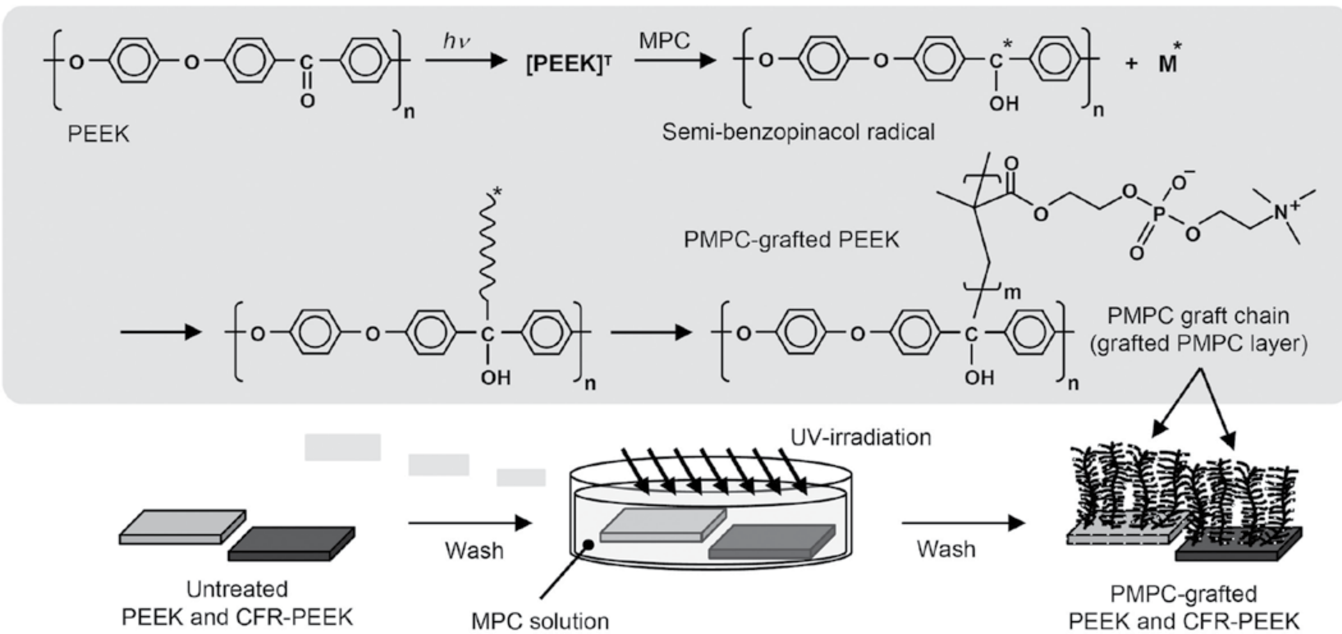

Figure 1. Schematic illustration of the preparation of PMPC-grafted PEEK and PMPC-grafted CFR-PEEK.

graft polymerization was subsequently carried out at 60°C for 90 min on the PEEK and CFR-PEEK surfaces under UV irradiation (UVL-400HA ultra-high pressure mercury lamp; Riko-Kagaku Sangyo Co. Ltd., Funabashi, Japan) with 5 mW/cm2 intensity. A filter (UV-D35; Toshiba Corp., Tokyo, Japan) was used to restrict the incident UV light to wavelengths of 350 ± 50 nm. After polymerization, the PMPC-grafted PEEK and CFR-PEEK specimens were removed from the MPC solution and washed with pure water and ethanol to remove the unreacted monomers and ungrafted polymers.

Surface morphological observation by atomic force microscopy and transmission electron microscopy

The surface morphologies of the PMPC-grafted PEEK and CFR-PEEK were analyzed by atomic force microscopy (AFM; Nanoscope IIIa; Nihon Veeco, Tokyo, Japan) in the tapping mode. The measurements were performed under dry conditions using a monocrystal silicon cantilever. A scan rate of 0.25 Hz, tip velocity of 5 µm/s, and imaging size of 50 µm × 50 µm were used for all samples.

Transmission electron microscopy (TEM; JEM-2010F; JEOL Ltd., Tokyo, Japan) at acceleration voltage of 200 kV was used to observe the cross section of the PMPC layer on the PMPC-grafted PEEK and CFR-PEEK surfaces. A thin film of the samples was prepared by the focused ion beam (FIB) technique (FB-2100; Hitachi High-Technologies Co., Tokyo, Japan) at an acceleration voltage of 40 kV. Untreated and PMPC-grafted CFR-PEEK specimens were precoated with a carbon film before the FIB process.

Wettability and friction evaluation

The static water contact angles on the PMPC-grafted PEEK and CFR-PEEK surfaces were measured by the sessile drop method using an optical bench-type contact angle goniometer (DM300; Kyowa Interface Science Co., Ltd., Saitama, Japan). Drops of purified water (1 µL) were deposited on the PMPC-grafted PEEK and CFR-PEEK surfaces, and the contact angles were directly observed by a microscope after 60 s of dropping. Fifteen points were measured for each PEEK and CFR-PEEK sample, and the average values were used.

A unidirectional friction test was performed using a pin-on-plate machine (Tribostation 32; Shinto Scientific Co. Ltd., Tokyo, Japan). Six specimens were prepared for each of the PMPC-grafted PEEK and CFR-PEEK surfaces. A 9-mm-diameter Co-Cr-Mo alloy pin was also prepared. The surface roughness (Ra) of the pin was <0.01 µm, which was comparable to that of femoral head products. The friction test was performed for each specimen at room temperature using a load of 0.98 N, sliding distance of 25 mm, frequency of 1 Hz, maximum of 100 cycles, and pure water for lubrication. The mean coefficients of dynamic friction were determined by averaging the measurements for five data points from 96–100 cycles.

Pin-on-disk wear test

Multidirectional wear tests were conducted using a POD testing machine (Ortho POD; AMTI, Watertown, MA, USA). Untreated PEEK, untreated CFR-PEEK, and PMPC-grafted CFR-PEEK pins with 10-mm diameter were used for the wear tests and control soak tests to correct the water-absorption increments (n = 3). As the control, untreated CLPE pins (n = 3) with 10-mm diameter were prepared; these were machined from a compression-molded bar stock of PE (GUR1020 resin; Quadrant PHS Deutschland GmbH, Vreden, Germany) irradiated with a 50-kGy dose of gamma-rays in N2 gas atmosphere and annealed at 120 °C for 7.5 h in N2 gas to facilitate cross-linking. The Co–Cr–Mo alloy disks had a surface roughness of Ra < 0.01 µm. A mixture of bovine serum with a protein content of 30 g/L, 20 mM ethylenediamine-N, N, N', N'-tetraacetic acid (EDTA), and 0.1 mass% sodium azide was used at 37°C as the lubricant. The multidirectional wear test was conducted on a rectangular sliding surface. The test conditions were specified as a static load of 213 N, sliding distance of 30 mm, and frequency of 1 Hz for a maximum of 1.0 × 106 cycles, according to the ASTM F732 standard. Gravimetric wear was determined by weighing the pins and disks. Soak controls were used to compensate for fluid absorption by the specimens.

Hip simulator wear test

A 12-station hip simulator (MTS Systems Corp., Eden Prairie, MN) using untreated PEEK and CFR-PEEK, and PMPC-grafted PEEK and CFR-PEEK cups (n = 3) with inner and outer diameters of 26 and 52 mm, respectively, was used for the wear test according to the ISO 14242-3 standard. A Co–Cr–Mo alloy ball of 26-mm diameter (K-MAX® HH-02; KYOCERA Medical Corporation, Osaka, Japan) was used as the femoral head. A mixture of 25-vol% bovine serum, 20 mM EDTA, and 0.1 mass% sodium azide was used as the lubricant. The lubricant was replaced every 0.5 × 106 cycles. Gait cycles were applied by simulating a physiological loading curve (Paul-type) with double peaks at 1793 and 2744 N and a multidirectional (biaxial and orbital) motion of 1Hz frequency. Gravimetric wear was determined by weighing the cups at intervals of 0.5 × 106 cycles. Load-soak controls (n = 2) were used to compensate for fluid absorption by the specimens according to the ISO 14242-2 standard. Testing was continued for a total of 3.0 × 106 cycles.

The wear particles were isolated from the bovine serum solution used for lubrication and observed using a scanning electron microscope (SEM). Isolation was accomplished by incubating the lubricant in a 0.4 g/mL sodium hydroxide solution for 1 h at 60°C and then adding methanol to it. The mixture was sonicated for 10 min to digest the degraded and precipitated adhesive proteins and then sequentially filtered through a 0.1-µm membrane filter. The membrane was directly observed under an SEM (S-3400N; Hitachi Ltd., Tokyo, Japan) using an acceleration voltage of 15 kV after gold deposition.

To evaluate the wear conditions, the features of the bearing surfaces of the femoral heads were observed after 3.0 × 106 cycles of the hip simulator wear test using a confocal laser scanning microscope (OLS1200; Olympus Corp., Tokyo, Japan) and a fluorescence microscope (Axioskop 2 Plus; Carl Zeiss AG, Oberkochen, Germany). For the fluorescence microscope observation, an appropriate exposure time (~0.2 s) was allowed to obtain best-quality sample images. The arithmetic mean of the surface roughness of the contact and non-contact areas of the retrieved femoral heads was determined using a surface roughness tester (Surftest SV-3100; Mitutoyo Corporation, Kawasaki, Japan) according to the ISO 7206-2 standard.

Statistical analysis

The mean values of the four groups (untreated and PMPC-grafted PEEK, and untreated and PMPC-grafted CFR-PEEK) were compared by one-factor analysis of variance (ANOVA) and the significance of differences was determined by post-hoc testing using the Bonferroni method. All statistical analyses were performed using an add-on software (Statcel 3; OMS Publishing Inc., Tokorozawa, Japan) for a computerized worksheet (Microsoft Excel® 2010; Microsoft Corporation, Redmond, WA).

Results

The preparation of the PMPC-grafted layer on the surface affected the morphologies of the PEEK and CFR-PEEK substrates. Nanometer-scale scratches (attributed to the surface finishing (polishing)) and pits (attributed to the removal of carbon fibers) were observed on the surfaces of the untreated PEEK and CFR-PEEK (Fig. 2). In contrast, the surfaces of the PMPC-grafted PEEK and CFR-PEEK were smooth; scratches and pits were hardly observed. For both PMPC-grafted PEEK and CFR-PEEK, an approximately 100-nm-thick PMPC layer was clearly observed on the surface of the PEEK substrate, and neither cracks nor delamination were observed on the PEEK substrate or at the interface between the PMPC layer and the PEEK substrate.

PMPC grafting affected the hydration and friction characteristics of the PEEK and CFR-PEEK surfaces. The contact angles of untreated PEEK and CFR-PEEK were ~90° (PEEK; mean = 92.5°, 95% CI = ±1.0, and CFR-PEEK; mean = 88.3°, 95% CI = ±1.6) and decreased to their lowest values of <10° after PMPC-grafting on the surfaces (PEEK; mean = 6.8°, 95% CI = ±0.9, $p < 0.01$ and CFR-PEEK; mean = 5.5°, 95% CI = ±0.8, $p < 0.01$) (Fig. 3). The coefficient of dynamic friction of untreated CFR-PEEK

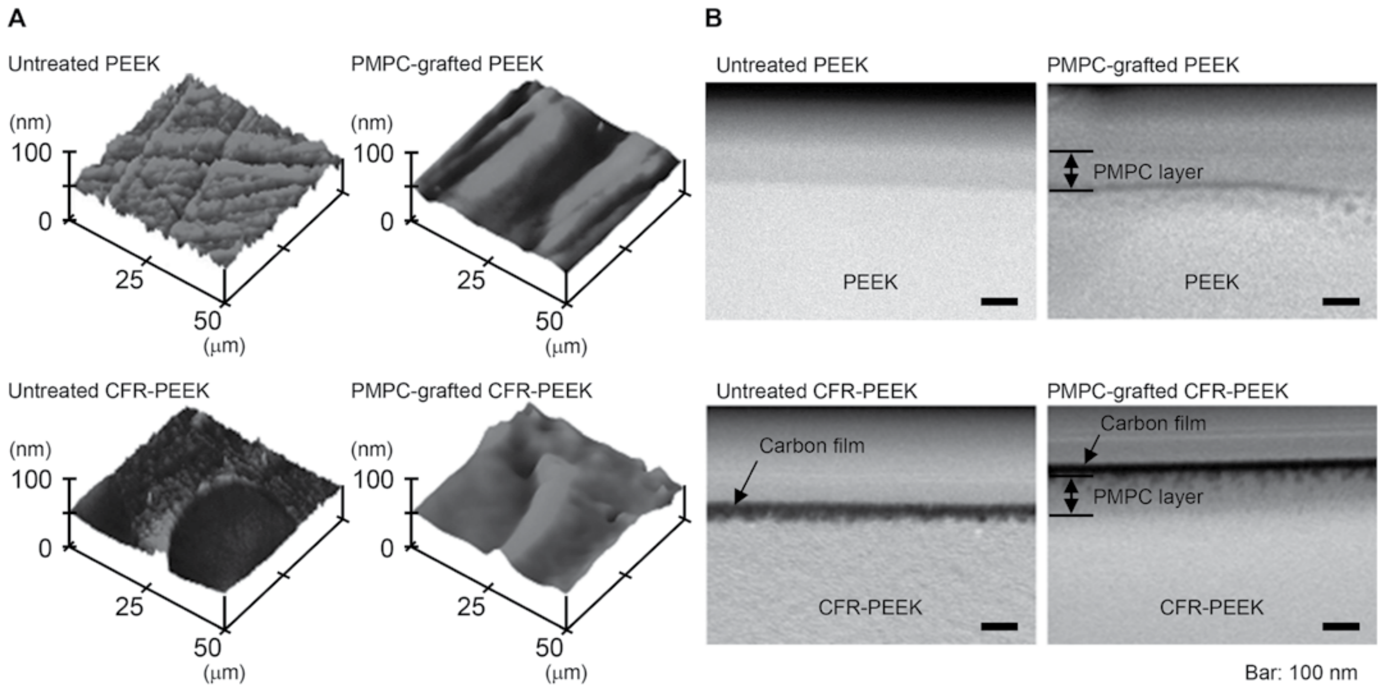

Figure 2. (A) Surface AFM images and (B) cross-sectional TEM images of untreated PEEK, PMPC-grafted PEEK, untreated CFR-PEEK, and PMPC-grafted CFR-PEEK.

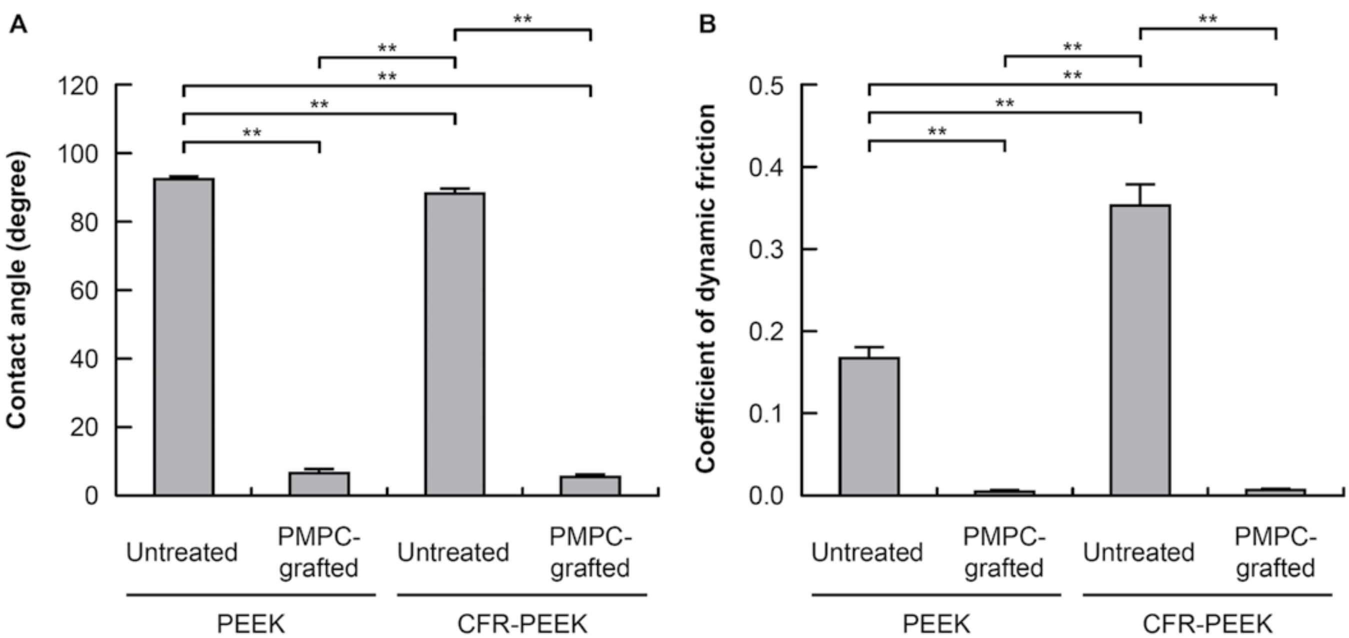

*Figure 3. (A) Static water contact angle and (B) coefficient of dynamic friction of untreated PEEK, PMPC-grafted PEEK, untreated CFR-PEEK, and PMPC-grafted CFR-PEEK. Data are expressed as mean ± 95% confidence intervals. **: One-factor ANOVA and post-hoc test, significant differences ($p < 0.01$) were observed in the comparison between four groups.*

(mean = 0.354, 95% CI = ±0.025) was two times that of untreated PEEK (mean = 0.167, 95% CI = ±0.013, $p < 0.01$). However, regardless of the carbon-fiber reinforcement, the lowest values of both coefficients of dynamic friction were <0.01 after PMPC grafting on the surfaces and were 97% lower (PEEK; mean = 0.005, 95% CI = ±0.001, $p < 0.01$ and CFR-PEEK; mean = 0.007, 95% CI = ±0.001, $p < 0.01$) than those of untreated PEEK and CFR-PEEK.

In the multidirectional pin-on-disk wear test, untreated CFR-PEEK (mean = –0.18 mg/106 cycles, 95% CI = ±0.10) and PMPC-grafted CFR-PEEK (mean = 0.01 mg/106 cycles, 95% CI = ±0.01) pins were found to undergo significantly less ($p < 0.01$) gravimetric wear rate than untreated PEEK (mean = 9.50 mg/106 cycles, 95% CI = ±4.14) pins (Fig. 4). On the other hand, the gravimetric wear rate of the counter Co–Cr–Mo alloy disks against the untreated CFR-PEEK pins (mean = 0.61 mg/106 cycles, 95% CI = ±0.46) exhibit higher wear ($p < 0.05$) than the CLPE pins (mean = 0.02 mg/106 cycles, 95% CI = ±0.02).

In the hip simulator wear test, the characteristics of the PMPC grafted surface affected the durability of the PEEK and CFR-PEEK cups. During 3.0 × 106 cycles of the hip simulator wear test, the PMPC-grafted PEEK cup (mean = 31.60 mg/106 cycles, 95% CI = ±19.54) was observed to experience less gravimetric wear rate than the untreated PEEK cup (mean = 216.97 mg/106 cycles, 95% CI = ±181.02) (Fig. 5A). However, the difference was not statistically significant owing to the wide deviation of the gravimetric wear of the untreated PEEK cups. The untreated and PMPC-grafted CFR-PEEK cups (untreated: mean = –2.46 mg/106 cycles, 95% CI = ±0.24; PMPC-grafted: mean = –5.49 mg/106 cycles, 95% CI = ±1.62) were found to undergo significantly less ($p < 0.05$) gravimetric wear than the untreated PEEK cups. Remarkably, fewer wear particles were isolated from the lubricants of the PMPC-grafted PEEK cups than from those of the untreated PEEK cups after 3.0 × 106 cycles (2.5–3.0 × 106 cycles) of the hip simulator test (Fig. 5B). Moreover, extremely small and barely observable wear particles were produced by the untreated CFR-PEEK and PMPC-grafted CFR-PEEK cups. The wear particles of the untreated PEEK and PMPC-grafted PEEK cups were micrometer-sized fibrils and sub-micrometer-sized granules. In contrast, those of the untreated CFR-PEEK and PMPC-grafted CFR-PEEK cups were only sub-micrometer-sized granules. PMPC grafting did not affect the morphologies of the PEEK or CFR-PEEK wear particles. In the confocal laser scanning microscope images shown in Fig. 6A, the surfaces of the Co–Cr–Mo alloy femoral heads against the untreated and PMPC-grafted PEEK cups and the PMPC-grafted CFR-PEEK cups were smooth. However, that against the untreated CFR-PEEK cups had a different morphology; the surface was worn and slightly roughened by scratches. In the fluorescence microscope image of only the femoral head against the untreated PEEK cup, fluorescence of the adhesives was observed (Fig. 6B). This is primarily attributed to the PEEK. The mean of the surface roughness of the worn femoral heads against the untreated CFR-PEEK cups (mean = 0.019 µm, 95% CI = ±0.005) was significantly higher ($p < 0.05$) than those of the other bearing couples (untreated PEEK: mean = 0.009 µm, 95% CI = ±0.004; PMPC-grafted PEEK: mean = 0.006 µm, 95% CI = ±0.001; PMPC-grafted CFR-PEEK: mean = 0.010 µm, 95% CI = ±0.003) (Fig. 6C). There were no differences among the mean surface roughness of the other three bearing couples.

Discussion

In this study, we developed the novel self-initiated surface graft polymerization technique, by which we demonstrate the fabrication of a highly hydrophilic and biocompatible 100-nm-thick smooth layer on the surfaces of PEEK and CFR-PEEK by the photo-induced graft polymerization of MPC without using any additional low-molecular-weight photoinitiators. Furthermore, we investigate the surface characteristics of PMPC-grafted PEEK and CFR-PEEK. We considered two research questions: (1) Will the PMPC grafting affect the lubrication characteristics of PEEK and CFR-PEEK surfaces? (2) Will the modifications affect their wear resistances? The results suggested that it was possible to improve the durability of orthopedic bearing materials.

It is important to optimize the water-wettability and lubricity of the bearing surface to improve wear resistance. The wettabilities of PMPC-grafted PEEK and CFR-PEEK surfaces are considerably greater than those of the untreated PEEK and CFR-PEEK surfaces (Fig. 3A). This is because of the presence of a smooth 100-nm-scale PMPC layer resulting from the polymerization of highly hydrophilic MPC monomer (Fig. 2). Fig. 3B shows that the coefficients of dynamic friction of the PMPC-grafted PEEK and CFR-PEEK surfaces were significantly lower than those of the untreated PEEK and CFR-PEEK surfaces. The wettabilities of the PMPC hydrated layer clearly affected the frictional properties of the PEEK and CFR-PEEK surfaces. The higher friction of untreated PEEK and CFR-PEEK surfaces is one of their disadvantages because it results in greater wear and the seizure of bearing couples. The higher frictional properties of untreated PEEK and CFR-PEEK surfaces actually affected the wear properties determined by the hip simulator wear test.

The wear properties of PEEK and CFR-PEEK when used as bearing materials in hip joint articulations have been reported in previous studies [26–30]. To the best of our knowledge, the wear resistances of these materials are not completely satisfactory. Scholes et al. reported that the wear rate was 1.16 mm3/106 cycles [28], and Brockett et al. reported that the wear rate was 0.30 mm3/106 cycles [30] for CFR-PEEK cups against alumina or zirconia-toughened alumina (ZTA) ceramic femoral heads, respectively. In the hip simulator wear test, the significant improvements in the water-wettabilities, frictional properties, and/or carbon-fiber-reinforced properties of the PMPC-grafted PEEK and CFR-PEEK cups resulted in substantial improvements in their wear resistances. The wear rate of the PMPC-grafted CFR-PEEK cups was almost zero (–3.81 mm3/106 cycles, as calculated using a specific gravity of

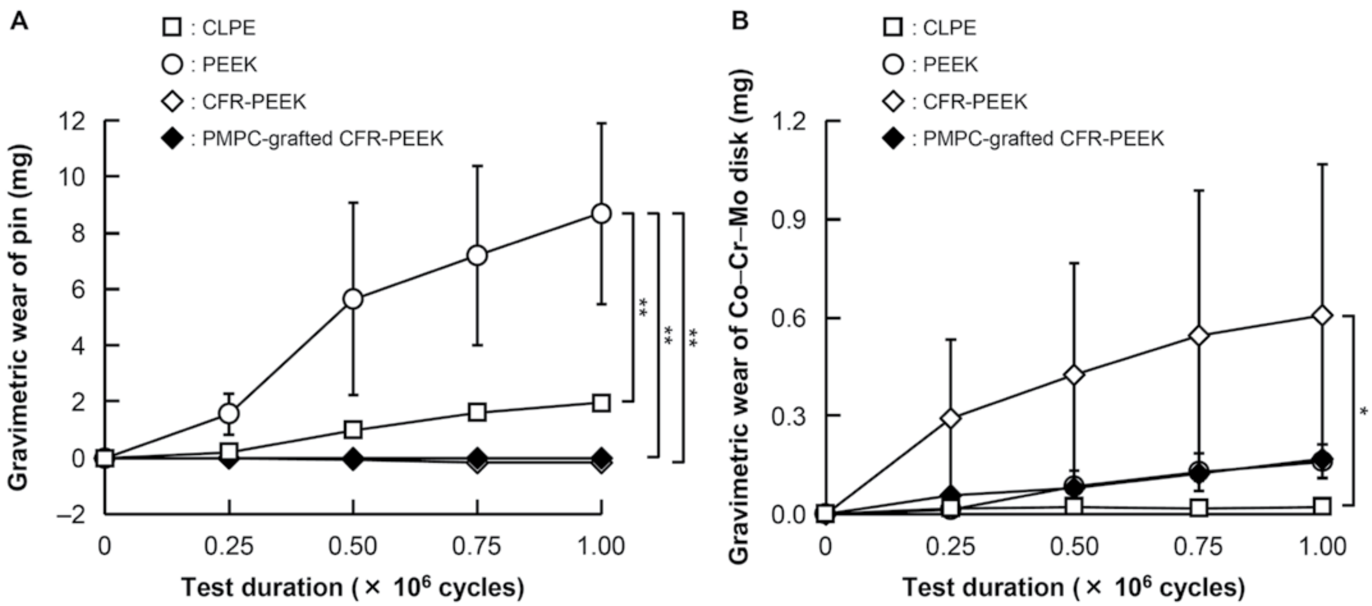

*Figure 4. Time courses of the gravimetric wear of the (A) untreated PEEK and untreated and PMPC-grafted CFR-PEEK pins, and (B) counter Co–Cr–Mo disks during the multidirectional POD wear test. Data are expressed as mean ± 95% confidence intervals. One-factor ANOVA and post-hoc test, significant differences (*p < 0.05, **p < 0.01) were observed in the comparison between four groups.*

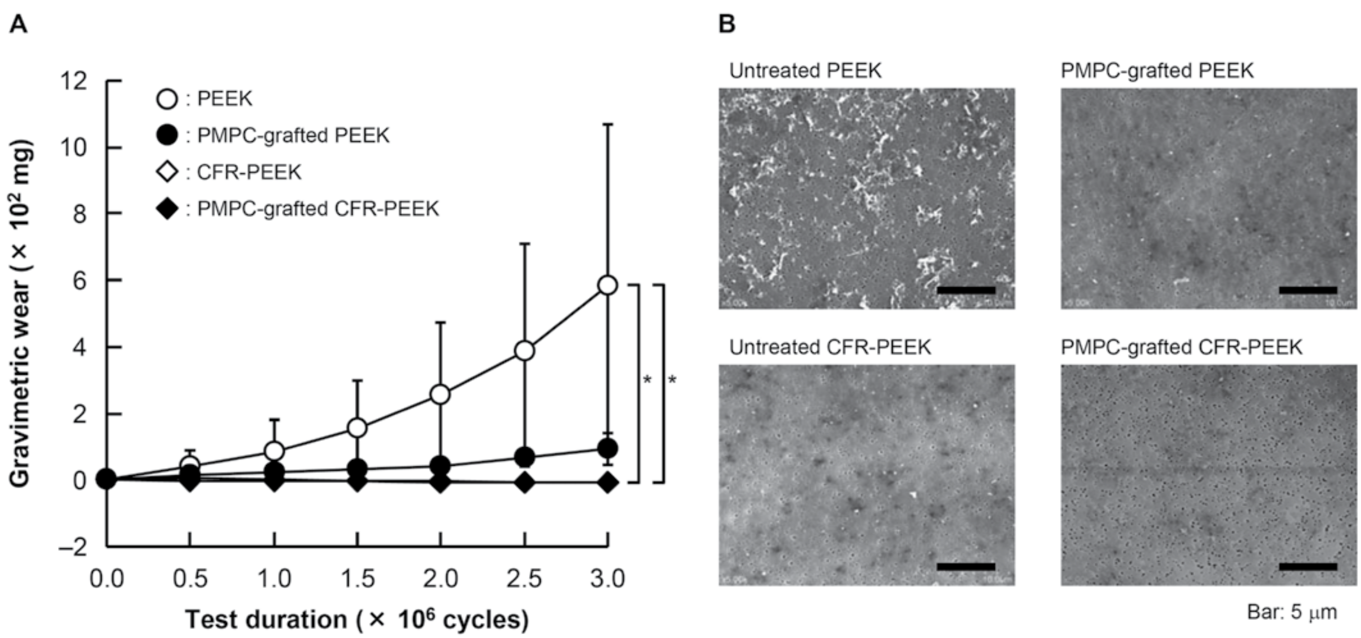

*Figure 5. Time courses of the gravimetric wear of the (A) untreated and PMPC-grafted PEEK and untreated and PMPC-grafted CFR-PEEK cups, and (B) SEM images of wear particles isolated from lubricants of the hip simulator wear test. Data are expressed as mean ± 95% confidence intervals. One-factor ANOVA and post-hoc test, significant difference (*p < 0.05) was observed in the comparison between four groups.*

1.44 g/cm3) even when articulated to Co–Cr–Mo alloy femoral heads. As noted earlier, PMPC is water-soluble because MPC is highly hydrophilic. Fluid-film lubrication (or hydration lubrication) with the PMPC-grafted surface was therefore afforded by the hydrated layer. It can be affirmed that an orthopedic bearing using PMPC mimics natural articular cartilage. The bearing surfaces of a natural synovial joint are covered by a specialized type of hyaline cartilage (i.e., articular cartilage) that protects the joint interface from mechanical wear and facilitates smooth movement of the joints during daily activity [31]. Articular cartilage consists of surface-active phospholipids, chondrocytes, and surrounding matrix macromolecules, such as proteoglycans, glycosaminoglycans, and collagens. Because of

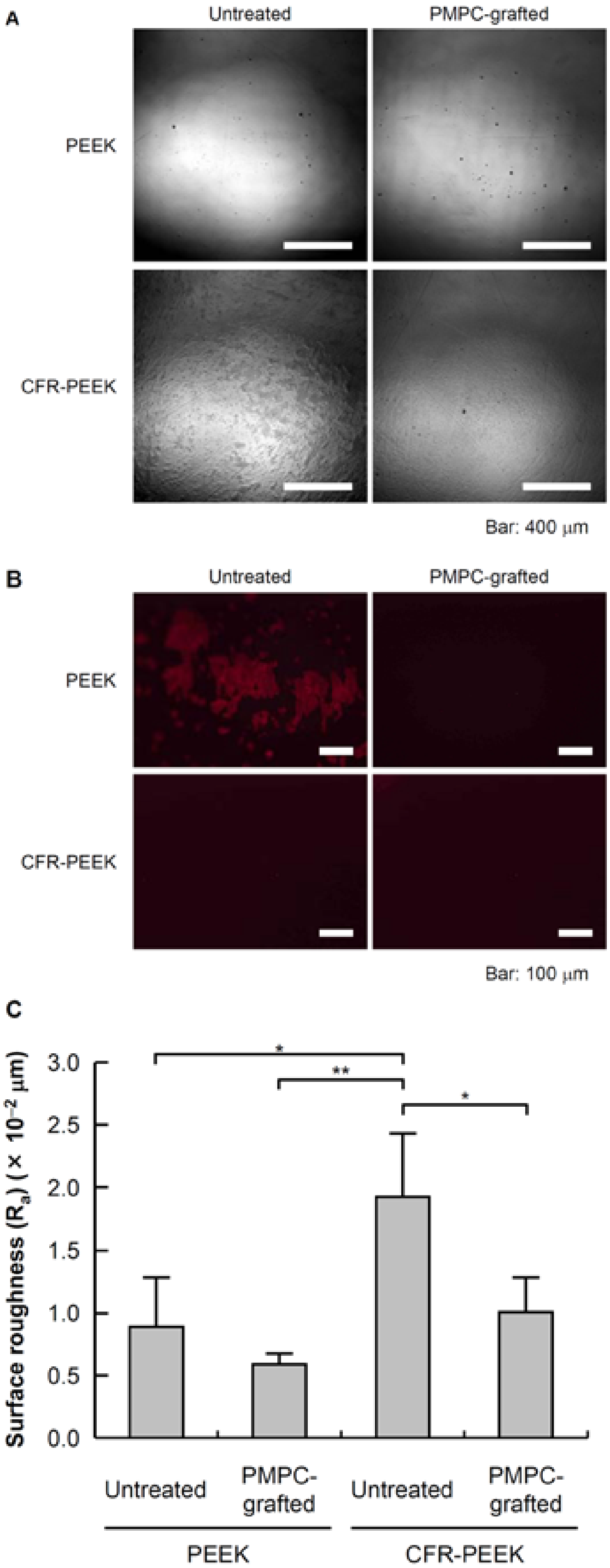

*Figure 6. Surface conditions of Co–Cr–Mo alloy femoral heads against PMPC-grafted PEEK and CFR-PEEK cups after 3.0 × 106 cycles. (A) Confocal laser scanning microscope images, (B) fluorescence microscope images, and (C) surface roughness of Co–Cr–Mo alloy femoral heads. Data are expressed as mean ± 95% confidence intervals. * indicates $p < 0.05$, ** indicates $p < 0.01$.*

their charge, they can trap water to maintain the water-fluid and electrolyte balance, which provides hydrophilicity and affords effective boundary lubrication [32]. The thin-film fluid lubrication of the hydrated layer of articular cartilage is essential to the smooth movement of natural synovial joints. Considering that the study and mimicking of nature has been widely successful in science and technology, an investigation of the bearing surfaces of artificial joints with the purpose of mimicking cartilage by surface modification appears promising [32].

There was a significant difference between the wear of PEEK and CFR-PEEK in both the multidirectional pin-on-disk wear test and hip simulator wear test. CFR-PEEK exhibited extremely low wear compared to PEEK. The PAN-based carbon fiber content of the composite must be sufficient to achieve high wear resistance, and it scratched the counter surfaces that exhibited high metal wear [27]. In contrast, the counter surfaces against PMPC-grafted CFR-PEEK were smooth. It is assumed that the fluid-film and/or hydrated layer produced by the PMPC graft suppressed direct contact between the counter-bearing face and the hard carbon fibers of the CFR-PEEK substrate (Fig. 7). This prevented the damage of the metal counter surface, regardless of the carbon fiber content of CFR-PEEK. Evans et al. reported that wear of the metal counter surface proved to be of little concern because it is one-hundredth-thousandth that of CFR-PEEK [33]. Similarly, in the multidirectional pin-on-disk wear test in this study, the wear of the metal counter is only a few percent that of CFR-PEEK or CLPE. However, we should focus on the increasing concern about the adverse local and systemic effects of elevated metal ion release (and electrochemical corrosion), which could cause serious problems such as local soft-tissue reaction and pseudotumor formation [34].

Brockett et al. reported that CFR-PEEK cups exhibited step-like wear with periods of higher wear rate (approximately 0.4–1.4 mm3/106 cycles) and lower wear rate (approximately <0.4 mm3/106 cycles) owing to the composition of the material [30]. The two wear phases were related to the loss of carbon fiber and PEEK matrix, a phenomenon that has been reported previously as well [28]. In contrast, the CFR-PEEK cups exhibited linear low wear [29]. It is assumed that the stepwise wear observed in previous studies was due to the polishing of the worn surface or removal of carbon fibers during the hip simulator wear test. Surface wear of the CFR-PEEK cups was hardly observed during the hip simulator wear test. Because of the surfaces, resulting in relatively linear low wear of carbon fibers and PEEK matrix and a smooth bearing surface, had been polished before the test.

Careful observation of wear particles for PEEK and

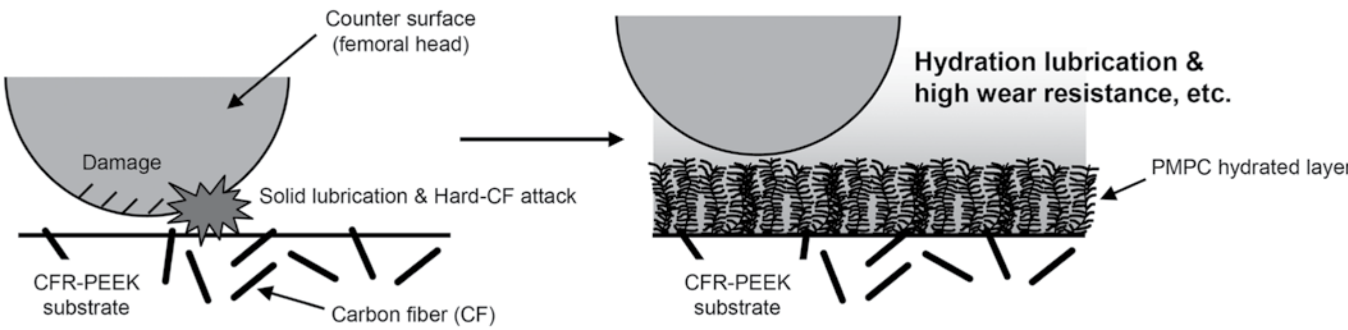

Figure 7. Schematic illustration of advantages of PMPC-grafted PEEK and PMPC-grafted CFR-PEEK.

CFR-PEEK is necessary because the production of wear particles in THA is recognized as the main factor that initiates periprosthetic osteolysis and aseptic loosening [1–3]. These wear particles are not biodegradable in vivo, and their deposition in the periprosthetic tissue activates macrophages and the subsequent release of cytokines, which stimulate bone resorption. The inflammatory cellular response to particles is thought to be dependent upon factors such as particle number, size, and shape; surface area; and material chemistry. In the wear particle analysis, remarkably fewer wear particles were isolated from the lubricants used for the PMPC-grafted PEEK and CFR-PEEK cups than from those used for the untreated cups. The wear particles from the PMPC-grafted PEEK and CFR-PEEK cups were almost sub-micrometer-sized. However, the procedure used for isolating the wear particles cannot entirely capture particles of diameter less than 0.1 µm. Moreover, because the amount of wear particles produced by the PMPC-grafted PEEK and CFR-PEEK cups was extremely small, the procedure could not separate them from those produced by the PEEK matrix and the blended carbon fiber. Considering the results of the wear particle analysis, we expect the biological response of the PMPC-grafted PEEK and CFR-PEEK cups in vivo to be comparable with those of PE or CLPE [12, 35]. This is supported by the cell culture experiments performed by Howling et al., who reported that CFR-PEEK wear particles had no cytotoxic effects and could not possibly cause adverse cellular (L929 and U937 cells) reactions [36]. Jones et al. reported that wear particles of CFR-PEEK cups exhibited no cytotoxic or mutagenic potential in the Ames test and the evaluation of chromosome aberration in human lymphocytes [12]. On the other hand, Lorber et al. suggested an increased proinflammatory potential of CFR-PEEK in the evaluation of cytokine (TNF-α, IL-1β, and IL-6) expression tests [37]. Additionally, no in vivo biocompatibility studies using an appropriate animal have been published on this subject. Therefore, we think that careful consideration for wear particles of PEEK and CFR-PEEK is necessary, regardless of PMPC grafting.

The design of a new implant with a well-characterized surface and substrate is a very important but difficult task. At present, the possibility of using PEEK and CFR-PEEK as orthopedic bearings in artificial hips is being earnestly investigated globally. The results do not yet demonstrate a clinical advantage of PEEK and CFR-PEEK over other well-established orthopedic bearings, such as CLPE and alumina or ZTA ceramics. The novel self-initiated surface graft polymerization technique proposed in this study, namely, the simple and innovative photoinduced graft polymerization technique would be very suitable for the surface modification of PEEK and CFR-PEEK orthopedic bearings. Indeed, smart PEEK and CFR-PEEK surfaces could usher in a new generation of orthopedic bearing implants.

Conclusions

In the present study, we successfully demonstrate the fabrication of a highly hydrophilic and biocompatible nanometer-scale layer on the surfaces of PEEK and CFR-PEEK by the photo-induced graft polymerization of MPC using self-initiated surface graft polymerization. The wettability of the PMPC-grafted PEEK and CFR-PEEK surfaces was considerably greater than that of the untreated surfaces. The coefficient of dynamic friction depended on the wettability. The PMPC-grafted layer was expected to significantly improve the wear resistance of the bearings; smart PEEK using the self-initiated surface graft polymerization of MPC should lead to the development of novel orthopedic bearings.

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