IN SITU (XPS) AND *EX SITU* (XPS and TOF-SIMS) STUDIES OF THE OF NYLON 6 AND PMMA TREATED IN REMOTE O_2 AND O_2-N_2 PLASMAS

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ABSTRACT
The functionalization and degradation processes of Nylon 6 and PMMA have been studied in the post-discharge area of microwave O2 and O2-N2 plasmas. Their evolution as a function of the dose of active species has been followed by *in situ* and *ex situ* surface characterisation methods (XPS and SIMS). The role of the C-N bond strength in Nylon 6 and the ester bond conformation in the PMMA has been highlighted. Treatments at low atomic oxygen doses induce stuctural changes at both the Nylon 6 and PMMA surfaces. The evolution of plasma treated surfaces after air exposure has been studied, showing sharp differences between PMMA and Nylon 6.

INTRODUCTION

In previous studies, the behavior of polyethylene (PE) and polycaprolactone (PC) surfaces treated in the post-discharge of a pure oxygen plasma has been investigated. The surface functionalization (creation of new chemical oxygen bonds) increases as a function of treatment time, until degradation (breaking of oxidized fragments) occurs. Since functionalization and degradation are complex phenomena it is of great interest to investigate on the one hand, the influence of the presence of a weak bond in the polymer chain, and on the other hand, the influence of chain conformation. Thus, we chose Nylon 6, which contains the weak C-N bonds, and polymethylmethacrylate (PMMA) for which the ester group is in a pendant chain.
We present a surface investigation of the treated Nylon 6 and PMMA by *in situ* and *ex situ* XPS and *ex situ* SIMS. XPS gives us information about the number of oxygen atoms chemically bonded at the surface (O1s/C1s ratios). Decomposition of O1s and C1s spectra allows us to follow the bonding formation. Owing to the molecular information it provides, its hight sensivity and its selectivity to the uppermost surface layers, SIMS is a good complementary technique to XPS.

EXPERIMENTAL

The experimental setup consists of a plasma microwave reactor directly coupled to a XPS apparatus. It allows analysis of the samples without any contact to the atmosphere between treatment and analysis.

The plasma device consists of a quartz tube bent at a 90° angle, with two different diameters: the gases are introduced in the narrower part and the discharge is generated by a surfaguide at 2.45 GHz, 300W. The samples are treated in the wider part of the tube at various distances X2, where photons, electrons and ions issued from the plasma are not present.

We can modelize via actinometry [1] the post-discharge medium in order to establish the density gradient of the different species in the post-discharge such as oxygen atoms [O] and oxygen molecules [O_2 ($a^1\Delta$)] [2].

Nylon 6, free from plasticizers and slip agents was spread on aluminum foils. PMMA, first purified to remove the majority of its additives, was spin-coated on glass.

Nylon 6 was treated in the post-discharge of a 20 sccm, 2 Torr, 300 W, pure oxygen plasma at the distances: X_2 = 12, 19 and 32 cm. The densities of atomic oxygen reaching a surface unit (cm^2) during one second are resp.: $4.5 \cdot 10^{18}$, $2.3 \cdot 10^{18}$, $6.6 \cdot 10^{17}$ at·cm^{-2}·s^{-1}. The dose is the density integrated along the time of treatment.

PMMA surfaces were treated either in pure oxygen plasmas or in O_2-N_2 plasmas at: 300W, 75 sccm, 0.5 Torr. The treatment distances are X2 = 12 and 25 cm. A, B, C, D are respectively the treatments made with 0%, 10%, 50% and 99 % nitrogen.. Pure N_2 plasma could not be produced because of an oxygen contamination on the quartz tube (<1%).

XPS analysis was performed in-situ using a VSW X-ray photoelectron spectrometer which uses a monochromatized Al Kα source. ToF-SIMS studies were performed at Louvain-La-Neuve three days after the plasma treatment with a Charles Evans and Associates apparatus as describe elsewhere [3]. In order to compare the both techniques we performed also *ex situ* XPS analysis after three days contact with air.

In order to performed TOF-SIMS spectra, a normalisation to the total intensity minus the hydrogen intensity (too sensitive to the setting adjustements) and contamination intesities (too variable) was performed. This procedure allows to obtain very reproductible values (maximum error: 10%)

RESULTS AND DISCUSSION

I Nylon 6

In situ results :

Fig. 1 shows the evolutions of the O/C, N/O, and N/C ratios with the time of treatment at each distance. It is quite similar for the 12 and 19 cm treatments *viz.* a steady increase of the O/C ratio and a drastic decrease of the N/O ratio at the beginning, immediately followed by a stabilization going along with an increase of the N/C ratio. The behavior at X2 = 32 cm is somewhat different: after the same initial variation, all ratios reach a plateau.

Fig. 2 shows the O/C ratio versus the dose of atomic oxygen. If, at the same dose, the surfaces treated at 12 or 19 cm show the same O/C ratio, at 32 cm, the ratio is higher at weak doses and seems to become lower after $1.5 \cdot 10^{22}$at·cm^{-2}. The N/O and N/C

of the C-N bond (degradation). It can be offset by the production of C-O bonds during the treatment, especially for X2 = 12 cm. In fact, the C-N bond is very weak and so its breaking is the first reaction occuring under the treatment. The behavior at 32 cm can thus be explained in the following manner: as the reactive medium is much poorer on atomic oxygen than at 12 and 19 cm, there is not enough atomic oxygen after the break of the C-N bond which generate a small functionalization, to allow the production of more radicals, base of the functionalization and the degradation mechanisms.

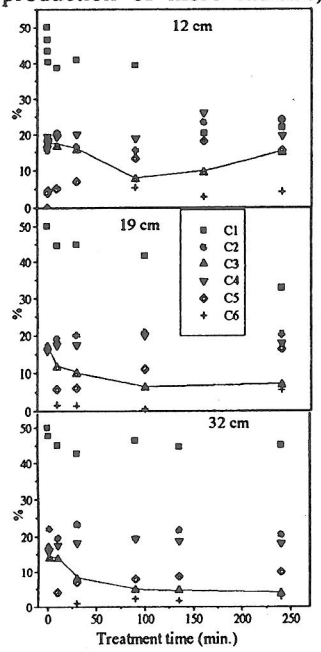

Fig. 3: evolution of the *in situ* C1s components with the treatment time

Ex-situ results:

1) XPS

There is not a sharp difference in term of O/C, N/C and N/O ratios measured *in situ* and *ex situ* except for samples 1 min., 12 cm and 10 min., 32 cm where the O/C ratio is lower after air exposure. For longer treatment times, only treatment at 19 cm shows a decrease of O/C and a simultaneous decrease of N/O, as compared to the *in-situ* analysis.

If we consider now the C1s components, the main result is that the decreases of C5 and C6 are large, especially at short treatment times. We also notice the absence of any modification of the C=O bond.

2) SIMS

The O^-/CH^- ratios, known as representative of the oxygen content at the surface, give the same trends as the XPS O/C ones: they increase with the length of the treatment at 12 and 19 cm. However, if the O/C ratios were lower at 32 cm with respect to the other distances, this is not the case for the O^-/CH^- except for the 1 min. treatment where the O^-/CH^- ratio is even less than for the untreated sample. Once more, the differences are noticeable on the surfaces treated in a rective medium poor in atomic oxygen.

SIMS analysis points out noticeable differences in the treated surface with respect to the untreated sample: at 12 cm there is an increase of the normalized intensities of the very oxidized ions (89, 124, 127 and 173 amu) with the time of the treatment. At 19 and 32 cm the obtained values are lower. This is consistent with the variation of the C5 and C6 components in the C1s peak. There is no variation of the yields of carbonyl ions (29 and 43 amu); this is also consistent with the absence of variation of the C4 component. In the C1 cluster, the increase of the yield of C^+ ions with respect with

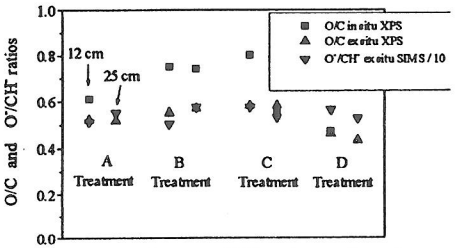

Fig 4: *in situ* and *ex situ* O/C ratios and *ex situ* O^-/CH^- ratios for the A, B, C and D treatments at X2 = 12 and 25 cm

ratios are lower at 32 cm whatever the dose. These results support the finding that the nature of the surface modification mechanism is different at low flux densities. Using an usual peak fitting method [4] based on the known chemical shifts [5] we decompose the C1s and the O1s spectra as shown in Table 1.

	C1	C2	C3	C4	C5	C6
peak position (eV)	285.00	285.70	286.40	288.00	290.05	291.00
	C—C C—H	C—C=O O	C—N C—O	C=O	C—C—O O	O—C—O O

Table 1: binding energy values (eV) of the different carbons in Nylon 6

As shown in fig. 3, the more noticeable effects are the decrease, for all distances, of the C3 component at the beginning of the treatment and the increase of the C5 and C6 components after a given time of treatment. The 32 cm treatment is aigain somewhat different: after 30 min. of treatment,there is no important variation in the percentages of the various components. The decrease of N/O can be related by the unsurprising introduction of new oxygen bonds. The fact that in the same time, the N/C ratio is also decreasing exhibit a degradation effect. The O/C ratio characterizes both the phenomena together. In this way, the increase of the O/C ratio at X2 = 12 and 19 cm with the N/O ratio constant, and the N/C one increasing can be only due to the loss of C, *i.e.* the degradation of aliphatic fragments. Here, the degradation is not a limiting factor for functionalization.

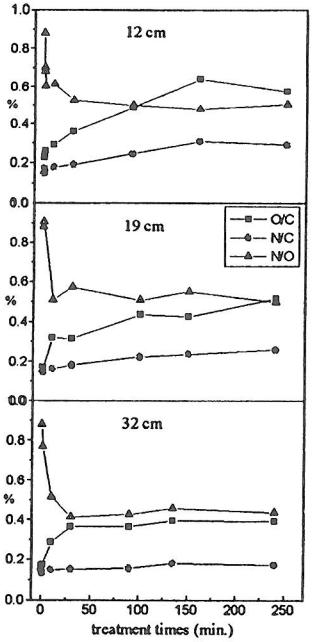

Fig. 1: evolution of the *in situ* O/C, N/C and N/O ratios with the treatment time

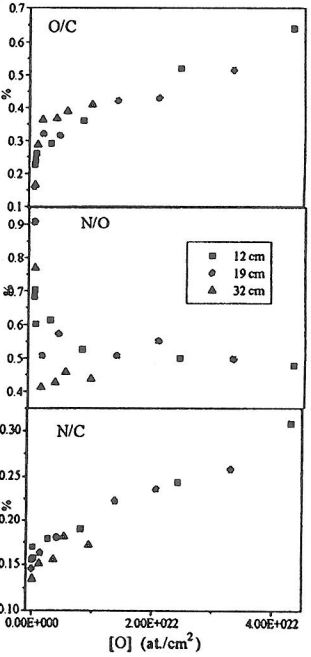

Fig. 2: evolution of the *in situ* O/C, N/O, N/C ratios with the atomic oxygen dose

That is backed up with the decrease of the C3 component which is characteristic of both C-N and C-O bonds. Since it concerns only C-N in the untreated polymer, the decrease of C3 at the beginning of the treatment comes from the break

the untreated surface shows the occurence of the break of aliphatic fragments. The observed differences are slight for the different treatments, except for the 1 min., 32 cm one. In fact, the relative intensities of ions that could be related to (but not only) carbonyl (29 and 43 amu), alcohol (31 amu), amine (44 and 56 amu) functions are lower than for the other treated sample and even for the untreated sample. Moreover, the C_8/C_2 ratio, which may be representative of branching and crosslinking for polyolefines [6, 7] is much higher. Hence, a small atomic oxygen dose is sufficient to induce noticeable modifications at the surface but gives functionalization and stucture that are different from those obtained for higher doses and from those of the untreated sample.

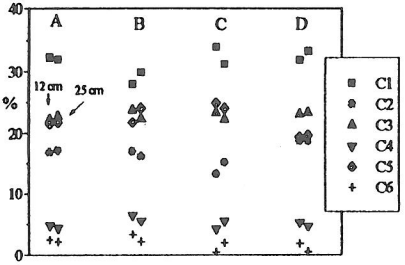

Fig. 5: *ex situ* C1s components for A, B C and D treatments

II PMMA

The values of O/C ratios obtained by *in situ* XPS or after a three days stay in air (*ex situ*) are shown in fig. 4. For the *ex situ* results, there is no sharp difference between A, B and C treatments and no differences between both distances. The D treatment alone shows a lower O/C ratio. It is also the only one presenting no difference between the O/C ratio measured *in situ* or *ex situ*. For the others samples and especially for the B treatment, the amount of O decreases drastically after air exposure.

		nitrogen content			
X_2	Untreated	0 %	10 %	50 %	100%
12 cm	3.00	5.14	5.03	5.75	5.63
25 cm	3.00	5.50	5.74	5.31	5.26

Table 3: O^-/CH^- ratios for the A, B, C and D treatments on PMMA

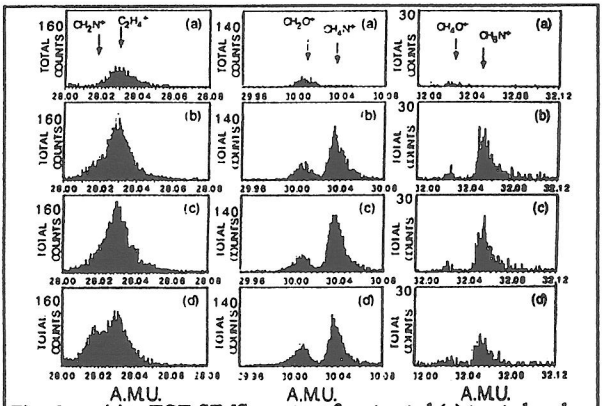

Fig. 6: positive TOF-SIMS spectra of untreated (a),treated under pure O2 (b), 50% N_2 (c), 99% N_2 (d) PMMA surfaces

The decompositions of the *in situ* C1s peaks show few differences between the A, B and C treatments. The D treatment differs by a smaller contribution of C5 and C6 components. If we consider samples transfered in atmosphere, the differences are even weaker (cf. fig. 5). The main facts are the decreases of C4, C5, C6 going along with the increase of C1 and C2. This means, that if the very oxidized parts are not bound to the polymer they can either go from the surface towards the bulk or be hydrolyzed with the air.

SIMS results are consistent with the above considerations insofar as there are again no sharp differences between the A, B and C treatments. Once more, only the D treatment presents typical features. If we consider the O^-/CH^- ratios in fig. 4 we can see that they are in good agreement with the XPS O/C *ex situ* ratios, except for the treatment at 99 % N_2 where they are not as small as in the case for the O/C ratios. Since SIMS is more sensitive at the extreme surface, it is reasonnable to think that the treated thickness in sample D is much more lower.
Otherwise, since the A, B and C treatments at 12 and 25 cm do not present reliable differences, the only differences on the D treatment are noteworthy. The most stricking effect is showed in fig. 6. It concerns the relative intensities of the different nitrogen containing ions: as a fuction of the N_2 content in the remote plasma ((b) to (d)), CH2-NH4+ at 32.05007 amu is decreasing, CH2=NH2+ at 30.03437 amu is constant and CH=NH4+ at 28.01872 amu is increasing. These ions are quite different by their hydrogen content. In fact, this evolution is going along with the decrease of the saturated fragments in the hydrocarbon clusters. There is also an increase on the C_2/C_8 ratio only for this treatment. This lead us to the clear conclusion of a structurally different surface in the case of the D treatment.

CONCLUSION:
From this study it appears that functionalization and degradation are always in competition in surface modification of polymers by post-discharge plasmas. The role of the dose of atomic oxygen has been demonstrated. The increase of oxygen concentration at the surface of Nylon 6 results not only from the appearance on new oxygen bonds but also to the loss of aliphatic fragments. It is clear that in this case the reaction mechanisms start from the C-N bond which is the weakest one. For both Nylon 6 and PMMA, the behavior of the surfaces is quite different at low doses than if they were treated in reactive medium richer in atomic oxygen: low doses induce primarily structural changes.
The Nylon 6 modified surfaces are indeed quite stable after air exposure as shown by *ex situ* XPS and SIMS experiments but some degradation is observed for PMMA after the contact with air.

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