MODIFICATION OF VARIOUS POLYMER SURFACES USING ATMOSPHERIC PRESSURE REDUCING PLASMA

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Abstract

This paper presents the results of surface modification of polymers induced by atmospheric pressure non-isothermal plasma generated in reducing atmosphere. The technology based on diffuse coplanar surface barrier discharge (DCSBD) was used with the aim to achieve highly hydrophobic surfaces. One rigid (polymethylmethacrylate-PMMA) and three flexible polymers (PMMA, polytetrafluoroethylene-PTFE and polyethylene terephthalate-PET) were modified by plasma. The changes in wetting phenomena and surface free energy were observed depending on plasma treatment conditions. The most significant modification occurred on flexible PMMA and PTFE. Using pure hydrogen plasma, we were able to achieve an increase of water contact angle up to ~115° from the original value 78° (untreated PMMA). On the contrary, the water contact angle on PTFE decreased to ~91° from the value 109° (untreated PTFE). Observed etching process on polymer surfaces and the changes in surface roughness were detected by a scanning electron microscopy (SEM) and atomic force microscopy (AFM).

Keywords: Non-isothermal plasma, reduction atmosphere, PMMA, PET, PTFE

1. INTRODUCTION

Plasma treatment of polymer surfaces is nowadays a highly exploited technique used to induce changes in surface wettability, for adhesion improvement, surface functionalization, sterilization, cleaning and etching. Plasma processing is widely applied in the industry e.g. for the production of functional coatings, in microelectronics, the modification of packaging materials as well as biomaterials.

The non-isothermal atmospheric pressure plasma sources provide the solution for efficient improvement of surface properties of low adhesive, chemically inert and heat sensitive polymeric materials such as polymethylmethacrylate-PMMA, polyethylene terephthalate-PET and polytetrafluoroethylene-PTFE.

Plasma-induced etching and surface structuring of polymers can result in the change of its wettability and surface morphology without the undesirable modification of the bulk and optical properties. The nano- and micro-scale surface structuring can result from the short and longer plasma exposures, respectively [1,2].

Plasma etching is widely studied for the fabrication of superhydrophobic and superoleophobic surfaces on polymers [3] with subsequent self-cleaning properties [4]. Ellinas et al. and Tserepi et al. [5,6] studied attachment of cells on highly hydrophobic surfaces for different biological applications. For this process, the low-pressure plasma generated mostly in Ar, He, O_2 and fluorocarbons containing gases is used [7,8].

Dry etching of different polymeric materials by plasma generated in various gas mixtures at atmospheric pressure was recently reported by authors of [9-11]. Reducing plasma can also be used for the improvement of the wettability and adhesion properties of chemically highly inert materials, such as PTFE [12,13].

In this paper, the diffuse coplanar surface barrier discharge (DCSBD), capable of meeting the industrial production requirements in reducing atmosphere, was used for surface etching and structuring at atmospheric pressure. The effect of high energetic plasma, with the electron density of 1.3×10^{16} cm^{-3} and mean electron

temperature of approx. 19×10^3 K [14], generated in pure hydrogen was tested on one rigid (PMMA) and three flexible (PMMA, PTFE, PET) polymeric substrates.

2. EXPERIMENTAL

Three flexible polymeric samples and one rigid polymer sheet were used in this work. Flexible PMMA foil (0.05 mm, DENZ BIO-MEDICAL GmbH, Austria), PET foil (0.25 mm) and PTFE foil (0.25 mm both from GOODFELLOW CAMBRIDGE Ltd., England) were used as samples. Moreover, 2-mm thick Acrylic sheet (CHO CHEN Ind. Co., Ltd, Taiwan) was also tested.

The polymers were treated by plasma generated by DCSBD plasma source. Single DCSBD unit generated a thin plasma layer on area of 20×8 cm^2 when powered by a high voltage generator VF700 (LIFETECH s.r.o., Czech Republic) with the frequency of 15 kHz and input power of 400 W. The samples were treated at the distance of 0.2 mm from the DSCBD ceramics in a dynamic regime. The schematics of DCSBD, as well as a picture of plasma generated in pure hydrogen, can be seen in **Figure 1**.

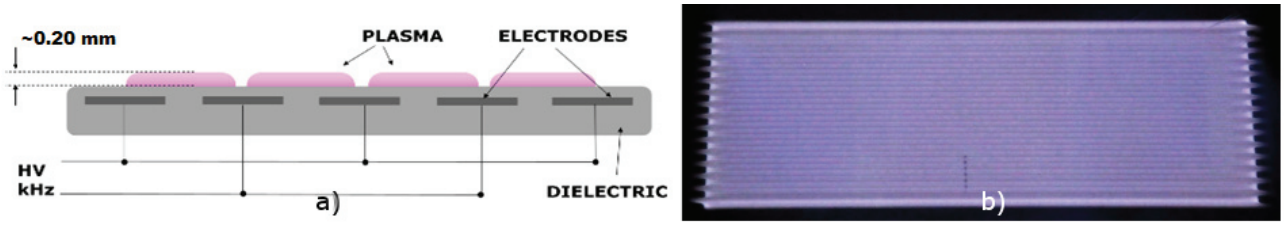


Figure 1 a) Schematics of DCSBD plasma unit and b) a picture of DCSBD plasma in pure hydrogen [15]

The DSCBD plasma source was placed in a sealed reactor chamber of volume approximately 2 l. The gas flow of pure hydrogen (99.998 %, MESSER TECHNOGAS s.r.o., Czech Republic) was kept at 1 l/min during the plasma treatment.

The changes in water contact angle (WCA) and surface free energy (SFE) were measured using surface energy evaluation system See System (ADVEX INSTRUMENTS s.r.o., Czech Republic). The WCA value was estimated as an average of contact angle measurement of 10-15 water droplets with a volume of 1 µl. The SFE value was measured using the average contact angles of three different liquids: water, ethylene glycol and diiodomethane (SIGMA-ALDRICH, Inc., USA), estimated in analogy with the WCA measurement. The surface free energy was then calculated according to the Owens-Wendt regression method [16].

The morphological changes of polymer surfaces after the plasma treatment were measured using Scanning Electron Microscope Mira3 (TESCAN s.r.o., Czech Republic) with an accelerating voltage of 5 kV using secondary electron emission detector. To prevent charging of the polymer surface, the samples were coated with 10 nm of Au/Pd composite layer. The change of surface roughness was measured using Atomic Force Microscope NTEGRA Prima (NT-MDT, Russia) in a semi-contact mode.

3. RESULTS AND DISCUSSION

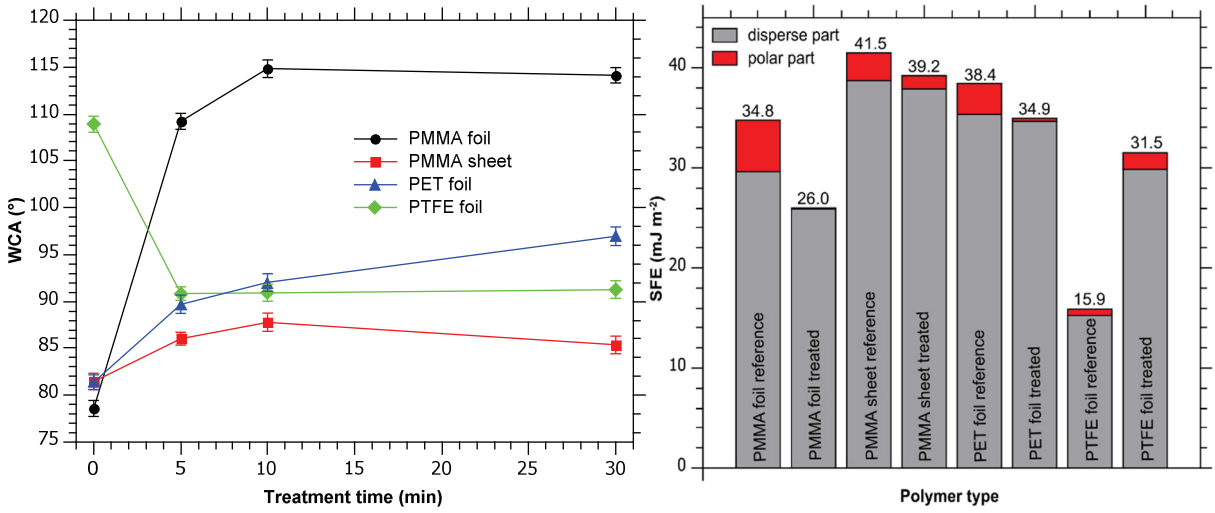
Figure 2 shows the results of contact angle measurement (a) and surface energy analysis (b) of plasma-treated polymers after 5, 10 and 30-min modification in pure hydrogen DCSBD plasma.

The contact angle analysis revealed the increase of WCA on both PMMA samples and PET surface. The maximum value of WCA on both PMMA substrates was achieved already after 10 minutes of treatment by reducing plasma. The increase of WCA was rather steep for the PMMA foil from initial 78.6° to 109.2° after 5 minutes and to 114.8° after the 10 minutes of treatment. The slighter increase of WCA on PMMA sheet can be related to the thickness and rigidity of the substrate. The observed PMMA changes after DCSBD plasma

treatment are similar to the results of chemical fluorination of PMMA presented by [17] and the treatment of PMMA by fluorocarbon plasma at low-pressure [8].

The WCA on PET foil increased from initial 81.4° to the measured maximum 97.0° after 30 minutes of the reduction plasma treatment. The slower increase of WCA and the previous work of Krumpolec et al. [10] is indicating, that the further change in contact angle can be achieved by the plasma etching of the substrate surface after extended treatment time.

The surface energy of PMMA and PET surfaces decreased because of a decrease of polar component of SFE. In both cases, the disperse component of SFE mostly preserved its value. It is apparent that a decrease of SFE by reducing plasma is due to the substantial decrease of the polar component and the mechanical structuring of the substrate surface observed by microscopy, which will be described in more detail later.



a) b)

Figure 2 The WCA (a) and SFE values (b) measured on plasma-treated polymer surfaces after 30 minutes in hydrogen DCSBD plasma and the comparison with reference values

On the other hand, the wettability of PTFE showed different results. A decrease of WCA from reference value 108.9° to 90.8° was observed after 5 minutes exposure in hydrogen plasma. No further decrease of WCA with increasing treatment time was observed.

Similar WCA and SFE results were observed by Jie-Rong and Wakida [12] who modified PTFE in low-temperature low-pressure hydrogen and methane plasma for several minutes. Authors related the result of an increase of the polar and disperse component to the plasma induced changes of chemical composition on the surface. The electron spectroscopy for chemical analysis revealed a decrease of fluorine concentration and an increase of carbon, oxygen and nitrogen intensity on the PTFE surface. However, authors didn't analyse the changes in surface morphology.

Figure 3 and **Table 1** present the roughness data measured on PMMA samples. The AFM analysis revealed similar tendencies in the roughness increase. The measured roughness for both substrates increased approx. 10 times after 10 min treatment in hydrogen DCSBD plasma. The maximum average roughness after the 30 min treatment achieved similar values for flexible PMMA and PMMA sheet. However, the structures created on the surface have different density, shape and diameter of the peaks. As revealed, the shape of the structures significantly influences the surface wettability.

Table 1 The average roughness of flexible and rigid PMMA after the DCSBD plasma treatment in pure hydrogen (area 5×5 μm^{-2})

Treatment time (min)	PMMA foil		PMMA sheet	
	Roughness (nm)	Δ (nm)	Roughness (nm)	Δ (nm)
0	2.8	0.1	1.1	0.2
5	20.1	0.3	7.1	3.2
10	22.7	4.5	11.6	3.0
30	65.8	1.4	59.1	3.9

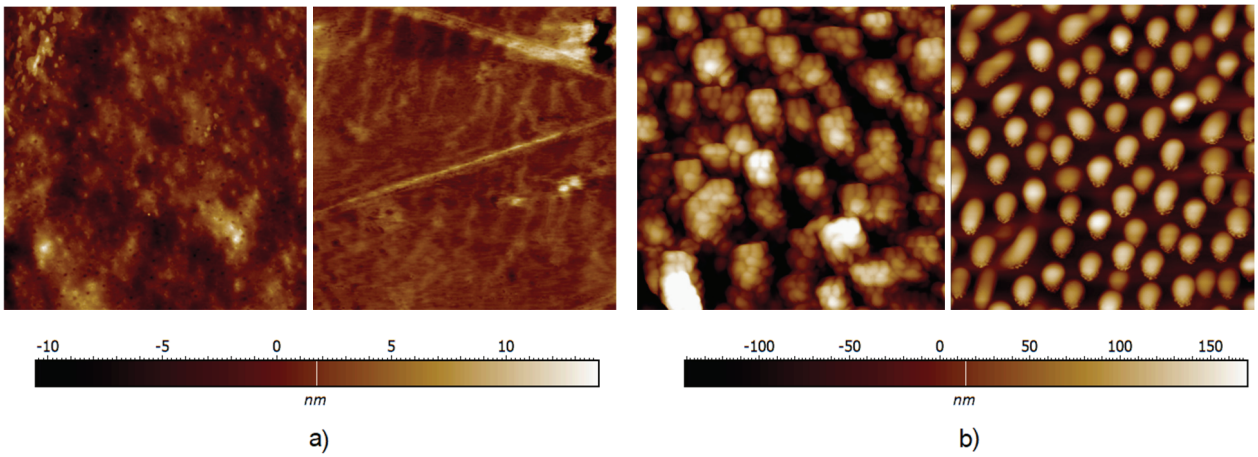


Figure 3 The AFM images (from left to right) of flexible and rigid PMMA references (a) and after 30 min (b) of DCSBD plasma treatment in pure hydrogen (area 5×5 μm^{-2})

SEM images show the morphology of plasma-treated polymers in **Figure 4**. A time-dependent formation of pillar and dot like structures on both PMMA and PET foils was observed. This type of morphology was reviewed in [18] and associated with bactericidal properties of naturally occurring, self-cleaning superhydrophobic surfaces. Coen et al. [1] observed a similar effect on PMMA foil treated by low-pressure helium plasma. As reported, small pillar structures (called worm-like chains) appeared after short treatment times. The thicker grooves were formed after the further (longer) treatment with small pillars preserved on top. Simultaneously, the authors linked this similar time-dependent change of the structure with kind of melting process involving chain scission and etching effect.

The SEM microscopy of PTFE surface revealed the arise of root-like nanoscale lines on the surface. These structures had no effect toward the improvement of surface hydrophobicity. In [1], the root-like structure grew more visibly after several minutes of helium plasma treatment. This effect was explained as the etching of amorphous part of the polymer. Then the appearing root-like structures can be composed of a backbone of crystallised polymer chains surrounded by the amorphous part. This assumption can be verified by long-lasting etching by atmospheric pressure hydrogen plasma treatment in the future.

4. CONCULUSION

The effect of atmospheric pressure DCSBD plasma generated in pure hydrogen was studied on one rigid substrate and three different polymeric foils. The change of the wetting phenomena towards hydrophobic properties and structuring of the surface was confirmed for both PMMA samples and PET foil. The contact angle analysis performed on these substrates revealed a substantial decrease of polar component of surface energy. The microscopic analyses showed the change of morphology and formation of submicron structures

on both PMMA and nanoscale structures on PET substrate. On the other hand, hydrogen plasma led to the increase of contact angle and improvement of wettability of PTFE foil with an insignificant change of substrate topography and morphology.

The atmospheric pressure low-temperature DCSBD plasma in pure hydrogen is presenting a novel approach to structuring the polymeric surfaces on a submicron scale. At the same time, it can improve the wettability and adhesion of the chemically inert polymer like PTFE without the need for low-pressure or time-consuming chemical processing of the substrate.

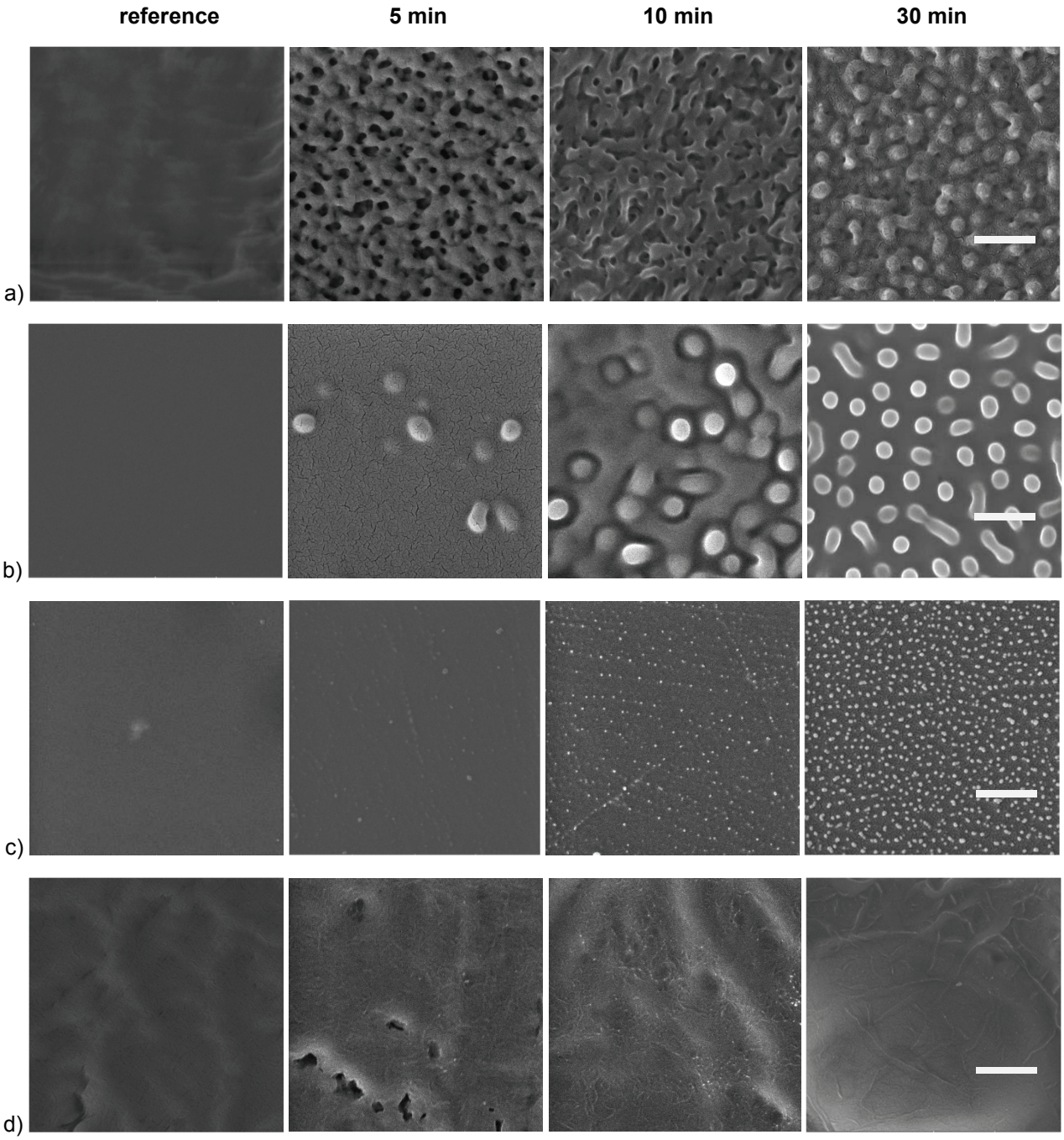


Figure 4 SEM micrographs of the PMMA foil (a), PMMA sheet (b), PET (c) and PTFE foil (d) (from left to right) reference sample and the samples after 5, 10 and 30 min treatment by DCSBD plasma generated in pure hydrogen (scale bar 1 μm)

ACKNOWLEDGEMENTS

The authors would like to acknowledge financial support from the project LO1411 (NPU I), funded by Ministry of Education, Youth and Sports of the Czech Republic and from the project TJ01000327, funded by Technology Agency of the Czech Republic.

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