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Improved adaptability of polyaryl-ether-ether-ketone with texture pattern and graphite-like carbon film for bio-tribological applications

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ABSTRACT

With the development of surface treatment technology, an increasing number of bearings, seals, dynamic friction drive or even biomedical devices involve a textured surface to improve lubrication and anti-wear. The present investigation has been conducted in order to evaluate the friction and wear behaviours of textured polyaryl-ether-ether-ketone (PEEK) coated with a graphite-like carbon (GLC) film sliding against stainless steel pin in biological medium. Compared with pure PEEK, the PEEK coated with GLC film shows excellent tribological performance with a low friction of 0.08 and long lifetime (wear volumes are about 3.78×10^{-4} mm^3 for un-textured one and 2.60×10^{-4} mm^3 for textured GLC film after 36,000 s of sliding) under physiological saline solution. In particular, the GLC film with appropriate dimple area density is effective to improve friction reduction and wear resistance properties of PEEK substrate under biological solution, which is attributed to the entrapment of wear debris in the dimples to inhibit the graphitization and the fluid dynamic pressure effect derived from the texture surface to increase the thickness in elastohydrodynamic lubrication (EHL) film during sliding motions. Moreover, the friction coefficient of GLC film under physiological saline solution decreases with the increase in the applied load. With the increasing applied load, the texture surface is responsible for accounting the improved wear resistance and a much lower graphitization of the GLC film during whole test.

1. Introduction

Biological synovial joints, e.g., hip, knee or shoulder joints, are complex and delicate structures capable of lubrication, damping, wear resistance and some other functions [1,2]. The excellent performance is due to the optimized combination of articular cartilage, a load-bearing connective tissue covering the bones involved in the joint and synovial fluid to protect bone-injury [3]. Unfortunately, osteoarthritis or degenerative joint diseases are caused by aging or repetitive injury, which can lead to damage of cartilage and bone [4]. Hence, transplantating prosthetic joint into bone can achieve a relief of pain and improve the joint mobility. However, the bio-compatibility between living tissues and non-living materials is the critical factor that limits the lifetime of implant materials [5]. In a historical and a practical perspective, a broad range of interactive behaviour occurs between tissues and prosthesis (metal or alloy) for substitution of hip and knee joints, and some wear debris particles may be generated in the human body to trigger a series of adverse biological reactions during this process, thus leading to the premature failure of the prosthesis [6,7].

Polyaryl-ether-ether-ketone (PEEK), one of the polymers as substitute for metal alloy in implant replacement [8], exhibits the desirable mechanical properties, high thermal stability, wear and chemical resistance, no toxicity as well as high resistance to gamma irradiation [9–11]. In particular, PEEK has an advantage that the stiffness is much closer to the cortical bone in contrast to metals, ceramics or other polymers, thus reducing the effects of stress shielding after implantation [12,13]. Recent research has also investigated the bio-tribology of PEEK composites as bearing materials and flexible implants used for joint arthroplasty and spine patients [14,15]. Wang et al. have investigated carbon fiber reinforced PEEK composites as bearing surfaces for total joint replacements [14]. It is found that those composites offer a far superior wear resistance compared with ultrahigh molecular weight polyethylene (UHMWPE). Moreover, Kurtz and Devine review the history of how

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PEEK biomaterials come to be increasingly accepted for spine and orthopaedic implants over other high-performance thermoplastics [16]. Nevertheless, reduction of wear is still a major challenge in PEEK research as wear particles are responsible for early loosening of prosthetic devices [8,17]. Currently, graphite-like carbon (GLC) films have been applied in biomedicine due to its low friction and specific wear rate as well as good chemical inertness [18,19]. Moreover, it is well known that medical implants not only experienced the wear from relative motion between bone joints but also subjected to the degradation through the physiological fluids [20,21]. While many authors have addressed that the GLC film has a good compatibility with different types of cells like macrophages, fibroblasts, human myeloblasts, osteoblasts, and so on [13,22]. Thus, GLC film would be one of the optimum candidates for the modification of PEEK.

To improve the prevention of inflammatory and allergic reactions of the GLC film, many researchers have adopted doping metal or non-metal elements in amorphous carbon matrix [23,24]. In this paper, we deposit GLC film on the textured PEEK surface to improve the bio-tribological performance, since the regularly distributed texture surface can generate fluid dynamic pressure effect to increase the carrying capacity of film [25], store lubricating medium to prevent interlocking between contact surfaces [26], and capture the wear debris to reduce abrasive wear [27], thus effectively improving the lifetime and reliability of GLC film. Moreover, laser surface texturing (LST) has been applied to the PEEK surface treatment for bio-tribological applications owing to its versatility, fast adaptability, high precision and cleanness of environment [28]. Kovalchenko et al. have reported that the tribological properties can be significantly improved by LST technology textured steel surfaces [29]. He et al. also verify that appropriate dimple area density by LST technology is effective in enhancing reducing-friction property of titanium alloys substrate under air friction and liquid lubrication conditions [30]. However, the synergistic effect of GLC film and surface texturing on the tribological properties of PEEK under biological medium has not received enough attention and extensive research.

In previous works [21,31], our team has systematically investigated the bio-tribological performance and friction mechanism of PEEK coated with metal or non-metal doping GLC films under biological media. A fundamental aspect of this work is to utilize the texturing design to optimize the bio-tribological performance of GLC film in biological lubricant. The possible friction reduction and wear resistance mechanisms are discussed by probing into the effect of dimple density and applied load on the bio-tribological behaviour of un-textured and textured GLC films. The present paper takes the first step of a wide program and the final objective is to apply the textured GLC film on human joint.

2. Experimental section

2.1. LST of PEEK substrates

The specimens, with a dimension of Ø25 mm × 3 mm, were cut from bulk semi-crystalline PEEK rod and subsequently polished with different grades of diamond paste to obtain a surface roughness of $R_a \leq 140$ nm. Micro-dimple patterns were then created on the surfaces of PEEK substrates through a neodymiumyttrium aluminum garnet laser with a wavelength of 1064 nm, pulse width of 4 ns, spot diameter about 40 μm, using a frequency of 10 kHz and 90% overlapping rate of laser spot, and the specimens were processed with an average power of 10 W at a 5 mm/s traverse speed. After laser texturing, a gentle polishing process was used to remove bulges or burrs around the rim of the dimples. Two dimple area densities were fabricated with the same dimple geometric parameters and labeled as PEEK-T15% and PEEK-T30%, respectively.

2.2. Deposition of GLC film

Prior to deposition, all specimens were ultrasonically cleaned in acetone and alcohol for 20 min and then cleaned with Ar+ ions at a substrate pulsed bias of −500 V in sequence before. The GLC films on the textured and smooth PEEK substrates were obtained by unbalanced magnetron sputtering technique in a multi-target PVD system. Before the deposition of GLC film, Si interlayer was deposited with a Si target in order to enhance the adhesion between the substrate and film. Subsequently, one graphite target (purity 99.95%) with dimensions of $6 \times 76 \times 153$ mm^3 for sputtering carbon was used. A base pressure of 2.0×10^{-3} Pa in the chamber was attained with a turbomolecular pumping system, and then the total pressure was set at a pressure of 0.6 Pa by Ar inflation with a flow rate of 120 sccm. As the pressure of the vacuum chamber was reached, PEEK substrates were sputtered in situ for 15 min with argon plasma at a DC bias voltage of −1000 V and a duty cycle of 50%. Meanwhile, the rotation speed of PEEK substrate was 5 rpm during the deposition process. Finally, GLC film was deposited at a DC current of 1.2 A and a bias voltage of −300 V. Two dimple area densities of 15% and 30% were achieved. The corresponding specimens were labeled as GLC-T15% and GLC-T30%, respectively. The total deposition process lasted for 100 min. The process flow diagram of textured GLC film was shown in Fig. S1 in Supporting information.

2.3. Characterization

The surface topography and cross-sectional micrograph of the as-deposited GLC films were examined by field emission scanning electron microscopy (FESEM, JSM-6701F). Atomic force microscopy (AFM, Benyuan CSPM 4000) with contact mode was used to measure the surface roughness of the GLC film. The nanohardness (H) and Young's modulus (E) of PEEK and as-deposited GLC film were determined by the Nanotest600 nanoindenter apparatus (Micro Materials Ltd.), the indentation depth was about 10% of the film thickness for GLC and 100 nm for PEEK substrate. The chemical states of as-deposited GLC film were analyzed by a PHI-5702 multifunctional X-ray photoelectron spectroscope (XPS) made by American Institute of Physics Electronics Company using K-Alpha irradiation as the excitation source. The binding energies of the target elements were determined at a pass energy of 29.3 eV, with a resolution of about ±0.3 eV, using the binding energy of contaminated carbon (C1s: 284.8 eV) as the reference. The morphology and depth of textured GLC film were measured using a MicroXAM 3D surface profiler. The microstructure of as-deposited GLC-smooth and textured GLC films were characterized by Raman spectroscopy equipped with a 532 nm argon ion laser (Raman, HR800 Raman spectroscopic measurement). The wear tracks of GLC films were checked by scanning electron miscroscopy (SEM, EVO18, ZEISS, Germany).

2.4. Tribological test

A CSM tribometer in the pin-on-plate reciprocating sliding was used for preliminary materials evaluation by friction and wear testing. The amplitude was 5 mm, and sliding frequency was 6.37 Hz corresponding to a velocity of 10 cm s^{-1}. The load of 3 N was applied through a stationary loading system. A 316L stainless steel pin with ball head (6 mm in diameter and surface roughness (R_a) value of 0.02 μm) was employed as counterpart, and the sliding direction was parallel to the LST patterns. The ambient temperature and relative humidity were 23 ± 2 °C and 23 ± 5%, respectively. Two