Photoinduced Surface Modification of PEEK with Biocompatible Phospholipid Polymers

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Statement of Purpose: Poly(ether-ether-ketone) (PEEK) is considered to be promising novel biomaterial for orthopedic applications, because PEEK exhibits excellent mechanical properties, chemical stability, non-magnetic nature as compared with polyethylene or metallic materials. However, since conventional PEEK cannot satisfy these requirements: e.g., wear resistance and biocompatibility for use as implantable medical devices. We propose here, new and safer method to construct nanometer-scale modified surface on the PEEK substrate by self-initiated photoinduced graft polymerization to form smart PEEK biomaterials. We have demonstrated the fabrication of highly hydrophilic and biocompatible nanometer-scale modified surface by photoinduced graft polymerization of 2-methacryloyloxyethyl phosphorylcholine (MPC) [1, 2]. The new and safer polymerization system was found out, that is, "self-initiated surface graft polymerization" and generated poly(MPC) (PMPC) layer on the surface of PEEK. This polymerization system is conducted in the absence of photo-active low molecular compound and in aqueous medium; this is human-friendly and excellent biocompatibility [3].

Methods and Materials: PEEK (450G; Victrex PLC, Thornton-Cleveleys, UK) and carbon fiber-reinforced PEEK (CFR-PEEK; Sumiploy CK4600; Sumitomo Chemical Co., Ltd., Tokyo, Japan) specimens were machined from extruded bar stocks, which was fabricated without stabilizers. PEEK and CFR-PEEK specimens were immersed in the 0.5 mol/L MPC (NOF Corp., Tokyo, Japan) aqueous solution. Photoinduced graft polymerization was carried out at 60°C for 90 min on the PEEK and CFR-PEEK surfaces under UV irradiation with an intensity of 5 mW/cm^2. Surface chemical properties of the PMPC-grafted PEEK and CFR-PEEK were examined by Fourier-transform infrared spectroscopy (FT-IR) and X-ray photoelectron spectroscopy (XPS). The fabricated PMPC layers on the PEEK and CFR-PEEK surface were observed using atomic force microscope (AFM) and transmission electron microscope (TEM). The static water-contact angle of the PMPC-grafted PEEK and CFR-PEEK was measured with a sessile drop method using an optical bench-type goniometer. The mechanical properties of untreated and PMPC-grafted PEEK were evaluated with tensile, flexural, small punch, and creep deformation tests according to ISO527, ISO178, ASTM F2183, and ASTM D621, respectively.

Results: After grafting, the peaks ascribed to MPC unit were clearly observed in both FT-IR and XPS spectra. Smooth PMPC layers with 100-nm thick were clearly observed on the surface of the PEEK substrate (Fig. 1). The contact angle of both the untreated PEEK and CFR-

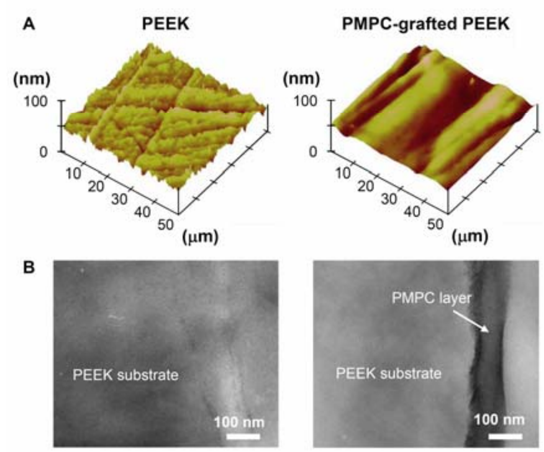

Figure 1. (A) Surface AFM and (B) cross-sectional TEM images of the untreated and PMPC-grafted PEEK.

PEEK was 90°, and it decreased markedly to 7°, after PMPC grafting. The coefficient of dynamic friction of PMPC-grafted PEEK was considerably decreased to 0.010; these are more than 90% reduction compared to those for the untreated PEEK.

We successfully demonstrated the fabrication of highly hydrophilic and biocompatible nanometer-scale modified surface by PMPC-grafting onto the surface of self-initiated PEEK and CFR-PEEK. The wettability of PMPC-grafted PEEK is considerably greater than that of the untreated PEEK, because of the presence of a PMPC layer: MPC is a highly hydrophilic compound. A significant reduction in static water-contact angle of PMPC-grafted PEEK resulted in a substantial improvement in friction property. The mechanical properties of the PEEK are unchanged even after PMPC-grafting. The self-initiated photoinduced graft polymerization proceeds only on the surface of the PEEK substrate, while 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 surface-functional materials but also as structural materials *in vivo*.

Conclusions: The "smart PEEK" with PMPC making unique properties such as biocompatibility and high wear resistance is novel phenomena, and can result in the next-generation implantable medical devices applications.

References: [1] M. Kyomoto *et al. ACS Appl Mater Interface*, 1, 537 (2009), [2] M. Kyomoto *et al. Biomaterials*, 31, 1017 (2010), [3] T. Tateishi *et al. JBMR* in press (2013)

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