SURFACE CHARACTERIZATION OF POLYTETRAFLUOROETHYLENE TREATED BY ATMOSPHERIC PLASMA

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Polytetrafluoroethylene surface was treated by atmospheric DBD plasma for 1 min in ambient conditions. The effect of DBD plasma introduces significant increasing of the surface energy (wettability) within 24 hours after treatment. However, the surface starts recovering to the original state with ageing. The surface elemental composition shows enhancing in oxygen content which suggests presenting the polar functional groups. The surface roughness exhibits a mild reduction within 24 hours after treatment. Whereas, the roughness values start to increase with the function of time.

Keywords: PTFE, surface characterization, atmospheric plasma treatment

1. Introduction

Polytetrafluoroethylene (Teflon) is one of the most used polymers in the industry due to its good mechanical properties, self-lubrication and surface hydrophobicity [1]. The effect of different plasmas on polymer surface characterization has been widely reviewed in literature especially during the last three decades. Earlier, it was achieved that exposure of PTFE to oxygen and argon plasma for a short time enhanced the surface wettability while no morphological alteration could be noted. However, longer time of oxygen plasma treatment leads to deeply etched PTFE surface [2]. In a related context, XPS results show that mild argon plasma treatment of PTFE surface is sufficient to cause substantial surface defluorination and oxidation [3]. The treatment of PTFE by low-power plasma utilizing a variety of feed gases (O₂, Ar, N₂, and NH₃) resulted in light etching into the surface. However, the nature and extent of chemical modification varied considerably where Ar plasma was the most efficient and O₂ plasma the least [4]. Vacuum DBD plasma signifi-

cantly improves the PTFE surface energy which is due to the changes in surface chemistry and microstructure [5]. Furthermore, Ar remote and direct plasma treatment of PTFE surface can modify the surface in morphology and composition, and form some polar functional groups which is due to the surface oxidation of PTFE films; thereby improvement in polymer wettability [6]. The influence of nitrogen plasma-based ion implantation (N PIII) introduces a sharp decrease in the F/C atomic ratio, whereas topography measurements show an increase in the mean surface roughness [7]. The polymer surface characterization is the major role which controls the polymer behaviour in terms of tribology and adhesive bonding, for instance, the wear rate of PTFE composite is reduced to the half approximately due to low-pressure plasma treatment [8]. However, the atmospheric plasma may introduce better tribological properties for PTFE composite [9]. In the present paper, the effect of atmospheric DBD plasma on PTFE surface characterization (wettability, chemical composition and topography) will be investigated within 24 hours also after the time shift.

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2. Methods and materials

2.1. Material and preparation

Polytetrafluoroethylene commercial type (distributed by Quattroplast Ltd., Hungary and produced by Ensinger GmbH, Germany), were utilized in bulk conditions: Polytetrafluoroethylene or virgin PTFE grad Docaflon-PTFE-N. The mechanical properties of the used material are as follows: tensile strength $\sigma = 22$ MPa, glass transition temperature $T_g = -20$ °C, shore D hardness = 55. Polymer samples were manufactured into pins with a diameter of 10 mm and thickness of 2 mm with an extruded surface for all tests except the topographical investigation where the surface was subsequently polished with wet SiC paper (grid numbers P1200 and P2000) and felt sheet towards required surface roughness. For more precision, the samples were cleaned in an ultrasonic bath with distilled water and 96% ethanol (Reanal, Hungary) before testing.

2.2. Plasma treatment

The plasma was generated in the air by diffuse coplanar surface barrier discharge DCSBD plasma source at AKI, Research Centre for Natural Sciences. Plasma works depending on a coplanar dielectric barrier discharge (DBD). The electrodes have comb-shape within a dielectric [10]. The diffuse plasma is generated in thin 0.4 mm thick flat layer on alumina ceramic; the DCSBD was designed to be utilized primarily for flat surfaces treatment (Roplass s.r.o., Brno, Czech Republic), the apparatus is shown in Fig. 1.

The DCSBD electrode system was powered by AC High-Voltage source with frequency approx. 10–20 kHz and voltage approx. 20 kV peak-to-peak while the total discharge power in plasma during the experiments is 320 W. The total area of generated plasma is 170 cm². The system is supported with oil cooling system to maintain the system at the proper temperature range which keeps the surrounded gas temperature at 370 K. The DCSBD plasma is described in detail [11]. The plasma treatment was performed in dynamic treatment mode, and the distance between the treated polymer surface and DBD reactor was 0.5 mm. The treatment has been done under air atmosphere conditions ($T = 23$ °C, $H = 50\%$). The treatment time for each specimen was 1 min determined by preliminary experiments and all the recent experiments were done within 24 hours from the treatment then repeated after shift time to verify the ageing effect on the surface characterization.

2.3. Wettability

The wettability was evaluated according to contact angle measurements by using the static sessile drop method at 23 °C, with double distilled water and diiodomethane (CH₂I₂) (Sigma–Aldrich, Reagent Plus 99% grade), applying the Surface Energy Evaluation (SEE) System apparatus (Advex Instruments, Czech Republic) as shown in Fig. 2. A Hamilton syringe was used to inject 2 μ l droplets. The results of the contact angle are an average of 5 measurements, always performed on previously non-wetted parts of the samples. The surface energy component calculations were based on Owens–Wendt method [12].

Fig. 1. DBD laboratory equipment which used for polymer surfaces treatment

Fig. 2. Surface energy evaluation (SEE) system apparatus

2.4. Chemical composition

The X-ray photoelectron spectroscopy (XPS) was carried out on a XSAM 800 spectrometer (Kratos, Manchester, UK), as shown in Fig. 3, equipped with a non-monochromatic Mg $K_{\alpha 1,2}$ radiation source (1253.6 eV) operating under a fixed analyzer transmission mode (chamber pressure $< 10^{-7}$ Pa). The pass energy was set at 80 eV for survey spectra (wide scan) and 40 eV for high resolution (detailed) spectra. The wide scan spectra were recorded at 0.5 eV steps in the 50 to 1300 eV energy range while the detailed spec-

tra were recorded at 0.1 eV steps for the respective main elements. As a reference, the C1s line for the hydrocarbon $C-H_x$ component was set to a binding energy of 285.0 eV. The accuracy of binding energy determination was ± 0.2 eV. The data acquisition and processing were performed with the Kratos Vision 2 software, applying a Shirley type background subtraction and decomposition of the peaks by using a mixed Gaussian-Lorentzian shape (70/30 ratio) of equal full-width-at-half-maximum (FWHM). The quantitative analysis of the surface composition was based on integrated peak areas calculated by the XPS MultiQuant

Fig. 3. X-ray photoelectron spectroscopy (XPS)

program [12] and is expressed in at.-%. The photoionization cross-section data of Evans et al. [14] and asymmetry parameters of Reilman et al. [15] were experimentally utilized. The conventional model of the infinitely thick layer was used to estimate the surface chemical compositions.

2.5. Surface topography

The surface roughness was evaluated from non-contact profilometry, using a 3D optical profilometer Coherence Correlation Interferometry (CCI) HD type (Taylor Hobson, Leicester, England), as shown in Fig. 4, with

Fig. 4. 3D optical profilometer Coherence Correlation Interferometry (CCI) HD type

an ultra-high precision closed loop piezoless z-scanner having a resolution in z direction of $0.1 \text{ \AA}$. Fiber Lite DC-950 source was used to generate a white light illumination and measurements were done at 50% light intensity. The elaborated surface area is $330 \times 330 \mu\text{m}^2$ for each sample, and vertical scanning interferometry imaged it, with an objective lens of magnification $\times 50$ and numerical aperture (NA) = 0.55. The scanning arrays contained 2048×2048 pixels with a field-of-view (FOV) = $330 \mu\text{m}$, corresponding to a pixel size of $0.165 \mu\text{m}$. The images were further processed by Talymap software (Digiserve) to calculate the 3D surface roughness parameters according to ISO 25178, including S_a (average roughness), S_z (maximum height), S_{ku} (kurtosis) and S_{sk} (skewness). The roughness values were determined as average from three measurements at independent surface locations, with repeatability $S_a < 0.2 \text{ \AA}$ [16], more details about Coherence Scanning Interferometry in De Groot [17].

3. Results and discussion

3.1. Surface energy

The contact angle (water and CH_2I_2) values are illustrated in Table 1, whereas Fig. 5 shows the surface energies and their changes for pristine and a DBD plasma treated surface (after 24 hours and 80 days' shift

Table 1. Contact angle values for pristine and treated surfaces

Sample	θ_w (deg)	$\theta_{\text{CH}_2\text{I}_2}$ (deg)
PTFE untreated	108 ± 1.5	73 ± 3.2
PTFE treated, 24 h	75 ± 1	56 ± 1
PTFE treated, 80 days	98 ± 16	75 ± 7.1

Fig. 5. Surface energy parameters and tendency for pristine and DBD plasma treated surface (after 24 hours and 80 days)

Fig. 6. Analysis of chemical composition from high-resolution XPS spectra

time). From that the substantial change in the wettability can be noted, where the contact angles significantly decreased, thereby the surface energies were enhanced due to DBD plasma treatment based on Owens–Wendt calculation. In parameters range, overall polar (γ_{pol}), dispersive (γ_{disp}) and total (γ_{tot}) components of the surface energy were increased, in particular, the polar component was increased by 3650% more than the reference state. After 80 days of ageing, the hydrophobic recovery takes place, resulting in decreasing the polar and dispersive component values. Thus, the polarity declined by 72% than the initial state after treatment.

3.2. Chemical composition

XPS analyzed the surface chemical composition change. The elemental composition values (at.-%) of PTFE are listed in Fig. 6 for theoretical, pristine and treated surfaces, respectively, which were calculated

from the wide-scan XPS spectra. The effect of DBD plasma on the surface chemical composition has presented an improvement in the oxygen content and reduction in the fluorine and carbon content, indicated by the increase of O/C atomic ratio and decrease F/C atomic ratio. The increased O content introduces the establishment of polar functional groups (oxygen-containing functional groups) onto the PTFE surface which in turn leads to improvement in the surface wettability.

3.3. Surface topography

Surface topography of pristine and plasma treated samples were monitored by non-contact profilometry, illustrated by 3D surface scan, presented in Fig. 7. The 3D surface roughness parameters and their changes due to plasma treatment are shown in Fig. 8. In general, the surface roughness was slightly decreased after DBD plasma. In parameters range, the average rough-

Fig. 7. Non-contact profilometry of pristine and treated samples of (330×330 μm^2 surface area)

Fig. 8. Surface roughness parameters of pristine compared to plasma treated samples (after 24 hours and 800 hours)

ness S_a decreased by 10%, the maximum height (S_z) decreased by 20%, S_{ku} (kurtosis) was destined closer to the three value whereas S_{sk} (skewness) exposed reduction in the negativity value after plasma treatment. The values introduce mild flattened surface probably owing to the removal of the top layer and melting of the surface asperities, while the original polishing grooves remain visible. The ageing effect was taken into consideration therefore the tests were repeated after 800 hours. PTFE exhibits increase in the surface roughness with the function of time which was attributed to the surface recovery. The surface smoothing is characteristic for the used plasma processing conditions and measurements at micro level scale.

4. Conclusions

In conclusion, the surface characterization of polytetrafluoroethylene was investigated for pristine, and atmospheric DBD plasma treated surface within 24 hours and after shift time. The SEE System apparatus evaluated the contact angle, and the surface energy was calculated based on Owens–Wendt method. The surface chemical composition was analyzed by XPS. The surface 3D topography was scanned by non-contact profilometry (CCI) HD type. Due to the atmospheric DBD plasma treatment, the surface energy components were improved where the polar component was increased by 3650% more than the virgin state. Surface chemical composition exposes increasing the oxygen content which leads to the establishment of polar functional groups thus enhancement in the surface wettability. The 3D topographical scan shows a mild decrease in the surface roughness after

plasma treatment where the average roughness was decreased by 10%. However, the surface roughness parameters start to increase with the function of the time due to the surface recovery effect.

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