Surface characterization of plasma-treated PTFE surfaces: an OES, XPS and contact angle study

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PTFE surfaces have been exposed to neutral atoms and molecules, and to electrons originating from a modified RF nitrogen plasma, able to filter out the cations. The changes in surface energy of the modified polymer, determined by the water contact angle, are linearly related to the increase of the nitrogen concentration at the surface, determined by XPS. The deconvolution of the spectral envelope of the C 1s photoelectron peak shows a strong modification of the nature of the chemical groups on the surface, depending on the treatment time and on the plasma power. Electrons are postulated to be mainly responsible for the appearance of the CF₃ group, while the major functions induced by nitrogen seem to be C=\(\text{N}\), C–\(\text{N}\) and a possible F–C–\(\text{N}\) group. Copyright © 2004 John Wiley & Sons, Ltd.

KEYWORDS: PTFE; nitrogen plasma; XPS

INTRODUCTION

Surface modification of polymers using plasma-based techniques has been the subject of many investigations in the last 20 years.¹–⁵ Amongst them, polyethylene (PE) and polypropylene (PP) have been the polymers most investigated. Gases such as oxygen, nitrogen, carbon dioxide and ammonia have been used in various low-pressure plasmas, such as DC, RF or microwave. Many industrial applications have been developed using high-pressure corona plasma. More recently, these plasmas have treated fluoride-containing polymers.⁶–⁹ The general goal of such treatments is to change the chemical and physical properties of the surface. Good probes for this are the surface composition and the surface energetics, the first one being determined mostly by SSIMS and XPS, the second one being determined by the water contact angle (WCA).

Plasma treatments are advantageous since they do not release toxic organic solvents into the environment, they are easy to control (current, pressure and voltage are the main parameters), they can be run at room temperature, (which is of interest for polymer surfaces), they have a low energy cost, and they are reproducible. However, some major disadvantages still exist, namely an ageing of the polymer after treatment, and the complexity of the processes involved during the plasma treatment. Indeed, the great variety of species created in a plasma (excited neutral atoms and molecules, molecular and monoatomic ions, electrons, photons) leads to a great number of (mostly unknown) interactions between the reactive species and the sample surface. Therefore, most of the studies published present the macroscopic effect of the application of a plasma on the modified polymer. The purpose of this paper is to try to look at PTFE surfaces treated by a modified RF \(\text{N}_2\) plasma. In our set-up, the sample, located outside the plasma, is placed above the anode grid and is submitted to the exposure of electrons and neutrals, avoiding most of the positive ions.¹⁰ We expect therefore, through this preliminary study, to be able to extract some selected effect of the neutrals and the electrons generated in the plasma on the surface modification of PTFE.

EXPERIMENTAL

The PTFE samples were from Goodfellow. After having been cut to size, they were cleaned in pure iso-octane and introduced into the plasma chamber. The plasma chamber consisted of a stainless steel based vessel surmounted by a Pyrex bell jar. Isolation was realized by a Viton O-ring. The pumping system consisted of an Edwards primary pump (up to 10⁻¹⁰ Torr) and a turbomolecular pump (Balzers 230 l/s) coupled to a membrane pump. Pure nitrogen from Alphagaz was used (N60, 99.9999% purity). Before introduction of nitrogen, the chamber was pumped down to a pressure lower than 10⁻⁶ Torr, and then backfilled to the working pressure. In order to avoid contamination, the chamber was continuously pumped during the experiments (dynamic regime). The RF plasma was initiated using a Huttinger PFG300RF generator, coupled to a PFM 1500 A matchbox. The samples were positioned outside the plasma region, above the anode grid, which could be either grounded or biased. A schematic diagram of the experimental set-up has already been published.¹⁰ The plasma chamber is also equipped with a fibre optic probe in order to detect...
the excited species generated in the plasma. The Sofie spectrometer operated in the 200–900 nm region.

After treatment the chamber was backfilled to atmospheric pressure using liquid nitrogen, and the sample was transferred either to the XPS chamber or to the contact angle room. XPS analysis was carried out in a UHV chamber (originally PHI AES 590 system) equipped with a VG clam II analyser. Spectra were acquired using the Mg anode (1253.6 eV), operating at 300 W. Wide surveys were acquired at 100 eV pass energy. Spectra of the C 1s, N 1s and F 1s regions were acquired with a pass energy of 30 eV. The deconvolution of the C 1s, N 1s and F 1s spectral envelope was performed using CasaXPS software. The FWHM of the C 1s peak, previously determined on clean PTFE on our instrument, for 30 eV pass energy was 2.8 eV. The philosophy of the deconvolution was to fit the spectral envelope with the lowest number of physically meaningful components needed. A critical use of the existing moieties detected reported in the literature helped us to identify species. When available, other techniques were employed to confirm the predictions. The average surface concentrations were determined with the usual formula, with the following sensitivity coefficients: N\text{D} = 0.477; C\text{D} = 0.296; F\text{D} = 1; O\text{D} = 0.711.

Water contact angle measurements were performed in the static mode, in a climatized room, with controlled humidity. Milli-Q water was used. Ten drops were deposited statistically on the modified surfaces, and the angle was measured on both sides of the drop. The results presented here are therefore an average of 20 measurements.

RESULTS AND DISCUSSION

An interesting property of RF plasmas is the inhomogeneous distribution of the charged species, with the cations remaining mostly close to the cathode. Figure 1 shows, as an example, the relative intensities of the N\text{2}^+ (391.4 nm)/N\text{2} (315.85 nm) lines in the dark space, the negative glow and the positive column of the plasma as a function of the plasma power. One can clearly see that the molecular ions are mostly located close to the cathode. The relative concentrations close to the sample (i.e. above the anode), therefore outside the plasma, indicate first a lower amount of cations, and second that this amount depends upon whether a positive bias is applied on the anode (see the insert in Fig. 1). As a conclusion, this set-up authorizes a partial ‘filtering’ of the ions, and the majority of the species reaching the sample surface are neutrals and electrons (the typical electron current on the sample surface was measured in Ref. 10). Although plasma-induced UV radiation may have a significant effect in the chain-breaking process at a polymer surface, it will not be studied in this paper.

Figure 2 presents the evolution of the contact angle, and the nitrogen concentration with the exposure time for 20 W and 50 W plasmas. A general trend is an increase of the surface energy and of the nitrogen surface concentration with the plasma power, and with the treatment time, with the grafting kinetics increasing with the plasma power. As expected, the increase of surface energy is faster for 50 W plasma. In all the cases, for long treatment times, a plateau regime is reached both for the surface energy and the nitrogen concentration. This indicates a saturation of the surface by nitrogen groups, with an average concentration between 16 and 20 at.%. This value is in agreement with Ref. 8 where PTFE was treated with NH\text{3} plasma, but is higher than the 9% reported in Ref. 6 where N\text{2} plasma was used. However, in their set-up the sample is located in the plasma (ours is outside), therefore much more exposed to nitrogen ion bombardment (see Fig. 1) which is known to induce a partial resputtering and etching of the surface, whereas neutral nitrogen species mostly graft onto the surface.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{Figure1.png}
\caption{Optical emission spectroscopy (OES) characterization of the plasma area. The relative intensity of the N\text{2}^+ /N\text{2} line is plotted as a function of the plasma power. The spectra were recorded in the positive column, the negative glow and the dark space. The intensities of the N\text{2}^+, N\text{2} and N\text{+} lines above the anode grid (close to the PTFE surface) are reproduced in the insert (for a 10 W plasma).}
\end{figure}
Figure 2. Evolution of the cosine of the water contact angle and the nitrogen surface concentration for PTFE surfaces with the plasma treatment time, at two different plasma powers. N₂ pressure = 5 × 10⁻² Torr.

Figure 3. Full plot of cos (WCA) as a function of the F surface concentration (bottom scale, full marks), and as a function of the N concentration (top scale, open marks). The circles, squares, and triangles represent the different plasma powers applied. For one single set of data (for instance the open circles), the only parameter varied is the time of exposure.

All the results (at plasma powers varying from 20 W to 70 W, and at treatment times varying from 5 to 30 min.) have been plotted in Fig. 3 where cos (WCA) is plotted as a function of the nitrogen surface concentration. A very good relationship is obtained; indicating clearly that the change in the contact angle is mostly a result of the increase in the nitrogen surface concentration, and the concomitant decrease of the fluorine concentration. A similar relationship was reported by Jie-Rong et al.⁹

The oxygen concentration never exceeds 5–6 at.% (in agreement with Ref. 9) and does not seem to depend on the plasma conditions. One cannot exclude in this case a slight contamination during the air transfer to the XPS chamber. Indeed, polymer surfaces modified by nitrogen plasma have proven to be very sensitive to water adsorption and post-plasma reactions do often occur with this molecule. We stress here that the amount of oxygen is much lower than, for instance, for PE-treated samples.¹⁰

The change in the shape of the C 1s photoelectron peak during the plasma treatment is presented in Fig. 4. For all the samples treated, a decrease of the CF₂ contribution at 292.0 eV, and of its satellite peak (in the lower binding energy tail of the C–C component), and the appearance of new contributions was detected. A higher binding energy contribution at 294.0 eV is attributed to CF₃, as postulated in the literature,⁷ and confirmed by the m/z = 69 fragment in the mass spectrometry (see hereunder). The other major contributions are C–C or C≡C at 284.6 eV. At least two
intermediate compounds at binding energies of 286.6 eV and 290 eV are also detected. Although there are many controversies in the literature, we could try to attribute the 286.6 eV component to C=N moieties, as it has been shown in previous papers that this is probably the major group grafted on PE surfaces when neutrals reach them, contrary to the C–N groups, mostly created when ions reach the surface (in the case of PE). C–N and C≡N groups on N₂ plasma-treated PTFE were also observed by Wilson et al.⁶

The 290.0 eV component could be attributed to C–F groups (also detected in mass spectrometry). Successful peak fitting could only be achieved by the introduction of an unknown component at a binding energy around 288 eV, which could correspond, from the chemical shift point of view, to a carbon surrounded by nitrogen and fluorine. This group is a reasonable consequence of the plasma treatment, but should be confirmed by another technique. One cannot exclude the presence of a more complicated environment, due to the presence of water vapour on the surface after treatment, which could react with the various nitrogen-containing species.

Fluorine-based polymers are known to be sensitive to an electron attack. The defluorination induced by the secondary electrons created in XPS has been studied by many authors.¹¹ Although for a short-term irradiation (a few minutes long) no significant effect is observed, allowing surface analysis for long irradiation times (>100 min) defluorination takes place. Figure 5 presents the mass spectra recorded in situ after 100 min XPS exposure for a clean PTFE sample and for a plasma-modified PTFE sample. Compared to the spectrum of the atmosphere of the XPS chamber, the CF⁺, CF₂⁺ and CF₃⁺ ions at masses 31, 50 and 69 are clearly detected on both samples. The presence of this last ion reinforces the validity of the C 1s peak deconvolution, where a 294.0 eV component appears after plasma treatment (see Fig. 4). It also indicates a clear chain breaking in the polymer, and a reorganization, probably induced by the electrons generated in the plasma.
Confirming our original assumption, this peak is larger for the plasma-treated sample (submitted to the effect of electrons) than on the pristine one, only irradiated by x-rays. The water-to-nitrogen intensity ratio (m/z = 18 and 28) is also higher for the plasma-treated sample, indicating the higher adsorption of water on such surfaces. No significant trace of ‘C–N’-like groups was found, but they produce mostly negative ions that are not detected in our mass spectrometer.

CONCLUSIONS

The exposure of PTFE surfaces to neutrals and electrons originating from a RF nitrogen plasma lead to an increase in the hydrophilicity of the surface. This property is directly related to the amount of nitrogen grafted on the surface. A defluorination of the surface is observed in all cases. The presence of a CF₃ component in the C 1s peak, as well as the CF₃⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻leness

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