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Plasma induced surface modification in relation to polymer characteristics

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This paper aims an analysis on the correlation between various plasma effects on polymers treated under a particular experimental configuration, dielectric barrier discharge-type. Experiments are carried out to relate relevant surface properties, as surface energy components, surface topography, structural changes and chemical composition, under conditions where plasma processing allows complex surface modification, by combined functionalization and crosslinking to polymer characteristics. In this respect, the degree of modification of the surfaces, in terms of adhesion work increase, incorporation of polar groups, crystallinity enhancement, is shown to depend both on the sample polarity prior to treatment and on the respective chemical structure of polymers, showing also correspondence with the crystallinity and average size of crystalline regions.

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1. Introduction

Among various surface modification techniques, plasma is a complex energy source for tailoring the surface properties of diverse materials. Plasma represents an unique large variety of components, as excited and ionized particles, both atomic and molecular, photons, radicals, all these species carrying significant energy to induce chemical reactions, both in the plasma volume and at its interface with solid surfaces. One important application of plasma processing technique is surface treatment of polymers.

Plasma treatment of polymers encompasses a variety of plasma technologies and polymeric materials, for a wide range of applications [1-4]. Polymer materials are generally chosen and developed for their remarkable bulk properties, however, many of the final properties of polymers rest on the surface chemical composition, material structure and surface orientation of specific chemical functionalities, all intrinsically related, and defining the interaction of the material with its environment. In this respect, plasma treatments are advantageous for their ability to modify a wide range of polymer surfaces, within short treatment times, the chemical effects of plasma treatments being usually confined to the surface regions. Depending on the choice of the process gases, treatment parameters, in relation to the chosen polymer, a wide range of surface chemistries can be achieved on many polymer materials. Three major effects are normally observed: functionalization, which can lead to covalent bonds suitable for further chemical attachment, crosslinking, which can cohesively strengthen the topmost surface layer, and surface ablation, which can also be used for surface cleaning. Generally, the different effects mentioned above are difficult to separate and analyze, due to their inherent structural and chemical complexity.

In this respect, this paper aims to provide an analysis on plasma effects on a range of polymers, selected for their representative varied structure, functionality, degree of oxidation, crystallinity. The relation between polymer characteristics and plasma-induced surface modification is underlined, resulting from complex mechanisms, by combined functionalization and crosslinking.

2. Experimental

Plasma is generated using dielectric barrier discharge (DBD) [5,6]. The experimental arrangement consists of an asymmetrical electrode configuration, with adjustable inter-electrode gap, between 1 mm up to a few cm. The HV electrode is a disc 2 mm radius and the grounded electrode (GND) is a metallic plate 50 mm × 50 mm, covered with a glass plate 1 mm thick. The samples to be treated are placed on the glass plate. The discharge is generated using a pulsed high-voltage supply, 2 kHz frequency, 25 μs pulse width, 4 kV amplitude. The peak discharge current is 10 mA, whilst the energy deposited in the discharge during one cycle of the DBD is 20 mJ/pulse.

The working gas is introduced in the interelectrode gap, at atmospheric pressure, by a gas shower placed near the HV electrode. During the treatments, the inter-electrode gap is adjusted to 1 cm. In this configuration, the gas flow generates a discharge beam, ~ 2 mm wide. The beam spreads on the polymer film placed on the grounded electrode, due to the dielectric effect, in a surface discharge covering ~ 5 cm^2. The electrical parameters measurement, i.e. discharge current, shows that DBD is obtained in the glow mode, presenting therefore no non-homogeneities due to filamentary streamers and ensuring thus uniform treatment over the entire exposed area of the samples.

Here He is selected as the most convenient gas while working at atmospheric pressure, since it easily allows stabilizing homogeneous glow discharges at this pressure compared to other gases, at lower sustaining voltages and interelectrode gaps as high as a few centimetres [7]. Helium is also very suitable for use in polymer surface treatments, with its low degradation effect and reaction enthalpy on heat transfer rate to the surface, and also high properties of crosslinking and functionalization onto the surface [8,9].

Treatments are performed on polymer commercial films (Goodfellow Ltd.), all exposed to the discharge as films 0.25 mm thick: polyamide-6 (PA-6), high density polyethylene (HDPE), polymethylmetacrylate (PMMA) and polytetrafluorethylene (PTFE). These polymers are suitable in this study for reason of their variety of structure, functionality, degree of oxidation, crystallinity. The respective chemical structures of the monomer units of the polymer materials studied are presented in Fig. 1.

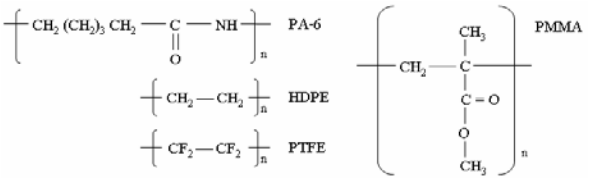

Fig. 1. Chemical structure of monomer units of selected polymers.

Treatments are performed for 10 s exposure time, chosen in correlation with previous experiments [6], since allowing effective and stable surface modification.

The discharge is characterised by means of electrical parameters measurement and optical spectroscopy. The electrical parameters, i.e. voltage applied to the electrodes, resultant discharge current and charge stored on the electrodes, are recorded with a Lecroy 9304CM digital oscilloscope. These parameters are then used for obtaining the current-versus-voltage or charge-versus-voltage plots and calculating the energy deposited at the electrodes during one pulse of the DBD. The emission spectra of the discharge are also digitally recorded in the UV-visible wavelength range, using Triax 550 and Oriel MS125 monochromators. The acquisition, control and data reduction is done using the software supplied along with the standard Grams 32 package.

The surface analysis is performed by X-ray diffraction (XRD), contact angle measurement and X-ray photoelectron spectroscopy (XPS).

XRD permits investigation of the crystalline structure of polymer films. The wide angle region of XRD spectra, for scattering angle $2\theta > 8°$, can be used to determine crystallographic aspects, as lattice spacing, average crystallite size, degree of crystallinity and preferred crystallographic orientation. The diffraction patterns show peaks, associated with diffraction on the crystalline phase, superimposed on an amorphous halo. These patterns are fitted with mixed Gauss-Lorentz functions, in order to estimate the area of the two phases. The degree of crystallinity (X_c) is calculated, from the ratios of the areas under the crystalline peaks (A_c) and the amorphous halos (A_a), as [10]

$$X_c = \frac{A_c}{A_c + A_a} \tag{1}$$

The average size of the crystalline regions (D) of polymers before and after DBD treatment is determined from the broadening of the peaks, using the Scherrer equation [11]

$$D = \frac{0.89 \cdot \lambda}{\beta \cos\theta} \tag{2}$$

where β is the half-width of the diffraction line at 2θ, θ the Bragg angle and λ the X-ray wavelength.

The average intercrystallite separation (R) in the amorphous region of the sample is evaluated from the position of the maximum of the amorphous halo [12]

$$R = \frac{5\lambda}{8\sin\theta} \tag{3}$$

Contact angle measurement allows evaluation of the surface energetic characteristics and monitoring the ageing behaviour of plasma-exposed polymer surfaces. Contact angles are obtained using the sessile drop technique, under controlled conditions of room temperature and humidity, at different intervals after the surface treatment, up to 30 days. An automated system is used to store the drop images, via Canon A85 camera, with PC-based control, acquisition and data processing. Bidistilled water and formamide are used as test liquids for calculation of the surface energy components.

The quantities characterizing the surface energetics and its adhesion properties in contact with the environment are calculated using the measured contact angles.

The adhesion work is defined as

$$W_a = \gamma_{lv}\left(1+\cos\theta\right) \tag{4}$$

where θ is the measured contact angle and γ_{lv} is the surface tension of the liquid used for measurement.

The surface energy is

$$\gamma_{sv} = \gamma_{sv}^{p} + \gamma_{sv}^{d} \tag{5}$$

where γ_{sv}^{p} and γ_{sv}^{d} are the polar and dispersive component of the surface energy, respectively

The surface polarity is

$$P = \frac{\gamma_{sv}^{p}}{\gamma_{sv}^{p} + \gamma_{sv}^{d}} \tag{6}$$

XPS spectra provide quantitative information permitting to identify functional groups and to determine the surface chemical composition. The high-resolution C_{1s}

spectrum was analysed, taking the 285.0 eV value of the hydrocarbon C_{1s} core level as calibration of the energy scale. The peak envelopes are curve-fitted using mixed Gauss-Lorentz component profiles, with linear-type background subtraction. Spectra are fitted based on standard measurement [13].

3. Results and discussion

Generation of surfaces and interfaces allowing control of the interaction with a specific environment, by means of definite surface chemical composition, structure and orientation of specific chemical functionalities, is a major challenge in the development of surface processing techniques. In this respect, plasma represents very reactive environment when in contact with a polymer surface, due to complex contributions from its large variety of energetic species. The physico-chemical reactions break the physical and chemical bonds, yielding active sites, polar groups and scission products onto the polymer surface. Then, depending mainly on the nature of excited species in plasma, plasma triggers the formation of a new functionalized surface layer or a crosslinked surface structure. The second mechanism is particularly favoured under inert gas environment, whereas presence of reactive species conducts to creation and incorporation of functional groups.

Information on the excited species present in the discharge is obtained by emission spectroscopy, which shows, in addition to the emission from the helium excited atomic species, emission from the molecular species present in air. This result is related to the presence of non-negligible amount of air entrained in the discharge by the working gas flow. The species identified on the DBD emission spectra are atomic helium He^*, neutral molecular nitrogen N_2 (bands of the first and the second positive systems), ionized molecular nitrogen N_2^+ (bands of the first negative system), and also atomic oxygen O^* (777.4 nm) and hydrogen H^* (lines of the Balmer series). It is then expected that plasma treatment results in high degree of surface oxidation, since oxygen, present even at very low levels, potentially represents very surface reactive species.

Nonetheless, competition between reactive oxygen species and helium species, with their large amount of energy available to transfer to the polymer surface, would end both in functionalization and crosslinking. The second process is particularly preferential in inert gases (Crosslinking by Activated Species in INert Gases - CASING) [14], where the plasma active species experience practically no chemical reactions with the radicals created onto the surface, which may thus link one to the other. The formation of chemical links between the molecular chains, by covalent bonds, yields an extremely stable ordered three-dimensional surface structure, with high density and cohesion, chemical resistance and lower friction coefficient. A higher degree of crosslinking is beneficial for the stability of the surface properties. The surface crosslinked layer acts like a barrier to the diffusion of molecules between surface and bulk, limiting the random movement of the polymer chain and restricting permeation.

Here, surface functionalization is directly substantiated by XPS and contact angle behaviour, whereas surface crosslinking is indirectly rendered to evidence, by XRD and ageing behaviour of treated polymers.

XRD spectra for polymer samples (examples presented in Figure 2), show well defined diffraction peaks, assigned to the crystal planes in the polymer, superimposed on the wide component due to the amorphous phases. Deconvolution of the spectra allows separation of the peaks, as presented in Table 1. The same peaks are present in the spectra of the treated samples, with different amplitudes compared to the untreated polymers. Areas of the peaks are used for calculating the crystallinity index X_c. The shape and position of the peaks permit calculation of the average size of the crystalline regions (D) and the average intercrystallite separation (R). The most prominent peak on all samples, at $2\theta = 21.4°$, is used to calculate D. The results obtained are presented in Tables 2-4, emphasizing the variations in the polymer crystallinity.

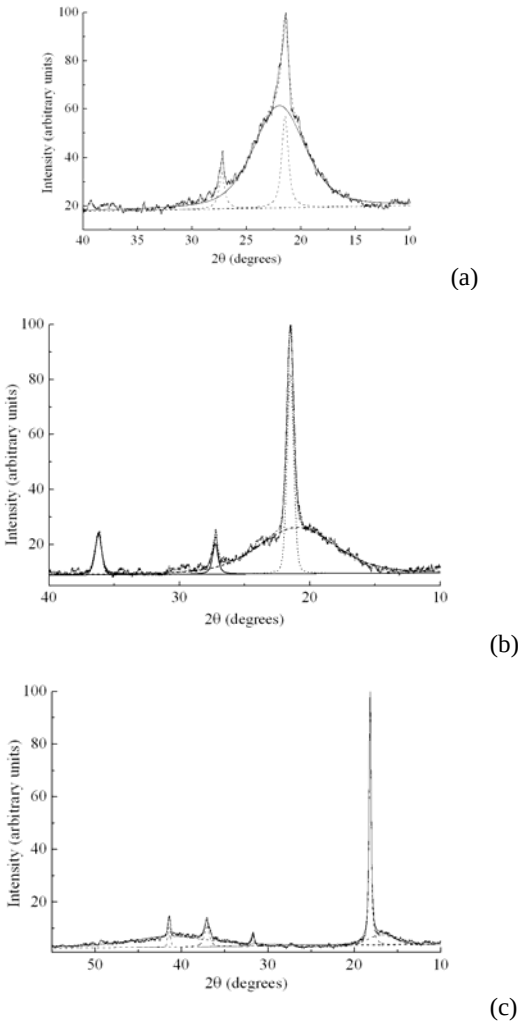

Fig. 2. XRD spectra for (a) PA-6, (b) HDPE, (c) PTFE sample.

Table 1. XRD peaks of various polymers.

Polymer	PA-6	HDPE	PMMA	PTFE
2θ (°)	21.4	21.4	21.4	21.4
2θ (°)	27.3	27.3	27.3	27.3
2θ (°)		36.2		37.0
2θ (°)				41.4
2θ (°) (amorphous)	21.0	21.0	18.0	16.8

Table 2. Crystallinity index (X_c) for various polymers, before and after DBD treatment (10 s treatment time).

Sample		PA-6	HDPE	PMMA	PTFE
Crystallinity index	untreated	0.11	0.26	0.44	0.48
	treated	0.14	0.30	0.60	0.62

Table 3. Average size of the crystalline regions (D) for various polymers, before and after DBD treatment (10 s treatment time).

Sample		PA-6	HDPE	PMMA	PTFE
D(nm)	untreated	13.24	15.76	25.80	34.68
	treated	15.03	17.88	28.03	36.29

Table 4. Average intercrystallite separation (R) in the amorphous region of various polymers, before and after DBD treatment (10 s treatment time).

Sample		PA-6	HDPE	PMMA	PTFE
R(Å)	untreated	6.14	6.14	7.15	7.67
	treated	6.08	6.10	7.11	7.66

The quantities characterizing the surface energetics and its adhesion properties are calculated using the measured contact angles. Treated polymer surfaces exhibit enhanced wettability, compared to the untreated ones, as shown by the adhesion work of water (Figure 3). The surface energy components are also modified by plasma treatment, resulting in steeply enhanced surface polarity (Figure 4), due to the increase of the polar component of the surface energy.

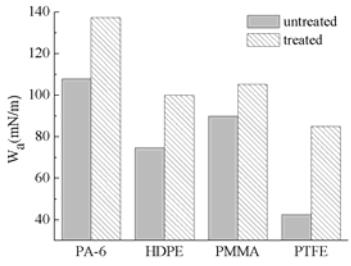

Fig. 3. Adhesion work of water on DBD plasma treated polymers.

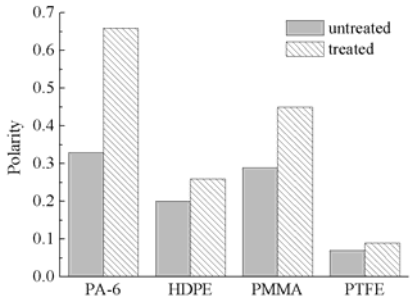

Fig. 4. Surface polarity of DBD plasma treated polymers.

Importantly, the measured contact angles show similar low-dispersion (3-4º) on all polymers and for all treatment conditions, immediately after treatment and also on aged samples, showing that the surface is not degraded after such short treatments, with the result that the modification of the surface properties is stable with time (Fig. 5).

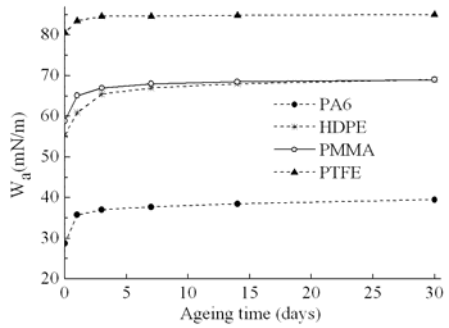

Fig. 5. Adhesion work of water on DBD plasma treated polymers, vs. ageing time.

XRD results and ageing behaviour of polymers are consistent with surface crosslinking, associating well with the properties of He plasmas, known to efficiently produce crosslinking reactions [9,14].

XRD measurement allows characterizing the ordered and disordered structural regions of the polymer. Tables 2, 3 emphasize the variations in the polymer crystallinity, as increase of the crystallinity index (X_c) and average size of the crystalline regions (D) is observed. Such behaviour is consistent with the formation of an ordered three-dimensional surface layer due to crosslinking. Importantly, the augmentation of X_c and D, reported to untreated polymers, shows higher variation for the polymers with higher content in amorphous phase.

The crosslinked structure created at the surface may as well explain the remarkable stability with time of the surface properties after treatment. Figure 5, presenting the evolution of the water adhesion work W_a with ageing time, shows that the post-processing recovery of the surface properties is very limited, with only a few percent loss in W_a on the 30 days-aged treated samples, compared to untreated ones.

Nonetheless, plasma affects the surface in much more complex manner, since the enhanced surface polarity is due to the creation of polar functional groups onto the surface (Figure 4). Whereas the He-DBD can be efficient in the ablation of small fragments from the surface and the formation of free radicals, enhancing thus subsequent crosslinking reactions, the molecular species in the discharge, due to residual air, create hydrophilic groups onto the polymer surface. In this respect, the chemical composition of the polymer samples, presented in Table 5, indicates significant surface functionalization, with oxidation only functional features.

Table 5. Surface oxygen atomic content (in atom %) of DBD plasma treated polymers (10 s treatment time).

Sample		PA-6	HDPE	PMMA	PTFE
O (at %)	untreated	14.2	1.1	32.0	—
	treated	24.3	15.3	38.0	1.0

In addition, the degree of modification of surfaces, in terms of polar groups, seems to depend in the present case both on the "polarity" of the samples prior to treatment and on the respective chemical structure of the polymers. Thus, the highest degree of modification is obtained for the PA-6 and HDPE samples. PA-6 is the sample with the highest polarity (Figure 4), which seems to make it most susceptible to be surface-modified, whereas HDPE has the simplest structure, bearing no functional groups other than $-CH_2-$.

Functionalization of PA-6 sample, compared to that of untreated material, represents an increase in oxygen content by a factor 1.7, whereas the increase observed for PMMA, which is ranked second in terms of polarity among tested polymers, is by a factor only ~1.2. Here the correspondence with the chemical structure is again apparent, given that PMMA has the highest content in intrinsically structurally bonded oxygen (Table 5).

Furthermore, the degree of chemical modification shows correspondence with the crystallinity and average size of crystalline regions of the polymer (Tables 2, 3). Modification is higher for polymers with lower crystallinity index (X_c) and lower average size of the crystalline regions (D), supporting the assumption that the mechanism of surface modification is triggered by preferential etching of the amorphous regions.

4. Conclusion

Mechanisms taking place at plasma-polymer interface, under He-DBD environment, allow complex surface modification. Active plasma species, bearing high energy, as helium metastables, and high reactivity, as oxygen-related species, generate active sites, as radicals and polar groups onto the polymer surface, that can then recombine to trigger branching and crosslinking. The resultant surface modification takes thus place by combined functionalization and crosslinking. Results presented here, obtained by various surface analysis techniques, for selected polymers, correlate well, emphasising the relationship between the surface polarity, the chemical structure and composition and the crystalline/amorphous phase ratio in the surface modification mechanisms. In this respect, the degree of modification of the surfaces, in terms of adhesion work increase, incorporation of polar groups, crystallinity enhancement, is shown to depend both on the sample polarity prior to treatment and on the respective chemical structure of polymers, showing also correspondence with the crystallinity and average size of crystalline regions.

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