



# Formation of bone-like apatite on plasma-carboxylated poly(etheretherketone) surface



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## ABSTRACT

Poly(etheretherketone) (PEEK) has attracted considerable research interest as a biomaterial for orthopedic or dental implants due to its bone-like stiffness and reasonable biocompatibility. However, PEEK is naturally bioinert, leading to limited biomedical applications, especially when direct bone-implant integration is desired. In this investigation, carboxyl groups were introduced on PEEK sheet surface using plasma polymerization of acrylic acid (AAc) for the first time. XPS confirmed the presence of carboxyl groups. When placed in stimulated body fluid for 4 weeks, apatite formed uniformly on plasma-carboxylated PEEK sample surface. SEM, EDS and FTIR results confirmed the formation of bone-like apatite. This study provides a simple method to enhance the bioactivity of PEEK without sacrificing its excellent mechanical properties.

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## 1. Introduction

Poly(etheretherketone) (PEEK), a semicrystalline thermoplastic polymer, is approved as an implantable biomaterial by the U.S. Food and Drug Administration, and widely used in a variety of biomedical applications, such as spinal, trauma and orthopedic implants [1]. Not only does PEEK exhibit appropriate biocompatibility, but its outstanding mechanical properties, including its bone-like stiffness unlike that of metal and their alloys which cause bone resorption via stress shielding, are analogous to those of natural bone. However, the bioinert nature of PEEK is not conducive to fast bone–cell attachment [2], and limits its further application to devices, e.g. orthopedic or dental implants, where implants have contact with the bone and tissue fixation at the bone–implant interface is severely critical. Therefore, it is necessary to improve its bioactivity to extend its biomedical applications.

Hydroxyapatite [ $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ , HA], which is similar to the main mineral phase of bone, is considered osteoconductive and directly bonded to bone [3]. Therefore, several studies have been performed to enhance the bioactivity of PEEK via incorporation of bioactive HA fillers or by thermal plasma spray deposition of HA coatings on PEEK surface [4,5]. Unfortunately, these methods have several drawbacks, such as the compromising between mechanical properties and bioactivity or non-uniformity in coating density,

weak adhesion to substrate and chemical inhomogeneity [4,6]. Biom mineralization, a natural biological apatite formation process, can be mimicked *in vitro* to produce calcium phosphate coating on various substrates by soaking the substrates in stimulated body fluid (SBF) with ion concentrations nearly equal to human blood plasma [7]. Surface functional groups play vital roles in nucleating calcium phosphate deposition on substrates in SBF. Abundant studies have confirmed that strong negative groups such as carboxyl groups ( $-\text{COOH}$ ) on substrates surface have a pronounced ability to induce nucleation of calcium phosphate in SBF [7–9]. It is difficult to functionalize PEEK surface on account of its inherent chemical inertness. Fortunately, plasma polymerization is a versatile method for surface modification of non-reactive substrates like PEEK, because plasmas can functionalize surfaces with various chemical groups without altering materials bulk properties, including its mechanical properties [10,11].

The purpose of this study was to enhance the bioactivity of PEEK while retaining its bulk mechanical properties through a simple formation process of bone-like apatite layers on plasma-carboxylated PEEK surfaces.

## 2. Materials and methods

PEEK (Victrex 450G) surface was modified using poly(acrylic acid) (PAA) thin films deposited by plasma polymerization. Distilled AAc was injected into a plasma-induced grafting reactor (Suzhou OPS Plasma Technology Co., Ltd., DJ-01). Vacuum before

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glow discharge was 8 Pa and the working temperature was 20 °C. The PEEK substrates were pretreated with argon gas at 32 Pa and a plasma power of 300 W for 3 min. The plasma was generated using a radio-frequency generator (Suzhou OPS Plasma Technology Co., Ltd., DT-04) operating at 13.56 MHz. Then, the stainless steel reaction chamber was evacuated at 7 Pa and, subsequently, AAC monomers were grafted using the grafting reactor, while maintaining the vacuum at 19 Pa. Plasma polymerization lasted about 5 min at 50 W. After returning the chamber to atmospheric pressure, the samples with plasma-polymerized thin films were removed, and subjected to soxhlet extraction with water overnight to remove any non-bonded polymers or monomers adhered to its surface. These specimens were named PEEK-COOH. The chemical structures of PEEK before and after plasma polymerization were investigated through static water contact angle (Krüss DSA100, 3  $\mu$ l drops) studies and X-ray photoelectron spectroscopy (XPS, XSAM800) at a take-off angle of 20°. The mechanical properties of PEEK and PEEK-COOH were evaluated based on tensile and flexural tests done on a CMT 4503 testing machine (SANS, Shenzhen, China) according to the ASTM D638 and ASTM D790-10 procedures, respectively.

A solution, 1.5 SBF, with an ionic concentrations 1.5 times that of normal SBF, was prepared by dissolving the following chemicals in distilled water in sequence: NaCl, NaHCO<sub>3</sub>, KCl, K<sub>2</sub>HPO<sub>4</sub>·3H<sub>2</sub>O, MgCl<sub>2</sub>·6H<sub>2</sub>O, 1 M HCl, CaCl<sub>2</sub>, Na<sub>2</sub>SO<sub>4</sub>; the ion concentrations (in mM) were as follows: Na<sup>+</sup> 213, K<sup>+</sup> 7.5, Ca<sup>2+</sup> 3.8, Mg<sup>2+</sup> 2.3, HCO<sub>3</sub><sup>-</sup> 6.3, Cl<sup>-</sup> 221.7, HPO<sub>4</sub><sup>2-</sup> 1.5, and SO<sub>4</sub><sup>2-</sup> 0.75. This solution was buffered to pH 7.40 with (CH<sub>2</sub>OH)<sub>3</sub>CNH<sub>2</sub> and 0.1 M HCl at 36.5 °C, additionally, NaN<sub>3</sub> (0.1%, w/v) was added to inhibit bacterial growth [12].

PEEK-COOH and untreated PEEK sheets were immersed in 40 ml of 1.5 SBF in polyethylene bottles and kept in an incubator at 37 °C for 4 weeks; the 1.5 SBF solution was refreshed every week. After incubation, the specimens were gently rinsed with distilled water and after drying, the surface deposits were examined by Fourier transform infrared (FTIR, Nicolet, 200SXV) spectroscopy and scanning electron microscopes (SEM, JSM-6300, Japan) equipped with energy dispersive spectrometry (EDS).

### 3. Results and discussion

XPS survey spectra of PEEK and PEEK-COOH are presented in Fig. 1a and b, respectively. Both show the same peaks, although the relative intensity of carbon and oxygen peaks varied after plasma polymerization of AAC (Table 1), because of AAC's higher oxygen content. This is also indicated by the chemical component ratio O1s/C1s (Table 1). In comparison with PEEK (Fig. 1c), a new contribution at 289.0 eV, typical of carboxyl groups [13,14] and in good accordance with previously published data on plasma-deposited AAC film or plasma-induced grafted polymerization of AAC onto various substrates [15,16], is visualized in the high-resolution C1s spectra of PEEK-COOH (Fig. 1d). Additionally, the water contact angle decreased dramatically from 90.2° ( $\pm$  1.29) to 20.4° ( $\pm$  2.25) after plasma polymerization, which modifies the first few layers of the surface while keeping the bulk material properties [11]. Therefore, the tensile and flexural strengths (MPa) of PEEK-COOH, respectively 87.32 ( $\pm$  3.31) and 135.82 ( $\pm$  2.27), were not significantly different ( $P > 0.05$ , Student's *t*-test) from

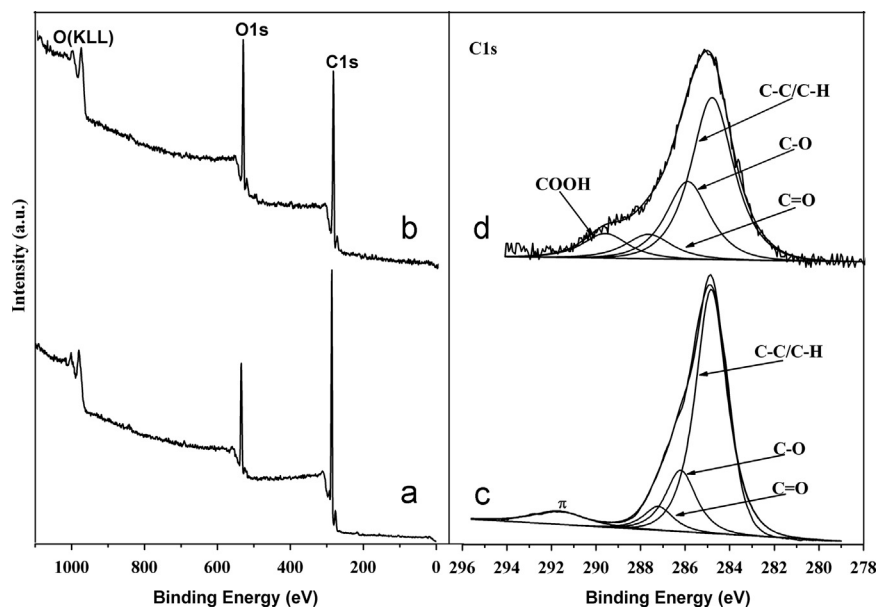


Fig. 1. XPS survey scan (on the left) for (a) PEEK and (b) PEEK-COOH; and C1s spectra (on the right) for (c) PEEK and (d) PEEK-COOH.

Table 1  
XPS analysis of PEEK and PEEK-COOH.

B.E. (eV)	Attribution	PEEK			PEEK-COOH		
		Relative composition	Element (%)	O1s/C1s	Relative composition	Element (%)	O1s/C1s
284.8	C-C/C-H	70.11	87.08	0.164	55.40	75.66	0.269
285.9	C-O	17.11			26.86		
287.2	C=O	6.42			8.95		
289.0	COOH	-			8.79		
291.7	$\pi$	6.36			-		

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