

Surface modification of natural and synthetic polymers induced by pulsed atmospheric pressure plasma

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Comparison is carried out on plasma-induced effects under helium and argon gaseous environment, in pulsed dielectric barrier discharge (DBD), on natural and synthetic polymers. The two inert gas plasmas are conducting to similar results, in terms of surface wettability and functionalization, on both types of polymeric surfaces, due to the high rate surface oxidation by species present in the residual atmospheric air. An enhanced ablation effect is triggered in argon-gas environment, limiting the level of functionalization attainable.

1. Introduction

Polymeric materials offer an extraordinary range of bulk properties, thus playing an essential role in many applications. Nonetheless, many polymer properties rest on the surface chemical composition, material structure and surface orientation of specific chemical functionalities, all intrinsically related, and defining the material interaction with its environment.

Among various techniques developed for surface processing, plasma is a complex source of energy for surface modification of polymers, due to the large variety of components, as excited and ionized particles, photons, radicals, all these species being capable to induce chemical reactions, both in the plasma volume and at its interface with solid surfaces [1-5].

Taking this into account, a study is carried out on the plasma-induced effects under helium and argon gaseous environment, in pulsed dielectric barrier discharge (DBD), on synthetic and natural polymers, aiming to compare the effects of the two inert gases.

2. Experimental

A dielectric barrier discharge (DBD) system with symmetrical electrode configuration, in enclosed chamber, described in detail elsewhere [6], is used. The interelectrode gap is 3 mm. Positive voltage pulses with 2 kHz repetition frequency, 30 μ s pulse width and 4 kV amplitude were used to generate the discharge. The energy transferred to the discharge system during one pulse is 0.6 mJ [6]. The experiments are performed at atmospheric pressure, in inert gases - He and Ar (99.996% purity). The working gas is continuously injected in the interelectrode gap at different gas flow rate, without preliminary vacuum pumping.

The treatments are performed on synthetic and natural polymer films of polysulfone (PSU) (Goodfellow Ltd.) and grease-resistant paper (GRP) (S.C. Ceprohart S.A.), respectively. GRP is mainly based on bleached sulfate cellulose from hardwood and softwood mixed with some additives, as super hydrophobic fluoropolymer, cationic polymer as retention agent and alkyl ketene dimer as sizing agent. The plasma exposure time is varied from 5 s up to 120 s.

The surface analysis is carried out using contact angle measurement and X-ray photoelectron spectroscopy (XPS).

The contact angles are obtained by sessile drop technique. An automated system is used to store the drop images, via a Canon A85 camera, with PC-based control, acquisition and data processing. The values of the static contact angle presented are the average of minimum ten measured values obtained on the imaged sessile liquid drop profile, with a drop size of 1 μ l.

The XPS spectra are recorded on a PHI-Ulvac VersProbe 5000 spectrometer, using the Mg K α line ($h\nu = 1253.6$ eV), at 45° take-off angle. The value of 285.0 eV of the hydrocarbon C1s core level is used as a calibration of the energy scale. The peak envelopes are curve-fitted using mixed Gauss-Lorentz component profiles.

3. Results and Discussion

The DBD was previously characterized by measurement of the electrical and spectral parameters of the discharge [6].

Here two series of experiments are conducted. In one series the plasma treatment is performed for constant gas flow rate (3 L/min) and various

exposure times, while in the other series the exposure time is constant (20 s) and the gas flow rate is varied between 0.5 and 5 L/min. Yet, the experimental results show that the surface modification investigated is not significantly affected by a 10 times increase of gas flow rate.

The water contact angle is found to change for all treated samples. In this respect, the variation of the water contact angle as a function of the treatment time, for the He-DBD and Ar-DBD treated polymers, is presented in Figure 1.

The overall view shows that the contact angle decreases from 83° for the untreated sample, to the lowest value of 35.2°, for PSU (Figure 1.a), and from 98.8°, to the lowest value of 12°, for GRP (Figure 1.b). This is associated to an increase of the water adhesion work [6]. It results that the surface modification is very steep within the first 10 s of treatment, for both polymer surfaces. Then it reaches a plateau for PSU, while for GRP it continues at significant rate for higher treatment times.

XPS is used to investigate the chemical structure of the polymer surfaces, taking into account that the most reactive species in the discharge is oxygen, due

to residual air. In this respect, Table 1 lists the relative atomic composition of different components of the carbon species C1s for pristine and treated PSU samples.

For XPS spectra of untreated PSU samples, carbon atoms attached to hydrogen/carbon, sulfone, and ether groups exhibit C1s core level binding energies of 285.0 (C1), 285.6 (C2), and 286.5 eV (C3), respectively [7, 8]. Also, a fourth peak, the low energy π - π^* shake-up transitions accompanying core level ionization at around 291.7 eV (C4) is also present for both untreated and plasma treated PSU samples [7, 8].

The C1s spectrum changes for plasma-treated PSU samples. The deconvolution of the C1s peak reveals the presence of a new component. More precisely, the peak at binding energy of 289.3 eV (C5) corresponds to the carboxyl $-\text{O}-\text{C}=\text{O}$ group created by the plasma treatment.

Table 1 also presents the relative oxygen content of the polymeric sample, expressed as O/C ratio, calculated as $O/C = (C3 + C5)/(C1 + C2 + C4)$, which demonstrates significant surface functionalization. Thus, the O/C ratio increases by a factor more than 2 for short plasma treatment time (5 - 20 s).

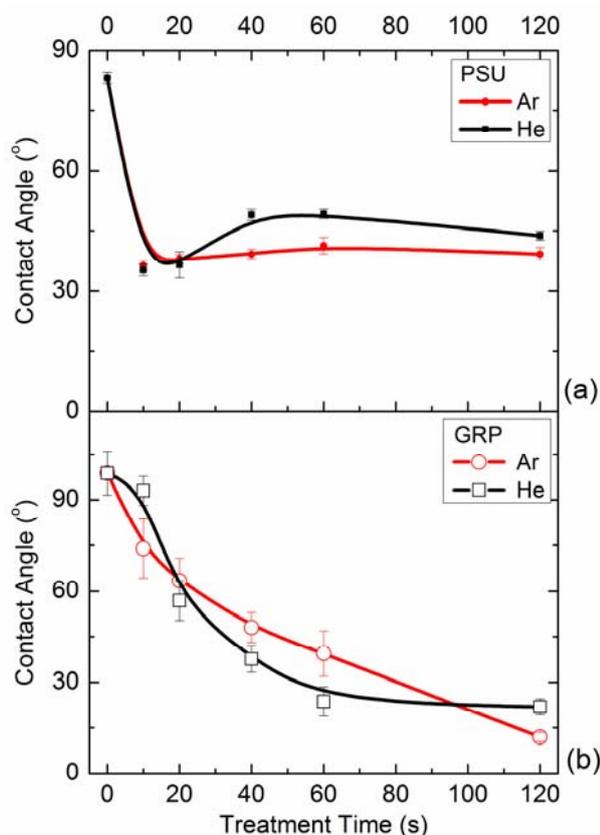


Figure 1. Contact angle versus treatment time, for PSU (a) and GRP samples (b), for He-DBD and Ar-DBD exposure.

Table 1. Atomic composition of the carbon species C1s on PSU surface (in atom %), as a function of the treatment time

t (s)	C1 (at%)	C2 (at%)	C3 (at%)	C4 (at%)	C5 (at%)	O/C
0	75.2	7.1	14.3	3.4	-	0.17
<i>(a) He-DBD plasma</i>						
5	63.9	5.3	23	2.6	5.2	0.39
20	58.6	9.5	21.9	2.9	7.1	0.41
120	64.8	10.1	18	3.8	3.3	0.27
<i>(b) Ar-DBD plasma</i>						
5	59.4	10.4	20.6	3.6	6	0.36
20	59.0	10.3	21.4	2.8	6.5	0.39
120	65.1	12.8	17.2	3.4	1.5	0.23

Table 2. Surface total composition (in atom %) for GRP samples versus the treatment time

	<i>untreated</i>	<i>5 s</i>	<i>20 s</i>	<i>120 s</i>
<i>(a) He-DBD plasma</i>				
C 1s	62.3	61.1	59.7	56.7
O 1s	37.7	38.9	40.3	43.3
<i>(b) Ar-DBD plasma</i>				
C 1s	62.3	64.0	60.1	58.5
O 1s	37.7	36.0	39.9	41.5

Then, for prolonged treatment, the inherent limiting level of oxidation of the sample is reached, conducting, eventually, to reversal of the surface functionalization for 120 s duration of plasma exposure (Table 1). This behavior renders to evidence combined mechanisms during surface modification, which are surface oxidation and ablation of low weight volatile fragments, occurring at different rates and producing opposite effects. The diminution of the level of oxidation arises due to higher rate ablation under such prolonged surface exposure into plasma.

The assessment of the results obtained in the two gaseous environments reveals comparable surface functionalization for the same treatment time, which could imply that the oxidation of PSU occurs at similar rate in He and Ar-gas plasma.

Nonetheless, the oxidation effect is somehow lower in Ar environment, since the *O/C* values for Ar-DBD treatment are 0.36 and 0.39, in comparison to 0.39 and 0.41 for He-DBD treatment, for 5 s and 20 s plasma exposure, respectively. More, for extended treatment (120 s), the diminution of the surface oxidation level is visibly more pronounced for Ar-DBD exposed surfaces (Table 1).

Such behavior is probably due to the physical effect of larger-size rare gas atoms, inducing more effective ablation of volatile oxidized fragments and, consequently, limiting the oxidation effect throughout.

The PSU surface reaching a limiting level of oxidation for plasma exposure shorter than 20 s, as established by XPS data, correlates well with the surface wettability behavior, since the water contact angle also stabilizes after 20 s treatment time (Figure 1.a).

The GRP samples do not exhibit the same trend of evolution as PSU, probably due to the more permeable structure of paper, compared to the compact polymer film, which allows plasma to modify a deeper layer. As a consequence, the alteration of GRP surface properties progresses on the entire range of exposure duration tested here, yet, at different rates.

As shown by the data from Figure 1.b, the water contact angle decreases very fast during the first 20 s of treatment, followed by lower rate decrease for exposure longer than 20 s. Interestingly, the contact angle for He-DBD treated GRP levels out for prolonged treatment (~ 60 s), whereas for Ar-DBD treated GRP it exhibits practically constant rate of variation throughout the 20 s - 120 s range, consistent with the physical effect of larger-size Ar atoms, compared to He atoms.

The XPS data presented in Table 2 correlate well with the contact angle trend of variation, showing continuous increase of the GRP oxygen content, in the 5 s - 120 s range tested here. Furthermore, the oxygen amount is lower for Ar-DBD treated samples, compared to He-DBD treated ones, for the same treatment times, relating, the same as for PSU samples, to higher rate ablation promoted by Ar atoms, which conducts to lower level of oxidation.

4. Conclusions

A study is carried out on the plasma-induced effects under helium and argon gaseous environment, in pulsed dielectric barrier discharge (DBD), on synthetic and natural polymers.

The results show that the two inert gas plasmas are conducting to similar results, in terms of surface wettability and functionalization, on both types of polymeric surfaces, due to the high rate surface oxidation by species present in the residual atmospheric air.

Nonetheless, Ar-gas environment triggers enhanced ablation effect compared to He-gas, due to the physical effect of larger-size Ar atoms, which reduces the level of functionalization attainable.

The compact PSU film exhibits limiting degree of oxidation induced by atmospheric-pressure plasma exposure, whereas the more permeable GRP structure allows for modification of a deeper subsurface layer.

5. References

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