Surface Properties and the Stability of Poly(ethylene Terephtalate) Films Treated in Plasmas of Helium–Oxygen Mixtures

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ABSTRACT: In this work, the surface treatment of poly(ethylene terephtalate) (PET) films in a low frequency (70 kHz) discharge in helium–oxygen mixtures is investigated. Optical emission spectroscopy and mass spectrometry are used to analyze the gas phase. Surface properties are analyzed via the X-ray photoelectron spectroscopy (XPS) technique and contact angle measurements. The treatment conditions are optimized in order to obtain a surface functionalization, which would show a reduced ageing effect. The stability of the treated surface via the crosslinking process seems to be closely correlated to the presence of the helium metastable species in the discharge. A very good stability with the ageing time is obtained for samples treated in gaseous mixtures that contain less than 5% O_2, conditions for which the oxidized polymeric structure seems to be formed on a reinforced crosslinked layer. The very efficient loss of He excited species, for amounts of O_2 higher than a few percent, affects the surface crosslinking. For high quantities of oxygen introduced in the reactor (more than about 50%), a balance is established between the introduction of oxygenated groups and the ablation of the surface. In this case, the surface degradation has, as a consequence, the ageing effect. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **66:** 1367–1375, 1997

Key words: He–O_2 mixtures; poly(ethylene terephtalate); oxidation; crosslinking; surface stability

INTRODUCTION

Plasma treatments with nonpolymerisable gases (He, Ar, O_2, N_2, etc.) are largely used to modify the surface layer of polymer films.[1-14] In order to develop plasma techniques on an industrial scale, the surface modifications should be stable with time. The ageing effect can be slowed down if a more cohesive and dense layer is obtained between the uppermost surface and the bulk material.

A so-called CASING process, well known from the literature,[15] consists of creating a crosslinked layer with a high cohesive energy as a result of an inert gas discharge action. Such discharge creates new bonds, such as C=C, which indicate the crosslinking.

Helium is the most efficient of the inert gases for the crosslinking of the uppermost few monolayers of a polymer,[1] with this feature being due probably to the large amount of energy available to transfer to the polymer surface via ion neutralization, Auger deexcitation, and Penning ionization in the polymer.[1]

Plasma treatments in so-called reactive gases (O_2, N_2, etc.) have surface functionalization as a

main effect. Oxygen plasmas are used largely for this purpose, with oxygenated functions such as ether, hydroxyl, carbonyl, or carboxyl being grafted onto the surface; reactive surfaces are thus obtained.[12]

The helium discharge has been used in a two-step process as a pretreatment before an ammonia plasma treatment in order to improve the adhesion of polypropylene (PP) to aluminium layer.[16]

Treatments in He–O_2 gas mixtures are interesting because they produce a surface oxidation simultaneously with a crosslinking reaction in a one-step process. These two mechanisms, when achieved at the same time, allow to obtain a reactive surface, which also presents good stability with ageing time. The competitive action of the two mechanisms will depend, in a critical manner, on the composition of the gaseous mixture. Such studies were performed earlier for pure gases and also for some He–O_2 mixtures,[2] but no detailed analysis was performed for the whole range of gas composition, with correlation between the plasma parameters and the surface modifications.

In a previous work, the influence of the gas flow rate on the "competition" between surface functionalization and crosslinking of poly(ethylene terephtalate) (PET), in a He discharge with oxygen as residual gas (0.3%) was investigated.[16]

Taking into account the above-mentioned aspects, the purpose of this work is to optimize the treatment conditions for PET in a low-frequency (70 kHz) discharge with a nonsymmetrical configuration of electrodes in He–O_2 mixtures, conditions for which the surface functionalization would show a reduced ageing effect. Optical emission spectroscopy and mass spectrometry are used to analyze the gas phase. Surface properties are analyzed via the XPS technique and contact angle measurements. In particular, evolution of these properties versus ageing time is investigated.

EXPERIMENTAL

Materials and Apparatus

The experimental setup is described in detail elsewere.[9] It consists mainly of a glass reactor with a non-symmetrical configuration of electrodes. Low-frequency power (70 kHz), provided by an industrial generator, is directly coupled to the blade-type electrode. The polymer film is enrolled on the grounded cylinder.

Helium and oxygen, provided by Alphagas at a purity of 99.995%, are used without further purification; the gaseous mixture is introduced through the powered blade electrode. MKS flow-meter/controllers measure and control the gas flow rate. The pressure is measured with a MKS 127A capacitance manometer and controlled by MKS 252 exhaust–throttle–valve controllers. The bell jar is pumped by a TPH 170 (Balzers) turbomolecular pumping system to a typical base pressure of about 10^{-3} Pa.

The optical emission from the center of the discharge is transmitted to the entrance slit of a Jobin–Yvon HRS2 (0.6 m focal length, 1200 grooves/mm grating) monochromator by a 200 μm optical fiber, permitting to record the 360–800 nm range.

Effluent gases are analyzed with a quadrupole mass spectrometer QMG 420-Balzers, attached to the reactor chamber via a silica capillary tube ($\phi = 16$ mm; $1 = 600$ mm). Such a configuration is favorable for the recombination of the reactive species as metastable or radicals. However, it is useful to survey the concentrations of the stable species.

The surface properties are determined as a function of ageing time in air, by contact angle measurements (sessile drop) with bidistilled water and methylene iodide, using an image processing system.[17]

XPS investigations are performed at the ITO-DYS laboratory (University of Paris VII) on a VG Scientific ESCALAB MKI apparatus, with a non-monochromatic Mg Kα X-ray source, operating in the constant analyzer energy mode. The electron take-off angle is 90° with respect to the surface. The pressure in the analysis chamber is about 5 $\times$ 10^{-8} mbar. Digital acquisition is achieved with a Cybernetix system, and data is collected with a computer. Charge correction is determined from peak fitting of the C1s line with three components, the C—C/C—H component being set at 285 eV.

PET 23 μm films are used after washing in alcohol.

Treatment Conditions

The influence of gas mixture composition on the discharge characteristics is investigated in the following conditions: constant applied electric power, 3.3 W; pressure, 1 mbar; total gas flow rate, 100 sccm. The PET film treatment is achieved for various compositions of the gaseous mixture: between 100% He (with 0.3% residual
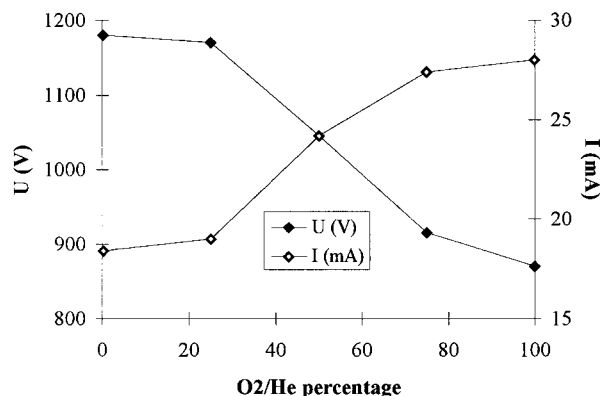
Figure 1 Values of the current and peak-to-peak voltage applied on the discharge versus the composition of the He−O₂ mixture.

O_2) and 100% O_2. In particular, the range for oxygen contents less than 5% is detailed.

RESULTS AND DISCUSSION

Electrical Parameters of the Discharge

Experiments are carried out at constant applied electric power. Measured current and peak to peak voltage depend on the relative percentages of He and O_2 in the gaseous mixture. A decrease in the voltage is observed, accompanied by an increase in electric current intensity, when oxygen density increases between above limits (Fig. 1). These parameters remain almost constant for either low (<20%) or large oxygen contents (>75%). Obvious dependence on the relative amounts of helium and oxygen takes place for intermediate values.

The electron energies necessary to sustain the He discharge are high because of the high energy levels of helium. Also, the plasma impedance is high, due to the low density of the charge carriers. Thereby, as long as He is the major component, a great amount of energy is necessary to sustain the discharge. The presence of O_2, molecular gas with much lower energy levels as compared to He, leads to an increase in the density of the charge carriers. The plasma impedance diminishes, leading to a consequent decrease in the applied threshold voltage necessary to sustain the discharge. The variation of these parameters with gas mixture composition is almost negligible as long as one of the gases is present in sufficient large amounts (>80%), which seems to indicate that the breakdown conditions in our discharge

are favorable for excitation and ionization of the He species, the other species present in the discharge being excited and/or ionized by Penning transfer by charge transfer processes.

We should also take into account the electronegativity of the oxygen, which leads to a supplementary loss of electrons by attachment and consequent creation of negative oxygen ions. This may induce a decrease of the rate of direct excitation by electronic collisions. Thereby, the effect of the decrease of the applied voltage and the simultaneous increase of the current on the discharge are someway attenuated by this mechanism. We might expect that in the presence of a less electronegative gas than oxygen, the variations of electrical parameters of the discharge would be steeper.

The diminution in electron energies by adding oxygen in the helium discharge is confirmed by measurements of the electron temperature using a Langmuir triple probe. These results will be presented later.

Optical Emission Spectroscopy

The spectroscopic study of the discharge allows to record spectra in the visible range of wavelengths. The emission spectroscopy investigations are accomplished with polymer sample in the discharge. The species identified are He, O, H, CO, N_2, and N_2^+.

Variation of the emission intensities of He atoms (all He* lines situated in the visible optical range are observed on our spectra), O atoms (I_O at 777 and 844 nm), and those species that are relevant to the degradation mechanism of the surface, i.e., CO (I_{CO} at 520, 561, 608, and 637 nm) and H ($I_{H\alpha}$ at 656 nm and $I_{H\beta}$ at 486 nm), are investigated. These intensities present different behavior versus gas mixture composition.

He* lines show a diminution in their intensity with the increase of O_2 content in the discharge, the decrease being greater for percentages less than about 5% O_2 (Fig. 2). The same type of variation is observed for H* lines, with the decrease being more pronounced, and may even vanish almost completely for O_2 contents higher than about 50% (Fig. 2).

The emission intensity for the O* lines shows a maximum for intermediate contents of O_2 (about 50%) (Fig. 3), a variation that also appears for the band heads of CO (Fig. 3).

The steep decrease in the He* lines emission intensity, observed for less than 5% O_2, implicates
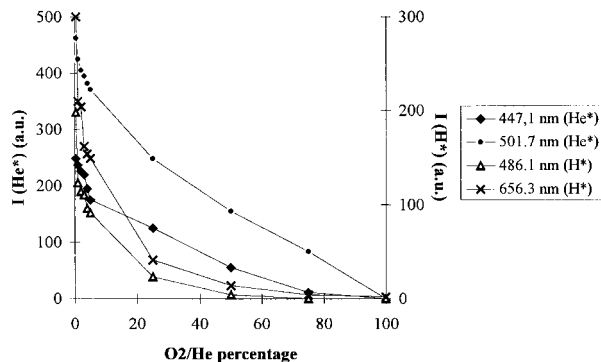
Figure 2 Emission intensities of some He* and H* lines versus the composition of the He–O_2 mixture.

a very efficient loss of He excited species by transfer to other species with lower energy levels and sustains the observation in connection with the electrical parameters.

The increase of the population of the radiative levels can take place by electronic collisions from the ground state or by stepwise processes: excitation of the metastable states $2\,^1S$ and $2\,^3S$ by electronic impact, i.e., the process which requires the lowest energy, followed by the "conversion" of these states, by collisions with electrons or with other He atoms, into radiative states. This stepwise process seems more probable because it implies lower electron energies and is justified also by the relatively low applied electrical power in the discharge. With the increase of the O_2 content in the mixture, the loss of the He metastable states by Penning transfer to oxygen species and the "conversion" processes of the metastables to radiative states are less probable.

The maxima obtained for the atomic oxygen emission lines in a gaseous mixture that contains about 50% O_2 can be explained by taking into account the excitation mechanisms for these lines. Generally, electronic collision mechanisms are proposed, i.e., direct excitation from the ground state and dissociative excitation of molecular species. Both processes can take place at electron energies greater than a threshold value (about 11 eV for the first and about 18 eV for the second); but the presence of He in the discharge renders very efficiently the Penning reaction, fast transfer ($\nu \cong 10^{-12}$ s), which requires practically no additional energy,[18] as follows:

$$He^m + O_2 \to He + O^* + O^+ + e$$

$$He^+ + O_2 \to He^+ + O + O^*$$

$$He^+ + O_2 \to He + O^+ + O^*$$
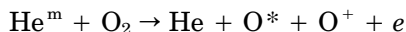
The transfer to O_2 is characterized by a high rate ($k \cong 20 - 30 \times 10^{-11}$ cm^3 s^{-1}). Thus, it seems probable that excited atomic oxygen species are produced by transfer from He species, especially the metastable ones.

It must be noticed that Penning ionization from He metastables ($2\,^3S$ state) is also very efficient in the case of other molecules, which are present in the discharge, as detected by mass spectrometry, such as CO ($k \cong 10 \times 10^{-11}$ cm^3 s^{-1}) or CO_2 ($k \cong 60 \times 10^{-11}$ cm^3 s^{-1}).[19]

The further decrease in the intensity of the O* emission lines, after the maximum reached at about 50% O_2, can be explained by O* loss in collisions with molecular oxygen, as follows:

$$O^* + O_2 \to O + O_2^*$$
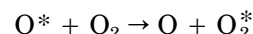
The efficiency of this reaction increases when the amount of oxygen in the discharge increases.

The variation of the emission intensity of band heads of CO, as detected in the experiments, can be explained by taking into account the same excitation transfer as for O*.

The steep decrease in the intensity of the H* lines seems to be the opposite of trend of variation of the H_2 species, as detected by mass spectrometry (compare with the next section). A large amount of H_2 is formed in the reactor with discharge-on, for all used mixtures. The important decrease in the intensity of emission seems to indicate a very efficient loss of excited hydrogen atoms, even in the presence of very small amounts of O_2. This fact may be presumably due to a rapid increase in the recombination rate that results from an increase in electron density.[20]
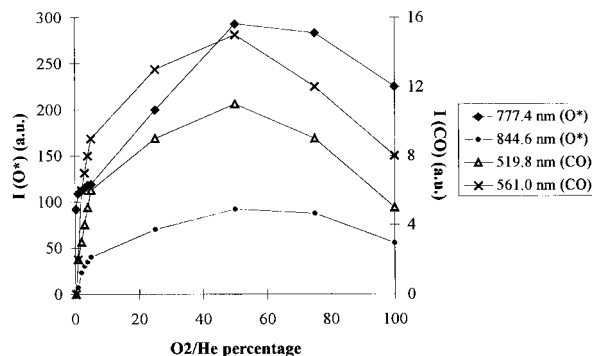

Figure 3 Emission intensities of some O* lines and some CO band heads versus the composition of the He–O_2 mixture.

Mass Spectrometry
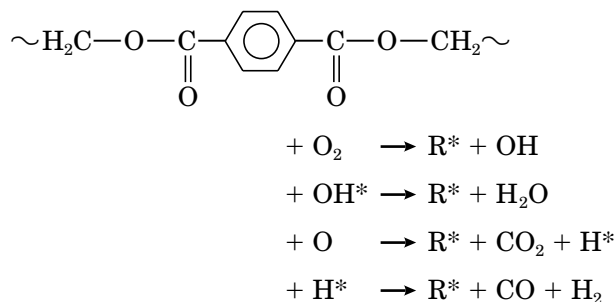
Mass spectrometry enables one to follow the neutral species resulting from the polymer degradation. Separation between the species with the same m/e value (N_2 and CO) is achieved by using the fragmentation patterns[21] corresponding to the value of 70 eV electron energy, which is used in our spectrometer. H_2, H_2O, CO, and CO_2 (m/e: 2, 18, 28, 44) are found to be the main degradation products.

Values presented in Figure 4 are the differences between the peak relative intensity with discharge-on and discharge-off.

The comparison with values obtained with PTFE films in the same conditions allows to separate the different contributions to the H_2 peak intensity: the hydrogen that results from the atomic hydrogen abstraction and the amount that originates from the desorption from the walls or different metallic parts of the reactor. Results confirm that almost all H_2 measured with discharge-on is a product of surface degradation.

The production of H_2 presents a continuous increase with the O_2 content in the discharge until about 50% O_2, followed by a decrease for higher quantities of the latter (Fig. 4). This variation is not correlated with the amount of He introduced in the reactor, which would thus indicate that the H_2 production is strongly related to the presence of reactive oxygen.

Hydrogen may then be produced by reactions that involve fragments, such as OH, CO, or CO_2, previously formed by the action of oxygen at the polymer surface.

$$\sim H_2C-O-\underset{\underset{O}{\|}}{C}-\hspace{-4pt}\left\langle\bigcirc\right\rangle\hspace{-4pt}-\underset{\underset{O}{\|}}{C}-O-CH_2\sim$$

$$+ \; O_2 \quad \longrightarrow R* + OH$$
$$+ \; OH* \longrightarrow R* + H_2O$$
$$+ \; O \quad\; \longrightarrow R* + CO_2 + H*$$
$$+ \; H* \quad \longrightarrow R* + CO + H_2$$

A fast increase in the CO concentration is observed for a small percentage of O_2. The maximum is followed by a slight decrease, almost reaching a plateau for high oxygen contents. The CO_2 concentration shows a similar behavior, but the slope in the CO_2 increase for the first few percentages of O_2 introduced in the gas mixture is
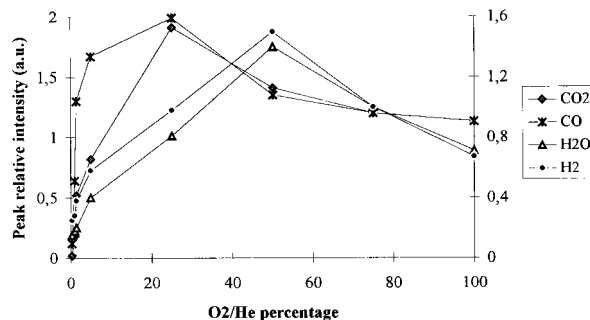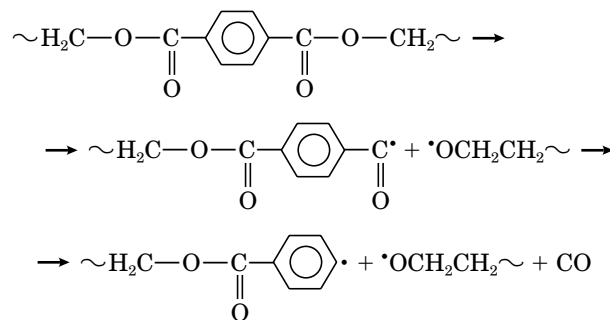
Figure 4 Mass spectrometer signals for different effluent gases, in percentages, measured as a difference between discharge-on and discharge-off, versus the composition of the He$-O_2$ mixture.
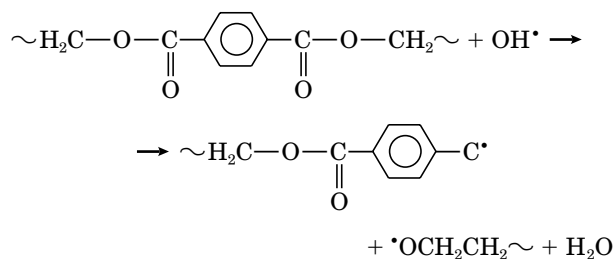
smaller than for CO. The maximum value is reached earlier for CO than for CO_2. After 5% O_2, the increase of CO_2 becomes faster than that of CO so that at 25% O_2, their relative intensities are almost equal, and they remain so until 100% O_2. This fact seems to indicate that CO_2 is instead formed in the discharge, through reactions such as

$$CO + OH* \rightarrow CO_2 + H*$$
$$CO + O \rightarrow CO_2$$
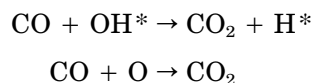
Consequently, the production of CO_2 could be dependent directly on the formation of CO, with the last one being a surface degradation product.

$$\sim H_2C-O-\underset{\underset{O}{\|}}{C}-\hspace{-4pt}\left\langle\bigcirc\right\rangle\hspace{-4pt}-\underset{\underset{O}{\|}}{C}-O-CH_2\sim \; \longrightarrow$$

$$\longrightarrow \sim H_2C-O-\underset{\underset{O}{\|}}{C}-\hspace{-4pt}\left\langle\bigcirc\right\rangle\hspace{-4pt}-C^\bullet + {}^\bullet OCH_2CH_2\sim \; \longrightarrow$$

$$\longrightarrow \sim H_2C-O-\underset{\underset{O}{\|}}{C}-\hspace{-4pt}\left\langle\bigcirc\right\rangle\hspace{-4pt}\cdot + {}^\bullet OCH_2CH_2\sim + CO$$

Water formation, which results from the action of OH* radicals, in reactions such as

$$\sim H_2C-O-\underset{\underset{O}{\|}}{C}-\hspace{-4pt}\left\langle\bigcirc\right\rangle\hspace{-4pt}-\underset{\underset{O}{\|}}{C}-O-CH_2\sim + OH^\bullet \; \longrightarrow$$

$$\longrightarrow \sim H_2C-O-\underset{\underset{O}{\|}}{C}-\hspace{-4pt}\left\langle\bigcirc\right\rangle\hspace{-4pt}-C^\bullet$$
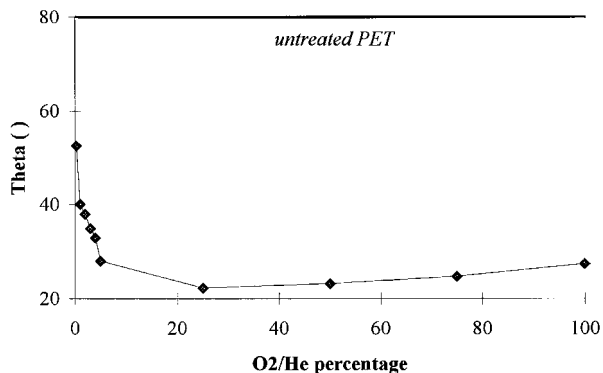
$$+ {}^\bullet OCH_2CH_2\sim + H_2O$$

Figure 5 Water contact angle of treated PET versus the composition of the He–O_2 mixture.

increases obviously slower than that of CO and CO_2. The trend of the formation of H_2O versus the composition of the gaseous mixture is very similar to that of H_2, thus indicating that oxygen species induce the dominant mechanisms at the polymer surface.

At low O_2 contents ($<5\%$), the formation of CO_2 and H_2O is limited by O-atom supply; therefore, the H_2O and CO_2 concentrations are lower than the H_2 and CO concentrations. At higher O_2 flow rates, the O-atom supply is sufficient to convert CO and H_2 to CO_2 and H_2O, respectively.

Contact Angle Investigations

The surface functionalization is shown by the decrease of the measured contact angle of water on

treated samples as compared to the untreated sample (Fig. 5). θ_{water} shows a considerable decrease, even for the He treatment (with a variation of about 34.5% as compared to untreated PET). Measurements made immediately after the treatment evidence the influence of the gas mixture composition on the surface properties for less than 5% O_2. For higher oxygen amounts, the measured values for water contact angle remain almost constant.

The study of the stability of the surface properties can be an indirect indication of surface crosslinking of treated PET samples. The He–O_2 treated PET films were aged in air at room temperature, with measurements being made during three months after the treatment (Fig. 6). A very good stability with time is obtained for samples treated in gaseous mixtures that contain less than 5% O_2 (about 10% variation of θ_{water}).

For 25% O_2–75% He and 50% O_2–50% He mixtures, the value for the water contact angle measured three months after the treatment shows a variation of about 100%, as compared with the value measured immediately after the treatment. For the 75% O_2–25% He and 100% O_2 discharges, this variation is about 120%. The values of the water contact angle on the samples treated in He–O_2 mixtures that contain more than 5% O_2, even if they present a considerable variation as compared to the values measured immediately after the treatment, continue to be smaller than those for untreated PET; i.e., the treated PET does not
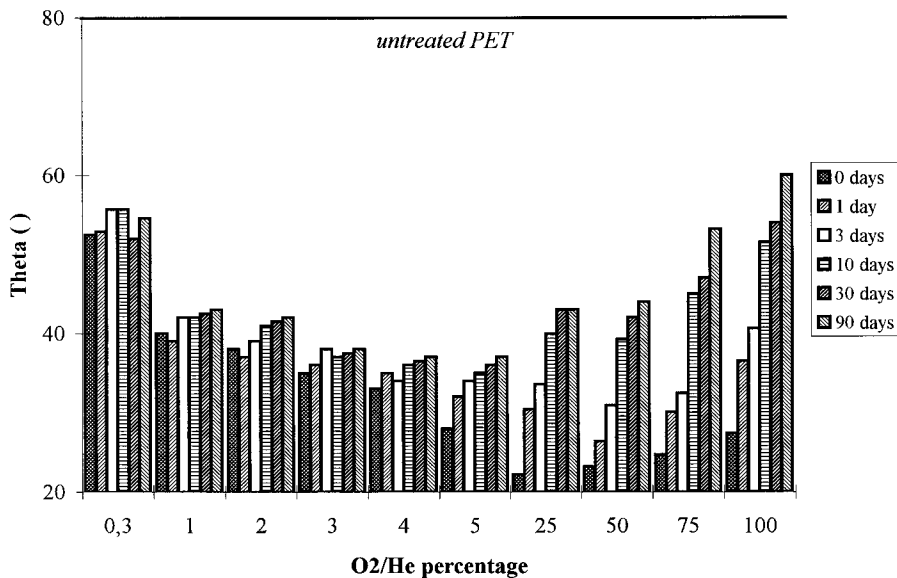

Figure 6 Variation of the water contact angle of treated PET with the ageing time versus the composition of the He–O_2 mixture.

get back to the untreated form of PET. Thus, it seems that the ageing process, which is very fast in the first 10 days after the treatment (about 75% of the total variation), keeps acting on rather long periods.

XPS Investigations

The C1s spectrum for untreated PET consists mainly of the following three distinct peaks, excluding the peak due to the $\pi - \pi^*$ shake-up transition: the carbon atoms in the benzene ring C1 (285.0 eV), the methylene carbon singly bonded to oxygen C2 (286.7 eV), and the ester carbon atoms C3 (288.9 eV). The O1s spectrum consists of oxygen atoms singly bonded to carbon O1 (533 eV) and oxygen atoms doubly bonded to carbon O2 (532 eV).

The effect of the He$-$O$_2$ plasma on the PET sample is to increase the oxygen functionalization at the surface as compared to the untreated sample (Fig. 7), as shown by the relative integrated intensity of the high-binding energy components C2 and C3 (arising from oxidative functionalization), with respect to that at low-binding energies (CH), C1, which shows a diminution for the He$-$O$_2$ treated samples. The intensity of the peak at 286.7 eV (C2) increases for treated PET due to the appearance of alcohol and phenol groups. The

same modifications in the 288.9 eV peak (C3) shows the introduction of acidic groups.

The variations of C1, C2, and C3 depend on the gas mixture composition. C2 and C3 increase with the oxygen amount introduced in the reactor up to a maximum value for about 50% O$_2$, then decrease for higher oxygen percentages. C1 presents an opposite type of variation: it presents a minimum value at about 50% O$_2$, then it increases for gas mixtures with oxygen as the major compound. This indicates the degradation action of an oxygen plasma, with the oxidative functionalities introduced at the surface being etched by action of the oxygen species.

The deconvolution of the O1s electron peak shows the change in the relative proportions of oxygen singly and doubly bonded to carbon. From the roughly 50 : 50 distribution (O—C to O=C) for the untreated material, the plasma treatments give rise to an increase of the proportion of oxygen singly bonded to carbon functionalities compared to the lower binding energy component arising from oxygen doubly bonded to carbon, a fact which may suggest a crosslinking surface process.

As is pointed out in the literature,[22] crosslinking of PET proceeds by a reaction chain that involves recombination of two aryl radicals obtained by hydrogen abstraction from the benzene ring, as follows:
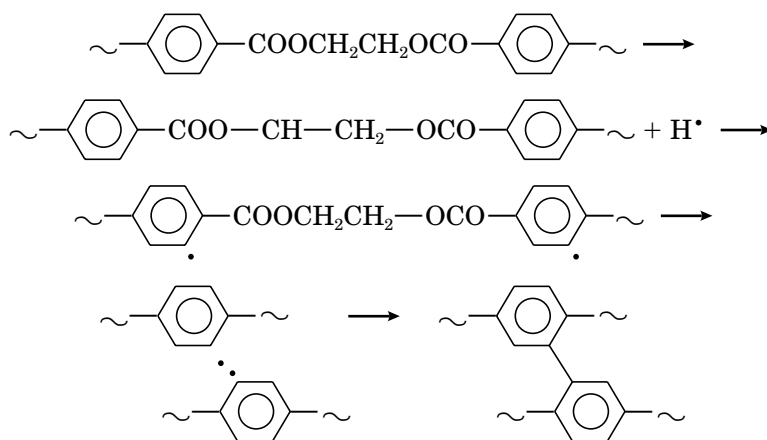
The presence of oxygen induces reactions that involve chain breaking and surface oxygenation.

The two competitive processes, i.e., crosslinking and functionalization, take place with different rates, depending on the composition of the gaseous mixture.

A large content of He seems to be necessary

to obtain a stable surface; but, at the same time, a balance between the contributions of the reactions from inert gas versus oxygen-containing species with the polymer surface is achieved when small amounts of oxygen are added in the reactor. As long as the added O$_2$ quantities are less then a few percent, the surface crosslinking
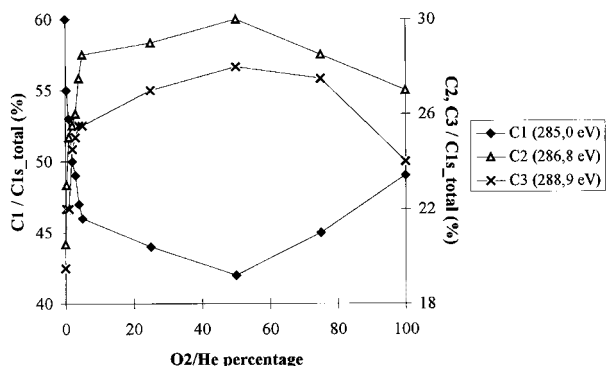
Figure 7 Intensities of various components of the C1s spectrum relative to C_{total} versus the composition of the He–O_2 mixture.

takes place simultaneously with the surface functionalization, as it was pointed out in a previous work[16] for treatments of PET with residual oxygen present in a He discharge.

The large amount of hydrogen that is formed in the discharge during the treatment of the polymer confirms the formation of the aryl radicals on the surface.

Oxygen has the tendency to trap the radicals formed on the surface, thus forming an oxidized polymeric structure. For the gaseous mixtures mentioned above, this structure seems to be formed on the reinforced crosslinked layer, thus permitting maintainance of the surface stable in time.

The presence of oxygen in excess is affecting, in a critical way, the density of He excited species. The very efficient loss of the He metastables for amounts of O_2 higher then a few percent will influence the surface crosslinking.

It is interesting to note that a certain degree of stability for the surface characteristics is obtained after treatments with He–O_2 mixtures that contain up to about 50% O_2. This fact might show that the elimination of stable small molecules such as H_2O, CO, or CO_2 could also favor other crosslinking reactions. In this case, the stability after such treatments extends only on short intervals of time. The formation of oxidized volatile products (CO, CO_2), which almost levels off after about 50% O_2 introduced in the reactor, indicates that a balance is established between the introduction of oxygenated groups and the ablation of the surface.

Thus, one can suggest that the stability of the surface is closely correlated to the presence of the He excited species in the discharge.

CONCLUSION

In this work, PET films are treated in plasmas of mixtures of helium and oxygen, aiming at obtaining stable surface properties with time. The results show that in He–O_2 mixtures, the two competitive processes, i.e., crosslinking and functionalization, can be optimized in order to limit the ageing. The latter is achieved when the O_2 content in the discharge is less than a few percent. The reinforced crosslinked layer that stabilizes the surface is formed under the action of the He active species, while the oxygen species induce the formation of an oxidized polymeric structure. The presence of O_2 in excess induces a depopulation of the excited levels of He, particularly the metastable ones, a fact which is reflected by a considerable decrease of the stability of the surface properties of the treated polymer.

REFERENCES

1. D. T. Clark and A. Dilks, *J. Polym. Sci., Polym. Chem. Ed.,* **16,** 911 (1978).
2. D. T. Clark and A. Dilks, *J. Polym. Sci., Polym. Chem. Ed.,* **17,** 957 (1979).
3. D. T. Clark and R. Wilson, *J. Polym. Sci., Polym. Chem. Ed.,* **21,** 837 (1983).
4. E. Occhiello, M. Morra, G. Morini, F. Garbassi, and P. Humphrey, *J. Appl. Polym. Sci.,* **42,** 551 (1991).
5. W. L. Wade, Jr., R. J. Mammone, and M. Binder, *J. Appl. Polym. Sci.,* **43,** 1589 (1991).
6. R. Foerch, N. McIntyre, and D. Hunter, *J. Polym. Sci., Polym. Chem. Ed.,* **28,** 193 (1990).
7. R. Foerch and D. Hunter, *J. Polym. Sci., Polym. Chem. Ed.,* **30,** 279 (1992).
8. A. Wrobel and M. Kryszevski, *Polymer,* **19,** 908 (1978).
9. F. Arefi, V. Andre, P. Montazer-Rahmati, and J. Amouroux, *Pure Appl. Chem.,* **64,** 715 (1992).
10. H. Yasuda, *J. Macromol. Sci. Chem.,* **A10,** 383 (1976).
11. F. Poncin-Epaillard, B. Cheret, and J.-C. Brosse, *Eur. Polym. J.,* **26,** 333 (1990).
12. D. Briggs, D. G. Rance, C. R. Kendall, and A. R. Blythe, *Polymer,* **21,** 895 (1980).
13. Y. De Puydt, Y. Bertrand, Y. Novis, R. Candano, G. Feyder, and P. Lutgen, *British Polym. J.,* **21,** 141 (1989).
14. J. M. Pochan, L. J. Gerenser, and J. F. Elman, *Polymer,* **17,** 1058 (1986).

15. H. Schonhorn and R. Hansen, *J. Appl. Polym. Sci.,* **11,** 1461 (1967).
16. M. Gheorghiu, F. Arefi-Khonsari, J. Amouroux, G. Placinta, G. Popa, and M. Tatoulian, *J. Plasma Sci. Technol.,* to appear.
17. M. Tatoulian, F. Arefi-Khonsari, I. Mabille-Rouger, M. Gheorghiu, D. Bouchier, and J. Amouroux, *J. Adhes. Sci. Technol.,* **9,** 923 (1995).
18. A. Ricard, in *Plasma-Surface Interactions and Processing of Materials,* O. Auciello, Ed., Kluwer, Dordrecht, 1990.
19. W. Lindinger, A. L. Schmeltekopf, and F. C. Fehsenfeld, *J. Chem. Phys.,* **61,** 2890 (1974).
20. L. St-Onge and M. Moisan, *Plasma Chem. Plasma Process.,* **14,** 87 (1994).
21. *Index of Mass Spectral data.* American Society for Testing Material.
22. *Plastics Additives Handbook,* R. Gachter and H. Muller, Ed., Hanser, Verlag, 1990.