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Treatment of polyethylene terephthalate in a He glow discharge

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Abstract This work is focused on the study of electrical and optical properties of a helium glow discharge during the treatment of polyethylene terephthalate films for the modification of their surface properties. The experimental results reveal that the change of the polymer surface properties, due to the bombardment by energetic plasma species, is accompanied by a profound change of the electrical characteristics of the discharge and a spatially uniform quenching of certain emitting metastable species. The threshold-like evolution of these phenomena with increasing rf voltage indicates that they are likely to be attributed to ions accelerated in the polymer-covered electrode sheath.

1. INTRODUCTION

Plasma treatment is known to be efficient in the modification of the surface properties of polymers without affecting their bulk properties [1-2]. The nature of this modification depends primarily on the gas used and is usually attributed to the presence of various species in the discharge such as electronically excited species, chemically active free radicals, charged particles and photons [3-4]. More precisely plasma treatment has been found to modify the surface structure, wettability, roughness, adhesivity, dyeability and biocompatibility of the subjected polymers [5]. The method is preferred over chemical treatment, because of its simplicity, the lack of chemical residues and environmental pollution, the possibility of large area uniform treatment, as well as the very short treatment times required.

Among the various gases that may be used for the treatment of polymer surfaces inert gases are often used either for cleaning or for improving the adhesive characteristics of polymers. The later is achieved through hydrogen abstraction and cross-linking by activated species of inert gases, procedure known as CASING [6-7]. These modifications find application in the improvement of the adhesion in polymer-polymer or polymer-metal interfaces and in the immobilization of surfactants on polymer surfaces [8].

Despite the large number of studies concerning the issue and the growing number of technological applications, no major attention has been paid to the glow discharge properties and their impact on the resulting surface properties. In this respect, a survey of the variation of plasma parameters during the polymer treatment and the simultaneous change of the surface properties could be a useful tool for fully understanding the process. Instead, the most common case in literature is the correlation of some plasma parameters with film properties. Two major problems exist in this approach: the first one is related with the lack of recording of the power actually consumed in the discharge, which is not a trivial measurement in rf discharges, whereas the second is related to the improper use of plasma emission ignoring the importance of the spatial characteristics of the discharge. The work presented here is an attempt to demonstrate the usefulness of rf power measurements and spatially resolved emission in the study of such processes. Helium has been chosen because it was proved very effective in the treatment of polyethylene terephthalate (PET) who has a wide applicability in packaging and numerous other technological applications.

2. EXPERIMENTAL

The experimental setup consists of a 160mm stainless steel high vacuum chamber, a fully characterized cell from the electrical point of view, having two parallel round stainless steel electrodes with a diameter of 55mm, equipped with four 50 mm in diameter quartz observation windows as described in reference [9]. The interelectrode distance was kept constant at 25 mm throughout the experimental procedure. A layer of polyethylene terephthalate film with a thickness of 23 μm is firmly mounted on the surface of the grounded electrode. Power is applied to the system from a 13.56 MHz rf generator (ENI model ACG-3) through an SWR meter and a proper impedance matching network. Voltage and current waveforms are monitored using adequate probes to a digital oscilloscope in order to determine the exact power consumed in the discharge according to the method described in reference [10]. The addition of the PET film on the grounded electrode does not impose any modifications in the method used for the determination of the power consumed in the discharge since the equivalent electric circuit used for this purpose includes only the elements from the powered electrode lead up to its surface.

A base vacuum of 10^{-7} Torr is achieved by a diffusion pump before the introduction of Helium provided by Air Liquide at a purity of 99.995%, used with no further purification. The gas flow into the chamber is controlled using mass flow controllers while the desired pressure is independently adjusted by a downstream throttle valve using the feedback of a capacitive manometer.

Spatially resolved optical emission profiles (OES), were obtained by moving the chamber and then recording the intensity value at a certain position of the interelectrode space [9], with a resolution of 0.5 mm. The light emitted from the discharge was collected using a 10 cm lens to the entrance slit of a JY THR-1000 monochromator.

In addition, a quadrupole mass spectrometer was used to detect species present in the effluent gas after 70eV electron impact ionization.

3. RESULTS

3.1 Electrical measurements

The experiments were carried out under the following conditions: the pressure was maintained constant at 500 mTorr, the total gas flow rate was fixed at 20 sccm while the applied peak to peak voltage was altered stepwise from 100V to 300V in 50V steps. Measurements were made with and without the presence of PET on the grounded electrode. From this point forward the experimental procedure which is carried out with no polymer layer attached to the grounded electrode will be referred to as Case I whereas the one involving the PET as Case II.

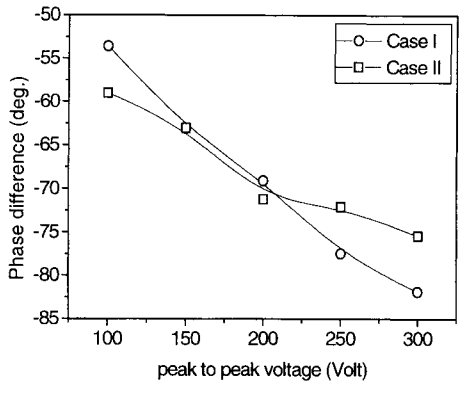

Figure 1. Plasma impedance phase versus applied voltage.

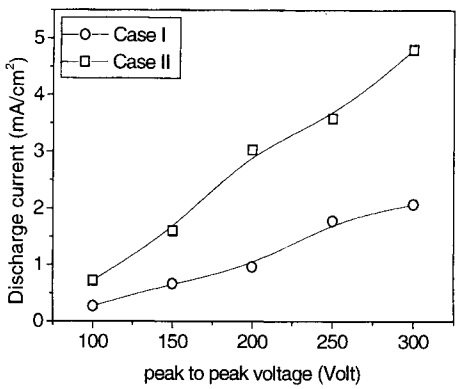

Figure 2. Current density versus applied voltage.

As presented in Figure 1 the plasma impedance phase is generally reduced with increasing voltage. However, in the presence of the polymer it is initially lower than without it while the situation is reversed

after a certain voltage (~200V) indicating a more resistive discharge behavior. This is generally confirmed by the behavior of the discharge current as a function of the applied voltage, as presented in figure 2, indicating an increase of the charge carriers with increasing voltage which is much more pronounced in case II compared to case I. The above observations lead to the conclusion that in the presence of the polymer layer the gas-phase is enriched with neutral and/or charged species resulting from the plasma-film interaction through polymer chain scission. The power density calculated from the current and voltage waveforms as a function of the excitation voltage is shown in Figure 3. One can observe the prevalence of the influence of the current to the shape of the two curves. In addition, the difference between the two cases increases with voltage due to an analogous increase of the charge carriers.

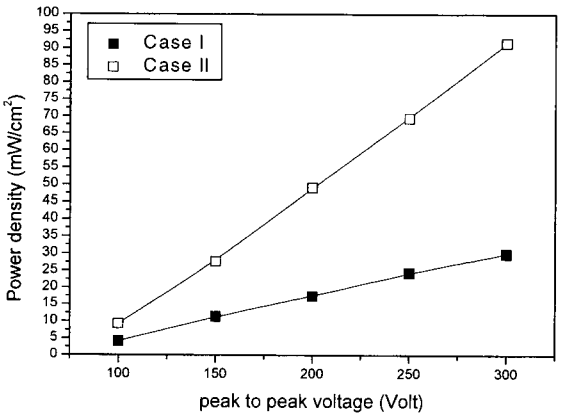

Figure 3. Power density as a function of the applied voltage.

The data presented here prove that the method is very sensitive and can be used for the diagnosis as well as for the accurate control of such surface treatment processes. If one uses the usual SWR meter measurements, there is no way to use power as an independent parameter when examining the influence of other parameters to the discharge. As an example, the variation of pressure under constant voltage conditions will also modify drastically the power consumed by the discharge, however this will not be observed in any SWR meter. In addition, the current-voltage data obtained when applying this method, can also be used for an accurate calculation of the potential of the plasma and the potential drop at each of the sheaths as well as of a series of plasma microscopic characteristics like field and electron density distributions through the adoption of proper discharge models [11]. Finally, these measurements can be used to insure reproducible discharge conditions since the discharge impedance measurements are sensitive even to the presence of usual vacuum impurities.

In conclusion, the electrical measurements reported here indicate an increase of the charge carriers in the gas-phase through the abstraction of species from the polymer surface. It is possible to distinguish between the abstraction of loosely bounded species, which occurs with a rate increasing with the discharge voltage and a threshold like process that appears after 200V and changes drastically the discharge characteristics.

3.2 Optical Emission measurements

Spatially resolved optical emission profiles of the 3^3 P -> 2^3 S line of He situated at 388.9 nm were recorded for various excitation voltages with and without the polymer. The respective intensity profiles ,

presented in figures 4 and 5, show a maximum that is invariably situated at a distance of 8mm from the powered electrode despite the increase of the voltage. The presence of the polymer does not have any impact on the position of the maximum or the shape of the curves, which reflects clearly the presence of the powered and grounded electrode sheaths and the prevalence of the wave riding electron heating mechanism under the specific conditions. One can easily observe here that the choice of the point of detection is extremely important since the variation of intensity with voltage scales with a different slope at each point of the interelectrode space. Therefore, the correlation of single point emission intensities with other discharge or material characteristics is simply erroneous.

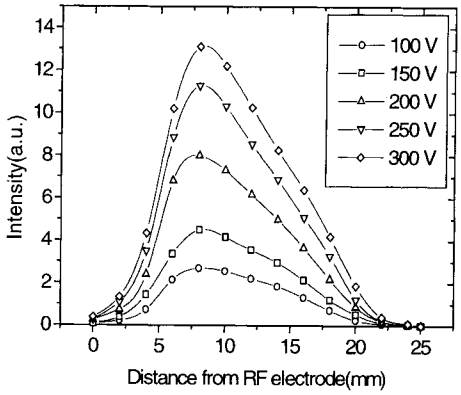

Figure 4. Emission profiles for Case I.

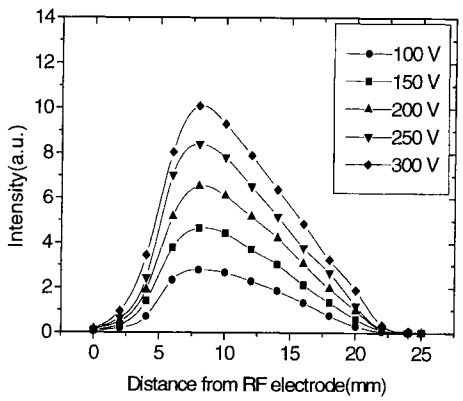

Figure 5. Emission profiles for Case II.

The observed intensity at each point of the interelectrode space increases normally with the raise of the excitation voltage for both cases. This appears to be as expected since more power is dissipated in the discharge inducing an analogous increase of the effective electron population for the specific process. On the other hand, the intensity in case I is higher than that of case II for each of the excitation voltages examined here. Indeed, this difference seems to be more pronounced with increasing voltage, despite the fact that, as shown in the previous section, the power consumed in the discharge is higher in case II.

To clarify the influence of the polymer to the emission profiles of the He metastable we have plotted the integral of the emission intensity in space for each excitation voltage in figure 6 and the difference between the profiles corresponding to the two cases at each point in figure 7. First, it appears that the emission profiles for the 100 and 150 volts are almost identical. When increasing the voltage to 200 volts or more a noticeable difference between the two cases appears which seems to be consistent with the change in the discharge character as observed in figure 1. The diminution of the emission intensity for Case II is a result of the quenching of the helium metastables by collision with free fragments resulting from the polymer surface. This is evident if one considers also the spatial distribution of this difference shown in Figure 7. The quenching of the He metastables appears to be homogeneous in space, fact compatible with the gas-phase regime which is expected to be diffusion controlled under these conditions. However, the most interesting observation is that the chain scission responsible for the enrichment of the gas-phase with quenching species is a threshold process occurring above a certain excitation voltage. This is a strong indication in favor of the candidacy of positive Helium ions as the species responsible for the observed phenomenon.

In an effort to identify the species resulting from the surface mass spectrometry was employed. The peaks observed in the 1-50 amu range were identified as due to molecules like CO, CO_2, H_2. For instance, the CO_2 percentage is increased by a factor of 2, while H_2 is three times larger with the polymer present than it is without it.

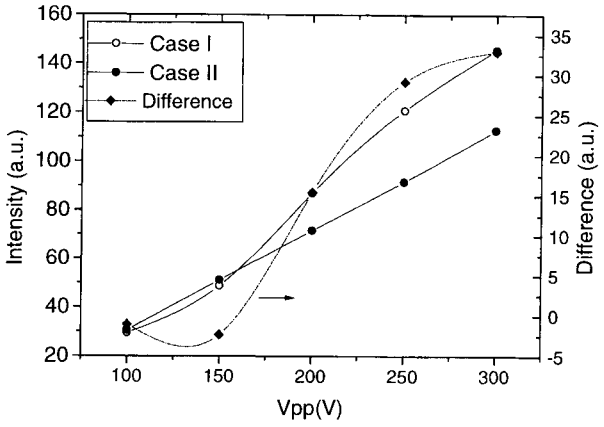

Figure 6. Total emission intensity versus excitation voltage.

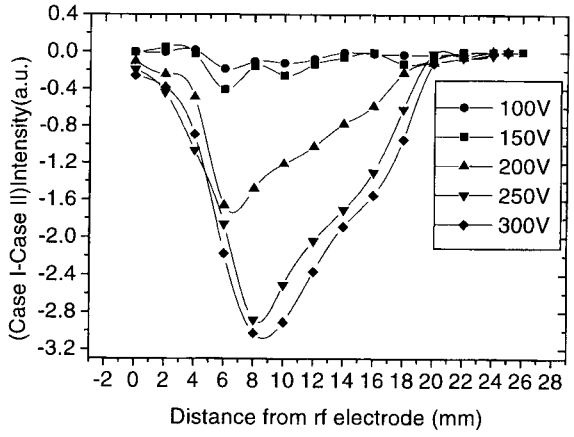

Figure 7. The difference of Emission Intensity for both cases as a function of the distance from the powered electrode.

4. CONCLUSION

The measurements presented here have shown their sensitivity for observing phenomena commonly present in polymer surface treatment with inert gas discharges. More specifically, a threshold-like process has been observed using either electrical or spatially resolved optical diagnostics.

In general, plasmas of inert gases can simultaneously bombard the polymer surface with various energetic species, capable of producing chain-scission and the subsequent cross-linking. The proposed possible candidates are mainly VUV photons, metastable species and positive ions and there is a debate among various research groups on the specific weight of each one of them [12-15]. The results presented here mostly favor the case of positive ions, however this is still not a straightforward proof. In this direction, more experiments, including the use of various pressures, electrical bias and in-situ measurement of the polymer etch-rate are underway.

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