

## Ammonia RF–Plasma on PTFE Surfaces: Chemical Characterization of the Species Created on the Surface by Vapor–Phase Chemical Derivatization

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A cylindrically configured plasma treatment system for Radio Frequency Glow discharges fed with ammonia was used to modify the internal surface of ePTFE arterial prostheses to improve their biocompatibility. For a better understanding of the effects of this type of treatment on the surface, RF-plasmas were also performed on PTFE films. The surface chemical composition was then characterized by XPS. The initial analyses showed that 15% of the surface atoms were replaced by nitrogen (N/C ratio of 0.3), whereas the F/C ratio decreased from 2 to 0.7–0.5 which indicates that the treated surfaces presented different chemical species, such as amine, imine, amide, acid groups, and insaturations. As XPS analyses could not lead directly to the nature of the N-species grafted on the surface (the chemical shifts being not significantly different), chemical derivatization was thus performed. Vapor phase chemical derivatization was carried out on model polymers to evaluate the reactivity and the selectivity of each reagent toward each of the expected functional groups. The results indicate that benzaldehyde derivatives were good derivatizing reagents for amine groups, whereas bromine was the reagent of choice to quantify the insaturations. Using these methods, the amine and alkene concentrations on the surface were found to increase according to plasma treatment time rising from their initial value of 3% for a 50 s plasma treatment to 6% for a 250 s plasma treatment. AFM studies on oriented Teflon films also demonstrated that the occurrence of chain breaking increased with plasma treatment time. It therefore appears that determining the treatment parameters should require the best compromise between several effects such as nitrogen grafting, amine and alkene formation, and chain breaking.

### Introduction

Low-pressure plasma surface treatments are promising techniques in the design and development of new materials because surface modifications can be achieved without altering the material bulk properties.<sup>1</sup> In this context, the surface modification of ePTFE vascular prostheses by plasma treatment is an interesting alternative to improve their hemocompatibility. A cylindrically configured plasma treatment system for Radio Frequency Glow Discharges fed with ammonia was therefore developed in order to modify the internal surface of ePTFE arterial prostheses by introducing reactive functional groups on the surface.<sup>2,3</sup> The amine groups expected to form are known to react fairly easily with other chemical functionalities, such as aldehyde<sup>4</sup> or succinimide derivatives,<sup>5,6</sup> therefore allowing covalent attachment.

Of particular interest was the nature of the chemical species created during an ammonia plasma treatment of PTFE surfaces. Indeed, it has been reported that amine groups are not the only species created during an ammonia plasma treatment, as was shown by the detection of oxygen by XPS<sup>7</sup> which therefore leads

to conclude that oxygen-containing species are readily formed on the freshly treated surface upon transfer from the plasma reactor to the XPS analysis chamber. The literature reports many conclusions regarding the surface characterization of ammonia RF-plasma-treated fluorinated polymers. For example, FTIR-ATR spectroscopy data recorded on ammonia RF-plasma-treated PTFE confirmed the presence of both amine and amide moieties on the polymer surface.<sup>8</sup> However, these conclusions should be questioned when considering the depth of analysis probed by FTIR-ATR, which is 1000-fold that of the surface modification thickness ( $\sim 1\mu\text{m}$  versus  $\approx 10\text{ \AA}$ ).<sup>9</sup>

More sensitive surface analysis techniques have therefore been used to obtain more precise information regarding the plasma-treated polymer surface chemistry. Among these techniques, XPS has certainly been one of the most successful in measuring the surface concentration of individual atoms or atomic ratios, such as N/C, F/C, and O/C, which are sensitive to surface nitrogen grafting, defluorination, and oxidation, respectively.<sup>7,10</sup> However, monitoring these parameters may have no bearing as their true significance is not known; certainly, at least, not in terms of N/C ratio. In addition, visual examination of the C1s High Resolution XPS (HR-XPS) spectra has clearly revealed the presence of various types of chemical moieties.<sup>11,12</sup> Unfortunately, the binding energy variation observed in the high-resolution C1s, F1s, or N1s spectra for the various chemical

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species found on the surface upon ammonia plasma treatment was too small to allow an accurate spectral curve fitting.<sup>3,7,13</sup>

Another method which may be used to more precisely identify the surface composition is the surface derivatization of the plasma-treated polymer surface.<sup>14,15</sup> Basically, it consists of inducing a chemical reaction between surface moieties created upon plasma treatment and a chemical reagent bearing at least one atom that is neither a part of the polymer structure nor the gas used to perform the plasma.<sup>1,13,14,16–31</sup> Following surface derivatization, the XPS signal from this particular atom can be used to quantify the surface concentration of the derivatized surface moieties. Surface derivatization can be performed in either liquid or vapor phases. However, derivatization performed in the liquid phase may produce questionable results because of possible interactions between the solvent and the surface chemical species, therefore impeding the expected surface reaction. Moreover, it has been demonstrated that the surface composition of an ammonia plasma-treated PTFE changes during storage in water.<sup>7,10</sup>

Only a few studies have been performed to characterize chemical species other than the amino groups on ammonia plasma-treated polymer surfaces, despite the fact that it is now clearly established that this surface modification technique induces several chemical phenomena.<sup>7,12,32</sup> In this context, it is worth mentioning the study by Pringle et al.,<sup>12</sup> who demonstrated the significant importance of the experimental conditions (pressure, input power, and duration) used to perform the plasma on the final surface chemistry. These authors basically demonstrated that PTFE defluorination was higher under conditions that yielded low ion energies or high concentrations of  $\text{NH}^{3+}$  ions and that these ions were much more reactive with PTFE surfaces than were  $\text{NH}^{4+}$  ions.

It therefore appears that plasma parameters (power, pressure, duration) should be carefully selected in order to reach an ideal compromise between nitrogen grafting, amine formation, defluorination, chain scission, etc. To gain further insight into the actual events occurring on the PTFE surface upon plasma treatment, the present study was conducted to characterize the surface in terms of the quantification of the species created on the surface by minimizing the number of resulting conclusions through indirect evidence. Amine and alkene groups were therefore characterized and quantified by derivatization reaction in the vapor-phase. An initial series of derivatization reactions with model surfaces enable us to verify the level of reactivity and selectivity of each derivatizing reagent toward each expected functional group. Thereafter, these reagents were used with plasma-treated PTFE surfaces to quantify the surface species created and elucidate the variation in their relative concentrations as a function of the duration of the plasma treatment. In addition, Atomic Force Microscopy (AFM) was used to characterize of the polymer chain-breaking event, which is considered to be a major impediment when using Radio-Frequency plasma treatments for surface modification. The combined results shed more light on the sequence of chemical events occurring on PTFE surfaces upon ammonia RF-plasma treatment and emphasize the importance of controlling of the plasma experimental parameters to achieve the desired polymer surface chemistry.

## Materials and Methods

**Standard Polymer Surfaces for Chemical Derivatization.** Polyacrylonitrile, polyacrylamide, poly(acrylic acid), and trans-polyisoprene were obtained (Aldrich, Milwaukee, WI) and used without further purification as standard surfaces for nitriles, amides, carboxylic acids, and alkenes, respectively. The standard

polymer films were prepared by spin coating on circular coverglasses (polyacrylamide-1% (w/w) in water; poly(acrylic acid)-2% (w/v) in methanol; polyacrylonitrile-2% (w/w) in DMF; polyisoprene *trans*-1% (w/v) in toluene). For amine model surfaces, 4,4'-oxydianiline (ODA — 4-aminophenyl ether) was used and prepared as pellets. The surface composition of these standard surfaces was measured by XPS analysis and the experimental atomic concentrations were found to match the values expected for each type of film considered. Pieces of PTFE films were cut (3 cm × 3 cm) from a 250  $\mu\text{m}$ -thick commercial film (Goodfellow, Berwyn, PA), washed twice with acetone as well as twice with methanol, then dried under vacuum overnight.

**Derivatization Reactions.** The vapor-phase derivatization reagents used were chlorobenzaldehyde, bromoacetyl bromide, bromosalicylaldehyde, and bromine (Aldrich, Milwaukee, WI). The derivatization reactions were performed in a sealed glass tube in which a 1 cm-thick bed of soda-lime glass beads was used to separate the reagent and the reactive surface. The reactions proceeded at room temperature for bromoacetyl bromide and bromine and at 40 °C for the 2 other reagents during chosen periods of time (30 min, 1 h, 2 h, 4 h, and 6 h). The surfaces were then outgassed under vacuum and analyzed by XPS. An identical protocol was used for plasma-treated PTFE films.

**Assessment of the Polymer Chain Scission.** Oriented PTFE films were obtained using a previously described method.<sup>33–35</sup> This technique consisted in rubbing a PTFE bar along the surface of a clean glass slide, both maintained à 300 °C which was slightly below the polymer's melting temperature. This allowed us to obtain a highly oriented polymer surface, with the PTFE chains oriented in the rubbing direction, well suited to visualize the polymer surface scission upon plasma treatment through atomic force microscopy (see below). The distance between two scissions (appearing as small pits in the acquired images) was measured with the analysis software supplied with the instrument and distributed in 50 nm-wide bins in column graphs. The resulting distributions displayed an evident Poisson-like shape. In fact, because a surface (and not a one dimension) phenomenon occurred, it was the distribution of the square of the distances which was fitted to a Poisson distribution. Therefore, the curves fitted to the distributions of distances were not exactly Poisson distributions, yet were closely related, and are given by the function

$$P_P(bd, b^2\mu_s) = \frac{a(b^2\mu_s)^{b^2d^2} e^{-b^2\mu_s}}{(bd)^2!}$$

where  $d$  is the value, in nm, of a distance bin, and  $\mu_s$  is the mean of the square of the distances. The constant  $a$  allows for variations in the total number of measurements used, which changes nothing to the distribution as far as the sampling is large enough. The constant  $b$  is a scale factor.

To use a continuous function, as opposed to the standard discrete one, the gamma function was selected to compute the factorials as  $\Gamma(x + 1) = x!$ <sup>36</sup>

**Plasma Treatment.** The plasma reactor and the treatment methodology are described elsewhere.<sup>2,3</sup> High purity ammonia gas was used for each plasma treatment in order to bind the amine groups on the PTFE film surfaces. Most of the treatments were performed in a cylindrical reactor at 20 W, 13.56 MHz, and 300 mTorr for 50, 100, and 250s.<sup>2,3</sup> This procedure was performed on flat PTFE sheets as well as on PTFE oriented films. Each experiment was reproduced in triplicate.

**Characterization.** XPS spectra were recorded on the flat PTFE films both before and after plasma treatment, as well as

**TABLE 1: Reactions of the Standard Polymer Surfaces with the Various Reagents—The Values Indicated Were Obtained by XPS Analyses**

functional group Model surface	chemical reagent			
	surface atomic concentration of the respective labeling atoms			
	Chlorobenzaldehyde → %Cl	Bromosalicylaldehyde → %Br	Bromoacetyl bromide → %Br	Bromine → %Br
AMINE → Oxydianiline (ODA)	6.7-7	6-6.3	8.1-8.7	13.6-15
AMIDE → polyacrylamide	0.1-0.2	0.6	2-2.4	2.5-3
ACID → poly(acrylic acid)	0.2	0.2	2-2.4	0.7-0.9
ALKENE → polyisoprene trans	0.1-0.2	0.2	15	27-31
NITRILE → polyacrylonitrile	0.6	0.2-0.3	0.6-0.9	1.8-3.4
TEFLON → PTFE film	0-0.1	0	0	0

on all of the surface-derivatized samples, using a PHI 5600-ci spectrometer (Physical Electronics, Eden Prairie, MN). A monochromatic aluminum X-ray source (200 W) was used to record the survey spectra, whereas high-resolution spectra were acquired with a monochromatic magnesium X-ray source (100 W). The detection was performed at 45° with respect to the normal of the surface. In addition, the oriented PTFE films were imaged both before and after plasma treatment using a Dimension atomic force microscope (Digital Instruments, Santa Barbara, CA), with silicon cantilever used in the tapping mode.

## Results and Discussion

**Selectivity of the Derivatization Reagents.** A set of standard surfaces, each with a single type of chemical functionality, were used to establish the protocol for the specific identification of the chemical functionalities potentially present on ammonia plasma-treated PTFE surfaces,<sup>2,3,10,37–39</sup> as depicted in Table 1. Moreover, a group of reagents (Table 1) bearing appropriate labeling atoms, were also chosen to selectively and quantitatively react with one or the other chemical moiety created on the PTFE surface upon plasma treatment. A cross-checking of the relevant literature has therefore allowed us to conclude that chlorobenzaldehyde and bromosalicylaldehyde should react fairly easily with amine moieties,<sup>1,13,16,24–26,29</sup> whereas a good reactivity is expected between bromoacetyl bromide on one side and acidic and amide functionalities on the other side.<sup>16,20,22,24,26–28,40,41</sup> Finally, the well-known halogenation reaction should occur between bromine and alkene moieties.<sup>15, 16, 40, 42, 43</sup>

Table 1 summarizes the reactions that effectively occurred between the various reagents and model surfaces investigated. This was ascertained by probing the XPS signal coming from the atoms used as markers in the various reagents. As is seen in this table, both the chlorobenzaldehyde and the bromosalicylaldehyde reacted almost exclusively with amino groups. On the other hand, bromoacetyl bromide reacted significantly with the amino, amide, acidic and alkene groups, while a less important reactivity was observed with the nitrile moieties. Finally, bromine reacted very significantly with both the ODA and the trans-polyisoprene model surfaces, while marginal reactions were observed with all of the other surfaces.

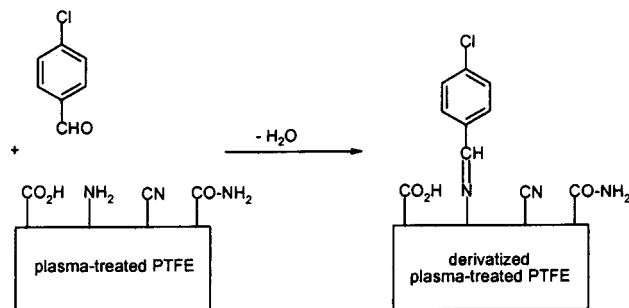
The selectivity of the various derivatization reagents toward the targeted surface moieties therefore appears to be confirmed only between the amino groups and the benzaldehyde derivatives. On one hand, bromoacetyl bromide was not specific at all, as it reacted with most of the surface chemical species investigated. This nonselectivity may possibly be explained by

the partial hydrolysis of the bromoacetyl bromide which led to the formation of HBr which may in turn have reacted with other functional groups through various reactional schemes. On the other hand, bromine gave rise to noticeable reactions with two of the model surfaces investigated, namely, trans-polyisoprene, as expected, and oxydianiline. Regarding the latter, organic chemistry has taught us that a reaction between bromine and amino groups is unlikely. For this reason, the addition of bromine on one or the other carbon atom located in the aromatic rings of ODA appears as a more probable cause of the XPS detection of bromine on the model aminated surface. This hypothesis was confirmed by an XPS study on the interaction between bromine and a polystyrene model surface, where the grafting of approximately two or three bromine atoms/aromatic ring was detected (results not shown). These XPS data therefore allow us to conclude to the specificity of this derivatization reagent toward double bonds. On the basis of the experiments described above, it is concluded that the reagents showing a more acceptable reactivity and selectivity toward the expected surface species following a plasma treatment of PTFE are benzaldehyde derivatives for the detection of amines and bromine for the detection of alkenes. Other reactions failed to satisfy either or both criteria of reactivity and selectivity.

**Level of Reactivity of the Derivatization Reagents and Quantification of the Surface Concentration of the Amino and Alkene Groups.** The quantification of amino or alkene groups proceeds via two different pathways, as XPS produces different spectroscopic information for these two chemical functionalities. On one hand, quantifying the amino groups requires knowing the total nitrogen concentration prior to the derivatization reaction. From an XPS analysis point of view, this information is obtainable through the survey scan by integrating the area under the curve of the feature assigned to nitrogen after the plasma treatment. Following the derivatization reaction with chlorobenzaldehyde (Figure 1), the chlorine surface concentration may be related to the amino groups surface concentration created after the plasma reaction using the equation

$$\% \text{ Cl} = \left( \frac{xN_0}{1 + 8xN_0} \right) * 100 \quad (1)$$

where %Cl is the experimentally determined surface concentration of chlorine after derivatization, as measured by XPS,  $x$  is the degree of conversion of the surface amino groups to imino



**Figure 1.** Derivatization reaction of a plasma-treated PTFE film with chlorobenzaldehyde.

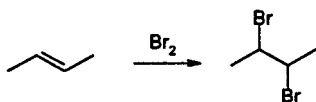
moieties upon surface derivatization (where  $x = 0$  in the case of no reaction and  $x = 1$  in the case of complete reaction), and  $N_0$  is the initial nitrogen concentration prior to derivatization. Basically, the denominator in the right term accounts for the eight added atoms coming from chlorobenzaldehyde, as well as the atoms lying underneath and probed by the XPS analysis. Equation 1 holds as long as the thickness over which the derivatization reaction takes place is greater than the XPS analysis depth.

A comparison of the values calculated using eq 1 with the experimental data confirmed that the former analyses and hypotheses were actually adequate. As shown in Figure 2, both chlorobenzaldehyde and bromosalicylaldehyde provided quantitative reactions on the ODA model surface, with almost identical reaction kinetics, which was 100% complete after 30 min.

Equation 1 leads only to the ratio of amines to nitrogen species grafted onto the surface. Therefore, the calculation of the amine concentration onto the surface should take into account the amount of nitrogen  $N_0$  grafted onto the surface following an ammonia plasma treatment, as described in the following equation

$$\% (\text{NH}_2)_{\text{on the surface}} = (\% \text{NH}_2 / N_{\text{total}}) * N_0 \quad (2)$$

On the other hand, no valuable quantitative information regarding the alkene moieties can be derived from the XPS C1s feature because of the important overlap noticed in this spectral region. Considering the stoichiometry of the halogenation reaction one



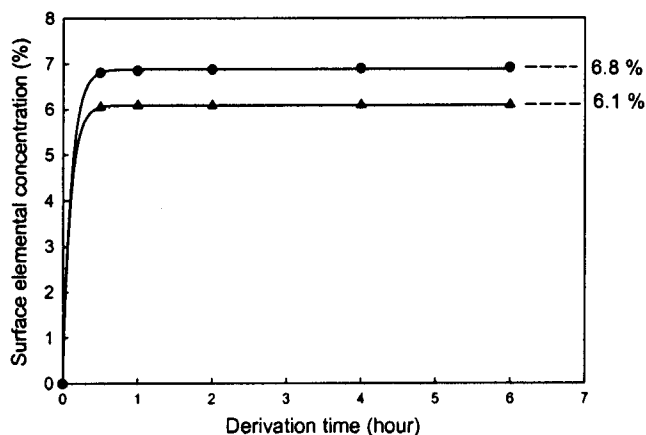
may simply calculate the fraction of double bonds on the polymer surface using the following equation

$$\% (\text{C}=\text{C})_{\text{on the surface}} = \frac{(\% \text{Br}/2)}{(\% \text{C})} \quad (3)$$

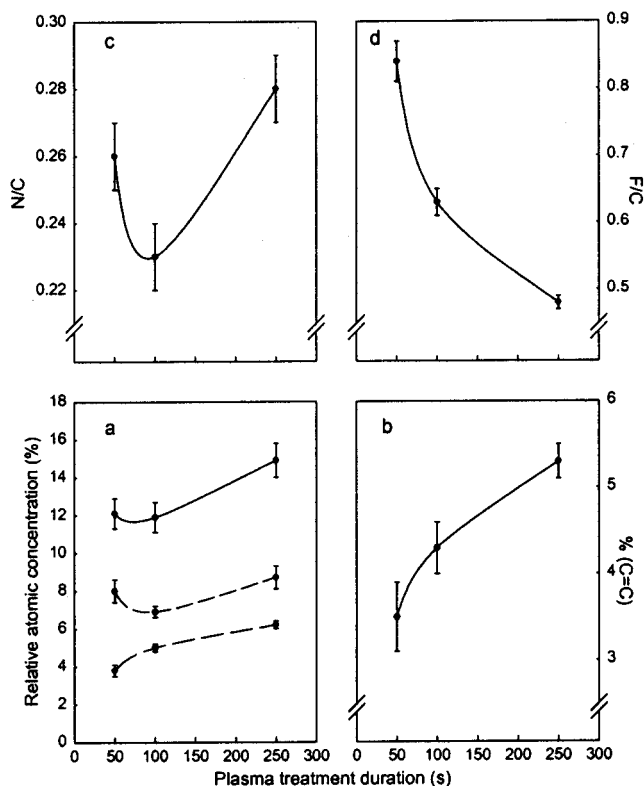
Again, the reaction between bromine and a polyisoprene trans model surface resulted in a 100% complete reaction after 30 min. This derivatization may therefore be considered as being accurate for the quantitative analysis of the concentration of alkene groups onto plasma-treated PTFE surfaces.

#### Characterization of the Plasma-Treated PTFE Films.

Contrary to what was observed for the derivatization on model surfaces, the chemical derivatization of the plasma-treated PTFE films only allowed the measurement of an underestimated value of the various chemical species concentration as the thickness of the treated layer of polymer film was approximately five times lower than was the XPS depth of analysis ( $\sim 10 \text{ \AA}$  vs  $\sim 50 \text{ \AA}$ ).<sup>44</sup>



**Figure 2.** Experimental atomic surface concentration of bromine and chlorine after different derivatization durations for the reactions between ODA and bromosalicylaldehyde (▲), or chlorobenzaldehyde (●), respectively. The surface concentration values indicated on the right-hand side of the figure are those expected for a 100% complete reaction.



**Figure 3.** Evolution of the surface concentration of nitrogen-containing species (a), of alkenes (b), N/C (c), and F/C ratios (d) as a function of the plasma duration.

Nevertheless, the data obtained enable us to confidently characterize with enough confidence the effects of the plasma treatment parameters relative to the creation of chemical functionalities on the PTFE surfaces. Indeed, the relative concentration values of the grafted species remained preserved despite the absolute underestimations.

Figure 3a displays the evolution of the nitrogen-containing species surface concentration as a function of the plasma duration. For the purpose of the study, the nitrogen surface concentration was divided into contributions comprising the one coming from amines, and those coming from all other nitrogen-containing species (essentially imines and nitriles in the oxygen-poor environment of the plasma reactor). The first striking information found relates to the important amount of total



nitrogen that had grafted on the surface after a treatment duration of only 50 s, e.g., 12.1% as detected by XPS. In addition, surface derivatization with chlorobenzaldehyde revealed that the amine formation, only 3.8%, was far from being the major phenomenon to explain this important formation of nitrogen-containing species on the PTFE surface with plasma treatment. A treatment of 100 s led to no further increase of the total nitrogen concentration (11.9%). However, a very interesting behavior was observed for this treatment duration, as the amine surface concentration slightly increased to 5%, whereas that of the other nitrogen-containing groups decreased with, as stated above, no major variation of the total nitrogen surface concentration. This observation therefore points toward a partial conversion of existing nitrogen-containing moieties to amino groups during the time interval between 50 and 100 s. Finally, a subsequent increase of the nitrogen surface concentration was noticed due to a simultaneous increase in the presence of both amino and other nitrogen-containing species: more than 6% of amines after a plasma treatment of 250 s for 14.9% of nitrogen grafted onto the surface. It is worth mentioning here that the amine surface concentrations measured for the entire set of experiments (between  $\approx 4$ –6%) fell within the nitrogen surface concentrations measured on ammonia plasma-treated PTFE surfaces after exposure to water, therefore indicating that the so-called other nitrogen-containing species were most likely imines, as these species readily hydrolyze in an aqueous environment.<sup>3</sup>

Figure 3b depicts the behavior of the alkene formation during the plasma process. From this figure, it is clear that the double bond formation kinetics on the polymer surface displays a behavior similar to that observed for the amino groups. Indeed, the percentage of double moieties with respect to any other carbon-containing species was 3.5% after 50 s, and reached a value of 5.3% after 250 s, which is to say that double bond formation occurred approximately every 30 carbon atoms for a plasma duration of 50 s, while the same phenomenon occurred every 20 carbon atoms after 250 s.

Figure 3, parts c and d, also present the behavior of two common XPS markers often used to investigate radio frequency plasma-treated fluorinated polymers with nitrogen-containing gases, namely the N/C and F/C ratios.<sup>3,7–10</sup> The former probes the nitrogen grafting onto the polymer surface, whereas the latter is, of course, sensitive to polymer defluorination. As may be seen by comparing Figure 3, parts a and c, the N/C ratio only allowed a gross estimation of the actual events occurring on the PTFE surface upon the ammonia plasma, as it failed to reveal any subtle changes for individual types of surface moieties or more restricted groups of nitrogen-containing species. Considering this singular information may therefore lead to a misinterpretation of the formation kinetics of the various nitrogen-containing species. As a matter of fact, the decoupling of the formation kinetics of amino groups, with respect to that of all other nitrogen-containing species, clearly demonstrates that the creation of the various species containing a given atom does not necessarily follow a similar trend. For example, with regard to the nitrogen surface concentration, the present study reveals a very complex behavior occurring in the formation of nitrogen-containing moieties, as described above. This observation (albeit being still incomplete because of the impossibility of monitoring the concentration of each individual nitrogen-containing species contribution) emphasizes that only sketchy information was obtainable by measuring the XPS atomic ratios.

Nevertheless, the F/C ratio definitely appeared as the better probe, at least for the double bond formation, as the surface concentration of alkenes clearly increased (3.5% to 5.3% for a

plasma treatment duration of 50 s to 250 s) with a decreasing level of fluorine (0.84 to 0.48, respectively). However, this result was not very surprising, as most of the surface reactions expected to occur in the plasma environment and for which defluorination should be observed (formation of amines, imines, nitriles, hydrogenation, chain scission, etc.), should continuously proceed, at an unknown rate, ever time. All of these reactions would therefore have led to a similar correlation toward surface defluorination, should derivatization been possible for these moieties. Thus, the alkene formation reaction should be considered as only one of the components that contribute progressively to the continuous removal of fluorine atoms from the surface with time.

As far as the formation of amino groups on the surface is sought for subsequent reaction with other molecules, all of the reactions leading to surface functionalities other than amines should be considered undesirable. Nevertheless, chain scission is undoubtedly the one occurrence which must be prevented as it may lead to surface delamination upon exposure of the material to fluids. Thus far, no surface characterization technique has allowed a quantification of this phenomenon or its occurrence as a function of time.

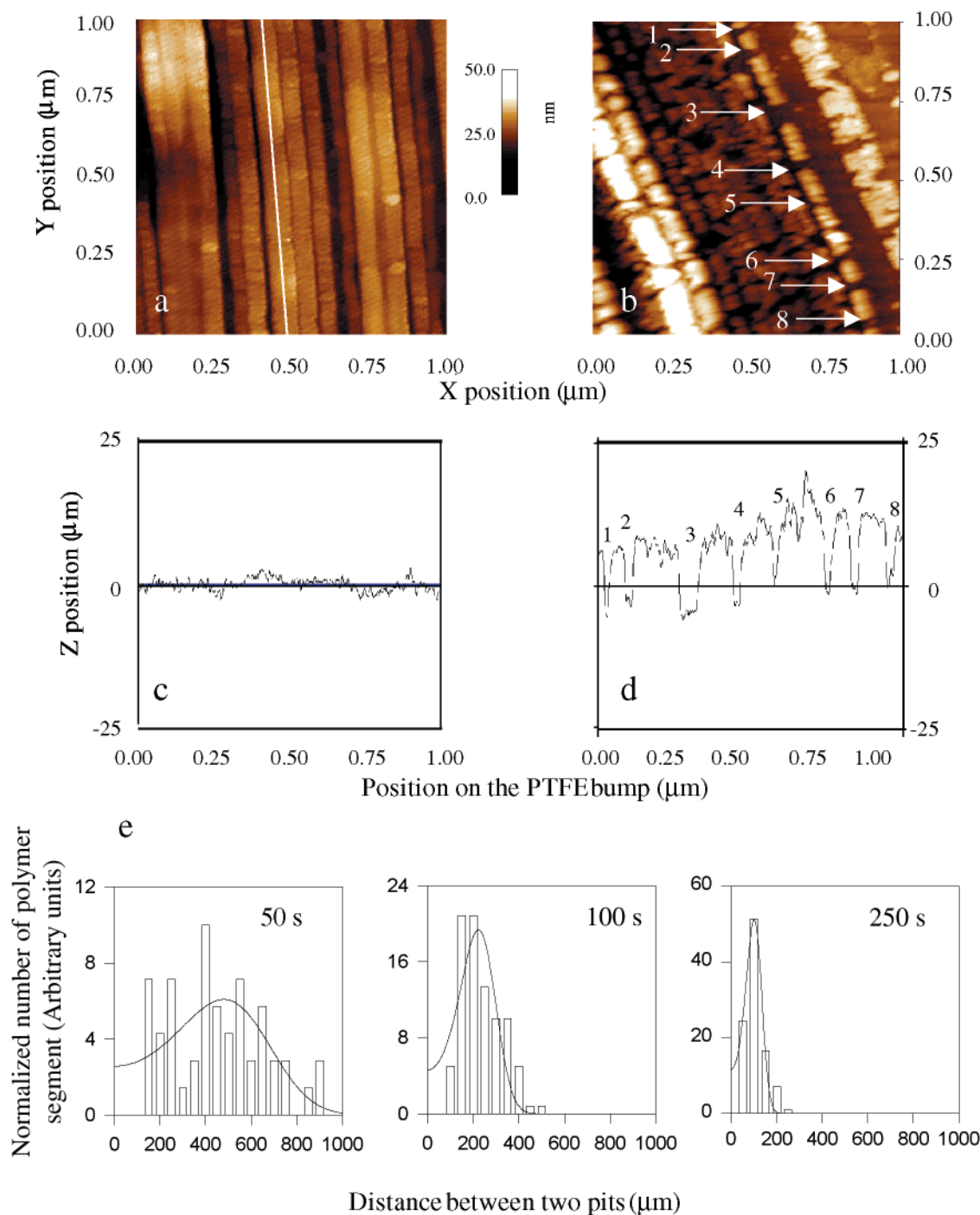
Figure 4, parts a and b, displays atomic force microscopic images of an oriented Teflon film before and after a plasma treatment time of 250 s. Before plasma treatment, the oriented PTFE film was made up of a succession of linear bumps of polymer and nude glass areas, in agreement with data published by Hansma et al.<sup>33–35</sup> Contrary to flat PTFE films, the oriented PTFE films allowed us to obtain AFM images with excellent contrast. This characteristic was particularly useful when attempting to observe the damages related to chain breaking caused by plasma treatment. As seen in Figure 4b, a plasma treatment of 250 s leads to the formation of several pits within the polymer linear structure (Figure 4d). Measurements of the distance between two consecutive pits in a same bump were therefore compiled into distribution curves for the various treatment durations, as depicted in Figure 4e.

As can be seen in these figures, the average length between two pits decreased with increasing treatment time, as did the distribution width. The most probable length went from 455 nm at 50 s to 246 nm at 100 s to 111 nm at 250 s. The fitted curves being, in fact, fitted to the distributions of the square of the lengths, the resulting Poisson distributions are displayed in Figure 5a. These curves were interpreted as the distributions of the intact surface surrounding a pit (which should be multiplied by a factor of  $\pi/4$  in a complete theoretical model). The reciprocal of the mean of these distributions was therefore interpreted as the mean areal density of the pits. This quantity is plotted in Figure 5b as a function of treatment time. The resulting curve appeared to be a straight line which intersects  $0 \mu\text{m}^{-2}$  at 48.7 s

$$\text{Density } \mu\text{m}^{-2} = 0,396 \text{ s}^{-1} \mu\text{m}^{-2} (\text{duration } s - 48,7 \text{ s}) \quad (4)$$

To verify the validity of the delay, extra samples were treated for 20 and 45 s. On the first one, absolutely no pits were found, whereas on the second, only a few, very dispersed pits could be observed (results not shown). The above-mentioned relation is thus validated and is representative of a second-order process. Some reaction must be required before a scission event can occur at a particular location. Additional theoretical and experimental work is required to further elucidate this phenomenon.

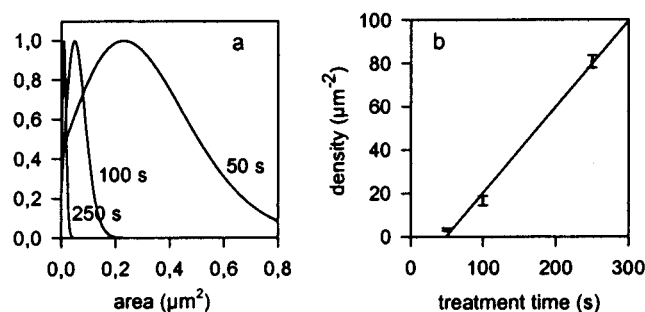
The present data have therefore shed more light on the events occurring on the PTFE surface upon ammonia radio frequency plasma treatment. On the basis of previously published results,



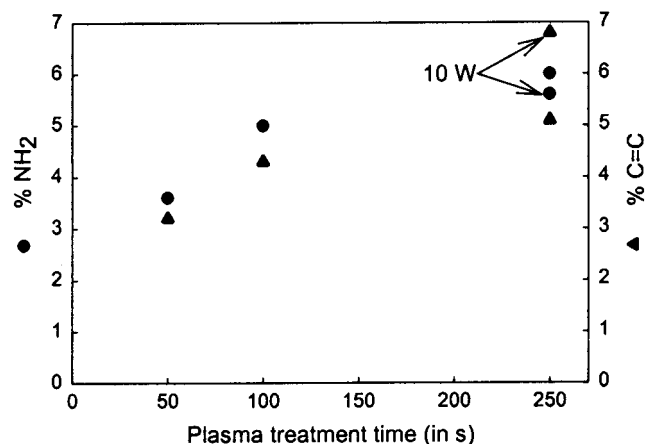
**Figure 4.** Atomic force microscopy images of an oriented Teflon film before (a) and after a plasma treatment time of 250s (b). Scan lines to determine the length separating two consecutive PTFE bump damages (c and d, respectively), and the distribution curves of the distance between two holes (e) for different plasma treatment times (50, 100, and 250 s).

the common opinion regarding such treatment of fluorinated polymers was that the amine formation was one of the first events to occur. In this context, the initial defluorination was thought to be accompanied by the insertion of one amino group along with, most of the time, one amino functionality replacing one fluorine atom. The formation of the other chemical functionalities was believed to take place through a complex surface reorganizations following subsequent defluorination. In addition, chain scission was also postulated as occurring throughout the entire plasma treatment process. The present study clearly supports a completely different scheme of reaction. It is obvious that the amine formation was not the major initial event, as approximately only one-third of the nitrogen-containing

species were identified as such after a 50 s plasma duration. For longer plasma treatments, a partial conversion of the nitrogen-containing species (other than amines) to amino groups was observed. Moreover, these events all occurred together with side reactions such as the formation of alkenes, for which the profile of formation kinetics closely follows that of the amino group formation. Finally, our data also confirms that the chain scission, pointed out as being the major weakness of the radio frequency plasma treatment technique and potentially limiting its application field, was in fact marginal for a treatment time of 50 s or less, occurring only after a certain period of time, contrary to previous assumptions. Optimizing other reactions will influence the chain scission rate.



**Figure 5.** Distributions of the square of the distances between consecutive pits for the different treatment durations (a). Deduced areal density of pits as a function of treatment duration (b).



**Figure 6.** Surface concentration of amines (●) and alkenes (▲) as a function of the plasma treatment time and radio frequency power.

With regard to the evolution of the formation of the various chemical species on the PTFE surface and its dependence on the duration of radio frequency plasma treatment, our observations raise the question whether it is possible to somewhat modulate the chemistry of the polymer surface through an appropriate selection of the plasma parameters, namely gas pressure and flow, radio frequency power, etc. This question is partially answered in Figure 6 which presents the amine and alkene surface derivatization data obtained for a plasma-treated PTFE surface using the above-mentioned experimental protocol at a radio frequency power of 10 and 20 W. This figure clearly shows that more alkene and less amino groups were formed under low-power experimental conditions. To our knowledge, this observation is the first to prove that the surface chemistry can be modulated through appropriate selection of the plasma treatment parameters. It also opens the door to a possible minimization of undesirable repercussive reactions, such as chain scission, through the appropriate selection and tuning of each experimental parameter related to a radio frequency-induced plasma such as treatment time, radio frequency power, treatment time, gas pressure and flow, possible magnetic confinement, and reactor configuration.

## Conclusion

The results of the derivatization on  $\text{NH}_3$ -plasma-treated PTFE surfaces indicate that the amine surface concentration increased with the plasma treatment duration, passing from 3.8% after 50 s to 6.2% after 250 s. In addition, the measurement of the bromine XPS signal following the derivatization reactions clearly indicated that insaturations were created during the plasma treatment and that their formation had increased with plasma treatment duration, ranging from 3.5% at 50 s to 5.3%

at 250 s. Moreover, a good correlation was observed between defluorination and alkene formation, as the higher the defluorination, the higher the double bond formation. AFM studies revealed that the polymer chain breaking events began occurring, to a measurable extent, just after 50 s of plasma treatment under the experimental conditions investigated. These combined data enable us to quantify the amine and alkene groups introduced on the surface, but also to better understand the kinetics involved in the various events occurring on the polymer surface in the plasma environment. Additional experiments are currently underway in which a Teflon surface is treated with an ammonia plasma, then exposed to water and dried, and finally analyzed by chemical derivatization. It is hoped that these experiments will provide invaluable information on the nature of other species present on the surface, such as imines, as well as a greater chemical knowledge of the reorganized surface.

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