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Mechanical and biological characteristics of diamond-like carbon coated poly aryl-ether-ether-ketone

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ABSTRACT

Poly aryl-ether–ether-ketone (PEEK) is an alternative to metal alloys in orthopedic applications. Although the polymer provides many significant advantages such as excellent mechanical properties and non-toxicity, it suffers from insufficient elasticity and biocompatibility. Since the elastic modulus of diamond-like carbon (DLC) is closer to that of cortical bone than PEEK, the DLC/PEEK combination is expected to enhance the stability and surface properties of PEEK in bone replacements. In this work, PEEK is coated with diamond-like carbon (DLC) by plasma immersion ion implantation and deposition (PIII&D) to enhance the surface properties. X-ray photoelectron spectrometry (XPS), Raman spectroscopy, and Fourier transform infrared (FTIR) spectroscopy demonstrate successful deposition of the DLC film on PEEK without an obvious interface due to energetic ion bombardment. Atomic force microscopy (AFM) and contact angle measurements indicate changes in the surface roughness and hydrophilicity, and nanoindentation measurements reveal improved surface hardness on the DLC/PEEK. Cell viability assay, scanning electron microscopy (SEM), and real-time PCR analysis show that osteoblast attachment, proliferation, and differentiation are better on DLC/PEEK than PEEK. DLC/PEEK produced by PIII&D combines the advantages of DLC and PEEK and is more suitable for bone or cartilage replacements.

1. Introduction

With increasing human longevity, more health care issues are looming and faster development of novel biomaterials, particularly tissue and organ substitutes, are imperative. Besides good mechanical properties and interfacial biocompatibility, biomaterials used in bone and joint replacements must offer good tissue tolerance without producing cytotoxic, carcinogenic, or mutagenic effects and provoke desirable biological responses *in vivo* [1]. The most popular orthopedic materials are metals such as titanium and its alloys which possess favorable attributes such as bio-inertness, high resistance to fatigue, and non-toxicity [2–5]. However, metals and alloys have some drawbacks. For instance, the elastic moduli of metal alloys are approximately 6–20 times greater than that of bones [6–8] causing bone resorption [9,10]. Moreover, the radiopacity of metal alloys and release of harmful metal ions *in vivo* are of concern. Therefore, it is necessary to develop better biomaterials for applications such as bone or cartilage grafting.

Polymers are receiving more attention as substitutes for metal alloys in orthopedic applications [9–12]. In particular, poly aryl-ether–ether-ketone (PEEK) with the basic structure of $(-C_6H_4-OC_6H_4-O-C_6H_4-CO-)_n$ is one of the candidates. PEEK is a linear polyaromatic and semicrystalline thermoplastic polymer boasting a suitable combination of high strength, stiffness, fatigue, and wear resistance [13]. In addition, it is easy to process, non-toxic [14] while possessing natural radiolucency as well as excellent thermal and chemical stability [15]. The elastic modulus of PEEK is 5 GPa which is closer to that of cortical bone (17 GPa) than titanium alloys (105–120 GPa). Consequently, the effects of stress shielding after implantation can be reduced if PEEK is used to substitute for metal alloys. Unfortunately, being bio-inert and hydrophobic has hitherto limited its applications.

The surface properties of biomaterials can be modified [16–19], and plasma immersion ion implantation and deposition (PIII&D) is particularly useful as a surface modification technique due to its simple operation and non-light-of-sight characteristics which bode well for biomedical implants with a complex shape [20,21]. Diamond-like carbon (DLC) films which have been demonstrated to be biocompatible both *in vitro* [22,23] and *in vivo* [24] possess many other desirable properties including excellent hardness, high stability, favorable tribological properties, and so on [25]. In this work, PIII&D is used for the first time to coat PEEK with DLC. The surface properties of DLC/PEEK are investigated and compared and the osteoblast behavior is also studied systematically.

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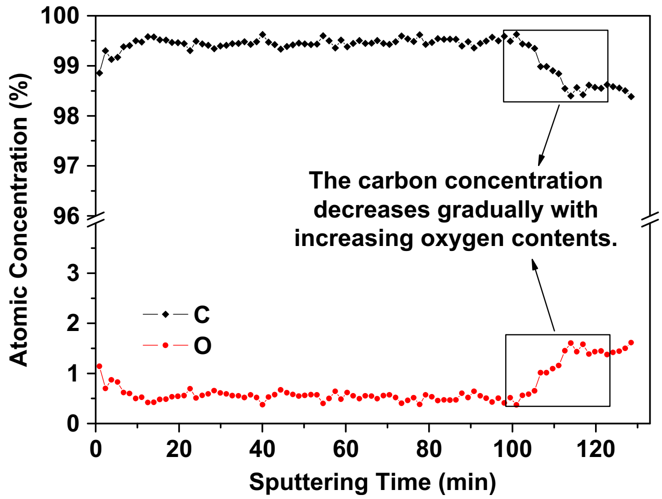

Fig. 1. XPS depth profiles of DLC/PEEK sample.

2. Materials and methods

2.1. Sample preparation

Implantable grade PEEK (Ketron LSG, Quadrant EPP, USA) was machined into round samples with a diameter of 5 mm and thickness of 3 mm, polished, and ultrasonic cleaned before DLC deposition by PIII&D. Prior to film deposition, the substrates underwent Ar^+ sputter cleaning for 3 min to remove surface contaminants and oxide. The base pressure in the vacuum chamber was 1×10^{-5} Torr. A mixture of acetylene (C_2H_2) and argon was subsequently bled into the chamber at an Ar to C_2H_2 flow rate ratio of 5:20 (sccm), and the plasma was triggered using radio frequency (RF). Film deposition was carried out at a constant RF power of 200 W and pressure of 8×10^{-4} Torr. The pulse duration was 200 μs and the repetition rate was 40 Hz. A negative bias voltage −5 kV was applied to the substrates during deposition to improve film adhesion via ion mixing.

2.2. Surface characterization

X-ray photoelectron spectroscopy (XPS) was conducted on a Physical Electronics PHI-5802 to determine the composition and chemical structure of the samples. Elemental depth profiles were obtained by XPS using argon ion bombardment at an approximate sputtering rate of 10 nm/min. The core peaks of C1s and O1s were recorded and analyzed every minute.

Raman spectra excited by a 633 nm Ar^+ laser were acquired to investigate the structural characteristics of the DLC films. The spectra were processed by Gaussian curve fitting and linear background subtraction. The molecular structure in the DLC was determined by a Perkin Elmer Spectrum One Fourier Transform Infrared (FTIR, ATR mode) spectrometry.

An atomic force microscope (AFM) made by Park Scientific Instruments/Auto Probe CP was used to evaluate the surface morphology of the DLC/PEEK and PEEK control (without DLC). The AFM images were obtained using the contact mode and the root-mean-square roughness (RMS) was determined by averaging results obtained from five different areas.

To determine the surface hydrophilicity, static contact angle measurements using distilled water and ethylene glycol as the media were performed by the sessile drop method on a Ramé-Hart (USA) instrument at ambient humidity and temperature. The drop size was 10 μl and each data point is the average of five measurements conducted on different parts of each specimen. Statistical analyses were performed by the student's t test.

The hardness and elastic modulus values were determined by nanoindentation measurements using a three-sided pyramidal diamond (Berkovich) indenter with

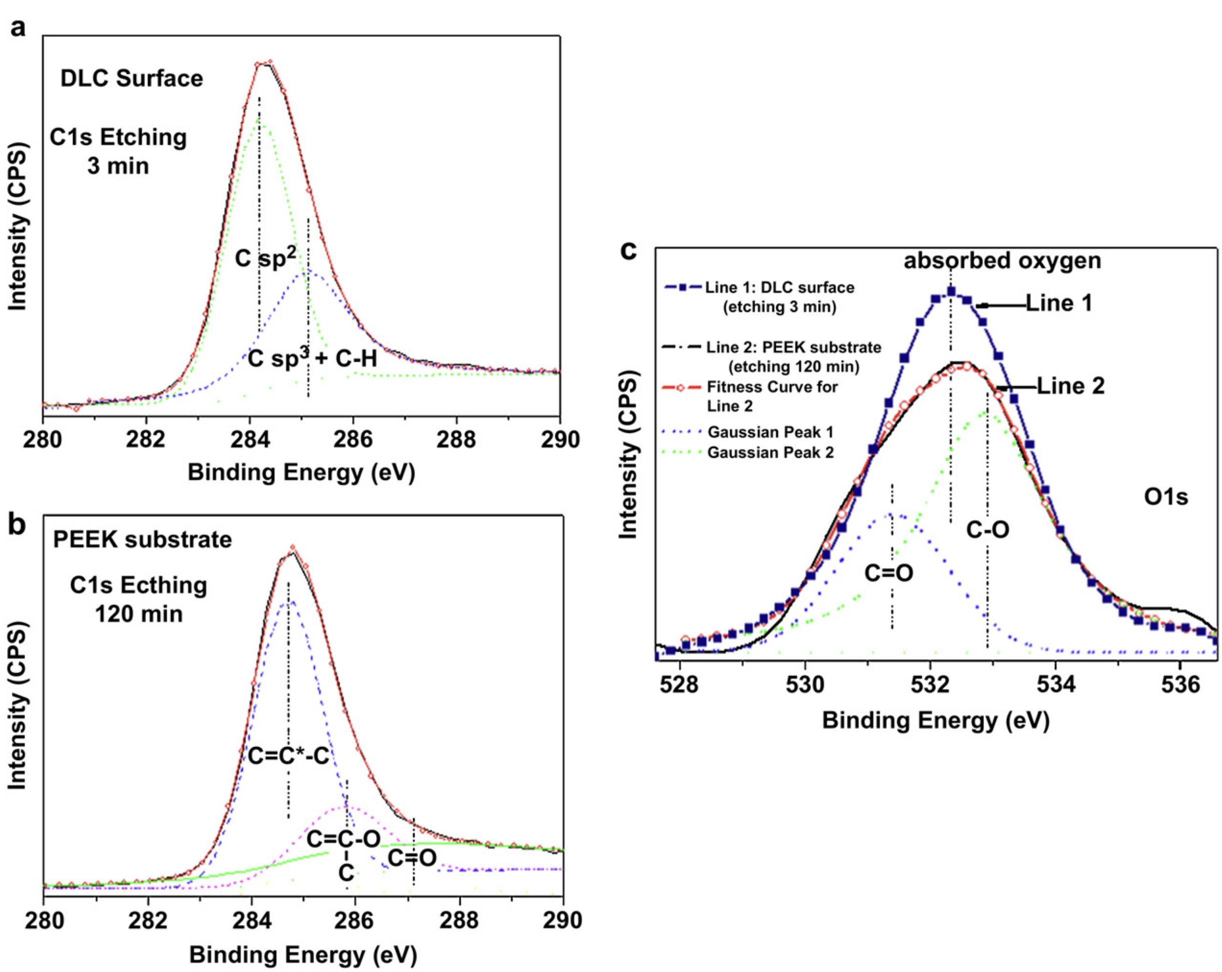

Fig. 2. C1*s* and O1*s* spectra acquired from the DLC film and PEEK substrate: (a) C1*s* at sputtering time of 3 min; (b) C1*s* at sputtering time of 120 min; (c) Shift of O1*s* from 3 min to 120 min.