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COMBINED TREATMENTS FOR THE IMPROVING OF THE PET SURFACES HYDROPHILICITY

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In this work plasma and ultraviolet light treatments are used separately and in combination in order to modify the wetting properties of polyethylene terephthalate (PET). This novel approach is an easy and fast method to obtain hydrophilic nano and microstructurated surfaces with many potential technological applications from which the biomedical ones are the most important. The surface characterization was revealed by atomic force microscopy (AFM), scanning electron microscopy (SEM), contact angle and x-ray photoelectron spectroscopy (XPS) measurements.

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1. Introduction

The modification and control of the surface properties of poly(ethylene terephthalate) (PET) is a research topic of current interest in view of its broad application range: adhesion, painting, dyeing, gas permeability or composites. Recent developments for obtaining hydrophilic polymers have yielded robust techniques like plasma or ultraviolet light treatments for controlled surface modification of polymers and the creation of nanostructural features at the polymeric surface [1]. Hydrophilic surfaces are preferred in applications where wetting and bonding are critical issues, especially in biomaterials applications. Several surface modification methods are employed to modify the polymer surfaces, such as chemical, thermal, mechanical and electrical treatments [2]. Separate and subsequent plasma etching and pulsed laser treatment have been reported by Akkan and collaborators [3] and they obtained a surface with a wide range of wetting properties.

PET is a semicrystalline polymer, used in textiles, reinforcement of tires and rubber goods, and food and beverage packaging [4,5]. Cardiovascular applications, one of the most important categories of implant materials, include arteries (vascular grafts) [6] and shunts in which PET is already wide used. However, PET proved to be, in some situations, an unsuitable material to use due to its low surface energy, leading to poor wettability and poor adhesion. Plasma treatment can be carried out by using chemically reactive (N_2, O_2, CO_2, etc.) or inert (H_2, Ar, He, etc.) gases. The former lead to the disruption of the polymer chains by the energetic ions and radiation generated in the plasma as well as to the introduction of chemical functional groups on the polymer surface [7-9], whereas the chemical effect is absent when inert gases are employed and only ion bombardment and radiation should in principle play a role [9-12]. It is thus interesting to compare the effect of plasma treatmentunder these different types of gases.

In the case of UV light treatment, the substrates absorb the UV energy from the light source, setting in motion a chemical reaction that quickly converts them onto a solid functionalized surface. The surfaces form monomers and oligomers after UV irradiation. Monomers can be mono- or multifunctional molecules, depending on the number of reactive groups they possess.

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The substrates become part of the polymer and because their reactive functional groups appear during exposure to UV light certain new properties are present to the surface of the polymer.

In the present work, two nonconventional methods, the UV irradiation and plasma treatment in nitrogen-helium atmosphere produced hydrophilic PET surfaces. The combination of both techniques revealed a hierarchically patterned hydrophilic surface.

2.Experimental set-up

2.1. Combined treatment

The PET biaxially oriented film samples (10 x 10 cm, 30 μm thickness), produced by S. C. TEROM of Iasi-Romania, were used.

The films were exposed to a combination of 10% nitrogen and 90% helium plasma atmosphere in a EMITECH RF plasma reactor, for 3 min at 50 W.

Films of the PET samples were irradiated for 2 hours in air at 25 ^{o}C with a UV- Philips lamp having a polychrome emission spectrum between 200 - 400 nm and light intensity of 30mW/cm^2. The distance between the light source and samples was 20 cm.

At last, the surface was subjected to the plasma etching and then UV treatment was applied.

2.2. Characterization

SEM micrographs were obtained with a Quanta 200 scanning probe microscope.

The surface composition analysis was run by X-ray photoelectron spectroscopy (XPS) (PHI-5000 VersaProbe photoelectron spectrometer ΦULVAC-PHI, INC.) with a hemispherical energy analyzer (0.85 eV binding energy resolution for organic materials). A monochromatic Al Kα X-ray radiation ($h\upsilon$ = 1486.7 eV) was used as excitation source. The standard take-off angle used for the analysis was 45^{o}, producing a maximum analysis depth in the range of 3-5 nm. The spectra were recorded from at least three different locations on each sample, with a 1 mm x 1 mm area of analysis. The low-resolution survey spectra were recorded in 0.5 eV steps with 117.4 eV analyzer pass energy and, in addition, the high-resolution carbon (1s) spectra were recorded in 0.1 eV steps with 58.7 eV analyzer pass energy.

AFM measurements were performed in airat room temperature, in the tapping mode using a Scanning Probe Microscope (Solver PRO-M, NT-MDT, Russia) with commercially available NSG10/Au Silicon cantilevers. In the tapping mode, the cantilever is oscillated at a frequency of 254.249 kHz, over a 5 x 5 μm^2 scan area, 256 x 256 scan point size images being thus obtained for each sample. The root-mean-squareroughness RMS was calculated as the average value for the set of AFM frames of certain scales [4]. The surface textures were characterized in terms of roughness parameters, such as root mean square roughness (RMS) and average height (Ha).

The contact angle measurements were made in a telescope-goniometer system CAM 101 Optical Video Contact Angle System, KSV Instruments LTD, Finland.

3. Results and discussions

On both micrometric (Fig. 1) and nanometric (Fig. 2) scale the pristine PET has a rather smooth surface, while the treated material is characterized by a granular topography of small features. The roughness of the surface films becomes significantly higher under the action of all described treatments. The combined method produces a surface with a roughness of approx. 3 times higher that the untreated one (Fig.2). From the height measurements, Ha is increasing from 5.9 nm for the untreated PET, 20 nm for the plasma-treated PET, 10 nm for UV treatment and 30 nm for the combined treatment.

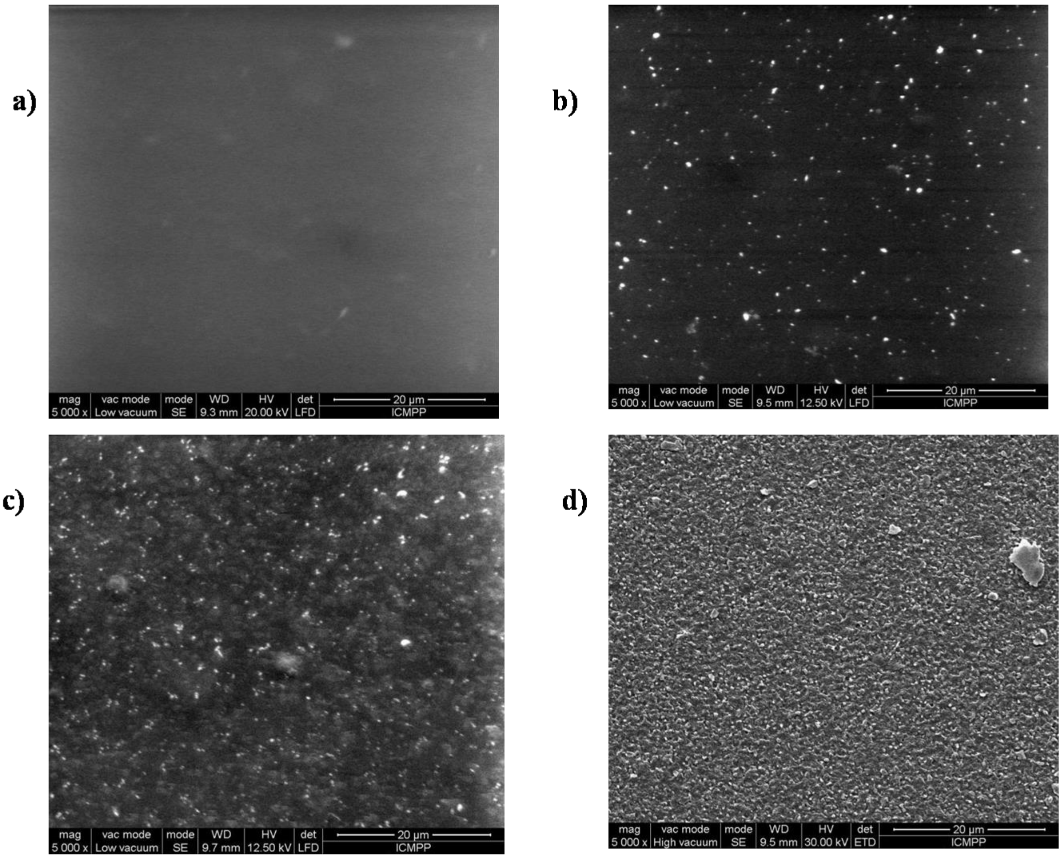

Fig. 1. SEM images for: the untreated PET film (a.); PET 2h UV (b.); PET 50 W, 3 min plasma (c.); PET 50 W, 3min plasma and 2h UV (d.).

The XPS spectra of the pristine and treated PET samples are shown in Fig. 3. The new groups, radicals or peroxides, generated at the treated polymer surface react with oxygen (and/or nitrogen) and lead to hydroxyl, carbonyl and carboxylic acid groups [6,8]. From XPS data it is clear that the combined treatment has a more significant influence than single UV light irradiation on the PET surface or plasma treatment. For the plasma treated samples, a decrease in the C (1s) peak was observed while the O (1s) peak increased suggesting that new oxygen-containing polar groups are formed on the PET films surface after treatments. It is evident that the combined treatment substantially increases the O/C ratio than single treatments.

The C1s high resolution spectrum of untreated PET film is shown in Fig. 3. The peaks are identified at 284, 285.5, and 288.1, respectively, which can be assigned to C–C/C–H (1), C–O (2) and O=C–O (3), respectively [9]. The spectra of treated films reveal, as well, peaks for C–C/C–H (1), C–O (2) and/or C–N, O=C–O (3) and/or N-CO-N and an additional peak at 287.1 eV, which may be attributed to N-C=O (4) groups [10]. The changes in content of each chemical component are given in Tabel1. The C–C component decreases significantly after all treatments and most of the C–O oxygen containing polar groups are increasing in the surface of the treated polymer surfaces (Table 1). These results indicate that some of the C–C/C–H bonds present in polymer surface are broken by the treatments, the broken C–C/C–H bonds recombining with the oxygen and the nitrogen atoms [11, 12].

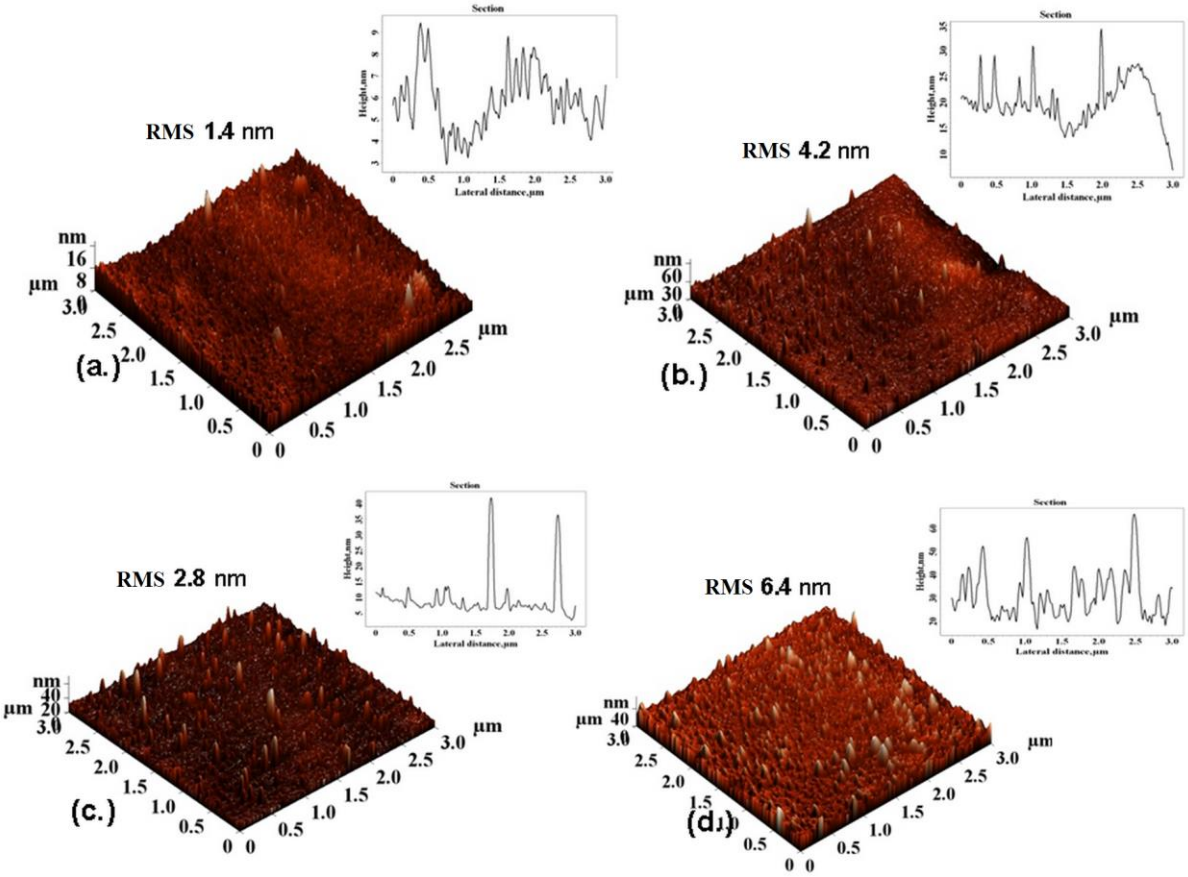

Fig. 2. 3D AFM images for: the untreated PET film (a.); PET 2h UV (b.); PET 50 W, 3 min plasma (c.); PET 50 W, 3min plasma and 2h UV (d.).

Table 1. XPS results

	Binding Energy(eV)	%	assignments
Untreated PET	284	79.4	C–C/C–H
	285.5	9.3	C–O
	288.1	11.3	O=C–O
PET 2h UV	284	42.52	C–C/C–H
	285.5	32.20	C–O/C–N
	288.1	15.25	O=C–O/N-CO-N
	287,1	10.03	N-C=O
PET 50 W, 3 min plasma	284	43.12	C–C/C–H
	285.5	30.00	C–O/C–N
	288.1	17.05	O=C–O/N-CO-N
	287,1	9.83	N-C=O
PET 50 W, 3min plasma and 2h UV	284	50.34	C–C/C–H
	285.5	30.62	C–O/C–N
	288.1	14.01	O=C–O/N-CO-N
	287,1	5.03	N-C=O

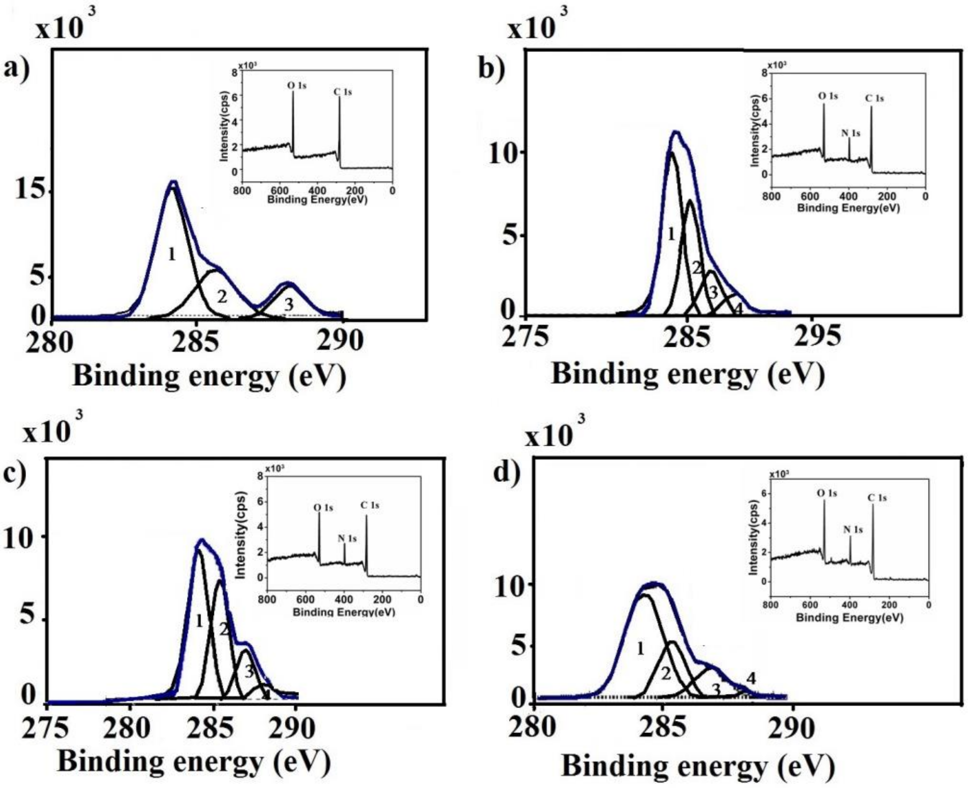

Fig. 3. XPS wide spectra and C1s high resolution spectra of: a) untreated PET; b) PET 2h UV; c) PET 50W, 3min plasma; d) PET 50W 3 min plasma and 2h UV.

The sessile drop method (in water and ethylene glycol) [12, 13] was used to determine γ_{SV} (the surface energy), γ_{SL} (the solid - drop interfacial tension), γ_{LV} (the liquid-vapour surface tension), and cos θ (the drop - surface contact angle) values listed in Table 2:

$$\gamma_{SV} = \gamma_{SV}^{p} + \gamma_{SV}^{d} \tag{1}$$

were p is polar and d is dispersive.

The interfacial solid–liquid tension (γ_{SL}) is given by the equations:

$$\gamma_{SL} = \gamma_{SV} + \gamma_{LV} - 2(\sqrt{\gamma_{SV}^{p}\gamma_{LV}^{p}} + \sqrt{\gamma_{SV}^{d}\gamma_{LV}^{d}} \tag{2}$$

The static contact angles values for PET film treated 2h UV compared with pristine sample is ~20°, for plasma treatment for 50W 3 min is~35°, while for the combined treatment a decrease of 41° in the water contact angle value compared with the untreated one was noticed (Fig.4).

Using the Young`s equation, it is possible to relate the work of adhesion (Wa) to the measureable contact angle of a liquid on a solid [14]:

$$W_a = (1 + \cos\theta)\gamma_{LV} = 2(\sqrt{\gamma_{SV}^{d}\gamma_{LV}^{d}} + \sqrt{\gamma_{SV}^{p}\gamma_{LV}^{p}}) \tag{3}$$

The calculated values of this energy demonstrate a higher polar component compared to the dispersive one for all the samples. Furthermore, the wettability of the PET surface treated with all methods increases but the higher value is obtained for the combined treatment. This is in agreement with XPS data which indicated the production of more polar functional groups at the film surface in the case of the combined treatments.

Table 2. Surface parameters of PET samples

Sample code	W_a (mN/m)	γ_{SV} (mN/m)	γ^p_{SV} (mN/m)	γd_{SV} (mN/m)	γ_{SL} (mN/m)
untreated PET	85,44	36,07	5,65	30,42	23.43
PET 2h UV	109.3	42.7	21.7	21.05	6.2
PET 50W, 3min	129.4	58.7	48.39	10.34	2,15
PET 2h UV and 50W, 3min	124.2	53.1	38.92	14.18	1.63

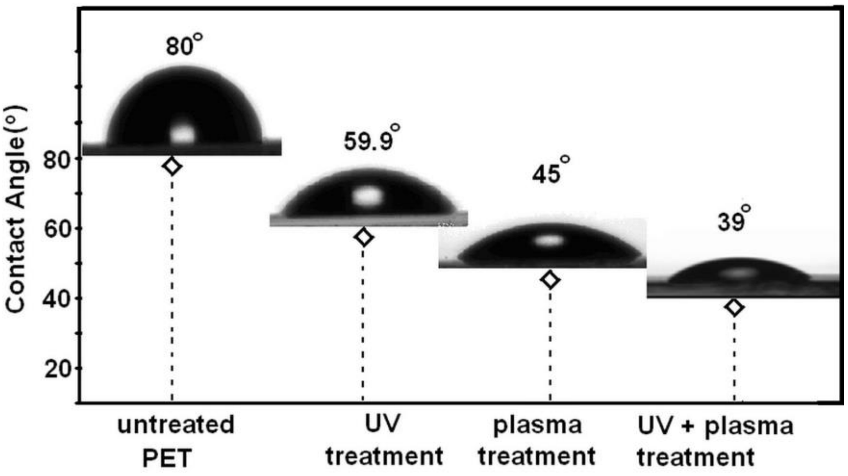

Fig. 4.Static contact angle values in water

4. Conclusions

The surface wetting is a critical parameter in biomaterial applications. The results presented in this research demonstrate that plasma and UV treatments should be used together as a functionalization procedure on the polymers, due to the efficiency in the creating of hydrophilic surfaces. The effect of the achieved topography on the surface parameters recommends this procedure as an easy and cheap method for a large area of applications.

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