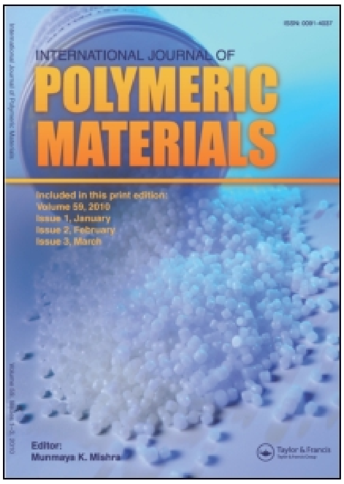

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Poly (Ethylene Terephthalate) Films with Different Content of Acid-Base Functionalities. II. Gas Phase Analysis and Proposed Mechanisms

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Poly (EthyleneTerephthalate) Films with Different Content of Acid-Base Functionalities. II. Gas Phase Analysis and Proposed Mechanisms

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The data about the plasma gas phase analysis and also a contribution to the mechanisms involved in such modifications are presented in this second part. Main 16 neutral species and their evolution in time, with and without PET sample in the treatment system, were investigated by MS. The fluences of atomic and molecular oxygen ions at the polymer surface were determined. A decreased content in neutral species higher is the ion energy is stood out when the PET sample is inside the treatment system. Appreciable differences between the treatments made in saturation regime and those in reimplantation regime were stood out. An enhanced etching mechanism is active in the treatments with ions of 100 and 300 eV, at the lowest dose, while an etching mechanism in stationary regime in a competition with a cross-linking process are important for the treatment with of 500 eV, the same dose. Treatments at this dose do not confer a prevalent acidic or basic character of the PET surface. A diminished etching process and an ion beam induced crystallisation are the main processes for treatments in a reimplantation regime. A more prevalent acidic or basic character of the treated PET surfaces is stood out. The ageing effects were explained by the surface oxygen content, the predominance of short or long range motion and the HSAB reactions.

Keywords: Neutral species; oxygen ionic species; saturation and reimplantation regime; acidic; basic character; etching mechanisms

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INTRODUCTION

Studies about the effects induced by ions with energies of keV or MeV magnitude order on polymers have started more than ten years ago. The interest was and it is still both for the fundamental and applied researches [1].

The interaction of the energetic ions with polymers involves some important differences in comparison with that between X-ray, γ or electrons [2]. The deposited energy per unit length (the so called linear energy transfer, LET) is higher for ions than for other ionising radiation. Typically, for ions of keV energy LET is in the range of 50÷500 eV. This energy is deposited in a very short time (10^{-14}–10^{-13} s), in a small volume surrounding the ion track. The ions of low energy (keV/a.m.u.) loss almost of their energy by nuclear (elastic) binary collisions and the volume of the deposited energy coincides with that for collision cascade. For high energy ions (MeV/a.m.u.) the electronic (inelastic) mechanism dominates and the radius of the ion track is determined by the kinetic energy of the electrons resulted from the ionising processes. Electronic or inelastic collisions can also be operative at low energies, although they are not so important as for very high energy ions. One of the main difference between the two above mentioned mechanisms for deposited energy in polymers is that the electronic collisions produce high excited species which relax in accordance with thermodynamic lows (minimum energy), while chain scission induced by elastic collisions is a random process which could also produce so called "non-thermodynamic" species like very unstable fragments. Primary created species could recombine or react in a volume that is much higher than the ion track and this due to the diffusion process of the active species or to propagation of the radical sites along the polymeric chain.

It must be also pointed out some differences between the metals and an organic solid with covalent bonds, as concerning the effect induced by ions [3]. There is a time distribution of the excited species in organic solids due to their low electrical and thermal conductivity and also to their long life excited species. Therefore, the excited species produced by successive collisions can effectively react each other, process that is no possible in metals because the superposition of the successive defects cannot take place due to their high relaxation rate. The nondirectional character of the metallic bond facilitates the reforming of the bonds, while the macromolecular chain scissions lead to low molecular weight fragments, usually volatile.

Some mechanisms about the oxygen ion beam assisted polymer etching are also given in the literature. For example Gokan and co-workers found that the C=O groups have the greatest sputtering yield due to the fact that CO is more stable and has a lower binding energy than the carbon. They proposed a so called etching mechanism induced by ion bombardment, chemical assisted by molecular oxygen. Their main conclusion was that the chemical process induced by ion bombardment is directly dependent on the ratio between the fuences of the neutral and ionic species and that this dependence dominates over that of the energy [4-6]. The main problem to which Gokan and co-workers do not find an answer is that the presence of the O_2 increase the emissions by a thermal spike mechanism or by a sputtering mechanism chemical enhanced. In Jurgensen's papers is shown that the thermal spike mechanism is active in the enhanced etching, in RIE and RIBE systems, in oxygen [7]. Also the same authors agree that atomic oxygen do not control the etching rate and consider that the main role is that of the ion bombardment [8].

Apart from the role played by the thermal effect in volatile product emission, it has been shown that such a thermal effect can produce drastic modifications in viscoelastic properties of polymers [9, 10].

The precedent paper presented the surface modifications of PET induced in an ion beam-low density plasma system, in oxygen [12]. The data about the plasma gas phase analysis and also a contribution to the mechanisms involved in such modifications are presented in this second part.

EXPERIMENTAL

The experimental set up has been described in previous papers [11, 12]. The treatment conditions and the methods for surface investigations are those given in the precedent paper [12].

Mass spectrometry (Hiden Analytical, PSM 300) was used to characterise both positive ionic oxygen species (O^+ and O_2^+), which act in the IB-LDP system and the main 16 neutral species for which chemical formula are given in Table I.

The evolution in time of the above mentioned neutral species, with and without polymer sample in IB-LDP system, were also registered. The fluence of the ionic oxygen species at the polymer surface were determined knowing the fluence registered at the sampling orifice of the mass spectrometer (in SIMS mode), as it is shown in [11].

RESULTS AND DISCUSSION

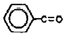
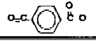
Gas Phase Characteristics

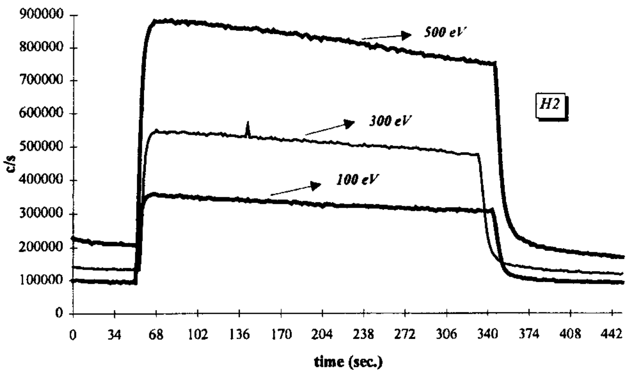
Neutral Species in IB-LDP System

The value for $m/q = 28$ signal was calculated starting from the intensity of $m/q = 14$ signal and taking into consideration the fragmentation reactions in the ionisation source of the mass spectrometer, for an electron energy of 70 eV [13].

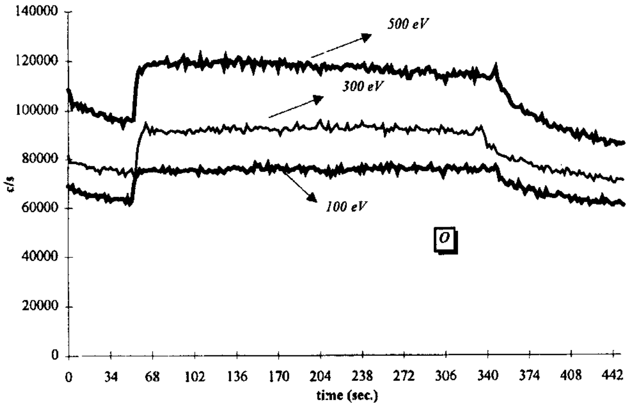
The MS signals for all investigated species increase with the increased ion energy, when the polymer sample is not in the IB-LDP system. This is well shown by the evolution in time for $[H_2]$ and $[O]$, presented in Figure 1. This feature can be explained mainly by considering the so

TABLE I The main species from the IB-LDP system investigated by MS

m/q	*Chemical formula*
2	H_2
14	N
15	CH_3
16	O
17	OH
18	H_2O
27	C_2H_3
28	$N_2(CO)$
32	O_2
43	$CH_2{=}C{-}OH$
44	CO_2
55	C_4H_7
76	
77	
104	
149	



a.

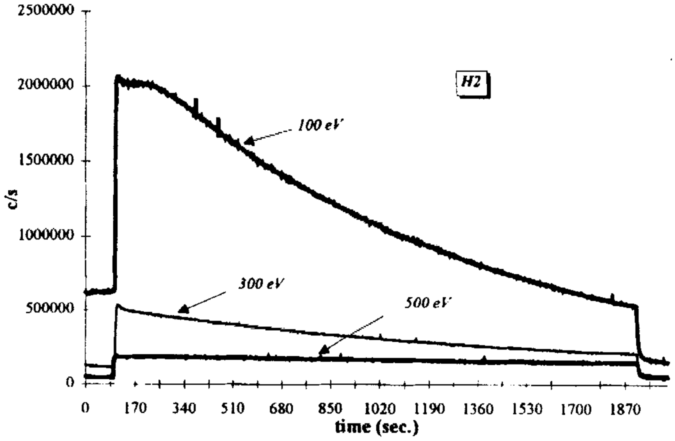


b.

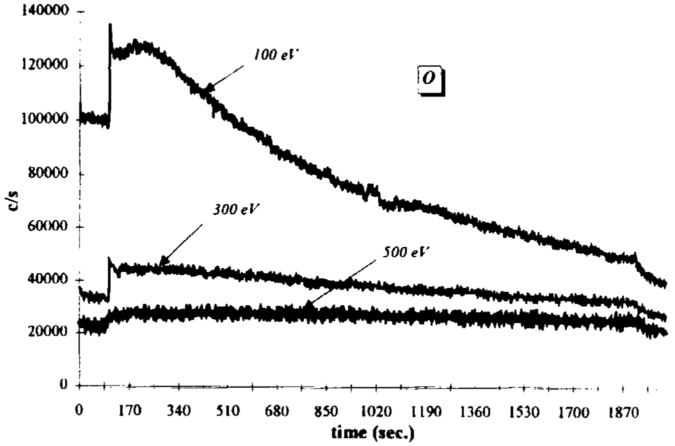
FIGURE 1 Evolutions in time of a) [H_2] and b) [O] at different energies, without PET sample in the IB-LDP system.

called electron stimulated desorption, process amplified in the presence of the more dense secondary plasma inside the channel of the ion beam.

An opposite situation, namely a decreased content in neutral species higher is the ion energy is stood out when the PET sample is inside the treatment system (Fig. 2). This apparently paradoxical result confirm



a.



b.

FIGURE 2 Evolutions in time of a) [H_2] and b) [O] at different ion energies, with PET sample in the IB-LDP system.

that obtained by Tead and co-workers in the case of the treatments of polystyrene, in RIBE or RIE systems, in oxygen [14, 15]. They explained the above mentioned feature by the fact that the systems with higher energy (or content) of the ions produce more reticulated polymer surface, but less damaged by chains scissions. The relative predominance of cross-linking at the higher ion energy may be possible due to an increase in the production of the secondary electrons and radicals. They didn't specify what are the involved species and specific mechanisms.

The treatment time dependence of the content for a given species in the two above mentioned situations (without and with PET sample in IB-LDP system) show also another aspect. The equilibrium between the yielding and the removing (consumption) of a given species is reached almost immediately after the switch on of the discharge (for almost all the investigated neutral species) when the polymer sample is not in the treatment system. Such an equilibrium is obtained after long exposure time, when PET sample is inside the treatment system.

The contents $[M]$ were determined from the $[M]=f(t)$ curves obtained in MID operation mode, by integration over an interval of ten seconds and in the Figures 3–6 are presented such curves [11].

Knowing that the content in a species M is the result of the emission and consumption processes, it must stood out that up to $t=10$ min. there is an important consumption process for treatment with ions of 100 eV; the consumption process is diminished in the case of 300 eV energy ions, for $1<t<10$ min. and for ions of 500 eV an important emission process takes place up to $t=5$ min. An equilibrium between the emission and the consumption rates is attained for $t \geq 15$ min., for the investigated ion energies.

The concentration $[H_2]$ is much higher than $[H_2O]$, in the case of the treatments wiht ions of 100 eV, but the difference is diminished for longer exposure times (Fig. 3, curves 1 and 1′). The difference between the contents of this two above mentioned species is diminished for treatments with 300 eV energy ions and even it arrives that $[H_2O]>[H_2]$ for longer exposure times (Fig. 3, curves 2 and 2′). $[H_2O]$ is higher than $[H_2]$ for all treatment times with ions of 500 eV (Fig. 3, curves 3 and 3′). [OH] is greater than [O] (Fig. 4) and $[CO]>[CO_2]$ (Fig. 5) for all investigated oxygen ion energy. Only for treatments with ions of 100 eV $[C_4H_7]>[C_6H_6]$ (Fig. 6, curves 1 and

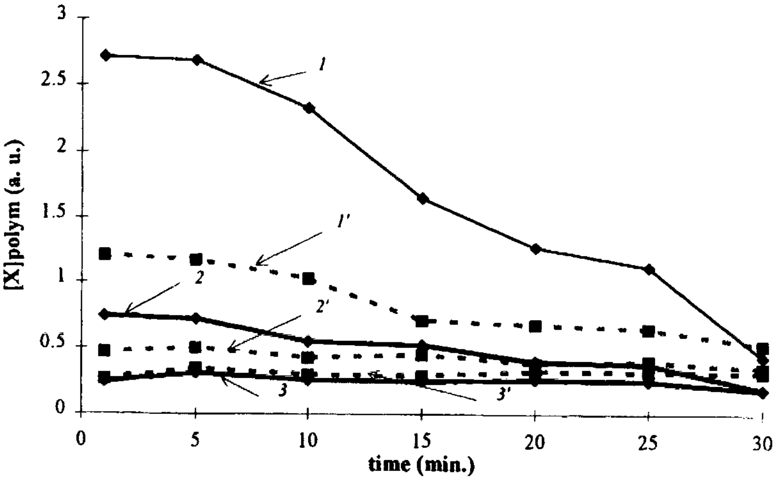


FIGURE 3 Dependence [X] = $f(t)$ for H_2 (curves 1 – 100 eV, 2 – 300 eV, 3 – 500 eV) and H_2O (1′ – 100 eV, 2′ – 300 eV, 3′ – 500 eV).

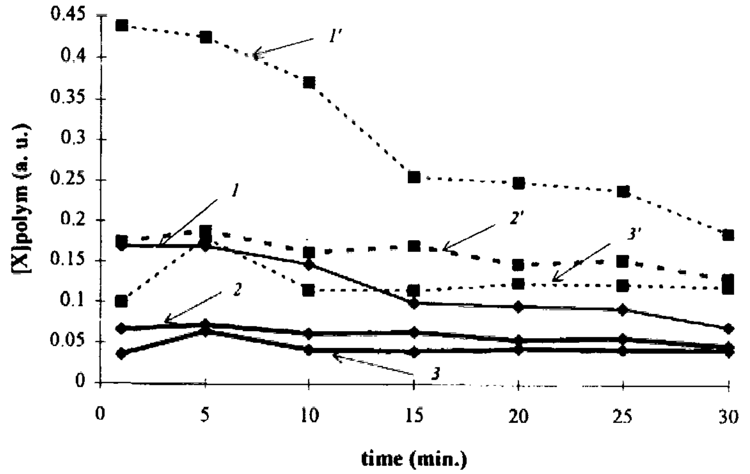


FIGURE 4 Dependence [X] = $f(t)$ for O (curves 1 – 100 eV, 2 – 300 eV, 3 – 500 eV) and OH(1′ – 100 eV, 2′ – 300 eV, 3′ – 500 eV).

POLY(ETHYLENE TEREPHTHALATE) FILMS WITH DIFFERENT CONTENT OF ACID-BASE FUNCTIONALITIES. II. GAS PHASE ANALYSIS

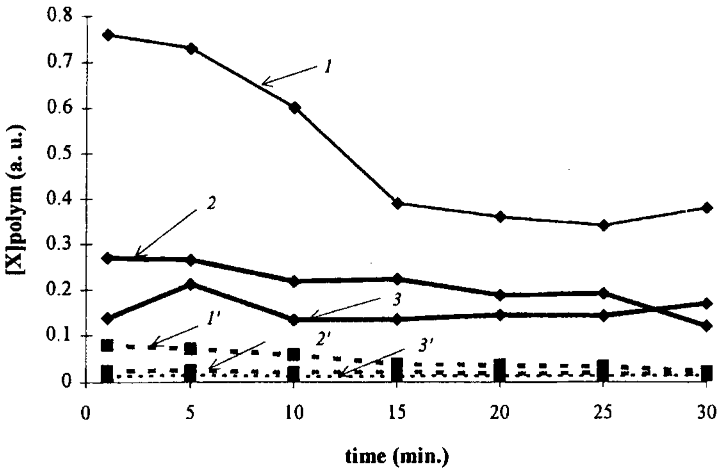


FIGURE 5 Dependence[X] = *f*(*t*) for CO (curves 1 – 100 eV, 2 – 300 eV, 3 – 500 eV) and CO_2(1′ – 100 eV, 2′ – 300 eV, 3′ – 500 eV).

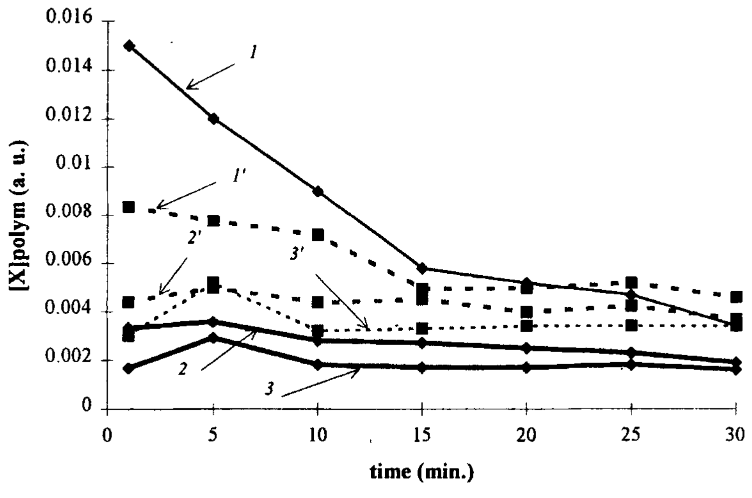


FIGURE 6 Dependence[X] = *f*(*t*) for C_4H_7 (curves 1 – 100 eV, 2 – 300 eV, 3 – 500 eV) and CO_6H_6(1′ – 100 eV, 2′ – 300 eV, 3′ – 500 eV).

1′). Conversely, $[C_4H_7] < [C_6H_6]$, for treatments with ions of 300 eV and 500 eV (Fig. 6, curves 2, 2′ and 3, 3′ respectively).

The ratio $(X_{\text{polym}} - X)/X_{\text{polym}}$ (where X_{polym} is the MS signal intensity for a given species, when the polymer sample is inside the system and X-the same as above when the PET sample is not inside the system) has been calculated for all the investigated neutral species. The values for the three investigated ion energies, at the lowest does δ_1 are given in Figure 7. The high, positive values of this ratio, for treatments with ions of 100 eV, means that the main part of the MS signal is due to the species released by the polymer sample. For treatments with ions of 300 eV only for $m/q = 28$ and $m/q = 77$ were obtained small, positive values, while for the other species were obtained negative values of this ratio. For all the investigated neutral species were obtained negative values in the case of the treatments with ions of 500 eV, higher than for treatments with ions of 300 eV. The negative values for $(X_{\text{polym}} - X)/X_{\text{polym}}$, when the polymer sample is in the IB-LDP system, suggest that these species are consumed by reactions on the polymer surface like the dissociative adsorption.

A short presentation of the main steps of the PET degradation or cross-linking reactions which could be possible in such a system is necessary now in order to explain the MS data.

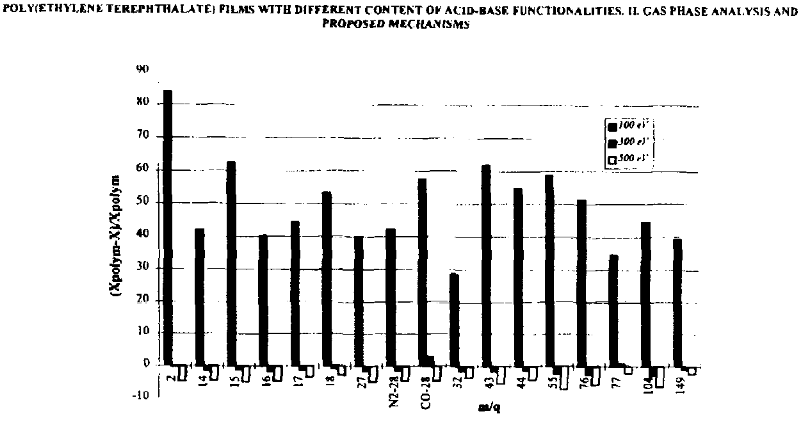


FIGURE 7 $(X_{\text{polym}} - X)/X_{\text{polym}}$, for the investigated neutral species by mass spectrometry, at different ion energies and the lowest dose.

The first step in chain scission reactions, promoted by the fast oxygen ion bombardment, in competition with atomic oxygen and UV radiation from the IB-LDP system, is determined by the dissociation energy required by such reactions. Therefore, is necessary [16]:

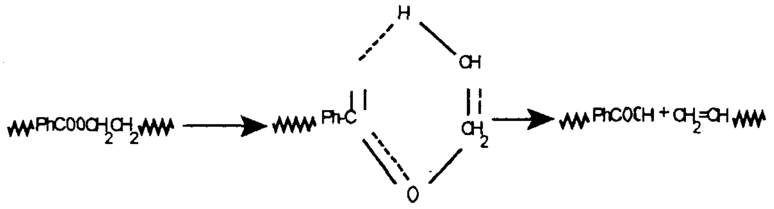
$$84\,\mathrm{kcal/mol\ to\ obtain}: \sim \mathrm{PhCOO{\bullet}+{\bullet}CH_2CH_2} \sim \qquad (1)$$

$$88\,\mathrm{kcal/mol}: \sim \mathrm{Ph{\bullet}+{\bullet}COOCH_2CH} \sim \qquad (2)$$

$$102\,\mathrm{kcal/mol}: \sim \mathrm{PhCO{\bullet}+{\bullet}OCH_2CH_2} \sim \qquad (3)$$

As a function of the LET value, which in turn is a function of the ion energy, one or other of the above mentioned reactions are more probable.

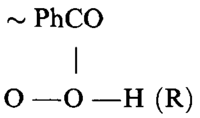
Another important reaction which leads to the formation of the carboxylic groups is a Norrish II type [17]:



(4)

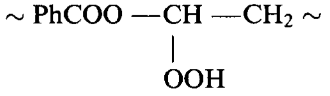
with Ph = ⏣. Such a reaction involves the intramolecular hydrogen reduction; *cis* phase, mainly from the PET amorphous phase, is favourable to the creation of the transient state in the reaction (4).

The primary and secondary polymer radicals can react with molecular or atomic oxygen. The reaction with molecular oxygen lead to the formation of peroxyesters/acids (5) or to hydroperoxydes (6):



$$\begin{array}{c}\sim \mathrm{PhCO}\\ |\\ \mathrm{O-O-H\ (R)}\end{array}$$

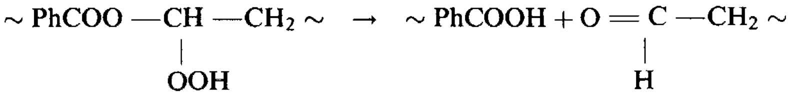
(5)



$$\begin{array}{l}\sim \mathrm{PhCOO-CH-CH_2} \sim\\ \qquad\qquad\quad\ |\\ \qquad\qquad\ \mathrm{OOH}\end{array}$$

(6)

Decomposition of hydroperoxydes to aldehydes takes place by the reaction:



$$\sim PhCOO-\underset{\displaystyle OOH}{\underset{|}{CH}}-CH_2\sim \;\rightarrow\; \sim PhCOOH + O=\underset{\displaystyle H}{\underset{|}{C}}-CH_2\sim \qquad (7)$$

Atomic oxygen attacks primary or secondary radicals inducing complete degradation of the chain and formation of formaldehyde. This last one on its turn reacts with atomic oxygen result in the formation of CO, CO_2, OH•, H• [18]:

$$CH_2=O+OH \rightarrow OH+H-C=O\cdot \xrightarrow{\bullet O,k_1} CO+OH\bullet \qquad (8)$$

$$\xrightarrow{\bullet O,k_2} CO_2+H\bullet \qquad (9)$$

$$\xrightarrow{\bullet H,k_3} CO+H_2 \qquad (10)$$

with $k_3>k_1>k_2$.

Radicals OH• are able to participate to different reactions, the main ones being [18]:

$$OH\bullet+RH \xrightarrow{k_4} R\bullet+H_2O \qquad (11)$$

$$OH\bullet+CO \xrightarrow{k_5} CO_2+H\bullet \qquad (12)$$

$$OH\bullet+H_2 \xrightarrow{k_6} H_2O+H\bullet \qquad (13)$$

with $k_4> k_5> k_6$.

The CO_2 content is the result of the balance between its yielding by reactions (9), (12) and (14) and its consumption (reactions (15) and (16)):

$$CO+O \rightarrow CO_2 \qquad (14)$$

$$CO_2 \rightarrow CO+1/2O_2 \qquad (15)$$

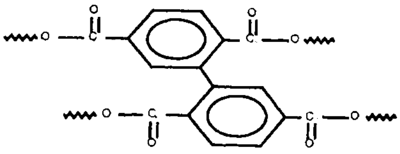
$$CO_2 + e \rightarrow CO + O \quad E > 10\ \text{eV/mol} \tag{16}$$

Atomic hydrogen is produced by reactions (9), (12), (13) and it is consumed mainly by the following reactions:

$$H-C=O\bullet + H\bullet \rightarrow H_2 + CO \tag{17}$$

$$RH + H\bullet \rightarrow H_2 + R\bullet \tag{18}$$

Therefore, reverting to MS data, it must pointed out again that a decomposition of PET is the main process for treatments at the lowest energy (100 eV) and dose δ_1 (Fig. 7). A cross-linking of PET is a process in competition with the chain scission reactions for treatments at higher energy and doses. Such a process is mainly due to the formation of a structure like [19].



via the recombination of two aryl radicals obtained by hydrogen abstraction from the benzene ring. The cross linking could also takes place by cracking of the aromatic rings and formation of polyenes [17].

Water formation mainly by reaction (11) and (13), in which are involved OH•, in correlation with the low reactivity of H• toward polymer in comparison with OH• and O•, explains the inequality $[H_2O] < [H_2]$, in the first minutes of the treatment with ions of 100 and 300 eV (Fig. 3). The less efficient degradation process at higher doses or energy could be the reason for the diminishing in the difference between $[H_2O]$ and $[H_2]$, in these conditions.

The higher rate constants for CO yielding (by reactions (8) and (10)) than for CO_2 (reaction (12)) could explain the higher value for [CO] than for $[CO_2]$ (Fig. 5). The higher reactivity of O• than OH• toward polymer could also explains the inequality [OH] > [O].

This is in contradiction with the data from the literature about the reactivity toward butane: $K_H = 2{,}5 \cdot 10^{-16}$ cm^3/molecule·sec, $K_{OH} = 2,\ 5 \cdot 10^{-12}$ cm^3/molecule·sec, $K_O = 2,\ 2 \cdot 10^{-14}$ cm^3/molecule·sec [18].

The chain scission with the formation of high weight molecular fragments, even its contribution to the total degradation product content is low, is more important in the case of bombardment with higher ion energy (Fig. 6).

Oxygen Ionic Species in IB-LDP System

The fluence of the ionic oxygen species (O^+ and O_2^+) at the polymer surface were determined from mass spectrometry data, as shown in [11]. Both the fast ions O^+_{fast} and $O^+_{2,fast}$ (with medium energy given by the difference between the potential of the source and target plasma) and the slow ones O^+_{slow}, $O^+_{2,slow}$(mainly from the target plasma) were taking into account. These fluences are given in Table II together with the values for $\Gamma_{O^+,fast}/\Gamma_{O_2^+,fast}$, $\Gamma_{O^+,slow}/\Gamma_{O^+,fast}$ and $\Gamma_{O^+_{2,slow}}/\Gamma_{O^+_{2,fast}}$. These ratios give informations about the importance of the physical effect of the collisional cascade, in which fast ions are involved, in comparison with the chemical desorption process promoted by slow ions bombardment. These ratios also give information about the depth of the altered layer into the sample, knowing that, at the same energy, the lowest atomic mass ions loss their energy in the deeper layers.

The $\Gamma_{O^+,fast}$ is almost the same for ions of 100 eV and 300 eV, but it is ten times greater for ions of 500 eV. The fluence of the fast molecular oxygen ions increases with ion energy, in the investigated domain. The $\Gamma_{O^+,slow}$ slightly decreases with ion energy, while the $\Gamma_{O^+,slow}$ remains unchanged.

Possible Mechanisms Involved in PET Modification in the IB-LDP System

The experimental results presented above and those shown in previous papers [11, 12] make possible to have an almost complete picture about the mechanisms involved in PET modifications in the IB-LDP system in oxygen.

Active Elements in IB-LDP System

The following factors are active in IB-LDP system, in oxygen:

i) O^+ *and* O_2^+ *fast ion bombardment.* Their fluences to the polymer sample obviously increase with ε_i (Tab. II). The $\Gamma_{O^+,fast}/\Gamma_{O^+_{2,fast}}$ ratio

TABLE II Data on the fluences of fast and slow O^+ and O_2^+ ions on the PET sample [11]

Characteristic	$\varepsilon_i = 100\,eV$	$\varepsilon_i = 300\,eV$	$\varepsilon_i = 500\,eV$
$N_O \cdot 10^{11} (cm^{-3})$	6,1	6,0	5,8
$N_{O_2} \cdot 10^{11} (cm^{-3})$	9,3	7,3	6,7
$\Gamma O^+_{fast} \cdot 10^6 (a.u.)$	1,2	1,6	58,8
$\Gamma O^+_{2,fast} \cdot 10^6 (a.u.)$	3,7	57,7	206,5
$\Gamma O^+_{slow} (a.u.)$	$1{,}1 \cdot 10^5$	$1{,}1 \cdot 10^5$	$1{,}0 \cdot 10^5$
$\Gamma O^+_{2,low} (a.u.)$	$0{,}8 \cdot 10^5$	$0{,}6 \cdot 10^5$	$0{,}5 \cdot 10^5$
$\Gamma O^+_{fast} / \Gamma O^+_{2\,fast}$	0,3	0,03	0,3
$\Gamma O^+_{slow} / \Gamma O^+_{2\,slow}$	1,4	1,6	2,0
$\Gamma O^+_{slow} / \Gamma O^+_{fast}$	0,1	0,06	$1{,}7 \cdot 10^{-3}$
$\Gamma O^+_{2\,slow} / \Gamma O^+_{2\,fast}$	0,02	$1{,}1 \cdot 10^{-3}$	$2{,}4 \cdot 10^{-4}$

has the same value for ions of 100 eV and 500 eV, but it is ten times smaller for ions of 300 eV, due to the ε_i dependence of both fast ion fluence to polymer sample and cross section of the involved charge transfer reactions [11].

ii) O^+ *and* O_2^+ *slow ions* for which the fluences are not appreciable modified by ε_i. The $\Gamma_{O^+_{slow}} / \Gamma_{O^+_{fast}}$ and $\Gamma_{O^+_{2,slow}} / \Gamma_{O^+_{2,fast}}$ ratios decrease with ε_i (Tab. II).

iii) *Atomic and molecular oxygen* concentrations decrease with ε_i (Tab. II).

iv) *The UV and thermal radiation* from the discharge which were considered to have the same intensity at the same treatment time, for all investigated ion energies.

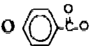
Possible Mechanisms in Connection with Ion Energy and Dose

The data presented in the actual and precedent papers [11, 12] prove that appreciable differences are stood out between the treatments made in so called saturation regime for ion dose (δ_1) and those in reimplantation regime (δ_2 and δ_3). The ion energy, in the investigated domain, is important by measure to which it determines the fluence of fast and slow, atomic and molecular oxygen ions at the polymer surface.

Treatments in Saturation Regime (δ_1)

An enhanced etching mechanism promoted by low fluence of O^+_{fast} and $O^+_{2,fast}$ and by slow ions bombardment (which contribute to the efficient desorption of the volatile products) takes place for PET treatments with ions of 100 eV [11]. The etching process, in a so called anomalous transport regime (with a higher etching rate than oxidation rate [18]), is facilitated by the presence on the pristine sample surface of an non-homogenous, amorphous layer and is sustained by the following experimental data. *Cis* shoulders are diminished in δ_{I}-100 (Fig. 10a [12]), which sustains that the etching process takes place mainly in the amorphous phase. The oxygen groups content is slightly increase which is shown by the relative small values for γ_s^{ab}, $\gamma_s^+$and γ_s^- (Fig. 3 [12]). The highest content of degradation products released from the polymer sample and the higher consumption rate in the first 10 min. (Figs. 3 – 7) sustain that the slow ion bombardment is important and leads to a more efficient desorption of the degradation products, leaving free surface active sites.

The intensive heavy $O^+_{2,\mathrm{fast}}$ ion bombardment is the main characteristic of the treatments with ions of 300 eV ($\Gamma_{O^+_{,\mathrm{fast}}}/\Gamma_{O^+_{2,\mathrm{fast}}}$ is ten times smaller than that for treatments with ions of 100 eV and 500 eV). The linear energy transfer LET for such ions is higher than for atomic light ions and makes that a cross-linking process be competitive with the enhanced etching process in a very thin uppermost layer. Content of (100) planes which make angle $\omega \neq 0$, $N_{(100)\text{-}\omega}$, is the greatest for δ_{I}-300 (Fig. 12 [12]), proving that the heavy ion bombardment affects not only the amorphous phase, but determines a distortion of the crystalline one. The surface oxygen group content of δ_{I}-300 sample is diminished in comparison with that of untreated and δ_{I}-100 samples (Fig. 3 [12]). A decreased neutral species content and a diminished consumption process are stood out in Figures 3 – 6, proving the competition between the above mentioned processes.

For treatments with ions of 500 eV an etching process in stationary regime (with an oxidative layer depth independent of dose) is in competition with a cross-linking process. These processes take place in deeper layers since they are determined mainly by the high fluence of O^+_{fast}, for which low value of LET is characteristic. Increased intensity of the 1578 cm^{-1} band assigned to  group (Fig. 10a [12]) together with a slight increase of γ_s^{ab}, γ_s^+ and γ_s^-(Fig. 3 [12]) sustain the introduction of oxygen surface functionalities. The lowest content of degradation products and its independence on the treatment time is stood out in Figures 3 – 6.

Generally treatments at δ_1 do not award a prevalent surface acidic or basic character of the PET samples.

Treatments in Reimplantation Regime (δ_2 and δ_3)

Treatments at δ_2 and δ_3 determine a diminished etching process and an ion beam induced epitaxial crystallisation as it is well argued in [11], for all investigated ion energies.

The PET samples treated at these high doses have a more prevalent acidic or basic character. The content in acid/base functionalities depends now not so much on the first step in the chain scission reaction, but much more on the thermal stability of the different carbon groups [19]:

carbonyl(hard basic) > hydroxyl(soft acid) > carboxyl(hard acid)

Therefore, the treatment at the highest dose (δ_3) and ion energy (500 eV), for which the thermal effect of the ion bombardment is more important, determine the diminishing of $\gamma_s^+$and increasing of γ_s^- (Fig. 3 [12]).

Ageing Mechanism

Data about ageing effects could be explained by considering the synergetic coupling of three factors: the surface oxygen group content, the predominance of short or long range motion [19] and the hard-soft acid-base (HSAB) reactions [20].

For the samples with a low content of oxygen functionalities and for which the cross-linking process is not too important, the long range motion explain the transient increased in acid/base surface component γ_s^{ab} (Tab. III [12]). A no prevalent acidic or basic character could mean that there are introduced groups of the opposite type (basic *and* acidic), but the same hardness and in the same proportion. Between such kind of groups faster reactions takes place according to HSAB principle and could provide a more stable surface.

A more pregnant acidic or basic character means that a high content of a given type of group (basic *or* acidic) is introduced; between such groups is much less possible to take place reactions and more probable are reactions with those of the same hardness, but the opposite type from the subsurface layers. Such mechanism is sustained, apart by surface energy data, by XPS results. Therefore, for δ_3-100 sample, which evolves with the ageing time from acidic to basic character, an increase of O = C/C in the uppermost layers concomitantly with the diminishing of the same ratio in the profoundness layers is stood out (Fig. 7c [12]). δ_3-500, which initially has a basic character and evolves to an acidic one, the increase in O—C/C ratio in the profoundness layers is observed (Fig. 9c [12]).

CONCLUSIONS

The main neutral and oxygen ionic species from the IB-LDP system were analysed by MS. These data and those presented in previous papers [11, 12] have allowed to propose some mechanisms for surface modifications and ageing effects.

Appreciable differences between the treatments made in saturation regime and those in reimplantation regime were stood out. An enhanced etching mechanism, promoted by the bombardment of O^{+}_{fast} and $O^{+}_{2,\ \text{fast}}$is active in the treatments with ions of 100 and 300 eV, at δ_1, while an etching mechanism in stationary regime in a competition with a cross-linking process are important for the treatment with of 500 eV, the same dose. Treatments at this dose do not confer a prevalent acidic or basic character of the PET surface. Treatments in a reimplantation regime are characterised by a diminished etching process and an ion beam induced crystallisation. Also, a more prevalent acidic or basic character of the treated PET surfaces is stood out.

The ageing effects were explained by considering the main three factors involved: the surface oxygen content, the predominance of short or long range motion and the HSAB reactions.

The samples with a predominant acid or base character are more unstable in opposition with those with a not prevalent one.

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