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Ronan Prat^{ab}; Ming-Kun Shi^{ac}; Françoise Clouet^a

^a Institut de Physique et Chimie des Matériaux de Strasbourg UMR 046 du CNRS Groupe des Matériaux Organiques (I.P.C.M.S.-G.M.O.) 23 rue du Loess, Strasbourg-Cedex, France ^b Faculty of Science and Technology, Sophia University, Tokyo, Japan ^c Département génie chimique, Ecole polytechnique, Montréal, Québec, Canada

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INTERACTIONS OF COLD PLASMAS WITH POLYMERS AND THEIR MODEL MOLECULES: DEGRADATION VS. FUNCTIONALIZATION

RONAN PRAT,*,[†] MING-KUN SHI,[‡] and
FRANÇOISE CLOUET[§]

Institut de Physique et Chimie des Matériaux de Strasbourg
UMR 046 du CNRS Groupe des Matériaux Organiques
(I.P.C.M.S.-G.M.O.)
23 rue du Loess, 67037 Strasbourg-Cedex, France

ABSTRACT

The influence of the chemical composition of polymers on their modification in argon or oxygen RF plasmas has been studied. Hexatriacontane (C36), octadecyloctadecanoate (OOD), and octadecyloctadecanamide (OAD) have been chosen as model compounds of the following polymers: high density polyethylene (HDPE), polycaprolactone and two polyamides [nylon 6 (N6) and nylon 12 (N12)]. Surface degradation and functionalization have been followed using gravimetry, optical emission spectroscopy, mass spectroscopy, XPS, and contact angle measurements. The presence of ester or amide functions in the composition of the polymers has an influence on the degradation which starts on the functions. The mechanisms of formation of the degradation products CO and CO₂, followed by mass spectrometry, are the same for all the investigated samples. The competition between degradation and functionalization limits the evolution of the O/C ratio and of the surface

[†]Present address: Faculty of Science and Technology, Sophia University, 7-1 Kioi-cho, Chiyoda-ku, Tokyo, 102, Japan.

[‡]Present address: Ecole polytechnique, Département génie chimique, 2900 Bld Edouard Monpetit, Station A Box 6079, Montréal, Québec H3C 3A7, Canada.

[§]Died April 17, 1993.

energy. A contact angle titration technique showed the formation during plasma treatment of functions which can participate in an acid/base reaction.

INTRODUCTION

Polymers are intensively used in nearly all sectors of industry, but their small surface energy and the existence of low cohesion layers can limit their applications in the design of composites. To overcome these drawbacks, the use of cold plasmas has increasingly developed in recent years [1-7]. This surface treatment technique improves the adhesion properties without affecting the characteristics of the bulk by increasing the surface energies of the polymers through the generation of functional groups [8-11].

The study of the mechanisms which occur during the treatment of polymers in cold plasmas is quite complex. The number of species in the plasma (electrons, ions, UV photons, excited molecules, . . .) likely to take part in the modification of the surface, and the complexity of the composition of the polymers (presence of additives, chains with different lengths) explain the difficulty in analyzing the plasma-surface interactions.

The action of numerous reactive species on the surfaces leads to bond breaking and radical formation [12, 13]. A complex chemistry takes place in which ejection of molecular fragments in the gas phase (*degradation*) and the appearance of oxygenated functions at the surface (*functionalization*) occurs.

To simplify this study, we chose to use organic molecules as models. They are well-defined chemically; they are 100% crystalline and can be compared to industrial polymers. These molecules are: hexatriacontane (C36), octadecyloctadecanoate (OOD), and octadecyloctadecanamide (OAD), which are respectively models of high density polyethylene (HDPE), polycaprolactone (PC), nylon 6 (N6) and nylon 12 (N12). C36 is a linear paraffin with 36 carbon atoms. OOD and OAD are the corresponding ester and amide with the replacement of the central methylene group by, respectively, an ester function and an amide.

By a comparison of these three model molecules which have the same length and are additive-free, the influence of the ester and amide functions will be clearly shown. The behavior of these molecules will be also compared with that of the corresponding polymers.

In previous works, studies on polyethylene, polycaprolactone, and their corresponding model molecules were made [14-18]. Here we complete these studies with the investigation of Nylon 6, Nylon 12, and OAD.

All studies were performed in a RF reactor (13.56 MHz). The plasma gas was either oxygen or argon. The degradation was followed by gravimetry, optical emission spectroscopy, and mass spectroscopy. The functionalization, i.e., incorporation of oxygen chemically bonded to the surface, was characterized by XPS (x-ray photoelectron spectroscopy) and contact angle measurements. It has been shown that the functionalization (and then the surface energy) is effectively dependent on the evolution of the oxygen/carbon atomic ratio.

EXPERIMENTAL: MATERIALS AND APPARATUS

Polymers (polyethylene, polycaprolactone, and the two polyamides) and hexatriacontane were purchased from Aldrich. The samples were prepared by molding under primary vacuum at their melting temperatures.

Octadecyloctadecanoate (OOD) was synthesized in our laboratory [19] by reacting octadecanol at 90°C with octadecanoyl chloride in chloroform (CHCl₃) in the presence of triethylamine as an HCl trap. The ester was purified by chromatography on a silica gel column and recrystallized from acetone. Melting point: 60–61°C.

Octadecylamideoctadecanoate (OAD) was synthesized in our laboratory [20] by reacting octadecylamine at 80°C with stearic chloride in pyridine. The amide was purified by chromatography on a silica gel column in hot chloroform. Melting point: 96°C.

The model molecule films were spread at their melting temperature with a Conway bar on 7 cm × 5 cm aluminum plates.

The plasma was created in a cylindrical reactor (7.5 cm in height and 21 cm in diameter). Its top was the cathode, capacitively coupled to a 13.56-MHz energy generator. The samples were clamped on the anode. The volume of the reactor was about 2600 cm³. The system was evacuated with a mechanical pump up to 10⁻² mbar. The gas flow was fed into the reactor through a mass flowmeter.

The formation process of the degradation products was followed by mass spectrometry (VG Instrument SXP 300). The concentrations of these different gaseous species issued from surface degradation were also studied by optical emission spectroscopy. The plasma emission, transmitted via a quartz optical fiber, was recorded using a 0.32-cm Jobin Yvon monochromator (HR 320). The photons were detected by a photomultiplier having its spectral response in the 185 to 870 nm range.

A VG ESCALAB MKII spectrometer was used for the analysis of surfaces using the AlK α x-ray emission line (1486.6 eV). The surface energies were determined by measuring the contact angles of three liquids on the modified surface. All the measurements were performed less than half an hour after the treatment. The drops on the surfaces were videorecorded on a optic bench. The shape of the drops was determined with the help of VISILOG software, and the values of the contact angles were calculated by the program ADSA-P. The liquids were distilled water, methylene iodide, and formamide. Their reference surface energies are listed in Table 1.

TABLE 1. Components of the Surface Energies (dyn/cm) [21]

| | H ₂ O | CH ₂ I ₂ | Formamide |
|------------|------------------|--------------------------------|-----------|
| γ_p | 51.0 | 2.3 | 18.7 |
| γ_d | 21.8 | 48.5 | 39.5 |
| γ_t | 72.8 | 50.8 | 58.2 |

For the contact angle titration technique, described later, the buffered solutions were purchased from Merck (Titrisol solutions).

RESULTS AND DISCUSSION

Degradation

Weight Loss

Influence of the Time of Treatment. We first studied the influence of the chemical composition of the organic samples on the degradation by measuring the weight loss during plasma treatment under the following conditions: Pressure = 0.3 mbar, power = 0.023 W/cm³, flow rate = 40 sccm.

We assume the effect of the plasma to be uniform on the whole surface of the samples inserted in the central part of the reactor.

For all samples the weight loss (W_D) increases linearly with the time of treatment, and the degradation is more important in an oxygen plasma than in an argon one. This degradation is due mainly to ion and electron bombardments of the surface [22]. In addition, oxygen recombination also occurs in the oxygen plasma to form molecular oxygen. This recombination produces $h\nu$. It releases enough energy to break any kind of covalent bond of the materials.

For the polymers, under the same conditions the degradation rate increases when replacing one of the methylene groups by a function which in fact weakens the chain (Table 2), allowing degradation to be initiated on these functions. This increase of the degradation rate is larger for the amide function than for the ester one. According to the bond energies of the ester (CO—O) and of the alkane (C—C), 393 and 343 kJ/mol respectively [23], the probability of breaking should be about the same but, in the case of the ester, breaking leads to radicals which are more stable because of their stabilization by resonance. Even with the energy value of 414 kJ/mol [24], the amide bond (CO—NH) seems to be most sensitive to RF plasma treatment.

Because of the small number of functions in the model molecules, a different way of preparation (evaporation) was needed to observe differences between the degradation rates: they are in the same order as for the polymers.

Influence of the Power. The influence of the power on the degradation was then followed. The degradation rates were determined for different powers ranging from 0.008 to 0.038 W/cm³.

The degradation rate increases linearly with power (W). It can be expressed by the equation (1):

TABLE 2. Degradation Rates ($\mu\text{g}/\text{cm}^2 \cdot \text{min}^{-1}$). Model Surfaces Prepared by Evaporation

| R_D | N6 | PC | N12 | PE | OAD | OOD | C36 |
|----------------|------|------|------|-----|------|------|------|
| O ₂ | 17.3 | 16.4 | 10.5 | 10 | 34.4 | 29.7 | 25.9 |
| Ar | 3.2 | 2.7 | 1.5 | 1.3 | 2.2 | 1.9 | 1.7 |

$$R_D = a_D W + b_D \quad (1)$$

For the model molecules as for the polymers, a_D varies in the following manner: $a_D(\text{CH}_2) < a_D(\text{COO}) < a_D(\text{CONH})$. The differences between the degradation rates (differences due to the functions) increase with the power. All the b_D values are positive. There is thus an enhancement of the degradation at small powers.

Influence of the Temperature. The influence of the temperature on the degradation was studied for the following conditions: 0.031 W/cm³, 0.3 mbar, 40 sccm, and 5 minutes of treatment. In this case we studied only the amide and the hexatriacontane. The temperature was maintained by the circulation of hot water controlled with a thermostat.

The modification of the degradation rate is roughly the same for both samples: a plateau at low temperatures, a noticeable increase with temperature, followed by another plateau near the melting temperature (Figs. 1 and 2).

A transition is observed by DSC (differential scanning calorimetry) for both the amide and the hexatriacontane before the melting temperature. These transitions are confirmed by observation under the polarizing microscope and show an orientation change of the crystals. Since we have seen that there is a difference in the degradation rates due to sample preparation (evaporation or spreading with a Conway bar), modification of the degradation rates could be due to the transition of crystal conformation. The temperature of the sample heated by plasma is certainly higher than the one obtained with hot water circulation, and this can explain the shift in temperature between the transition observed by DSC and the change of degradation rate observed by gravimetry. These results show the importance of crystalline conformation during treatment in a plasma discharge.

Mass Spectrometry

In order to better understand the degradation mechanisms the evolution of the degradation products with the time of treatment was followed by mass spectroscopy.

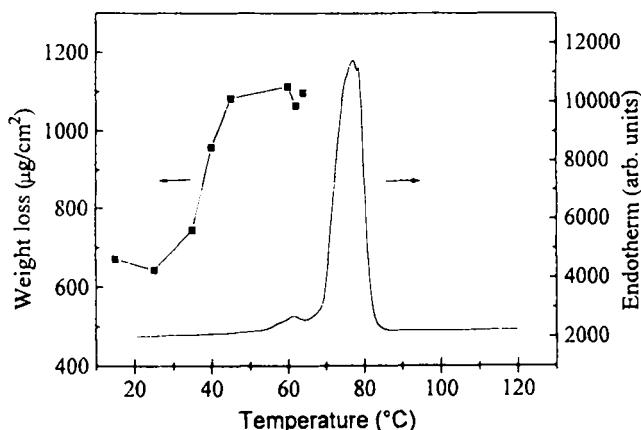


FIG. 1. Influence of the temperature on the C36 degradation: (■) weight loss in mg/cm²; (—) DSC.

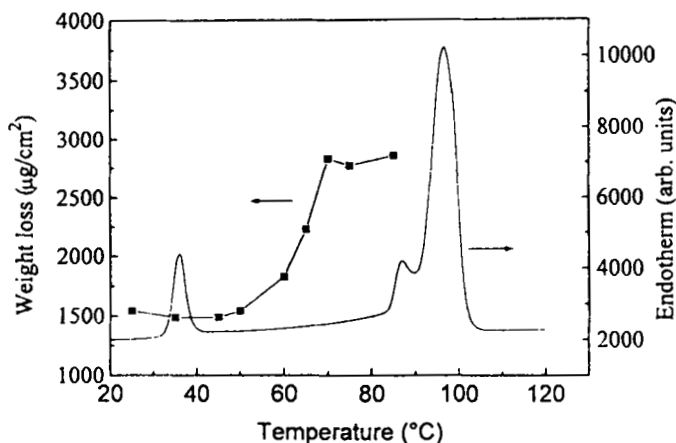


FIG. 2. Influence of the temperature on the amide degradation: (■) weight loss in $\mu\text{g}/\text{cm}^2$; (—) DSC.

Oxygen Plasma. The main degradation products observed with an oxygen plasma are CO_2 , CO , H_2O , and H_2 . Their evolution versus the time of treatment are shown in Figs. 3 and 4 for nylon 6 and OAD.

The mass intensities of these products evolve slightly to a plateau after 2 minutes. Typically there is a fast increase of the mass ratio intensities for CO_2 and CO , and a slower increase for H_2O and H_2 .

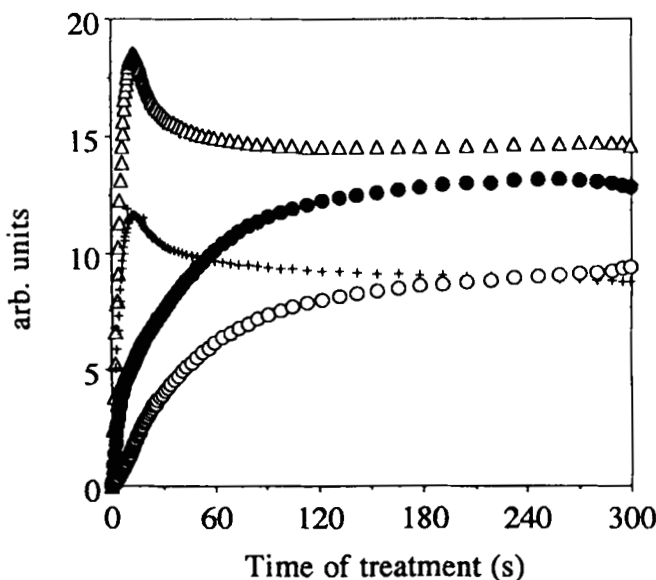


FIG. 3. Concentration of the species issued from the degradation of OAD versus time of treatment in an oxygen plasma: (Δ) CO ; (+) CO_2 ; (●) H_2 ; (○) H_2O .

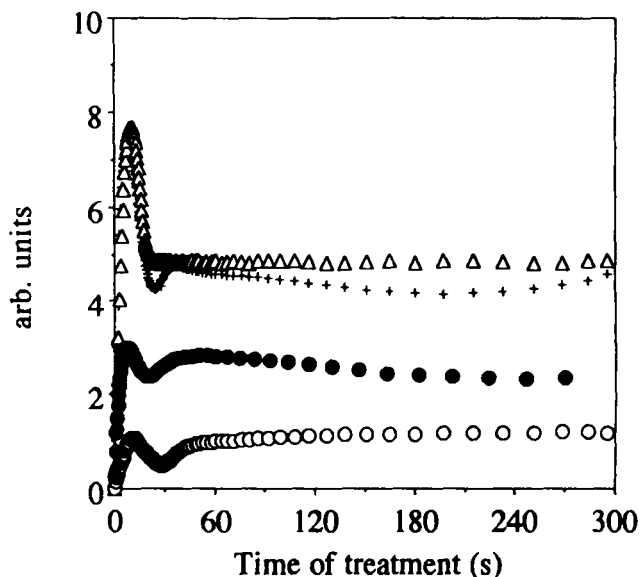


FIG. 4. Concentration of the species issued from the degradation of nylon 6 versus time of treatment in an oxygen plasma: (Δ) CO; (+) CO_2 ; (\bullet) H_2 ; (\circ) H_2O .

Figures 5 and 6 represent the evolutions of mass intensities of CO for the different compounds divided by the degradation rate (R_D). For both the polymers and the model molecules, the main observations are as follows.

For the three polymers and for the three model molecules, we obtain for CO a plateau at the same concentration (within the error bars). After 2 minutes of treatment the quantity of CO ejected from the surface of each material is thus proportional to their respective R_D s. The same observations were done for CO_2 (not shown).

When we divide the concentration by the degradation rate, we suppress the differences in the degradation rates due to the differences in chemical composition of the materials. Since the plateaus reach the same value, the degradation mechanisms, after the initiation steps, are identical for each materials.

The enhancement in the formation of CO (or CO_2) in the first seconds observed for the ester and amide is not seen for the compounds without functions (C36 and polyethylene). This enhancement is much smaller for model molecules than for polymers. There are indeed more functions in polycaprolactone and nylon 6 than on the corresponding model molecules (1 function for 5 methylene groups against 1 function for 35 for the model molecules).

The functions are thus responsible for this enhancement since 1) it does not happen for polyethylene and C36, which are functionless, and 2) it is larger for polymers where the number of functions is higher.

We also followed the mass intensities versus the time of treatment with different powers. The lower the power is, the largest is the enhancement observed in the first seconds of treatment. At the highest power range (0.038 W/cm^3) there is no more enhancement.

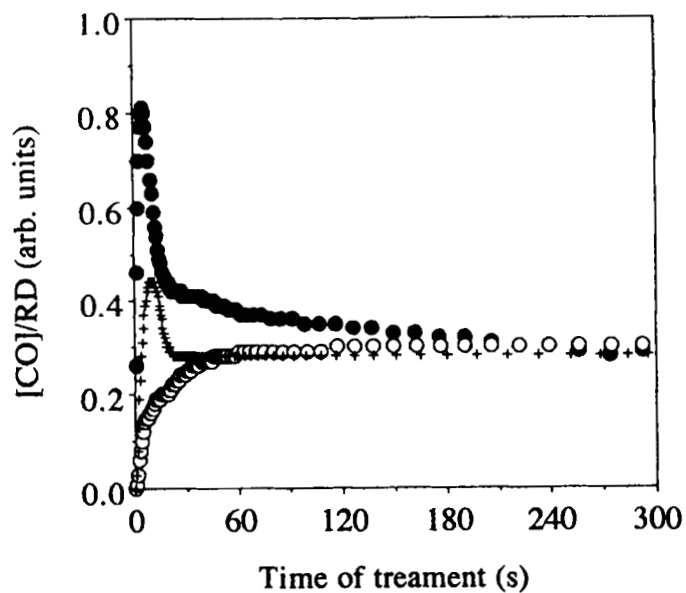


FIG. 5. CO concentration, determined by mass spectrometry, divided by the degradation rate versus time: (+) N6; (●) PC; (○) PE.

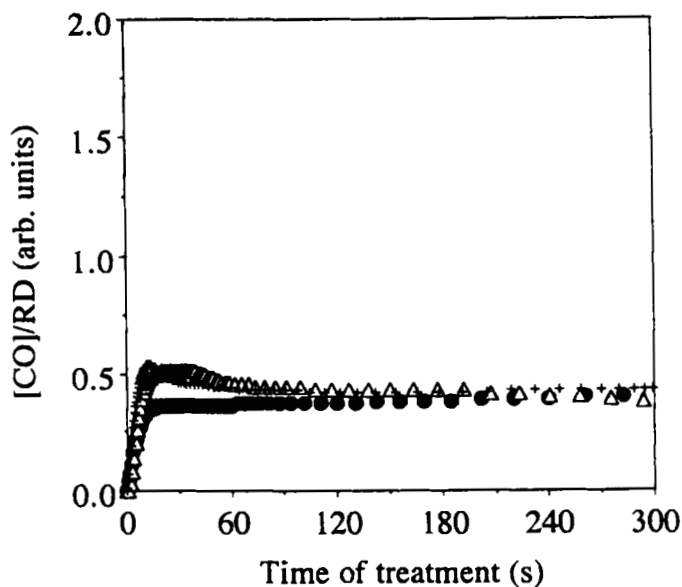


FIG. 6. CO concentration, determined by mass spectrometry, divided by the degradation rate versus time: (●) C36; (+) OAD, (△) OOD.

Two kinds of bonding can be considered: the bonds on the chains and the functional bonds, which are weaker. During the first seconds it is the latter ones which are broken faster. At high powers this difference is no longer possible. When the power increases, the energy of the species (ions, electrons, . . .) which reaches the surface increases too, and then their selectivity decreases. Furthermore, their number increases, enhancing the probability for two atomic oxygens to recombine at the surface.

Argon Plasma. In the case of argon the main degradation products are H_2 and CO (Figs. 7 and 8). We can make the same remarks as for the oxygen plasma, i.e., 1) enhancement in the first seconds except for polyethylene and C36, and 2) $[CO]_{eq}$ proportional to the degradation rate.

Optical Emission Spectroscopy

The emission spectrophotometer allows us to follow the presence of excited species in the vapor phase. The main species detected are CO_2 , CO, CH, and H_α . For all these species the maxima are reached in a very short time (less than 0.1 second). The excited CO and CO_2 concentrations are then constant during the time of treatment, contrary to the concentrations measured by mass spectrometry, but in the latter case we measured both the excited and unexcited molecules.

Figures 9 and 10 show the variation of the intensity vs power. The intensities increase linearly with power for CO_2 and CO and exponentially for CH and H. When the power is higher, an increase of the atomic oxygen emission (777.2 and 884.6 nm) and of the argon emission (750.4 nm) is observed [15]. This results from the increase in density and energy of the electrons. It is thus not surprising to also observe an increase with power of the emission of the species which come from the degradations.

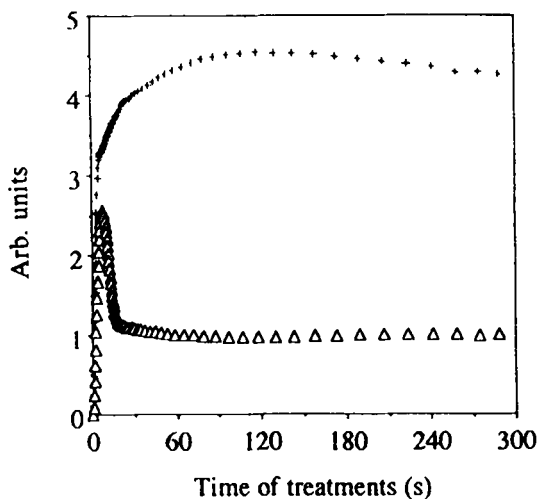


FIG. 7. Concentration of the species issued from the degradation of OAD versus time of treatment in an argon plasma: (+) H_2 ; (Δ) CO.

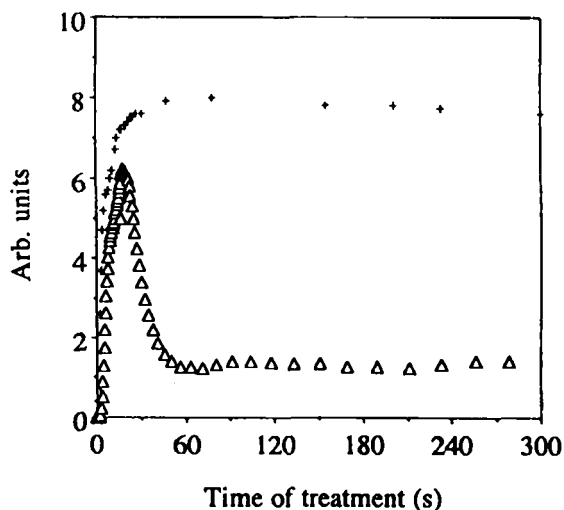


FIG. 8. Concentration of the species issued from the degradation of nylon 6 versus time of treatment in an argon plasma: (+) H₂; (Δ) CO.

Functionalization

XPS

The functionalization (or oxidation) rate is the result of the competition between the degradation and the functionalization itself. Indeed, the degradation affects not only the intrinsic functions but also the newly created functions.

In order to study the functionalization at the surfaces, we followed the O/C and N/C ratios obtained by XPS versus the time of treatment. They are obtained from area measurements of the C_{1s}, N_{1s}, and O_{1s} photopeak areas using relative sensitivity factors. The details of the calculation are given in Ref. 25.

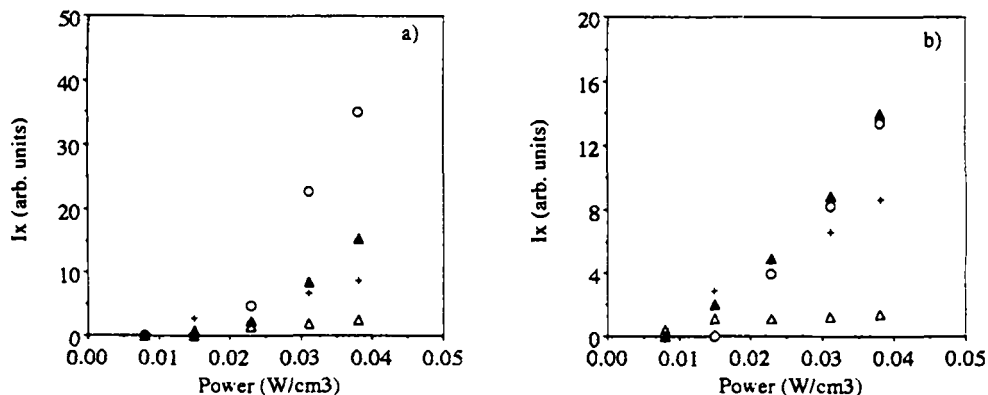


FIG. 9. Emission intensities of the species issued from degradation versus power in an oxygen plasma: (a) OAD; (b) N6: (○) CH; (▲) H₂; (+) CO; (Δ) CO₂.

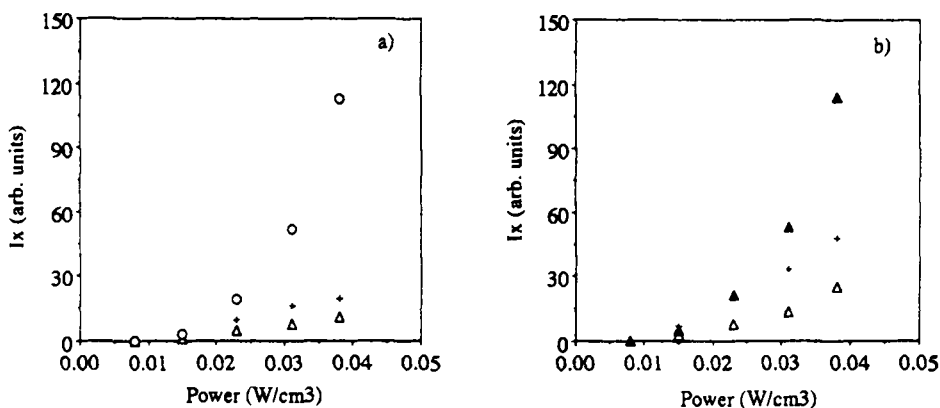


FIG. 10. Emission intensities of the species issued from degradation versus power in an oxygen plasma: (a) N6; (b) OAD: (○) CH; (▲) H_2O ; (+) CO; (△) CO_2 .

In our study the samples were treated by plasma, placed in high vacuum overnight, and analyzed the next day.

Before treatment, the oxygen/carbon ratios are very close to the theoretical values. The oxygen concentration at the surfaces seems to be the same as in the bulk. With time of treatment, the trend in the evolution of the O/C ratio is similar for each molecule. In argon plasma, the ratio increases during the first 20 seconds and then becomes constant (Fig. 11). The maximum is more rapidly reached (5 seconds) for treatment in an oxygen plasma. After the maximum, the degradation counterbalances the functionalization and the O/C ratio stays constant. An increase of the N/C ratio for the amide and for the nylons is also observed but it is smaller. One of the reasons for this increase of the number of nitrogen atoms can be the presence of a small contamination in the reactor (in addition to a selective loss of carbon atoms by degradation).

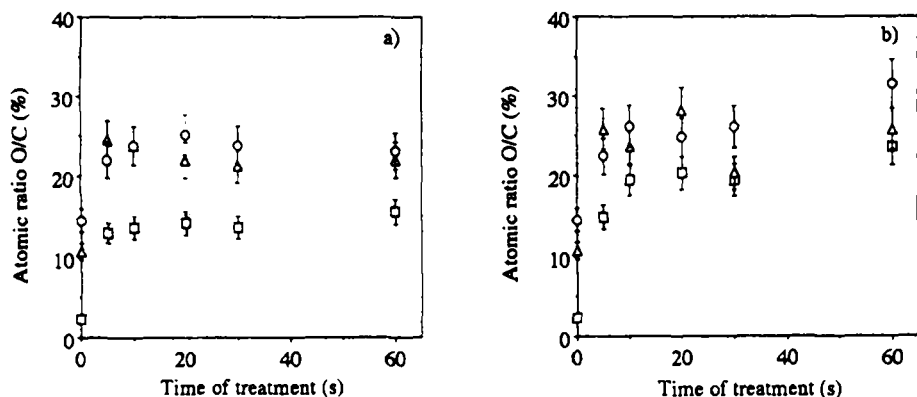


FIG. 11. Evolution of the O/C ratio versus time of treatment: (a) in an oxygen plasma; (b) in an argon plasma: (○) N6; (△) N12; (□) OAD.

The functionalization is more important for materials without oxygen in their initial composition.

The increases of the O/C and N/C ratios are more important with an argon plasma than with an oxygen one. This difference is due to post-plasma reactions, i.e., incorporation of oxygen at the surface by free radicals when the sample is brought back to an atmospheric environment [18, 20]. The oxygenated functions created in this way will not be subject to degradation. Furthermore, degradation is more important for treatment in an oxygen plasma.

Argon Plasma. In Table 3 we have collected the O/C ratio values for untreated samples and for treated samples (the O/C values included are those observed after O/C reached a plateau).

For the Ar plasma the main result is that the model molecules have a larger O/C increase [$d(O/C) = O/C_{\text{final}} - O/C_{\text{initial}}$] than their corresponding polymers because of the length of their CH₂ chains. Functionalization takes place preferentially on the CH₂ chain: $d(O/C)$: OAD > N12 > N6; OOD > PC (this last difference in behavior is emphasized by the loss of oxygen atoms from the ester functions). Since polyethylene and C36 lack functions, their $d(O/C)$ values are nearly the same.

Oxygen Plasma. The weak increase of O/C for polycaprolactone and OOD can be explained by the loss of oxygen atoms from the ester function during degradation, which compensates for the gain of oxygen atoms from the functionalization (this phenomenon is also visible for argon plasma but to a lesser extent).

The differences between the $d(O/C)$ of polyethylene and C36 are due to the desorption of short fragment chains into the gas phase. [An equivalent $d(O/C)$ is expected.] In the same way, this desorption also explains the difference in behavior with the argon plasma: $d(O/C)$: N12 > OAD; PC > OOD.

The N/O ratios decrease for the nylons and the amide. It is very important for the amide, less important for nylon 12, and even less important for nylon 6. These differences in behavior are emphasized for argon treatment: the functionalization of the chains on the unfunctional bonds is responsible of this since the amide has more CH₂ groups than nylon 12 and nylon 6 (in that order), and the observed N/O ratio decreases are in the same order.

Contact Angle Titration

This study of the functionalization of the surface was completed with a study of contact angles. Less than 30 minutes after the plasma treatment, small drops

TABLE 3. Oxygen/Carbon Atomic Ratios Before and After Plasma Treatment

| Atomic ratio O/C, % | C36 | OOD | OAD | PE | PC | N6 | N12 |
|---------------------|------|------|------|------|------|------|------|
| Before treatment | 0 | 4.9 | 2.3 | 0.4 | 26.0 | 14.5 | 10.7 |
| Theoretical values | 0 | 5.5 | 2.8 | 0 | 33.3 | 16.7 | 8.3 |
| Ar | 14.0 | 18.0 | 20.3 | 16.0 | 30.0 | 25.7 | 27.4 |
| O ₂ | 10.6 | 9.2 | 13.7 | 16.0 | 32.8 | 24.0 | 24.3 |

(<0.2 μL) of a liquid were placed on the modified surface. The surface energies were calculated from Wu's equation [26].

The contact angles (surface energies) are modified within the first seconds of treatment. Then, as the O/C and N/C ratios are measured by XPS, they become constant after 20 seconds of treatment. Plasma treatment has more influence on the polar component of the surface energy than on the dispersive one [5].

The order of augmentation of the polar component for the different surfaces studied is roughly the same as the order of O/C ratio increase as determined by XPS. Small differences could be due to the depth of analysis, which differs for the two methods.

Nearly all the surfaces have similar surface energies after treatment. We believe that there is a "common state of the surfaces" due to the very large degradation in glow discharge.

In order to determine more precisely the existence of new functions at the surface of the samples and to identify these functions, we measured the contact angles of a series of buffered aqueous solutions with pH values ranging from 2 to 11 before and after treatment. For a molecule without functions, the contact angle of all the buffered aqueous solutions must be equivalent. If there are some functions on the surface which can participate in an acid/base reaction in the 2–11 pH zone, the contact angles will be different and we can trace a contact angle titration curve. This technique was used recently [27, 28]. The information obtained from this technique is mainly qualitative: the pH value at which interfacial ionization take place ($\text{p}K_{1/2}$) must not be confounded with $\text{p}K_a$. The difference of value between $\text{p}K_{1/2}$ and $\text{p}K_a$ is usually around 2 pH units.

Our results for polyethylene are presented in Fig. 12. Before treatment, the values of the contact angles do not vary with the pH of the buffered solutions. After treatment, the value of the contact angles is lower and depends on the pH, which shows the existence of acid or basic functions at the surfaces of the treated samples. At low pH, the contact angle remains constant and the functions are not ionized (at $\text{pH} < 5$, all the carboxylic acid functions are in the COOH form). At high pH, the value of the contact angles reaches a new plateau which corresponds to a complete ionization of the functions (at $\text{pH} > 9$, the functions are in the COO^- form). There is no noticeable differences between the two treatments (O_2 and Ar). This confirms the XPS results (O/C equivalent) and the surface energy results.

In the case of polycaprolactone (Fig. 13), the values of the contact angles vary before treatment because of the presence of the ester function. The differences between the contact angles before and after treatment are equivalent for $\text{pH} = 2$ and $\text{pH} = 11$, which confirms the weak incorporation of functions as already observed in XPS.

Unlike polyethylene, the differences between the values of the contact angles for the two plateau are larger in argon plasma. The number of acid functions which can be ionized between $\text{pH} = 2$ and $\text{pH} = 11$ is then larger after argon plasma treatment than after oxygen plasma treatment. Furthermore, the equivalent point is higher after oxygen plasma treatment. The surfaces of the molecules are thus less polar and/or possess less ionizable functions after oxygen plasma treatment since a shift in the equivalence point is observed when the interphase is less polar, and then the ionization is more difficult: the location of the equivalence point yields information on the polarity of the surface.

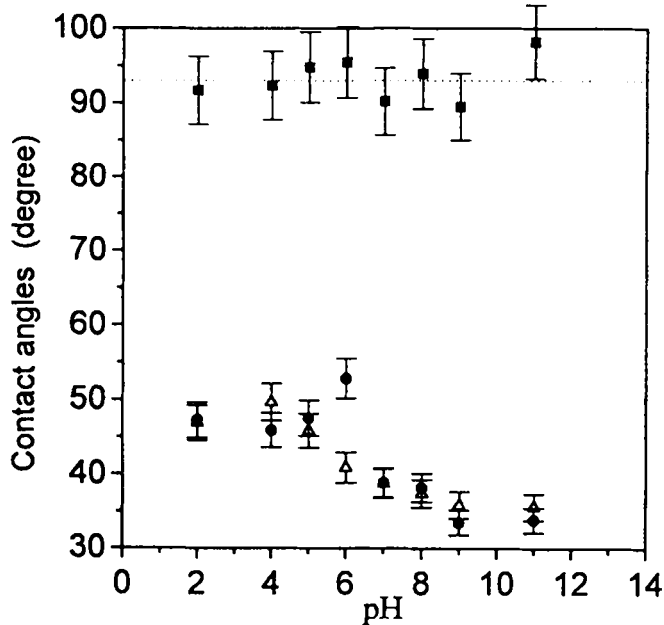


FIG. 12. Contact angles versus pH for polyethylene: (■) before treatment; (●) Ar; (△) O₂.

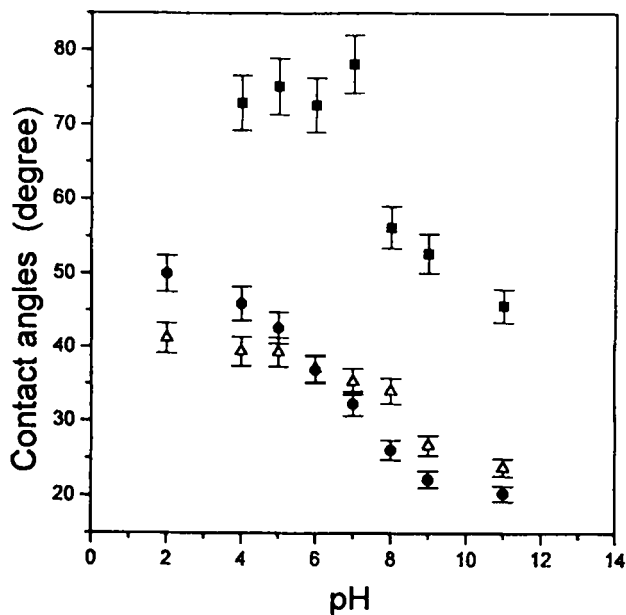


FIG. 13. Contact angles versus pH for polycaprolactone: (■) before treatment; (●) Ar; (△) O₂.

The creation of acid functions is very small in the case of polyethylene in argon plasma. Contrary to polycaprolactone, polyethylene does not have carbonyl radicals which can lead to the formation of acid functions. During the return of the sample to the atmosphere, many reactions take place. A path to the formation of such functions is presented in Scheme 1 [29].

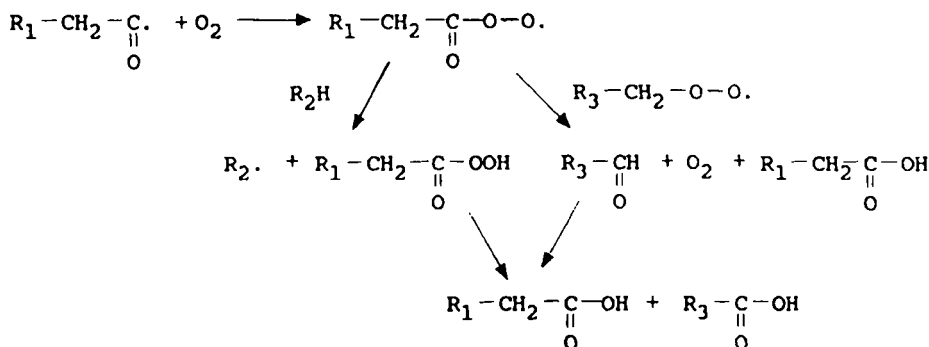
CONCLUSION

The main information we obtained is as follows. The presence of functions has an influence on the degradation which starts on the functions. The amide function is more sensitive to degradation than is the ester one. Mass spectroscopy analysis tells us that after the initiation step, the formation mechanisms of CO and CO₂ are the same for all surfaces and that there is an enhancement of the degradation in the first seconds of treatment due to breaking of the functional bonds. O₂ plasma is more powerful in the degradation process than is argon plasma. The experimental results show that degradation takes place on the functions (amide or ester) whereas the functionalization occurs on the methylenic groups (CH₂). The reaction mechanisms which take place at the surface of the polymer are numerous. For nylon 6 and OAD we can have, among others, the mechanisms presented in Scheme 2.

The behavior of the model molecules explains the mechanisms of one of polymers, and the conclusions related to the model molecules can be extended to all of the polymers.

We can see from the evolution of both the O/C ratio and the surface energy that there is competition between functionalization and degradation, but the RF glow discharge is too destructive. The functionalization is very quick (5 to 20 seconds) and never reaches O/C values larger than 20-30%. In the same way, these conditions lead to equivalent surface energies for all the samples, whatever their composition is.

Furthermore, the existence of post-plasma reactions hinders comprehension of the reaction mechanisms. We have shown the influence of the chemical composi-



SCHEME 1.

ment from reacting with the oxygen of air. A more powerful XPS analysis will also allow a more precise identification of the nature of the functions created at the surface. Furthermore, modeling of the medium in a glow discharge is possible and will allow more precise determination of the part of the different species in the plasma in modification mechanisms of the polymer surfaces.

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