Self-initiated surface graft polymerization from PEEK brings smart orthopaedic biomaterials

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Statement of Purpose: We propose here, new and safer method to construct nanometer-scale modified surface on the poly(ether-ether-ketone) (PEEK) substrate by self-initiated photo-induced graft polymerization to form smart PEEK biomaterials. The PEEK is considered to be promising novel polymer biomaterial for orthopaedic and spinal applications. However, since conventional PEEK cannot satisfy these requirements for these applications: e.g., wear resistance and biocompatibility for use as an artificial joint or intervertebral body fusion cage. Therefore, study on the PEEK as implants has also been focused on lubricity and biocompatibility of the polymer, either by reinforcing agents, or by surface modification.
We developed the modified PEEK with a biocompatible 2-methacryloyloxyethyl phosphorylcholine (MPC) polymer. The new and safer polymerization system was found out, that is, “self-initiated surface graft polymerization.” This polymerization system is conducted in the absence of photo-active low molecular compound and in aqueous medium; this is human friendly process.

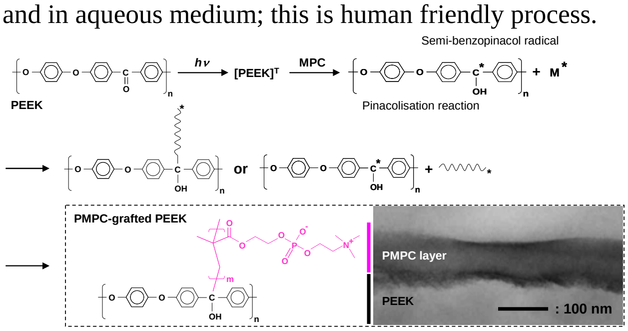

Figure 1. Scheme for the preparation and cross-sectional TEM images of poly(MPC) (PMPC)-grafted PEEK.

Methods: PEEK and Carbon fiber-reinforced PEEK (CFR-PEEK) specimens were machined from an extruded bar stock, and then their surfaces were polished. PEEK specimens were immersed in the 0.5 mol/L MPC aqueous solution. Photo-induced graft polymerization was carried out at 60°C for 90 min on the PEEK surface under UV irradiation with an intensity of 5 mW/cm^2. Surface chemical properties of the untreated and PMPC-grafted PEEK were examined by Fourier-transform infrared spectroscopy (FT-IR) and X-ray photoelectron spectroscopy (XPS). The cross-section of the PMPC layer fabricated on the PMPC-grafted PEEK was observed using a transmission electron microscope (TEM). The static water-contact angle of the untreated and PMPC-grafted PEEK was measured with a sessile drop method using an optical bench-type goniometer. The wear test of PMPC-grafted CFR-PEEK pin against Co-Cr alloy plate was performed by an AMTI Ortho-POD system. The wear tests were performed at 37°C with a load of 213 N, multidirection sliding, and frequency of 1 Hz. A mixture of 27 vol% bovine serum was used as a lubricant medium. A cross-linked polyethylene (CLPE) with 75 kGy gamma-ray irradiation pin against Co-Cr alloy plate was used as control.

Results: Photo-irradiation results in the generation of semi-benzopinacol containing radicals of the benzophenone units in PEEK molecular structure, which acts as a photo-initiator during the graft polymerization.
After grafting, the peaks ascribed to MPC unit were clearly observed in both FT-IR and XPS spectra. PMPC layers with 100 nm thick were clearly observed on the surface of the PEEK substrate (Fig. 1). The static water-contact angle of the untreated PEEK was 92.5°, and it decreased markedly to 6.8° after PMPC grafting.
The untreated and PMPC-grafted CFR-PEEK pins were found to wear significantly less than the CLPE pins (Fig. 2A). Co-Cr plate, when used with CFR-PEEK, exhibited higher wear compared with that with PMPC-grafted CFR-PEEK, with observations of scratching of the Co-Cr surface by the carbon fiber (Fig. 2B).

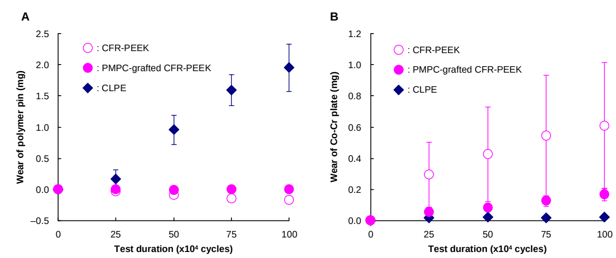

Figure 2. Wear of (A) the PMPC-grafted CFR-PEEK pin, and (B) Co-Cr plate. Bar: Standard deviations.

Conclusions: A highly hydrophilic nanometer-scale modified surface was successfully fabricated on the PEEK and CFR-PEEK substrate by the photo-induced graft polymerization of MPC in the absence of photo-initiators. The new and safer self-initiated surface graft polymerization on the PEEK surface making unique properties such as lubricity by PMPC grafting is novel phenomena in the field of orthopaedic and spinal surgery: e.g., PMPC layer prevents damages of metal counter surface, regardless of the carbon fiber content of the CFR-PEEK (Fig. 3).

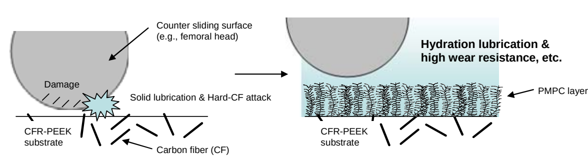

Figure 3. Schematic illustration of advantage of PMPC-grafted CFR-PEEK.

References:
1. Kyomoto M, et al. ACS Appl Mater Interfaces 2009;1:537–542.