Biomaterials 34 (2013) 7829–7839

Contents lists available at ScienceDirect

Biomaterials

journal homepage: www.elsevier.com/locate/biomaterials

Poly(ether-ether-ketone) orthopedic bearing surface modified by self-initiated surface grafting of poly(2-methacryloyloxyethyl phosphorylcholine)

Masayuki Kyomoto [a,b,d], Toru Moro [b,c], Shihori Yamane [b,d], Masami Hashimoto [e], Yoshio Takatori [b,c], Kazuhiko Ishihara [a,*]

[a] Department of Materials Engineering, School of Engineering, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan
[b] Division of Science for Joint Reconstruction, Graduate School of Medicine, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan
[c] Sensory & Motor System Medicine, Faculty of Medicine, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan
[d] Research Department, KYOCERA Medical Corporation, 3-3-31 Miyahara, Yodogawa-ku, Osaka 532-0003, Japan
[e] Materials Research and Development Laboratory, Japan Fine Ceramics Center, 2-4-1 Mutsuno, Atsuta-ku, Nagoya 456-8587, Japan

ARTICLE INFO

Article history:
Received 19 April 2013
Accepted 6 July 2013
Available online 24 July 2013

Keywords:
Poly(ether-ether-ketone)
Phosphorylcholine
Surface modification
Photopolymerization
Joint replacement
Wear mechanism

ABSTRACT

We investigated the production of free radicals on a poly(ether-ether-ketone) (PEEK) substrate under ultraviolet (UV) irradiation. The amount of the ketyl radicals produced from the benzophenone (BP) units in the PEEK molecular structure initially increased rapidly and then became almost constant. Our observations revealed that the BP units in PEEK acted as photoinitiators, and that it was possible to use them to control the graft polymerization of poly(2-methacryloyloxyethyl phosphorylcholine) (PMPC). This "self-initiated surface graft polymerization" method is very convenient in the absence of external photoinitiator. We also investigated the effects of the monomer concentration and UV irradiation time on the extent of the grafted PMPC layer. Furthermore, as an application to improving the durability of artificial hips, we demonstrated the nanometer-scale photoinduced grafting of PMPC onto PEEK and carbon fiber-reinforced PEEK (CFR-PEEK) orthopedic bearing surfaces and interfaces. A variety of test revealed significant improvements in the water wettability, frictional properties, and wear resistance of the surfaces and interfaces.

1. Introduction

Total hip arthroplasty (THA) has been one of the most successful joint surgeries over the last half century. Owing to the aging global population, the number of primary and revised THA has significantly increased annually [1]. Most patients have experienced dramatic pain relief and improvement in their quality of life after THA. The most popular artificial hip joint is a bearing couple composed of polyethylene (PE; currently cross-linked PE or CLPE) and a cobalt–chromium–molybdenum (Co–Cr–Mo) alloy. However, the incidence of osteolysis has significantly limited the duration and clinical outcome of THA [2–4]. Osteolysis is triggered by a host of inflammatory responses to PE wear particles produced at articular surfaces [5], which undergo phagocytosis by macrophages and thus induce the secretion of bone resorptive cytokines [6]. Although osteolysis is one of the most common reasons for late revision surgery, dislocation is the major short-term problem. A large femoral head not only increases the range of motion prior to the impingement of the femoral stem neck on the liner, but it also increases the jump distance. Hence, larger femoral heads have been frequently used in recent times for improving the stability of the bearing surface.

Efforts to reduce these particles, improve stability, and increase the longevity of artificial hip joints have focused on a number of bearing alternatives and improvement of the bearing materials [7–14]. Large femoral heads in metal-on-metal THA and hip resurfacing have been proposed to reduce the risk of dislocation and wear. However, regarding the use of metal-on-metal bearings, there has also been increasing concern about the adverse local and systemic effects of elevated metal ion release and electrochemical corrosion, which could cause serious problem, such as local soft-tissue reaction and pseudotumor formation [15].

It was recently discovered that poly(aryl-ether-ketone) (PAEK), including 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

---

* Corresponding author. Tel.: +81 3 5841 7124; fax: +81 3 5841 8647.
E-mail address: ishihara@mpc.t.u-tokyo.ac.jp (K. Ishihara).

0142-9612/$ – see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.biomaterials.2013.07.023

and ether functional groups (i.e., a benzophenone (BP) unit is included in its molecular structure). Polyaromatic ketones exhibit excellent mechanical properties, have a stable chemical structure, are resistant to chemical and radiation damage, and are compatible with several reinforcement agents (such as glass and carbon fibers). They are therefore potential high-performance plastic replacements for conventional implant materials. Consequently, the utilization of PEEK and/or carbon fiber-reinforced PEEK (CFR-PEEK) bearing materials has been increasingly important [16,17]. The tribological properties of PEEK and CFR-PEEK have been investigated in recent studies [18–20]. However, both PEEK and CFR-PEEK do not satisfy certain properties required in an artificial joint, such as low friction and high wear resistance [17]. To improve the applicability of PEEK and related composites in implants, they can be engineered by reinforcement agents or surface modification to exhibit a wide range of physical, mechanical, and surface properties [21,22]. Surface modification is one of the most important technologies in the development of new multifunctional biomaterials that are used to satisfy several requirements. Current surface modification methods include coating, blending, and grafting. Grafting is particularly advantageous because it forms an effective high-density multifunctional polymer brush interface.

2-Methacryloyloxyethyl phosphorylcholine (MPC), a methacrylate monomer containing a phosphorylcholine group, is used to synthesize highly hydrophilic and antibiofouling polymer biomaterials [23–30]. MPC polymers are potentially applicable in a variety of fields such as biomedical science, surface science, and bioengineering because they possess unique properties such as excellent antibiofouling and low friction. Thus, surface modification of orthopedic bearings using poly(MPC) (PMPC) is effective for obtaining low friction and high wear resistance [11,23,31]. Moreover, several medical devices (e.g., intravascular stents [32], soft contact lenses [33], and artificial hearts [27]) including artificial hip joints [31] have been developed by utilizing MPC polymers and clinically applied. The biomedical efficacy and safety of MPC polymers are therefore well established [27–33].

It is well known that when BP is exposed to photoirradiation such as ultraviolet (UV) irradiation, a pinacolization reaction is induced [34]. This results in the formation of semi-benzopinacol radicals (i.e., ketyl radicals), which act as photoinitiators. We therefore focused our study on the BP units in PEEK and formulated a self-initiated surface graft polymerization method that utilizes the BP units [10,11]. The polymerization reaction involving free radicals was photoinduced by UV irradiation. This technique enabled the direct grafting of the functional polymer onto the PEEK surface without using a photoinitiator.

In this study, we examined (1) whether photoirradiation produced semi-benzopinacol containing radicals (ketyl radicals) from the BP units in the PEEK molecular structure; (2) the component that acted as the photoinitiator and its controllability during graft polymerization on PEEK and CFR-PEEK substrates; and (3) whether the characteristics of the PMPC-grafted substrate could afford durable artificial hips.

2. Materials and methods

2.1. Self-initiated graft polymerization of MPC

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 were finished by polishing, which were fabricated without stabilizers or additives. The 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. The industrially synthesized MPC was supplied by NOF Corp. (Tokyo, Japan) and was dissolved in degassed water to obtain 0.25- and 0.50-mol/L MPC aqueous solutions. The PEEK and CFR-PEEK specimens were then immersed in the solutions. Photoinduced graft polymerization was subsequently carried out at 60 °C for 5–90 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) of intensity 5 mW/cm^2. 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. They were then dried at room temperature.

2.2. Electron spin resonance analysis of PEEK under UV irradiation

The free radical production of PEEK during UV irradiation was determined by the electron spin resonance (ESR) technique. The ESR spectra of PEEK (thin sheet specimens of thickness 100–500 μm sliced from the extruded bar stock) were obtained using an ESR spectrometer (JES-FA200; JEOL RESONANCE Inc., Akishima, Japan) at 9.4 GHz and 25 °C. This was done in a cylindrical TE$_{011}$ resonant cavity under UV irradiation using an ultra-high pressure mercury lamp (ES-USH500; JEOL RESONANCE Inc.) with glass filters (UV-35 and IRA-25; Toshiba Corp.). The external magnetic field was modulated at 100 kHz to detect the first-order derivative of the absorption line.

2.3. Surface morphological observation by atomic force microscope

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

2.4. Cross-sectional observation by transmission electron microscopy

Transmission electron microscopy (TEM) 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 using an FIB system (FB-2100; Hitachi High-Technologies Co., Tokyo, Japan) and an acceleration voltage of 40 kV. Untreated and PMPC-grafted CFR-PEEK specimens were precoated with a carbon film before the FIB process. An electron microscope (JEM-2010F; JEOL Ltd., Tokyo, Japan) and acceleration voltage of 200 kV were used for the TEM.

2.5. Gravimetric measurement of PMPC-grafted layer for various UV-irradiation times

The PMPC-grafted PEEK and CFR-PEEK specimens were weighed on a microbalance (Sartorius Supermicro S4; Sartorius AG, Goettingen, Germany) to determine the surface graft ratio of the PMPC. The surface graft ratio was obtained by the following equations:

$$\text{PMPC-graft extent}\left(\text{mg/cm}^2\right) = (W_g - W_0)/S \tag{1}$$

$$\text{PMPC-graft layer density}\left(\text{g/cm}^3\right) = (W_g - W_0)/S \times T \tag{2}$$

where W_0 is the initial weight of the untreated PEEK and CFR-PEEK substrates, W_g is the weight of the dry PMPC-grafted PEEK and CFR-PEEK substrates; S is the grafted surface area of the substrate; and T is the thickness of the PMPC-graft layer determined by cross-sectional TEM observation. Three samples of each of the untreated and PMPC-grafted PEEK and CFR-PEEK specimens were prepared. Each sample was weighed three times and the average value was used.

2.6. Surface analysis of PMPC-grafted PEEK and CFR-PEEK for various UV irradiation times

The elemental surface conditions of PMPC-grafted PEEK and CFR-PEEK specimens were analyzed by X-ray photoelectron spectroscopy (XPS). The XPS spectra were obtained using an XPS spectrophotometer (AXIS-HSi165; Kratos/Shimadzu Co., Kyoto, Japan) equipped with a 15-kV Mg-Kα radiation source at the anode. The takeoff angle of the photoelectrons was maintained at 90°. Five samples of each of the PMPC-grafted PEEK and CFR-PEEK specimens were prepared, and each sample was scanned five times.

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 sample of PEEK and CFR-PEEK, and the average values were used.