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Aqueous lubrication of poly(etheretherketone) via surface-initiated polymerization of electrolyte monomers

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ABSTRACT

Poly(etheretherketone) (PEEK) substrate surface was modified with charged cationic poly(2-(methacryloyloxy) ethyltrimethylammonium chloride) (PMTAC) and anionic poly(3-sulfopropyl methacrylate potassium salt) (PSPMK) polymer brushes through surface-initiated radical polymerization triggered by UV light exposure of benzophenone groups in PEEK backbone as an initiator. After extensive UV light exposure, the PEEK surface was covered with grafted polyelectrolyte chains and exhibited swollen polyelectrolyte brushes with high roughness under water, indicating high graft density and wide molecular weight distributions of PMTAC and PSPMK brushes. The hydrated polyelectrolyte brushes on PEEK surface induce significant air bubble repellency in water. Thus, thickening of swollen polyelectrolyte brushes dramatically reduces the friction coefficient of PEEK surface under a wet condition.

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1. Introduction

Poly(etheretherketone) (PEEK) is an engineering plastic with excellent thermal and mechanical properties, outstanding chemical resistance, and high strength-to-weight ratio [1–4]. Because of these advantages, PEEK has extensively been used to replace metal parts in many applications, such as biomedical, automotive and aerospace parts. However, the main drawbacks of PEEK are their hydrophobicity and high surface friction which lead to premature failure and shortened service life in harsh environments [5,6]. Various approaches have been proposed to overcome this issue, but often fail to meet the demands.

Polymer brushes have been widely used to modify functional properties on a substrate surface of interest. The “grafting from” and “grafting to” are two common approaches being practiced. The former forms highly concentrated polymer brushes by growing polymer chains from initiators on the surface, while the later approach gives low-density polymer brushes by tethering polymer chains with reactive end group. Therefore, the “grafting from”

approach has advantage of producing nearly defect-free, tightly packed polymer brush layer on the substrate surface. Benzophenone groups in PEEK generate radical species when they are exposed to UV light due to pinacolization reaction [1,7–11]. The radical species generated on PEEK surface initiate polymer chain growth to form brushes without a need for photoinitiator additives.

Polyelectrolyte brushes which are prepared by the “grafting from” procedure with surface-initiated atom transfer radical polymerization (SI-ATRP) show unique surface characteristics: excellent antifouling properties and low friction coefficient under wet condition [12–20]. Although there are many reports dealing with PEEK surface modification by surface-initiated polymerization [21–25], few has studied polyelectrolyte brushes and effect of graft density on anti-fouling and lubrication properties has not been fully understood. Herein, we report preparation of two kinds of polymer brushes, a cationic poly(2-(methacryloyloxy) ethyltrimethylammonium chloride) (PMTAC) and an anionic poly(3-sulfopropyl methacrylate potassium salt) (SPMK), on PEEK surface by surface-initiated free radical polymerization through UV light induced pinacolization reaction. The effect of UV exposure time on surface properties of PEEK substrate will also be investigated. Usefulness of the present finding for controlling surface properties of polymers is discussed.

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2. Experimental

2.1. Polyelectrolyte brush preparation using surface-initiated radical polymerization

50- μm thick VICTREX PEEKs were used in this experiment. [2-(Methacryloyloxy) ethyl] trimethylammonium chloride (MTAC) (80 wt% in water) was purchased from Sigma-Aldrich. 3-Sulfopropyl methacrylate potassium salt (SPMK) was purchased from Tokyo Chemical Industry Co. Ltd. All the chemicals were used as received.

Scheme 1 shows the synthetic strategy of PMTAC and PSPMK brushes on PEEK surface. PEEK plaques were cleaned by sonication in ethanol, subsequently dried under vacuum overnight. The MTAC solution was purged with argon to prevent side reactions. PEEK was immersed in the MTAC solution (80 wt% aqueous solution), and UV light with wavelengths ranging from 240 to 400 nm with the maximum intensity approximately at 365 nm was exposed at room temperature for 5–90 min at an overall light intensity of 5 mW/cm² (LA-410UV, Korin Electronic Co. Ltd. Japan). The PEEK substrate was placed about 5 mm beneath the solution for UV-light exposure at an intensity of 4.5 mW/cm². The PMTAC-grafted PEEK sheet (PMTAC-g-PEEK) was washed by deionized (DI) water and methanol to remove residual monomers and non-grafted polymers, then dried under vacuum. For PSPMK-g-PEEK, the same procedures were carried out but SPMK was first dissolved in degassed DI water (55 wt % aqueous solution). After the polymerization, PSPMK-g-PEEK was washed by DI water and dried under vacuum.

2.2. Characterization

Attenuated total reflectance infrared (ATR-FTIR) spectroscopy was performed by Spectrum One FTIR spectrometer (PerkinElmer, USA) equipped with an ATR accessory (Ge crystal, 45°). Each spectrum was obtained with 4 cm⁻¹ resolution and 64 scans in the range of 4000–650 cm⁻¹. X-ray photoelectron spectroscopy (XPS) was conducted by PHI-5000 VersaProbe II (ULVAC-PHI Inc. Japan) at 1 \times 10⁻⁹ Pa using a 150 W monochromatic Al-K α X-ray source. XPS data were acquired at a take-off angle of 45°, and a low-energy of 25 eV electron flood gun was used to minimize charging. Atomic force microscope (AFM) observation was carried out by Cypher ES

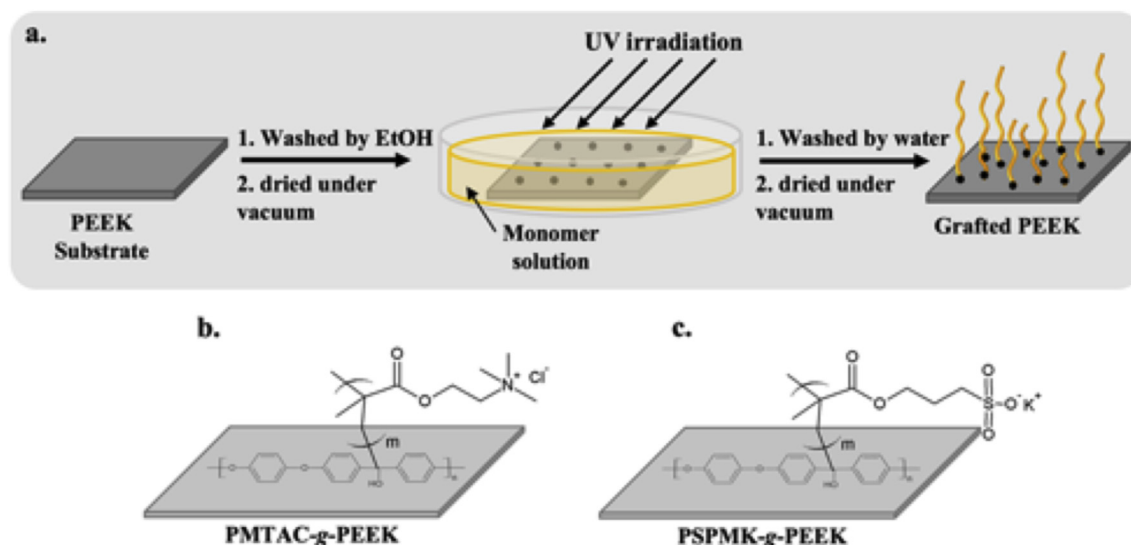
(Asylum Research, Santa Barbara, CA) installed with environment control scanner. Topographic images were obtained in tip contact mode at 298 K with a back-side Au-coated silicon nitride triangular cantilever (OMCL-TR800PSA-1, Olympus Corporation, Tokyo, Japan; size: 200 μm , spring constant: 0.15 Nm⁻¹, tip radius: less than 20 nm). Contact angle for air bubble in water was recorded with a droplet placing and droplet shape analysis system equipped with a video camera Theta (Biolin Scientific AB, Stockholm, Sweden). A 10 μL air bubble was placed on the polyelectrolyte brush grafted PEEK surfaces. The mean value was calculated from 6 measurements. The friction test was performed on Tribostation Type32 (Shinto Scientific Co. Ltd. Japan) by sliding 10 mm diameter stainless steel ball under normal load of 0.49 N in wet condition. Sliding velocity and distance was set at 120 mm/min and 7 mm, respectively. Fifteen tests were conducted per condition to obtain an average value.

3. Results and discussion

3.1. Characterizations of PMTAC-g-PEEK and PSPMK-g-PEEK

Fig. 1 shows typical ATR-FTIR spectra of unmodified PEEK, PMTAC-g-PEEK and PSPMK-g-PEEK. Characteristic peaks were observed at 1651 cm⁻¹ (carbonyl group), 1600 cm⁻¹ (phenyl ring), 1490 cm⁻¹ (phenyl ring) and 1225 cm⁻¹ (ether group) on the PEEK substrate. IR absorption peaks assigned to ester carbonyl group and quaternary amine group are clearly observed at 1725 cm⁻¹ and 953 cm⁻¹ in PMTAC-g-PEEK, respectively. IR absorption peaks assigned to ester carbonyl group and sulfonate group are observed at 1721 cm⁻¹ and 1045 cm⁻¹ in PSPMK-g-PEEK, respectively.

The surface chemical composition of the polyelectrolyte brush grafted PEEKs was further examined by XPS (**Fig. 2**). The XPS survey scan of PMTAC-g-PEEK exhibit the nitrogen (N_{1s}: 401 eV) and chlorine (Cl_{2s}: 266 eV; Cl_{2p3}: 196 eV) peaks, whereas the sulfur (S_{2s}: 232 eV; S_{2p}: 168 eV) and potassium (K_{2s}: 377 eV; K_{2p}: 293 eV) peaks are found in PSPMK-g-PEEK. The chemical composition calculated from the peak intensity corresponds well with the theoretical chemical compositions of PMTAC and PSPMK (**Table S1**). The FTIR and XPS results indicate that the PMTAC and PSPMK chains are successfully introduced on PEEK surface using the surface-initiated free radical polymerization method through UV light induced



Scheme 1. (a) Preparation of polyelectrolyte brushes on PEEK surface. Chemical structures of (b) PMTAC-g-PEEK and (c) PSPMK-g-PEEK.

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