

COMPARING THE MODIFICATION INDUCED BY PLASMA AND UV RADIATION TO POLYMER SURFACES*

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Received November 3, 2010

Abstract. The treated polymer surfaces perform as a function of their chemical structure, type of exposure, i.e. plasma or UV radiation, and exposure time. It results that processes at the very surface are dominated by reactions involving ions and metastables, while the radiative energy transfer dominates processes in the bulk.

Key words: Atmospheric pressure plasma, UV radiation, polymer, surface energy, polarity, ageing.

1. INTRODUCTION

Among various surface modification techniques, plasma is complex energy source for tailoring the surface properties of diverse materials. Plasmas are chemically active media, representing unique large variety of components, as excited and ionized particles, both atomic and molecular, photons, radicals. All these species are carrying significant energy to induce chemical reactions, both in the plasma volume and at its interface with solid surfaces. In addition, among various types of plasmas, cold plasmas do not cause thermal damage to surfaces they may come in contact with. This characteristic provides their application for low-temperature plasma chemistry and for treatment of heat-sensitive materials including polymers and biological tissues [1–6].

In the case of the surface modification of polymers, the specific roles of each plasma component are difficult to separate and analyze. In this respect, the still debated issue concerning whether the major contribution in surface reactions belongs to the electromagnetic component, or to the plasma heavy particles, presents practical interest, since there is need to optimize plasma treatments as to lower energy consumption.

* Paper presented at the National Conference on Physics, September 23–25, 2010, Iași, Romania.

Taking into account the above, this paper presents results on the surface processing of polymer films, by exposure under the entire plasma beam and exposure only under the UV radiation plasma component, in the same plasma reactor working at atmospheric pressure. Different treatment times were tested and the stability with time of the surface properties was also monitored. Results allowed to conclude on the paramount role of plasma particles in triggering surface modification, and to consequently optimize the plasma treatment parameters as to efficient and stable surface modification.

2. EXPERIMENTAL

The plasma is generated using a dielectric barrier discharge (DBD). The plasma reactor arrangement has an asymmetrical electrode configuration, with adjustable inter-electrode gap, between 1 mm up to a few cm. The HV electrode is a disc with radius 2 mm and the grounded electrode is a metallic plate, covered with a glass plate 1 mm thick. In this configuration, the gas flow generates a discharge beam, about 2 mm wide, which spreads on the polymer film, due to dielectric effect, in a surface discharge covering about 5 cm² [7].

The samples to be treated are placed on the glass plate. The discharge is generated using HV pulses at 2 kHz frequency, 20 μs pulse width, 4 kV amplitude. The peak discharge current is 12 mA, whilst the energy deposited in the discharge during one cycle (pulse) of the DBD, calculated using voltage *versus* charge Lissajous figures, is 78 μJ. Figure 1 presents, as example, the DBD voltage and current intensity waveform, where the single-peak current, without spikes due to filamentary streamers, emphasizes the homogeneous diffuse discharge regime obtained in the present arrangement.

Helium is used here as working gas, at 60 sccm constant flow rate, where the gas selection is based on He being the most convenient gas while working at atmospheric pressure, since it allows stabilizing homogeneous glow discharges much easier compared to other gases, at lower sustaining voltages and interelectrode gaps as high as a few centimeters. 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 [8–10].

Importantly, in the present flow-through system, non-negligible amount of air is entrained in the plasma beam by the gas flow, conducting to occurrence of excited atomic and molecular oxygen species in the discharge. In this respect, it is well known that oxygen, present even at very low levels, potentially represents very surface and volume reactive species.

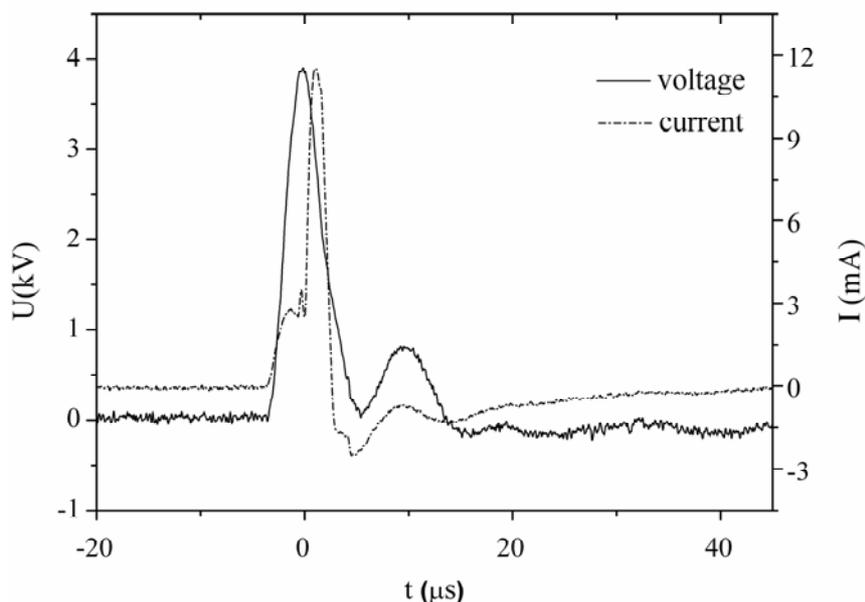


Fig. 1 – DBD voltage and current waveform.

Under such conditions, the species most susceptible to be taken into account in reactions at the plasma-polymer interface are the two He metastables, 2^3S and 2^1S , known to bear remarkable high excitation energy, 19.8 eV and 20.6 eV, respectively, the highly reactive atomic and molecular oxygen species and the very high energy UV photons.

Taking into account the above, two experimental situations are explored, in order to separate the contribution of the electromagnetic plasma component to surface reactions, by firstly exposing directly the polymer samples to DBD plasma, and then setting up the exposure with the sample covered with a quartz slide, 0.5 mm thick. In the first situation, all reactive plasma components, *i.e.* particles and radiation, reach the surface, whereas in the second situation there is only the radiation component, with $\lambda > 230$ nm, which interacts with the surface.

Treatments are performed on two types of polymer commercial films (Goodfellow Ltd.), presented to the discharge as films 0.25 mm thick, polyamide-6 (PA-6) and polytetrafluorethylene (PTFE), selected due to their very different chemical structure (Fig. 2) and susceptibility to surface modification. Whereas PA-6 is high surface polarity polymer, being thus expected to show significant modification after rather short plasma exposure, PTFE has high chemical inertness and resistance to external agents and is presumed to show negligible modification unless large energy is available to transfer at the surface [7].

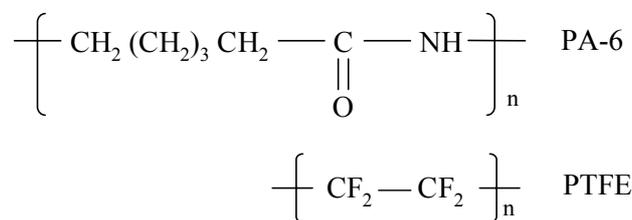


Fig. 2 – Chemical structure of PA-6 and PTFE polymers.

Treatments are performed for 10 s exposure time, chosen in correlation with previous experiments, as allowing effective and stable surface modification [4].

The surface analysis is performed by contact angle measurement, technique which is very sensitive to changes occurring in the one-two near-surface monolayers. Contact angle values allow 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 15 days. Bidistilled water and formamide are used as test liquids for calculation of the surface energy components.

The quantities characterizing the surface energetic and its adhesion properties in contact with the environment are thus calculated: adhesion work W_a , surface energy of the solid surface γ_{sv} , polar γ_{sv}^p and dispersive γ_{sv}^d component of the surface energy, surface polarity P . All these parameters were calculated for untreated samples, DBD and UV-treated samples, immediately after the treatment and after ageing.

3. RESULTS

The treated polymer surfaces perform differently, as a function of their chemical structure, type of exposure, *i.e.* plasma or UV radiation, and exposure time. In this respect, Tables 1 and 2 display the values of the adhesion work of water, the components of the surface energy and the surface polarity for various exposed samples, generally indicating increase of the surface hydrophilicity and polarity after treatment.

These data point out that the degree of modification is significantly higher for PA-6 than for PTFE, for all treatment conditions, and that increase of exposure time induces higher modification of the surface. Nonetheless, the modification induced only by the UV plasma component is considerably lower than that induced by total plasma exposure, although the exposure duration was deliberately selected much higher for the UV component.

Table 1

W_a of water, γ_{sv}^p , γ_{sv}^d and P , for DBD and UV radiation treated PA-6, as a function of the exposure time

Treatment / exposure time	W_a [mJ/m ²]	γ_{sv}^p [mJ/m ²]	γ_{sv}^d [mJ/m ²]	P
untreated	106.6	11.99	37.73	0.24
DBD / 10 s	129.7	32.10	27.39	0.54
DBD / 30 s	135.6	40.69	22.76	0.64
DBD / 1 min	135.6	42.21	22.07	0.66
UV / 30 s	108.5	13.04	37.42	0.26
UV / 2 min	114.3	17.45	37.08	0.32
UV / 5 min	121.1	21.28	31.92	0.40

Table 2

W_a of water, γ_{sv}^p , γ_{sv}^d and P , for DBD and UV radiation treated PTFE, as a function of the exposure time

Treatment / exposure time	W_a [mJ/m ²]	γ_{sv}^p [mJ/m ²]	γ_{sv}^d [mJ/m ²]	P
untreated	37.6	0.18	11.51	0.015
DBD / 10 s	57.3	1.06	28.38	0.036
DBD / 30 s	60.0	1.14	22.93	0.047
DBD / 1 min	64.5	2.01	28.72	0.065
UV / 30 s	38.4	0.24	13.88	0.017
UV / 2 min	40.8	0.40	18.65	0.021
UV / 5 min	41.1	0.44	16.48	0.026

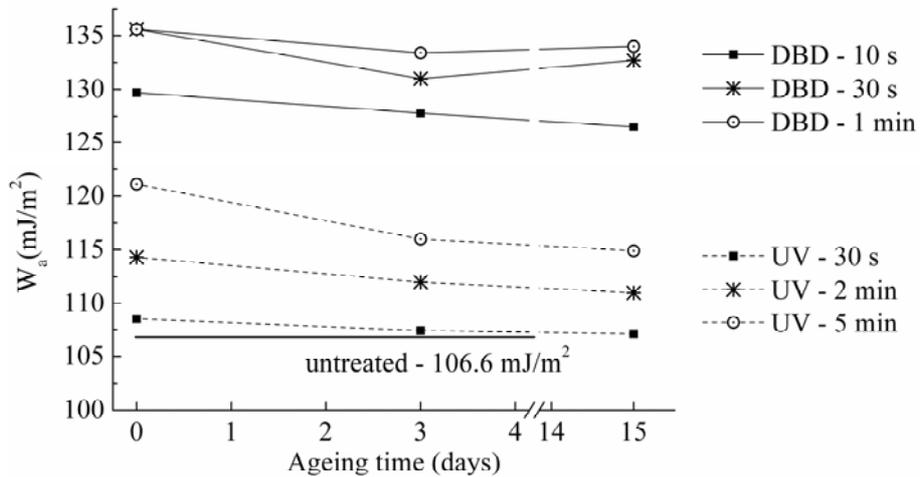


Fig. 3 – Adhesion work of water on DBD (solid line —) and UV radiation (dash line ---) treated PA-6, vs. ageing time.

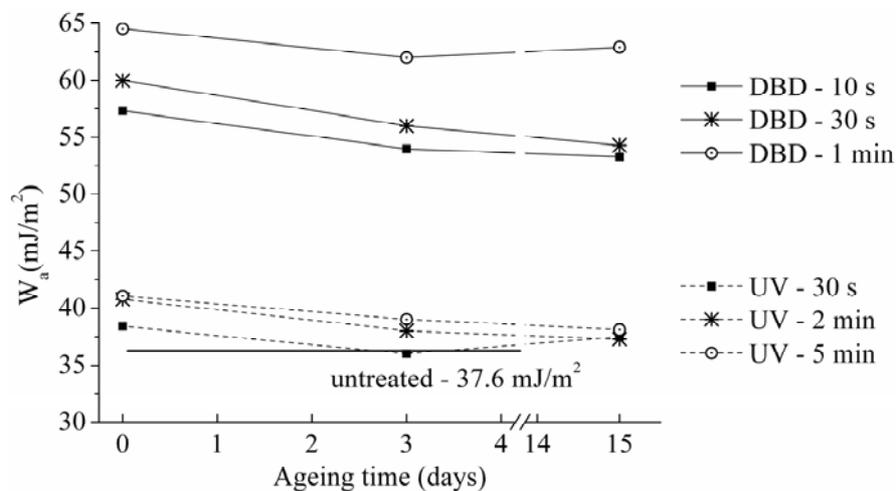


Fig. 4 – Adhesion work of water on DBD (solid line —) and UV radiation (dash line ---) treated PTFE, vs. ageing time.

The modification of the surface hydrophilicity by DBD exposure is very rapid, as 22% increase for W_a and 125% for P , and 52% increase for W_a and 133% for P , is observed for 10 s DBD treated PA-6 and PTFE, respectively. The surface modification by DBD also levels out rapidly, as values obtained for exposure longer than 30 s remain almost constant. It is noteworthy the increase by a factor 1.7 in adhesion work and 4.3 in polarity of the 30 s DBD treated PTFE.

Although the modification by UV component increases continuously with exposure time, it remains at a lower level than the modification by DBD, even for a few minutes exposure, compared to 10 s DBD. The UV component of the plasma seems to have very reduced effect on the PTFE sample, whereas the increase of W_a and P is only by a factor 1.1 and 1.6, respectively, for 5 min UV treated PA-6.

The ageing behaviour of the samples is illustrated in Figs. 3 and 4, showing the variation of the adhesion work with water as a function of the ageing time, for various exposed samples. For all samples, the degree of recovery of the surface hydrophilicity is reduced, pointing out to the stability of the surface properties achieved by treatment.

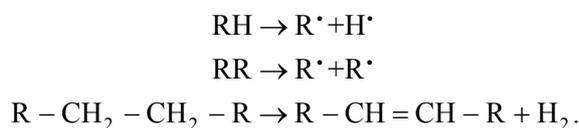
4. DISCUSSION

Plasma represents a very reactive environment when in contact with a polymer surface. The physical-chemical reactions break the physical and chemical bonds, yielding active sites, polar groups and scission products onto the polymer surface. Plasma treatment promotes thus removing the small molecules and

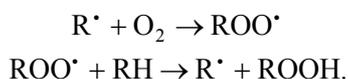
fragments, limiting their interfacial diffusion and other specific interactions across the interface, and triggers formation of a new functionalized surface layer.

In the first place, the plasma treatment can ensure a clean surface of exposed materials, by breaking the weak chemical bonds and removing the small molecules and contaminants with low molecular weight that are typically formed on the surface during the manufacturing and storage. This cleaning effect generates changes in surface texture, wettability, improves surface wettability, print quality, dyeability and adhesion, cross-linking, bondability etc., whereas radicals formed at the surface trigger secondary reactions, such as functionalization and intermolecular crosslinking.

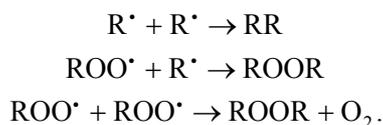
Generally, as the first step in surface chemical modification by plasma, the following set of free-radical reaction pathways and molecular reaction products are known to occur



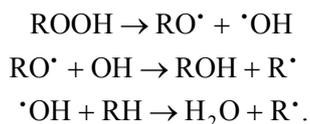
Importantly, these reactions are triggered by a source of energy capable of bond breakage, as metastable atomic and molecular species, energetic ions or UV photons. In presence of an oxidizing agent, as is the case for practically all plasmas, due either to residual air present or entrained by gas flow in the plasma reactor, or gas desorption (H_2O , air) from walls or samples, these reactions are followed by chain-propagating radical reactions



Then, the peroxy radicals ROO^\bullet can lead to three possible reaction pathways, namely crosslinking, and functionalization with or without scission of the polymer chain. Examples of crosslinking, which terminate the chain reaction, are



Examples of functionalization and further chain propagating reactions are



There are, of course, more possible reactions, for example ionization reactions under VUV photons with $\lambda < 100$ nm. The result of all possible reaction pathways is a wide variety of oxidation products, including C-OH (alcohol), C=O (carbonyl, ketone, or aldehyde), C-O-C (ether), COOH (carboxylic acid), COOC (ester) etc. [11].

The considerable changes in surface composition, particularly the presence of highly polar groups, such as hydroxyl or carbonyl, radically alter the surface energy of a polymer, and particularly its polar component γ_{sv}^p . This rise in surface energy is readily demonstrated by our results.

Yet, the degree of surface modification appears to be clearly different for DBD and UV radiation exposure, demonstrating the role of bombardment of the polymer surface by heavy particles from plasma, as the primary source of energy for surface reactions.

It is exact that UV radiation is an important component in many plasmas of technological interest, namely those of H₂, N₂, O₂, He and Ar, in the VUV to visible wavelength range, *i.e.* ~100–400 nm [11]. Hydrogen plasma, particularly, shows very intense VUV emission below 160 nm due to the Lyman and Werner bands, and the Lyman atomic resonance line 121.5 nm. Nitrogen and oxygen also possess certain intense emission lines in the VUV, for example the 130.5 nm resonance line of atomic oxygen, accompanied by weaker molecular bands.

However, it is the rare gas (He and Ar) spectral emissions which display rather remarkable characteristics, in that many of the intense VUV features do not originate from these gases, but rather from omnipresent impurities such as water vapor, or small air leaks. Due to the well-known Penning energy transfer from long-lived He* or Ar* metastables, even trace amounts of impurities can lead to quite intense emissions. Taking this into account, yet also by the fact that the environmental stability of polymers depends on the photochemistry of polymers in the near-UV and visible ranges, the interaction of UV radiation with polymers has been thoroughly studied [12, 13], being established that polymers are sensitive to extended exposure to UV radiation.

For example, studies on the plasma and VUV photochemical processes in low-pressure reactors showed that UV radiation induces polymer crosslinking [11, 14, 15].

Nonetheless, all results pointed to those UV-induced effects occur well below the immediate surface region of plasma-treated polymers, being noticeable for rather long exposure times, whereas the rapid modification of the outermost monolayer, at least in what concerns crosslinking, could be attributed to the direct energy transfer from ions and metastables.

Present results are evidently pointing to the primary contribution of heavy particles in the modification of the surface outermost layer. It results that processes

at the very surface of a sample are dominated by reactions involving ions and metastables, while the radiative energy transfer dominates processes in the bulk of the material [14, 16]. Nonetheless, surface modification is due to complex processes, involving free radicals and polar groups created by the plasma, that can then recombine to trigger branching and crosslinking, whereas effective and stable surface modification can be attained by plasma exposure as short as a few seconds.

5. CONCLUSION

Mechanisms responsible for surface modification in plasma are complex, involving excited and ionized particles, photons, radicals. Even though all these species possess enough energy to induce surface chemical reactions on polymers, their respective role in surface modification is different. Present results, on surface properties of polymer films processed by exposure under plasma and then only under the UV radiation plasma component, in the same plasma reactor, allow to conclude on the paramount role of plasma particles in triggering surface modification. The treated polymer surfaces are shown to perform differently, as a function of their chemical structure, type of exposure, *i.e.* plasma or UV radiation, and exposure time. Surface analysis results point out to the primary contribution of heavy particles in the modification of the surface outermost layer. It follows that processes at the very surface of a polymer sample are dominated by reactions involving ions and metastables, while the radiative energy transfer dominates processes in the bulk of the material. These aspects should be taken into account in surface processing using plasma, in order to optimize the plasma treatment parameters as to efficient and stable surface modification.

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