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Influence of atmospheric pressure dielectric barrier discharge on wettability and drying of poly(ether-ether-ketone) foils

Radka Štefaníková, Tereza Kretková, Anna Kuzminova, Jan Hanuš, Mykhailo Vaidulych, Ondřej Kylián*, Hynek Biederman

Department of Macromolecular Physics, Faculty of Mathematics and Physics, Charles University, V Holešovickách 2, 180 00, Praha 8, Czech Republic

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ABSTRACT

Wettability and water droplet drying dynamics on poly(ether-ether-ketone) (PEEK) foils treated by atmospheric pressure air dielectric barrier discharge (DBD) has been investigated. It has been found that plasma treatment causes significant increase of PEEK wettability that is predominantly connected with alterations of its chemical composition (oxidation) induced by DBD plasma. The hydrophilization of PEEK surface was not temporally stable and substantial increase of water contact angle up to 67° was observed with increasing storage time, which is consistent with loosening of polar groups as confirmed by means of XPS. Characteristic restoration time of the contact angle was 6.7 days. Furthermore, a large alteration of the dynamics of water droplets drying on PEEK after the plasma treatment was also observed: whereas for untreated PEEK three drying phases were clearly distinguishable, the phase of constant contact angle disappeared in the case of PEEK exposed to the atmospheric pressure air plasma. In spite of substantial decrease of PEEK wettability with storage time the constant angle phase didn't appear within 51 days after the plasma treatment. As a result of this plasma treated and aged PEEK exhibits much higher water contact hysteresis as compared to untreated PEEK. This effect may be explained by the formation of randomly distributed nanostructures on PEEK surface exposed to DBD plasma that increase the spatial heterogeneity of the PEEK surface and enhance droplet pinning during its drying.

1. Introduction

Poly(ether-ether-ketone) (PEEK) is a high-performance polymer consisting of an aromatic backbone molecular chain interconnected by ketone and ether functional groups (Fig. 1a). The first mention of PEEK in the literature dates back to the early 80s of the last century [1]. Since then, PEEK has become widely utilized in various fields, with global market expected to reach USD 765.7 million by 2020 [2]. The possible applications of PEEK include aerospace, automotive and medical industries, where it is considered as a promising candidate for replacing metal implant components [3,4]. The reasons for this are outstanding properties of PEEK such as its chemical and thermal stability, processing flexibility, good mechanical properties, as well as resistance to radiation damage. However, similarly to other common polymers, PEEK possesses relatively low surface energy and low biocompatibility, which represents a serious obstacle for its broader use.

Among various methods developed with aim to improve surface properties of polymeric materials, non-equilibrium plasmas are widely used as they enable for tailoring the surface characteristics of polymers without compromising their bulk properties. In this case the surfaces of polymers are subjected to fluxes of energetic ions, electrons and photons or chemically active radicals produced in the plasma volume. The plasma treatment of polymers, including PEEK, was traditionally performed at low pressures [5–11]. It has been shown that this results in a rapid alteration of the chemical structure of surfaces of treated polymers and with it associated changes in their surface energy, chemical composition as well as surface morphology. In the case of PEEK the low pressure plasma treatment operated in different gases revealed a dramatic decrease of water contact angle [6,7,11], and, at certain conditions, also a rapid increase of surface roughness [12]. Furthermore, markedly higher peel and lap-shear adhesion to plasma treated PEEK as compared to untreated PEEK as well as its enhanced biocompatibility were also reported [10,13].

However, the necessity to use relatively costly vacuum equipment triggered the interest in plasma systems that enable plasma generation at atmospheric pressure. One of such systems that can be operated in laboratory air, which substantially reduces the treatment costs, is dielectric barrier discharge (DBD), i.e. discharge operated in between two electrodes among which at least one is covered by thin dielectric layer [14,15]. Indeed, numerous studies performed on different polymers

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* Corresponding author.
E-mail address: Ondrej.Kylian@mff.cuni.cz (O. Kylián).

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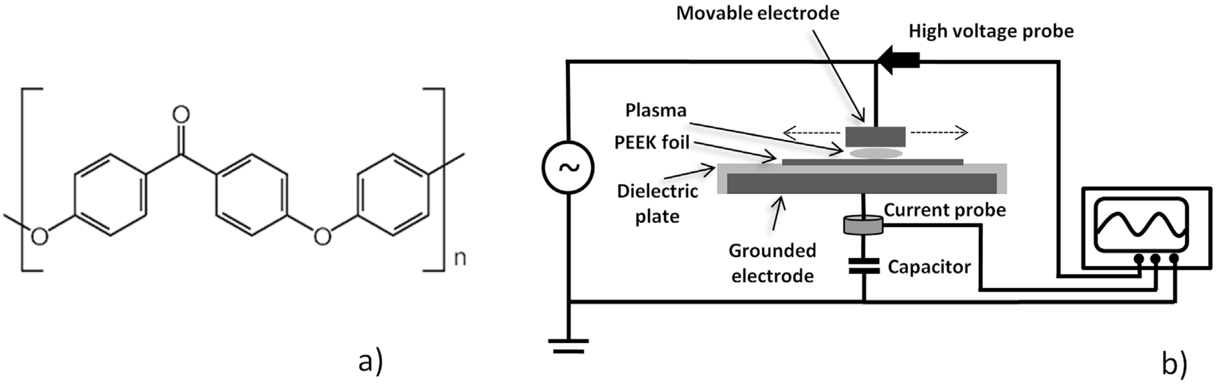

Fig. 1. a) Chemical structure of PEEK. b) Schematic drawing of DBD reactor used for PEEK air plasma treatment.

clearly demonstrated the capability of various types of DBDs operated in air at atmospheric pressure to effectively modify a wide range of conventional polymers (e.g. Refs. [16–25]), including PEEK [20,22,25–27], and to increase their surface energy and wettability. Unfortunately, the changes in surface wettability induced by plasma treatment are in general not temporally stable: a gradual decrease of the wettability was observed with increasing storage time of plasma treated PEEK. For instance, Borcia et al. [22] reported increase of water contact angle of DBD plasma treated PEEK from approximately 40° measured immediately after the treatment up to 60°-70° measured 30 days after the treatment. Similar results were observed also by Upadhyay et al. [20]. This effect, that is sometimes termed hydrophobic recovery, is explained either by reorientation of polar functional groups on a polymeric surface, outward-diffusion of low-weight oligomers or additives and/or by accumulation of air-born impurities [28–31].

Besides wettability and its temporal stability also dynamics of droplet drying is important phenomenon. This process, which is often overlooked in the works devoted to the plasma treatment of polymers, strongly influences the morphology of stains left after the evaporation of aqueous suspensions and is thus crucial in various applications such as for instance ink-jet printing [32], self-assembly or patterning [33], drop-coating techniques for biodetection [34] or even for fabrication of novel biological assays [35].

The main aim of this study is evaluating the effect of DBD plasma treatment on PEEK foils, with emphasis given not only to the wettability changes, but also to the evaluation of the dynamics of water droplets drying and to the effect of storage time on plasma treated PEEK surface.

2. Materials and methods

A schematic diagram of employed DBD treatment system that was previously used for processing of various common polymers [23–25] is shown in Fig. 1b. The plasma was operated in open air at a pressure of 1 atm in the filamentary mode between two parallel planar electrodes, the top one conductive (stainless steel, 20 × 20 × 50 mm) and the bottom one (72 mm × 160 mm) covered with dielectric (sintered alumina, 1 mm thick). The electrodes were spaced at a distance of 2.0 mm.

The plasma was driven with a high-voltage (~10 kV), low-frequency (~20 kHz) power supply. The power, which was measured from Lissajous figures (discharge voltage measured by a high-voltage probe versus the voltage on a 100 pF current-integrating capacitor in series with the discharge, as described e.g. in Ref. [36]), was 30 W.

The strips of PEEK foils (Goodfellow, 200 μm thick and approximately 10 cm^2, used as received) were placed on the dielectric covered bottom electrode. The upper electrode was scanning over the PEEK up to 40 times, which corresponded to the total exposure time of PEEK foils to DBD plasma up to 20 s. This dynamic mode of operation allowed to treated relatively large samples as well as it significantly lowered the thermal load on treated foils – according to previous experiments [25] the PEEK temperature was after 1 min exposure time 60°.

Surface wettability and surface energy of PEEK foils before and after the plasma treatment was evaluated by a goniometer of custom construction that consisted of substrate holder, manually operated syringe and a camera connected to a PC. Surface free energy as well as its polar and dispersive components were determined from the contact angles of deionized water and diiodomethane (Sigma Aldrich) according to Fowkes' theory [37]. Each value represents average of three droplets (volume 3 μl).

The drying dynamics was evaluated by means of an evaporation method [38] using the same goniometer as for surface wettability and surface energy measurements. The water droplets were manually placed onto the PEEK foils by a syringe and allowed to dry under ambient conditions. The images of the drying droplets were taken from side by a camera connected to PC with an interval of 10 s. Image analysis of water droplets was done to determine the contact angle and contact radius. The measurements were performed at room temperature (25–26 °C) and relative humidity 35–40%. In addition, the mass reduction of the water droplets during their evaporation was monitored by Mettler Toledo XS205 balances with a time step of 60 s.

Chemical changes of PEEK foils induced by DBD treatment were determined by X-ray photoelectron spectroscopy (XPS) that was carried out using a XPS spectrometer equipped with a hemispherical analyzer (Phoibos 100, Spec). The XPS scans were acquired at a constant take-off angle of 90° using Al Kα X-rays source (1486.6 eV, 12 kV, 200 W, Specs). Survey spectra that were used for the evaluation of surface elemental composition were acquired for binding energies in the range of 0–1100 eV with a step of 0.5 eV at pass energy of 40 eV. High resolution spectra of C1s and O1s regions were acquired with a step of 0.05 eV at pass energy of 10 eV with 10 scans. Recorded XPS spectra were referenced to the binding energy of C-C/C–H bonds of carbon atoms in the phenyl ring at a binding energy of 284.7 eV. The fitting of high resolution XPS spectra of C1s and O1s regions was performed after Shirly background subtraction with mixed Gauss-Lorentzian lines (50% Gaussian and 50% Lorentzian) using the CasaXPS software following the procedure described in Ref. [39].

Morphology of the PEEK foils was evaluated by atomic force microscopy (AFM, Quesant Q-scope 350) operated in the semi-contact mode using ACLA-10 Si probes (tip radius < 10 nm, nominal spring constant 58 N/m, AppNano). The acquired AFM images (10 μm × 10 μm scans, scan rate 2 s, resolution 512 × 512 points) were analyzed by Gwyddion software.

3. Results and discussion

3.1. Effect of DBD treatment on morphology, surface chemical composition and wettability

The first step of this study was the evaluation of wettability changes