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Surface modifications of polymer induced by atmospheric DBD plasma in different configurations

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The plasma treatment is an efficient method used for improved wettability of the polymer film surface and for increasing the surface roughness. In the present paper the surface modifications of polyethylene terephthalate (PET) and polyethylene terephthalate with TiO_2 additives (PET+TiO_2) by atmospheric dielectric barrier discharge (DBD) treatment in different configurations have been studied. The surface modifications of PET+TiO_2 samples were analyzed by two complementary methods: the contact angle method and Atomic Force Microscopy (AFM) technique. It was found that he shorter treatment durations, the asymmetric DBD configuration is more efficient than the others methods.

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Keywords: Dielectric barrier discharge, Atmospheric pressure glow discharge, Polymer surface treatment, AFM, contact angle

1. Introduction

Polyethylene terephthalate (PET) and PET with $Ti0_2$ seems to be promising material in many fields, especially in medicine. Novel applications such as in orthopedics, drug delivery systems and blood contacting surfaces are in continuous development. Surface properties like morphology and topography, degree of crystallization, wettability, adhesion, chemical structure can be modified by means of different chemical and physical treatment techniques.

Plasma treatment is probably one of the most used techniques for polymer surface treatment [1]. Function on the research purposes, the plasma can be generated in different gases, range of pressures or discharge geometries. The plasma parameters (particles density, collision frequency, mean energy of particles, presence of chemical active species) will influence the main processes at plasma-polymer interface. In this way by controlling the plasma parameters we will control both the quality and magnitude of the treatment effects on the polymer surface (etching, functionalization, crosslinking). For example, the resulting free radicals will react and form small oligomer chains at the polymer surface or will crosslink the polymer in the near surface regions. These processes are possible during plasma exposure of the polymers, in spite of the fact that the interaction volume is different.

The surface incorporation of polar groups, such as carbonyl, carboxyl and hydroxyl, during the treatment will increase the surface energy of the polymers. This grafting process will produce a more wettable surface after the treatment. Still, the increased wettability can be a combined effect of surface functionalization and increase in surface roughness [2].

In the present paper the surface modifications of PET and PET with TiO_2 additives foils after DBD treatments are studied by two complementary methods: contact angle method and Atomic Force Microscopy technique.

2. Experimental set-up

The dielectric barrier discharge (DBD) was produced in two reactors with two different configurations: plane-parallel and point-plane electrodes (Fig. 1.a) and b)). The dielectric materials used in both configurations was glass. The gas gap is always maintained constant at 3 mm. The high voltage power supply generates monopolar semi-sine pulses of 1 to 10 kV, pulse duration between 10 μs to 45 μs and frequency in the range 10 Hz to 10 kHz (TERAFLUX).

The experiments are made at room temperature, in spectral helium (Linde Gas, purity 4.6) without preliminary vacuum pumping. This mode of operation is motivated by the conditions used in industrial system for plasma surface treatment of the materials.

Using a 350 MHz digital oscilloscope (LeCroy WaveSurfer 434) the voltage U_a applied on the electrodes and the total current, I_t, were stored (Fig.2 a) and b)).

In both configurations the polymer sample was placed on the ground electrode. The treatment time of polymer film with the DBD plasma was varied from 30 to 450s.

Atomic Force Microscopy (AFM) analyses of the polymer films were performed using a standard silicone nitride tip (NSC21) and tips radius 10-20 nm. The analysis was made in tapping mode with 0.1 nm resolution in *z* direction.

Information about energetic properties of the surface was obtained by measuring contact angles on PET samples using distilled water as test liquid. The water droplets of 1μl were placed on the polymer surface using a pipette. The photos of each droplet, deposed on the polymer surface, were taken using a digital camera. The contact angle was determined from these photos using the open-

source software *ImageJ* [3]. The presented values are the average of at least 5 measurements on the same sample, the typical error in contact angle determination being ±1°

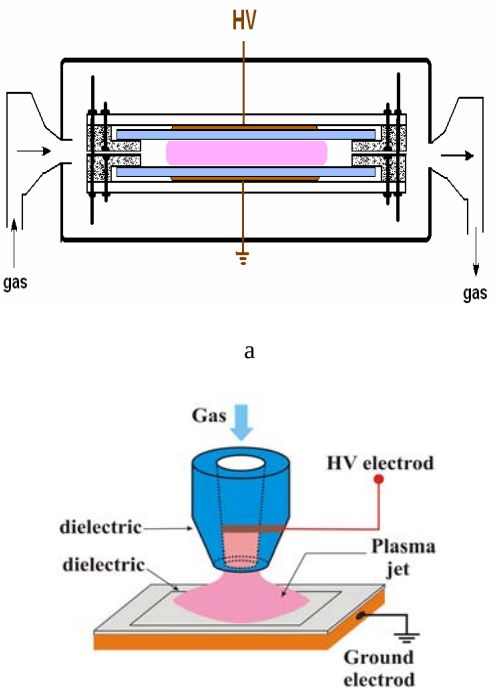

Fig. 1. Experimental set-up (a) of plan-parallel and (b) point-plan configurations

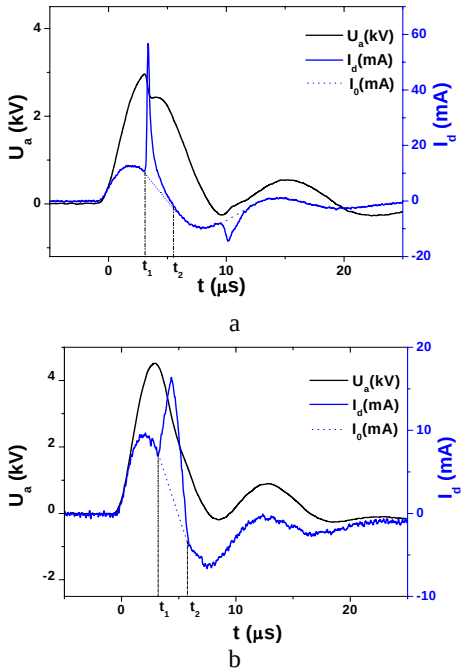

Fig. 2. The current - voltage characteristic in (a) the plan-parallel and in (b) the point - plan configurations

3. Results and Discussions

The surface modifications of PET+TiO_2 samples were analyzed by two complementary methods: the contact angle method and Atomic Force Microscopy (AFM) technique. In all configurations, for both polymers, after 20-30 seconds of the plasma treatment an improved wettability of the polymer film have been observed, while in order to increase the surface roughness longer treatment duration is needed. But, in order to obtain a pronounced modification of polymer surface roughness, different treatment duration is needed for those two configurations used.

More exactly, in order to obtained a significant change in roughness of the polymer film the shorter treatment duration (200 s) was necessary in the point-plane configurations. In contrast, treatment produced by DBD plane electrode structure, more than 450 s has been used for similar value of the surface roughness (Table.1.). This result might be related to the fact the electrical charge arrived on the sample surface ($Q_{el} = \int_{t_1}^{t_2} I_d \, dt$, t_1 and t_2 are the time limits for the current intensity of the plasma discharge peak) is about 20% higher in the former case than that in the later one, in spite of the fact that the peak current intensity was about 50% smaller. Larger electrical charge arrived on the sample surface, larger ion flux is produced and consequently larger modification of the surface is expected. The R_{rms} value of the untreated foils of PET samples is 1.1nm (Fig.3), and for PET+TiO_2 samples is 1.2nm. It is also proved by the result that the root mean square roughness (R_{rms}) values increase with the treatment duration as shown in the below table:

Table.1. The R_{rms} value in symmetric and asymmetric geometries.

	Symmetric geometry	Asymmetric geometry
Treatment time (s)	PET Rrms (nm)	PET Rrms (nm)
30	2.0	2.1
200	2.6	5.7
450	5.3	7.9

	Symmetric geometry	Asymmetric geometry
Treatment time (s)	PET+TiO_2 R_{rms} (nm)	PET+TiO_2 R_{rms} (nm)
30	1.4	2.7
200	3.2	3.7
450	3.0	15.3

Table.2. The plasma current intensity and the electric charge in different DBD plasma configurations

DBD geomeries	I_d (A)	Q_{el} (nC)
Asymmetric (He)	0.034	36.2
Symmetric (He)	0.068	23.9
Symmetric (He+O_2)	0.07	25.2

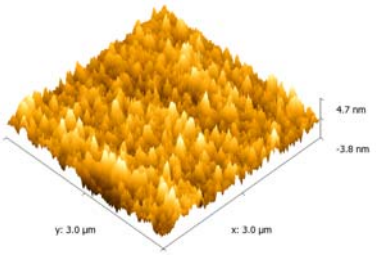

Fig. 3. 3D AFM images of 3µmx3µm of untreated PET samples.

The results obtained by the AFM technique are restricted mainly to 3D images of the treated polymer samples (Figs 4 and 5). Investigations made in a rather broad range of the discharge current show that plasma treatment does not significantly change the morphology of the polymer surface, for the short treatment duration (Fig.4. a) and c), Fig.5. a) and c)), while significantly modifications of the contact angle were observed. This shows that plasma treatment is mainly produced at atomic and molecular level. From Figs. 4 b), d) and 5 b), d) it can be seen that the topography and roughness of the PET foils are significantly changed only for the longer duration of the plasma treatment (over 400 s).

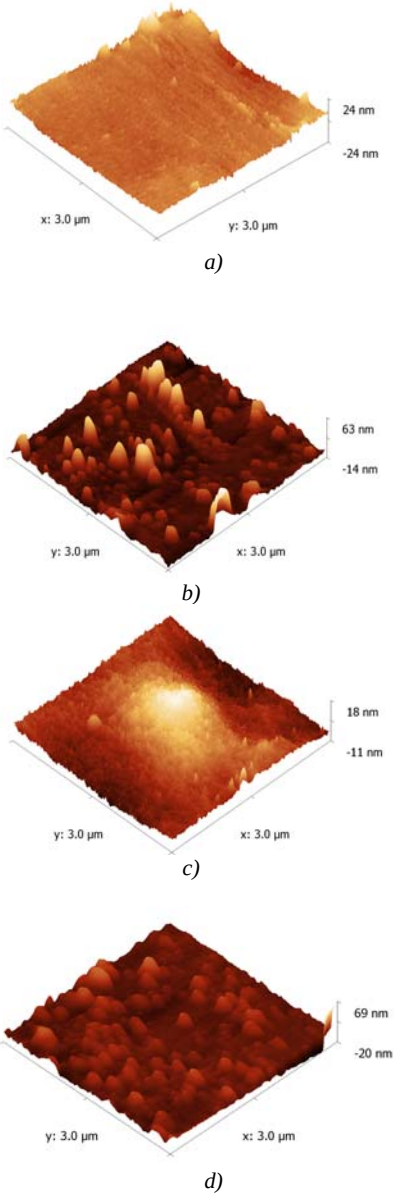

*Fig.4. 3D AFM images of 3µmx3µm of **PET samples** treated in DBD plasma, **symmetric geometry 30s (a), 450s (b)** and asymmetric geometry **30s (c), 200s (d)***

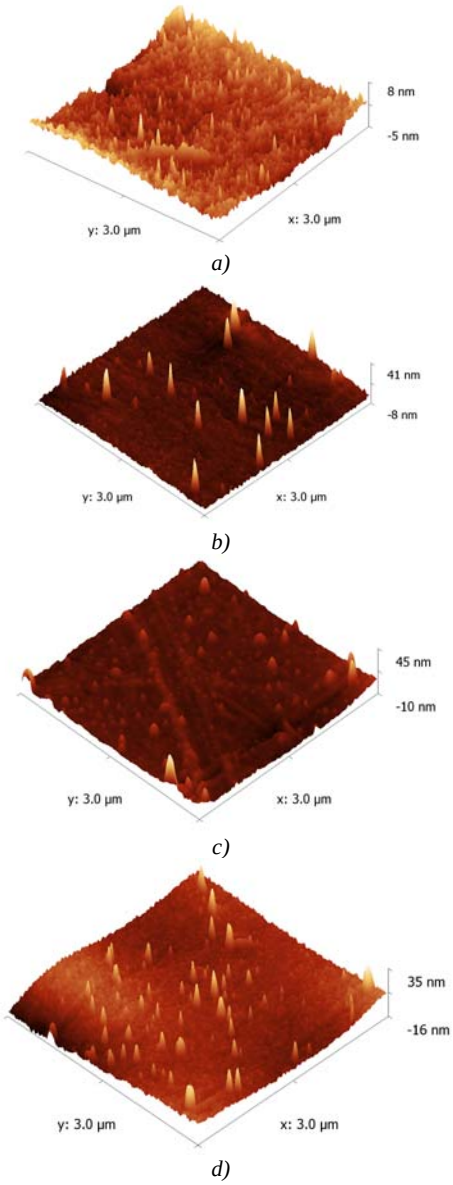

*Fig.5. 3D AFM images of 3µmx3µm of **PET+TiO_2** samples treated in DBD plasma, **symmetric geometry 30s (a), 450s (b)** and asymmetric geometry **30s (c), 200s (d).***

After treatment the localized picks are preserved and became more pronounced.

It appears that for longer treatment durations the polymer surface is totally reconstructed. This process can be due to the surface reorganization of polymer chains together with bond breaking and crosslinking reactions [4]. It is worthnoticing notice that the value of the root mean square roughness (R_{rms}) increases with the DBD plasma treatment duration (up to 7,92nm for PET samples, and up to 15,32nm for PET+TiO_2 samples, both for the asymmetrical geometry).

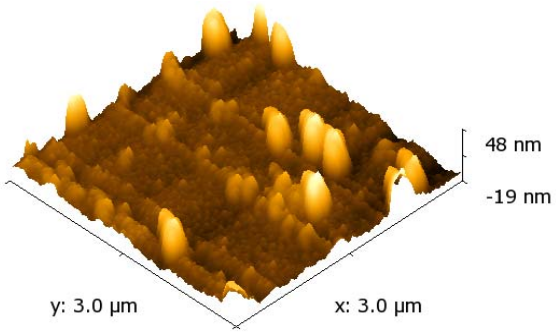

Fig. 6. ***3D AFM image of 3µmx3µm PET+TiO_2 samples treated in DBD plasma, symmetric geometry, He+ 3% O_2, Rrms = 8.89 nm.***

In the case of DBD symmetric configuration, adding 3% oxygen (as shown in Fig.6.), topographically modifications of the both polymer treated surfaces were stronger, but with lower intensity than in the asymmetrical configuration, for the same value of the treatment duration (450 s).

The contact angle value for untreated PET sample is 79°, and for untreated PET+TiO_2 samples is 76°. After DBD plasma treatment the contact angle decreases down to 35° (Fig. 4). This is a direct proof of surface functionalization [5].

For shorter treatment time (between 10s and 60s), the DBD plasma treatment is very efficient in terms of surface functionalization.. This is reflected in the contact angle measurements (Fig. 7). Thereby for 30s of DBD plasma treatment the PET samples contact angle is 44° (in both geometries), and for PET+TiO_2 samples is 42° (in the symmetric geometry), and 46° (in the asymmetric geometry). Increasing the treatment duration till 450s of DBD plasma treatment time, the contact angle value decreases to 41° for both polymers in the point-plane geometry. But, in the plane-parallel geometry the contact angle value decreases down to 34° for PET+TiO_2 foils and to 36.7° for PET foils, for the same DBD plasma treatment duration (450s).

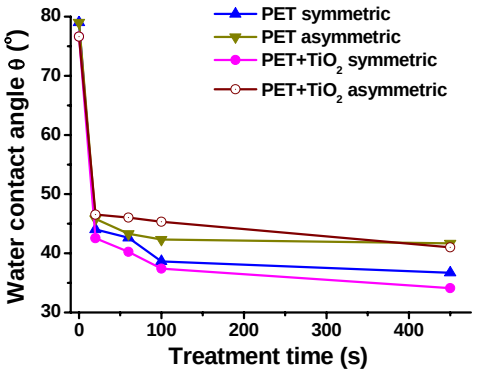

Fig.7. Contact angle evolution of the PET and PET+TiO_2 foils treated in DBD plasma, for different treatment times

However, as it can be seen in figure 7, the contact angle value for both PET and PET+TiO_2 treated polymer foils shows saturation process for longer treatment duration (>400s).

4. Conclusions

An improved wettability of the PET and PET+TiO_2 polymer foils have been observed in both configurations, after 20-30 seconds of the plasma treatment, while longer treatment time is needed in order to increase the surface roughness. Most probable the improved wettability and increased surface energy of both treated polimer samples stand as a fact of surface functionalization.

A shorter treatment time (200 s) was needed in order to obtained a significant change in roughness of both PET and PET+TiO_2 samples in the asymmetric configurations, due to the fact that the electrical charge value is about 30% higher than in the symmetric configurations, in spite of the fact that the discharge current intensity was about 50% smaller that in the first configuration.

For the DBD symmetric configuration, adding 3% O_2 in helium, localized picks are preserved on the both polymer treated surfaces, but less pronounced than in the asymmetrical geometry, for the same value of the treatment time (450 s).

The roughness of the treated surface is the equal, for both PET and PET+TiO_2 samples, for the same electrical power injected in the discharge.

Acknowledgements

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