Surface & Coatings Technology 265 (2015) 92–98

Contents lists available at ScienceDirect

Surface & Coatings Technology

journal homepage: www.elsevier.com/locate/surfcoat

Evaluation of the surface properties of PEEK substrate after two-step plasma modification: Etching and deposition of DLC coatings

Witold Kaczorowski *, Damian Batory, Witold Szymanski, Piotr Niedzielski

Institute of Materials Science and Engineering, Lodz University of Technology, 1/15 Stefanowskiego St., 90-924 Lodz, Poland

ARTICLE INFO

Article history:
Received 8 October 2014
Accepted in revised form 20 January 2015
Available online 28 January 2015

Keywords:
Diamond-like carbon
PACVD
Nanoindentation
Atomic force microscopy (AFM)
X-ray photoelectron spectroscopy XPS
Raman spectroscopy

ABSTRACT

This paper presents results of research on the change of the surface properties of poly (ether–ether–ketone) PEEK substrates under the influence of two-stage processes of the coatings production. Those modification processes included the etching procedure in oxygen, nitrogen and methane atmosphere, as well as synthesis of carbon coatings in methane plasma. After both the etching process and the synthesis of diamond like carbon DLC coating, the modified samples were analysed in terms of the changes in surface geometry, its chemical composition, nano-scale mechanical properties, the contact angle and the surface free energy, as well. The work also includes a comparison of changes in the friction coefficient for each set of process parameters applied in the synthesis of carbon coatings.

1. Introduction

PEEK is a polymeric material that is becoming increasingly dedicated to be used in the biomedical engineering [1–4]. In the literature, studies related to the implementation of PEEK, inter alia, to: disc arthroplasty [5], dental implants [6], reconstruction of the cranial vault [7], bone-implant [8] hip prosthesis [9], and artificial heart valve disks [2,10] can be found. Moreover, apart from biomedical applications, PEEK is also proposed in the structures dedicated to the automotive industry and electronics [11,12]. Such a broad application of the described polymer is caused by its significant useful parameters, especially biological [13–15] and mechanical ones [1,9,11]. Additionally, today the possibilities of application of PEEK are determined by the specific treatments to improve its surface properties, dominated by the modifications using both atmospheric and low pressure plasmas [4,10,16–18]. In most reports in the literature, ionized gas is used for etching or surface functionalization, less for the synthesis of coatings (e.g., hydroxyapatite HAp, diamond-like carbon DLC). However, this latter aspect of plasma techniques, despite the difficulties even in the appropriate matching of the Young's modulus of polymer and the coating, seems to be one of the most interesting ways to modify the surface of PEEK.

According to the literature, the plasma modification of polymer substrates is useful for changing their surface properties. Due to that fact, it is possible to change the surface roughness, the cross-linking ratio, to produce the specific chemical bonds or coatings on their surface or to combine the chains of other polymers [19]. The subject of this work includes, in particular, the manufacturing processes of DLC coatings on the PEEK substrates. According to the literature data, the DLC coatings connected with the substrate material by an intermediate layer expose the greatest application potential. This layer should increase the mechanical parameters (e.g., Hardness, Young's modulus) of the polymer, by their gradual change on the cross-section. To meet those requirements, the most common synthesis procedures are preceded by the processes of polymer cross-linking [20,21]. In the literature we can find various divisions of carbon coatings. However, most often we meet with the interpretation of the results based on the ternary phase diagram proposed by Ferrari and Ferrari and Robertson [22,23]. Hydrogenated amorphous carbons coatings can be also divided according to the band gap value. Here we have polymer-like a-C:H (PLCH) coatings with a band gap of more than 2 eV, diamond-like a-C: H (DLCH) coatings with a band gap of 1 to 2 eV and graphite-like a-C: H (GLCH) coatings with a band gap of less than 1 eV [24]. Of course, the one and the other interpretation are linked to the mutual proportions of sp^3 C – C, sp^2 C═C bonds and hydrogen content as well. Each of these classes of carbon coatings will be characterised by their individual properties due to which they find specific applications. Each of them is also manufactured under strict plasmochemical conditions adjusted to the modified substrate (the material and dimensions).

The objective of the presented paper is to show the changes of the surface properties of PEEK remaining under the influence of two-step modification: etching and the production of carbon coatings performed using the CVD reactor with radio frequency plasma discharge. These processes, combined together, enable to achieve the excellent mechanical properties [10]. The main purpose of this work was to analyse the changes of PEEK surface occurred after each of the processes (etching,

* Corresponding author. Tel.: +48 42 631 30 69; fax: +48 42 631 30 38.
E-mail address: witold.kaczorowski@p.lodz.pl (W. Kaczorowski).

http://dx.doi.org/10.1016/j.surfcoat.2015.01.053
0257-8972/

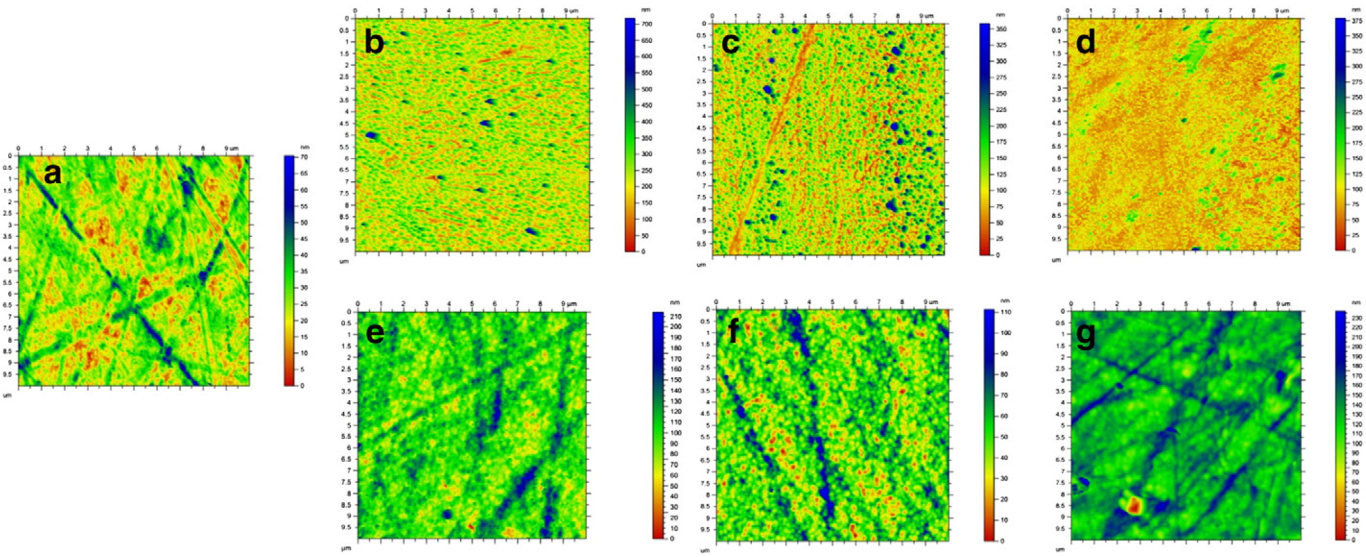

Fig. 1. AFM pictures of: a) unmodified substrate, PEEK etched in: b) oxygen plasma, c) nitrogen plasma, d) methane plasma, carbon coating deposited onto PEEK using the preliminary plasma processing in: e) oxygen, f) nitrogen, g) methane.

coating synthesis) and to determine their effect on the final properties of the obtained composite (PEEK/carbon coating). In the planned experiment, the etching processes were designed to provide the best wear resistance of deposited coatings.

2. Material and methods

Polymer PEEK OPTIMA LT1 was used for the research. The samples with a diameter of 14.4 mm and 2.5 mm thick were made by the high-pressure injection method. Before conducting the modification processes, the samples were cleaned for c.a. 10 min in the isopropyl alcohol using an ultrasonic washer and dried in the stream of compressed air. Prepared PEEK discs were placed in the chamber of plasmochemical reactor on the water cooled high frequency electrode. Processes of modification of PEEK substrates were carried out using the hybrid MW/RF PACVD (microwave/radio frequency plasma assisted chemical vapour deposition) technology, working with plasma frequency of 13.56 MHz [25]. The choice of excitation frequency was based on the results obtained in our earlier work [10]. Plasma etching process have been carried out using the three process gasses: oxygen, nitrogen and methane, introduced into the working chamber in the amount of 10 sccm, using a constant negative autopolarization bias of 500 V within the time limit of three minutes. Application of methane and oxygen for the etching procedure was dictated by their different influence on the PEEK surface [26,27]. In case of the methane plasma the quality and quantity of bonds formed on the surface are determined by its degree of dissociation. On the other hand due to the application of oxygen plasma it is possible to create the C – O bonds on the surface of PEEK substrates, which will be characterized by the highest bonding strength [27]. Processes of carbon coatings synthesis were carried out subsequently after conducting the etching procedure. Diamond like carbon layers were manufactured using methane in an amount of 60 sccm, under the negative bias of 500 V within the time limit of eight minutes. Thicknesses of synthesised coatings were ca. 200 ± 20 nm. Observation of morphology and surface topography was carried out using an atomic force microscope Veeco Multimode, equipped with a Nanoscope V (Bruker Corporation, USA) controller, operating in the intermittent contact mode (tapping mode). Measures of hardness (H), Young's modulus (E) of researched coatings were conducted using MTS NANO INSTRUMENTS device, model G 200. For nanoindentation a diamond Berkovich tip with roundness of 20 nm and the continuous stiffness measurement (CSM) mode was used. The overall penetration depth for all samples was 1000 nm. The values of hardness and modulus of elasticity for each substrate configuration were registered at different depths depending on: superposition of the mechanical properties of the layer and the substrate and the thickness of the layer as well. For the unmodified samples the average values of H and E were calculated for the range of penetration depth between 103 and 967 nm, which corresponds to normal forces in the range between 0.066 and 5.1 mN. For PEEK substrates after the etching process the minimum depth of penetration (h_{min}) for which values of H and E were determined was 44 nm and the maximum (h_{max}) was 135 nm, which corresponds to the maximum forces in the range of 0.02–0.12 mN. Whereas for substrates modified with carbon coatings H and E values were registered for $h_{min} = 7.7$ and $h_{max} = 51$ nm, which corresponded to forces of 0.06 and 0.11 mN respectively. The penetration depth in all cases of substrates modified with carbon coatings did not exceed 25% of the thickness of the layer. The tip shape was calibrated by conducting the experiments on a

Table 1
The analysis of the surface geometry of modified and unmodified PEEK substrates.

Roughness parameters/SD [nm]	Type of modification			
	PEEK	O_2/CH_4[a]	N_2/CH_4[a]	CH_4/CH_4[a]
Ra	4.70 ± 0.58	47.00 ± 6.90	30.60 ± 3.88	16.20 ± 3.06
		12.40 ± 1.89	9.81 ± 1.31	9.64 ± 3.00
Rz	26.60 ± 3.56	248.00 ± 44.20	168.00 ± 20.20	92.80 ± 19.70
		65.50 ± 10.80	52.30 ± 7.65	49.00 ± 14.70
RMS	5.90 ± 0.73	57.40 ± 8.89	38.00 ± 4.90	20.40 ± 4.30
		15.30 ± 2.34	12.20 ± 1.64	12.00 ± 3.86

[a] The first values in each chart cell correspond to data obtained after the process of etching, second ones — after etching and deposition.