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Surface modification of polymethylmetacrylate films using dielectric barrier discharge

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In this paper, continuing previous work, we report on the surface modification of a polymer, PMMA (polymethylmetacrylate), which already contains intrinsically structurally bonded oxygen in its structure prior to treatment, in an experimental DBD reactor run in an atmospheric pressure gaseous environment. Here the effects of He+N_2 and He+O_2-DBD treatment on the polymer surface are examined, discussed and compared to the He-DBD treatment. The surface analysis and characterization are performed using X-ray photoelectron spectroscopy (XPS), contact angle measurement and atomic force microscopy (AFM) before and following the DBD processing described. The discharge parameters used are correlated with the changes in the surface characteristics found following DBD treatments, in order to select the most convenient gas mixture for the efficient modification of the surface properties and the subsequent stabilization with time of the modified surfaces. The treated PMMA films exhibit improved surface characteristics and potentially better application performance, as demonstrated in relation with the surface morphology and roughness, the surface and interfacial energetic characteristics, and the chemical structure. The treatment is efficient and reproducible for short treatment times and the surface properties have high post-processing stability.

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1. Introduction

Polymers play an important role as structural materials, films and foils for packaging, supporting substrates, protective coatings, sealing applications etc. Although known polymer properties such as their thermal stability, chemical inertness, low surface energy and low friction may be desirable in several applications, for many uses these properties are a disadvantage and have to be overcome. Due to their low surface energy, their normally poor chemical reactivity and the presence of a weak cohesion layer at the surface, polymer surfaces are often difficult to wet and offer poor adhesion to other contiguous materials. Thus, surface pre-treatment is usually required to achieve satisfactory adhesion. In particular the immobilization onto the polymer surface requires a pre-treatment in order to increase the surface reactivity and to permit selective linkage onto the surface of species of interest in specific applications.

On account of the numerous applications of the common polymers, the methods used to treat and modify such polymer surfaces are many and varied. These include chemical, mechanical, thermal, photochemical and plasma-based processing. Among these, the various types of discharges and plasmas encountered have advantages compared to the other methods when seeking to change chemically and physically the polymer surface of interest. Plasma modification techniques should be capable of modifying only the topmost layers of the chosen material, rendering the polymer concerned better suited to the post-treatment processing required without affecting its bulk properties. Alterations to the polymer surface can arise in different forms: removal of the weak cohesion layer or other contamination present at the surface, introduction of new chemical functionalities or adding such to those already present, and increased surface roughness. These changes, in their distinct ways, contribute to the improvement sought in the wettability and in the adhesion properties of the surfaces of interest.

A number of non-equilibrium "cold" plasma discharge processes have been developed in this context that provide, by surface modification, the surface properties required of the polymers concerned. Among these various plasma techniques, dielectric barrier discharges are demonstrably very convenient for the activation or modification of polymer surfaces, as they offer the possibility of inducing significant surface chemical modifications on a material exposed to the discharge at or near atmospheric pressure, thus avoiding the high engineering costs usually associated with vacuum-based plasmas [1-3].

In many applications, the surface structure is the key parameter and it is very important not only to induce local modifications of surface roughness, but also to characterize and control the thin film roughness at interface. For example, in the actual and promising field of biomedical applications, the controlled creation and/or modification of the granular structure at interface could overcome the compatibility problems of implants. Furthermore, the modification of the surface roughness is usually accompanied by an increased or decreased wettability of surfaces, which is also a critical parameter for the selective adsorption of species from the biological environment. In this way, the identification of biocompatibility properties at interface should be made in relation with the surface morphology and roughness, the surface and interfacial energetic characteristics, and the chemical structure in terms of specific functional groups.

Recognizing the above, here a dielectric barrier discharge (DBD) at atmospheric pressure, optimized to work in helium and mixtures of helium with reactive gases, was used aiming to improve the surface properties of polymer films. The effects of He+N_2 and He+O_2-DBD treatment on the polymer surface were examined, discussed and compared to the He-DBD treatment. Surface analysis and characterization were performed using X-ray photoelectron spectroscopy (XPS), contact angle measurement and atomic force microscopy (AFM), before and following the DBD processing described. The discharge parameters used were correlated with the changes in the surface characteristics found following DBD treatments, in order to select the most convenient gas mixture for the efficient and controlled modification of the surface properties, such as surface morphology and roughness, surface and interfacial energetic characteristics, chemical structure, and the subsequent stabilization with time of the modified surfaces.

2. Experimental

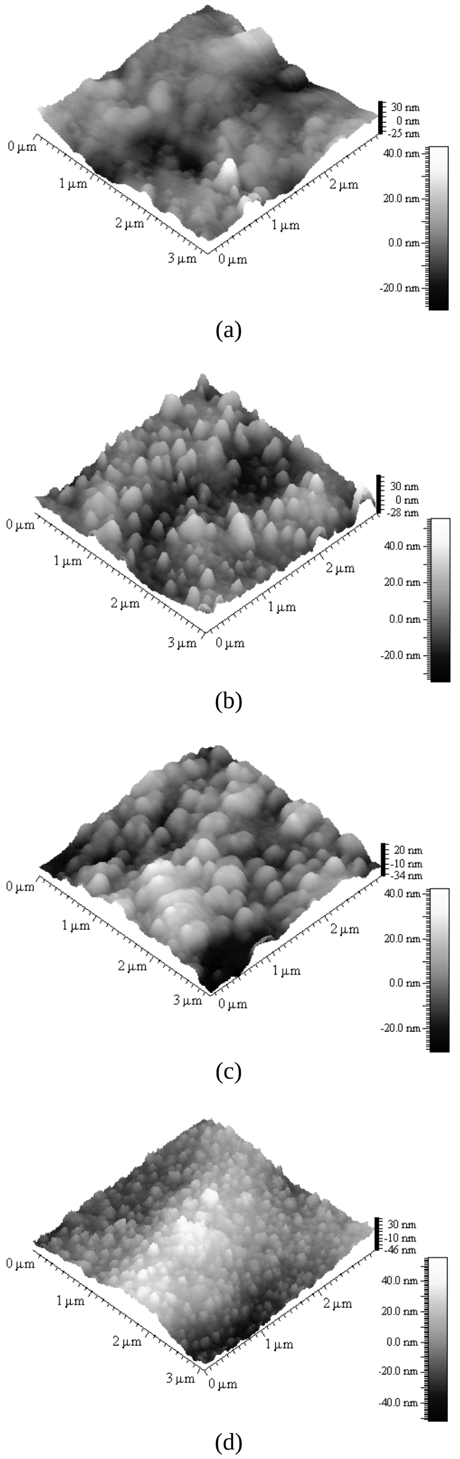
The in-house designed DBD system was described in detail elsewhere [4,5]. The discharge, working in the glow regime, was generated in a disc-to-plan geometry, with adjustable inter-electrode gap, using a pulsed high-voltage supply, peak-to-peak 4 KV, frequency 12 KHz. During the treatments, the inter-electrode gap was adjusted to 10 mm. In this arrangement the discharge, of conic shape, was uniformly distributed over an area of about 1 cm^2 on the polymer sample. The gas mixture was introduced into the inter-electrode gap at controlled flow rate for all components, at atmospheric pressure, by a gas shower placed near the disc electrode.

The composition of the He/reactive gas mixture was selected according to previous experiments, where an extended range of reactive gas flow rate was investigated during surface treatments of polyethylene films [6]. Therefore, treatments under 100 cm^3/min He are compared to the DBD exposure under He+10%N_2 and also under He+10%O_2 environment. The treatments were performed for 10 s exposure time, chosen in correlation with the previously mentioned experiments [6].

The treatments were performed on commercial films of polymethylmetacrylate (PMMA), thickness 0.25 mm (Goodfellow Ltd.), selected as widely used polymer for biomedical applications, for example being preferred in ophthalmology, for intraocular and contact lens. The surface characterization was performed using contact angle measurement, AFM imaging and XPS analysis.

3. Results and discussion

The morphological modification of the PMMA films was investigated by AFM. The AFM images recorded on treated and untreated samples show that the DBD treatment creates a new granular structure on DBD exposed samples, with distinct and well-organized features in the nanoscale domain (Fig. 1). Moreover, the treated surfaces present an increased area (increased roughness) compared to the pristine ones. In this respect the absolute roughness $\left| R \right|$ and the root mean square roughness R_{rms} are presented in Table 1. The granular structure has variable dimensions in the nanoscale domain, depending on the gaseous mixture, as demonstrated by the characteristic size $\overline{d}$ of the grains or crystallites, calculated as the average value on area of 9 μm^2, presented also in Table 1.



(a)

(b)

(c)

(d)

Fig. 1. AFM images of PMMA films (3μm × 3μm): untreated (a), and 10 s DBD treated in He (b), He+10%N_2 (c) and He+10%O_2 (d).

Table 1. Absolute roughness $|R|$ *and rms roughness* R_{rms} *for PMMA, 10 s DBD treated, vs. gaseous mixture composition.*

	untreated	treated		
		He	He+N_2	He+O_2
$\left\|R\right\|$ (nm)	8.03	11.06	11.49	16.02
R_{rms} (nm)	6.05	8.65	9.22	13.73
$\bar{d}$ (nm)	—	20	100	200

The observed effects could be due to several mechanisms. The discharge very probably has a cleaning effect, by preferential physical sputtering of amorphous regions [7]. The grains or crystallites could be hidden, on the untreated surface, by the outermost amorphous regions, becoming visible after the sputtering of the amorphous low cohesion surface layer, known to have high chemical inertness. The DBD treatments may thus produce such effects as removal of contaminants, oligomers and amorphous layers existing on the surface, allowing the chemical activation of the material. Then, the sputtering of the amorphous regions may continue as well by a migration of free radicals and contaminants, after treatment, providing an increase in size of the grains. Furthermore, a nucleation process is also possible. In this type of treatment, due to the high energy of the DBD, that is concentrated on a small area on the surface, and also because working at high pressure, a heat transfer phenomenon might be important. Nevertheless, the nucleation is less probable due to the local heating of the surface, this assumption being sustained by previous experiments during which the temperature monitoring showed constant values on the sample during treatment. Moreover, a Joule heating of the surface is not expected, since the discharge current was less than 5 mA [4]. The nucleation might be actually initiated on the surface electrical active sites created by DBD exposure, which act as attractors for the propagation of grains and crystallites existing on the surface. There is also a great probability that the defaults inherently present onto the substrate are acting as nucleation centers leading to the peaks and grains formation.

The observed effects are resulting in an enhanced physical adsorption at the surface, as the increased exposed area can subsequently undergo linkage by chemisorption of particles and reactive species from the environment. For example, in medical applications, the surface morphology, specifically the particles dimension and their distribution could significantly enhance the human endothelial cell attachment at the surface of an implant [8]. Thus, the molecular-sized surface structures could have a significant and direct effect on the preferential adsorption of biological components from blood and tissues and on the immobilization of enzymes, antibodies, drugs, antibacterial agents, antithrombogenic agents etc. [9,10].

Furthermore, the modification of the surface roughness is usually accompanied by an increased or decreased wettability of surfaces, which is also a critical parameter for the selective adsorption of species from the biological environment [11-13]. In this way, the identification of biocompatibility properties at interface should be made in relation with the parameters related to the surface and interfacial energetic characteristics, which were calculated using the contact angle measurement.

The adhesion work is a thermodynamic parameter relevant for the adsorption characteristics of the surface, since it controls all physical interfacial events. The strong increase of the adhesion work on the treated surfaces suggests that new functional hydrophilic groups are introduced onto the surface. This is confirmed by the surface polarity, defined as

$$P = \frac{\gamma^p}{\gamma^p + \gamma^d}$$

where γ^p and γ^d are the polar and dispersive component of the surface energy, respectively.

The DBD exposure induces a strong increase of the surface energy, especially due to the increase of the polar component, as shown in Fig. 2. The polarity is modified by a factor at least 2. The higher polymer surface energy could enhance the performance of the material in contact, for example, with a biological environment, as demonstrated by the strong reduction of the interfacial tension γ_{sl} after treatment, as shown in Fig. 3.

The stability with time of the treated samples was also monitored for two weeks after treatment. The reversal of the surface modification is particularly limited, since PMMA exhibits only ~10% reduction in the adhesion work after ageing, compared to that of the untreated material, as displayed in Fig. 4, confirming thus the high post-processing surface stability acquired by samples treated under helium environment.

The modification of the surface and interfacial energetic characteristics is very steep for the treated samples compared to the untreated ones, for all gaseous mixtures used. Nevertheless, results suggest that the He+10%N_2 mixture ensures better surface functionalization compared to He-DBD and He+10%O_2. The wettability of the surface is similar for the He and the He+10%O_2 treatment. This behaviour demonstrates the high level of oxidation induced by the He discharge, due to the molecular oxygen which is inherently entrained in the inter-electrode gap from the contacting air and activated, ionized and dissociated in the discharge to give extremely reactive oxygen species that react readily with the substrate surface. The surface might be already "saturated" with oxygen moieties so no further oxidation occurs while adding oxygen in the gaseous environment. On the other hand, the better results obtained for the He+10%N_2 discharge suggest that the nitrogen species are the most efficiently activated due to transfer from helium species [5]. These species could thus induce surface functionalization by moieties other than the oxygen-related ones, as the oxidized species are the only present for He-DBD treatments.

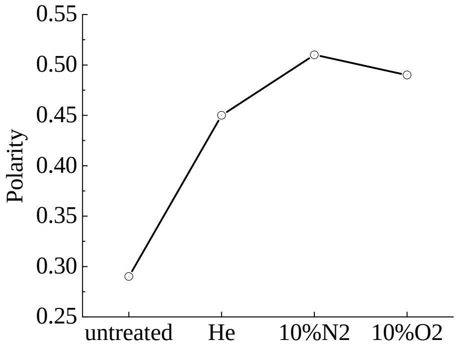


Fig. 2. Surface polarity of PMMA films, 10 s DBD treated, vs. gaseous mixture composition.

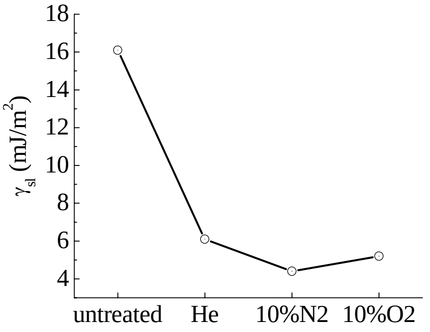


Fig. 3. Interfacial tension with water of PMMA films, 10 s DBD treated, vs. gaseous mixture composition.

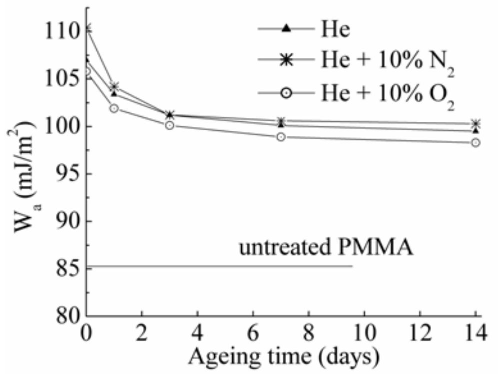
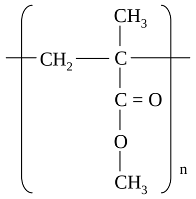


Fig. 4. Adhesion work of water on PMMA samples, 10 s DBD treated, vs. gaseous mixture composition and ageing time.

The XPS analysis allowed separating the respective contributions of the oxygen- and nitrogen-related species to the surface functionalization. PMMA is a polar functional polymer carrying intrinsically bound oxygen, with the following repetitive unit



$$\left(-CH_2-\underset{\underset{\underset{\underset{CH_3}{|}}{O}}{\underset{|}{C=O}}}{\underset{|}{\overset{\overset{CH_3}{|}}{C}}}-\right)_n$$

The carbon 1s XPS spectrum of untreated PMMA, presented in Fig. 5, consists of four distinct peaks. The C1 component, calibrated at a binding energy of 285.0 eV, corresponds to carbon atoms involved in C-C and C-H bonds. C2 at 285.7 eV is assigned to the quaternary carbon atom in the α-position to the ester group, C3 at 286.8 eV to the carbon atom involved in the methoxy- group of the ester chemical function, and C4 at 289.0 eV to the carbon atom of the carboxylic group.

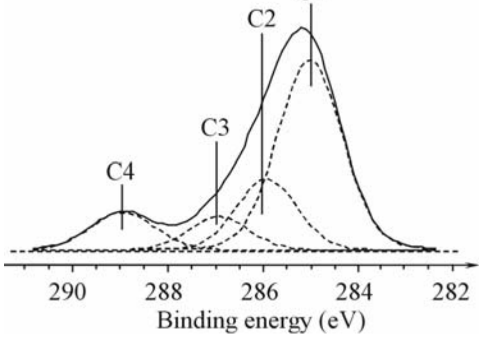


Fig. 5. C1s XPS spectrum of untreated PMMA.

Due to the high level of oxidation of the untreated sample and to the relatively similar binding energies of various oxygen- and nitrogen-related functional groups, it is difficult to identify new peaks on the XPS C1s spectra of treated PMMA. These spectra were therefore fitted with the same four components as in the example in Fig. 5. The atomic concentration percentages for oxygen and nitrogen were determined taking into account the corresponding area sensitivity factor for the different high-resolution spectral regions (C1s, O1s and N1s). Table 2 summarizes the elemental surface compositions for the pristine and the treated samples. These data indicate contributions from both nitrogen and oxygen in the attendant surface reactions.

Table 2. Elemental surface composition for PMMA samples, 10 s DBD treated, vs. gaseous mixture composition.

	untreated	treated		
		He	He+N$_2$	He+O$_2$
C (at. %)	68	62	59	58
O (at. %)	32	38	36	42
N (at. %)	0	0	5	0

It results, in the case of He+N$_2$-DBD treated PMMA, taking into account their respective binding energies and the level of nitrogen incorporation, that the species that could be relevant for nitrogen incorporation at the surface are C3 and C4, assignable to various nitrogen-single-bonded-to-carbon groups. Here it is worth noting that it is well known from other work that it is rather difficult to incorporate nitrogen at polymer surfaces, even in the case of very well controlled N$_2$ environment vacuum plasmas run for extended treatment times. It is, thus, reasonable to assume that only nitrogen-singly-bonded-to-carbon groups exist in the surface at such levels of nitrogen incorporation.

The incorporation of nitrogen by He+N$_2$-DBD exposure is significant, itself an encouraging outcome in respect of the possibility of implantation or generation of nitrogen-related functional groups by atmospheric pressure processing, since the untreated surface shows no nitrogen signal and the He and He+O_2-DBD treatment induces only surface oxidation. The surface oxidation is 6 at.% after the treatment in helium and increases to 10 at.% while adding 10% oxygen into the discharge, showing the efficiency of the present experimental arrangement, which can induce further oxidation on a polymer that already counts 32 at.% O in its chemical composition. The amount of additional oxidized groups which could be incorporated onto a polymer surface strongly depends on its initial oxygen content, becoming more limited as this content is higher [14]. On the He+N_2-DBD treated sample the "total" level of functionalization is 9 at. %, similar to that of the He+O_2-DBD treated one, excepting that nitrogen replaces oxygen, the incorporation of nitrogen being higher than the oxygen one. Nonetheless, the oxygen remains a very reactive species, although the values in Table 2 show that the incorporation of species other than oxygen at a polymer surface is possible at atmospheric pressure.

4. Conclusions

Here the effects of the dielectric barrier (DBD) treatment on the surface of polymethylmetacrylate (PMMA) films are investigated, aiming to enhanced performance of the polymer surface in contact with other materials or environment. The He+N_2 and He+O_2-DBD surface treatment is examined, discussed and compared to the He-DBD treatment, in order to select the most convenient gas mixture for the efficient modification of the surface properties and the subsequent stabilization with time of the modified surfaces. The surface analysis and characterization are performed using X-ray photoelectron spectroscopy (XPS), contact angle measurement and atomic force microscopy (AFM) before and following the DBD processing described.

The surface treatment induces increased roughness and creates a new granular structure on the DBD exposed samples, with distinct and well-organized features in the nanoscale domain, having variable dimensions depending on the gaseous mixture. The observed effects are resulting in an enhanced physical adsorption at the surface, as the increased exposed area can subsequently undergo linkage by chemisorption of particles and reactive species from the environment.

The DBD exposure induces a strong increase of the adhesion work and the surface energy, especially due to the increase of the polar component, which leads to enhanced adhesion properties. This effect could enhance the performance of the material in contact, for example, with a biological environment, as demonstrated also by the strong reduction of the interfacial tension after treatment.

The surface chemical functionalization and the enhanced adhesion properties of the DBD treated polymer are due, in the case of He and He+O_2 gaseous environment, only to oxygen-related polar groups, demonstrating that a polar functional polymer carrying intrinsically bound oxygen, can be further oxidized on exposure to DBD, whereas both oxygen and nitrogen-related species contribute to the attendant surface reactions for He+N_2-DBD exposure. The incorporation of nitrogen is significant, itself an encouraging outcome in respect of the possibility of implantation or generation of nitrogen-related functional groups by atmospheric pressure processing, viewing also the interest in creating amino-groups onto polymer surfaces aimed to be compatible with a biological environment.

The treatment is efficient and reproducible for short treatment times and the surface properties have high post-processing stability.

The DBD treated PMMA films exhibit thus improved surface characteristics and potentially better application performance, as demonstrated in relation with the surface morphology and roughness, the surface and interfacial energetic characteristics, and the chemical structure. These are key parameters in the identification of the biocompatibility properties at the interface between a material and its environment, so allowing planning of further experiments, where specific biocompatibility tests will be performed.

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