Plasma-modified polymer surfaces: Characterization using XPS

N. Vandencasteele*, F. Reniers*

Université Libre de Bruxelles, Faculty of Sciences, cp 255, Bld Triomphe, 2-B-1050 Bruxelles, Belgium

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ABSTRACT

Amongst all the available surface treatments, the plasma techniques have taken a major importance these last decades, both in fundamental studies and for industrial applications.

This paper presents the utility of X-ray photoelectron spectroscopy for the characterization of plasma-modified polymer surfaces. Due to the originality of the reactivity of the plasmas (generation of radicals), and to the surface-selective character of the plasma treatments, some specific uses of XPS are emphasized, such as peak fitting, derivatization, angle-resolved XPS. We also show several selected examples of typical XPS analysis of plasma-treated polymers: ageing, biocompatibility, plasma polymerization, adhesion, surface grafting of polar functions.

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1. Introduction

In the framework of this special issue of Journal of Electron Spectroscopy and Related Phenomena, we detail in this review the utility of X-ray photoelectron spectroscopy for the characterization of plasma-modified polymer surfaces. This introduction will present the general scope of plasmas, followed by their use for the surface modification of polymers.

The second section of the paper continues with the specific uses of XPS in this field. First the issue of surface charging and energy scale calibration, crucial for most polymers, is described. Second, the XPS characterization using peak fitting (mostly of the C 1s peak) will be presented, as it is the major tool used, especially for the surface modification of polymers. As in some cases, peak fitting is not sufficient to identify the surface functionalities grafted by plasma, the derivatization technique will be presented. Finally, the interest of ARXPS for plasma treated polymers will be emphasized.

After these topics, more specific to XPS, the paper will focus in its third section on some typical applications of XPS for surface-treated polymers: ageing, plasma polymerization, adhesion, membranes, and biocompatibility. Although the reader could have the feeling of some redundancy, we think that this double entry approach (first focusing on the analytical technique XPS, then on specific examples for each topic more dedicated to the modified material) will provide to the scientist the information he is looking for.

2. Section 1: Plasmas

Plasmas, sometimes called the fourth state of matter, have been known for a very long time now. The term plasma itself is often attributed to Langmuir [1]. Atmospheric plasmas for the generation of ozone are also used for a long time, as the Siemens process was presented in 1857 [2]. Plasmas are often defined as a partly or fully ionized gas. The energy required for the ionization process can be provided by various sources (heat, electromagnetic field, light, etc.). For the surface modification of polymers the energy is usually coming from an electric field. The electric field accelerates electrons which collide with atoms or molecules and ionize them, producing new charged particles (electrons, atomic or molecular ions) that are also accelerated.

A plasma can be characterized by several parameters such as: its degree of ionization, the energy of the various species it contains (electrons, ions, neutrals and photons), the pressure, the mode of generation of the discharge (AC, DC, RF, HF, etc.), or the density of the plasma (often expressed in electrons per cm$^2$).

The degree of ionization ($\alpha$) represents the ratio of ionized atoms/molecules over the total amount of particles:

$$\alpha = \frac{n_e}{n_e + n_0} \tag{1}$$


\begin{align*}
\text{ne} & \text{ is the electron density (m$^{-3}$); } n_0 \text{ is the neutral species density (m$^{-3}$).}
\end{align*}

Depending on the value of $\alpha$, two major kind of plasmas can be defined; the weakly ionized one with $\alpha$ values between $10^{-7}$ and $10^{-4}$ and the strongly ionized plasma where $\alpha$ is close to 1. Plasmas used to modify polymers are usually weakly ionized.

In plasmas, each species have their own energy range. It is therefore possible to define an electronic temperature ($T_e$), an ionic temperature ($T_i$) and a neutral temperature ($T_0$). In an equilibrium...
plasma, all the particles have the same range of energy $T_e \approx T_i \approx T_0$. In non-equilibrium plasma, electrons have a much higher energy than neutrals and ions $T_e \gg T_i \approx T_0$. Plasmas used to modify polymers are mostly of the times non-equilibrium plasma. The energy of the neutrals and ions is usually in the range of 300–1000 K, whereas the energy of the electrons can vary from 1000 to 100 000 K, with an average of a few eV (a few 10 000 K). Therefore, the gas phase is referred as ‘cold’. This allows to modify the surface of polymers samples without destroying them. The very high reactivity of cold plasma for the surface treatment of polymers originates in the collisions in the gas phase between the high energy electrons and the atoms/molecules that create very reactive excited species (with a high potential energy) that are able to react with even the most unreactive samples such as polytetrafluoroethylene (PTFE, or Teflon®). Several techniques are used to obtain non-equilibrium plasma. The easiest approach is to operate at low pressure, this minimizes the number of collisions between the light (electrons) and heavy (ions and neutrals) particles, and therefore no thermalization of the plasma can take place. One can also use a high frequency generator (kHz to GHz). At those high frequencies the mobility of the ions is strongly reduced because of their much higher mass compare to the electrons (a proton is 1836 times heavier than an electron). Special plasma geometries, like the dielectric barrier discharge, allow to operate at high (atmospheric) pressure, while minimizing the number of highly energetic collisions. This leads also to cold plasmas.

More detailed information about plasma can be obtained from the following books [3,4].

Plasmas are very complex media full of highly reactive particles (radicals, ions, electrons, UV photons), all of these reaching the polymer surface. As a consequence, due to this complexity, the mechanisms involved in the surface modification of polymer are not yet fully understood. Also, because of the many “reactants”, the end result often contains a wide variety of “products”, which can be for instance different functionalities grafted. It is therefore very difficult to have a full identification and quantification of all the species.

Low pressure and high pressure plasma have been used empirically for the treatment of surfaces for many decades, but it is only since the 80s that the plasma treatment of surfaces really started to gain importance. Fig. 1(a) and (b) shows the results of a SciFinder search using the Keywords: “plasma and surface” and “glow discharge and surface” present in the titles of papers published. Although the word “plasma” is dangerous (as it refers also to the blood component); a clear trend can be seen in both figures. This is correlated with the development of commercially available surface analysis techniques; mostly X-ray photoelectron spectroscopy.

Plasma treatment of polymers results mainly in two mechanisms: ablation of the polymer and/or grafting of new species on the surface of the sample. The two reactions are taking place at the same time but depending on the experimental conditions one is more important than the other. The most commonly use is the grafting of new functionalities on the sample surfaces.

There are major scientific and technological reasons for the use of plasma for the surface treatment of polymers. The most important one in terms of industrial applications is certainly the increase of the adhesion properties of the polymer [5–11]. Indeed, most polymers, despite their very good properties (chemical inertness, good weight to strength ratio, transparency, barrier properties, etc.), exhibit very poor adhesion properties. Plasma treatments are used to increase their surface energy by grafting polar species on their surfaces. As plasmas modify only the surface, that can be solved, while maintaining unaltered the bulk properties of the polymers. Moreover, plasmas are environmentally friendly, contrary to traditional wet chemistry, and they are fast.

![Fig. 1. # of references containing both the concept: “plasma” and “surface” (A) (SciFinder, March 2009) or “glow discharge” and “surface” (B) (SciFinder, May 2009).](image)

Another use of plasma for polymer science is plasma polymerization (Fig. 2). In this case a precursor is sent into the plasma, the reactive species from the plasma will activate the precursor molecules that will react with each other and polymerize. A very large variety of polymers can be created by this technique ranging from diamond like carbon [12] to polystyrene [13] and PTFE [14].

![Fig. 2. # of references containing the concept “plasma polymer” (SciFinder, May 2009).](image)
films. This technique allows to deposit polymers on a very large amount of substrates. Those plasma polymers (pp) are used for dielectric coating (microelectronic), corrosion protection, biocompatible surfaces, gas barrier (food packaging). They present several advantages over traditional polymers. For instance, these films exhibit usually a higher degree of crosslinking, and have therefore superior mechanical properties which allow to deposit ultra-thin films that present good adhesion on various substrates. Plasma polymer films also exhibit uniform surfaces with a full coverage of the substrate [15–17].

As plasmas modify only the top layers of the sample, therefore surface specific techniques are required to analyze polymers modified by plasma. Two of the main techniques used to characterized plasma-modified polymers are XPS and water contact angle (WCA). WCA is a “true” surface analysis technique, with a depth analysis of around 0.5 nm [18]. During water contact angle measurements a drop of water is deposited on the sample, then the angle between the drop and the surface is measured (Fig. 3a). Hydrophilic surfaces have low WCA values as the water spread on the sample; hydrophobic samples exhibit high WCA values as the drop tends to minimize its contact surface with the sample (Fig. 3b–d). The surface energy is related to the cosine of the WCA by the Young–Laplace equation (Eq. (2)):

\[ \gamma_{SV} - \gamma_{SL} = \gamma_{LV} \cos \Theta \]

\( \gamma_{SV} \) is the solid/vapour surface tension; \( \gamma_{SL} \) is the solid/liquid surface tension; \( \gamma_{LV} \) is the liquid/vapour surface tension; \( \Theta \) is the contact angle.

Another useful value is the adhesion work, defined by the Dupré equation (Eq. (3)). It is defined as the reversible work required to separate the interface from the equilibrium state of two phases to an infinite distance:

\[ W_a = \gamma_L + \gamma_S - \gamma_{SL} \]

\( W_a \) is the work of adhesion; \( \gamma_L \) is the liquid surface tension; \( \gamma_S \) is the solid surface tension.

WCA is not only a relatively low cost (and therefore easily available) technique, but it also provides an immediate information on the adhesion properties of the modified surface.

Other surface analysis techniques can also be used, and are presented in Table 1. Fig. 4 presents a typical experimental strategy to study a plasma-modified polymer. XPS analysis of plasma-modified samples became relatively common only in the 90s with the increase in the commercially available XPS equipments. Indeed, it is useful to remind that XPS is still a relatively young technique, as Siegbahn was awarded the Nobel prize for it only in 1981. Fig. 5 presents a SciFinder Scholar statistic study of the number of hits containing both the items “XPS” and “plasma”. From a few papers per year until the mid 80s, it reached around 100 papers at the beginning of the 90s, to jump to an average of 800 papers these last years. Not only XPS instruments became easily commercially available, but the improvement of the technology was also a significant factor. The development of new detectors (multiple channeltron or channelplates) lead to a spectacular increase in the number of counts per s (cps), and therefore to a higher sensitivity and to a

Table 1
Some example of techniques used to analyze polymer modified by plasma or plasma polymers.

<table>
<thead>
<tr>
<th>Technique</th>
<th>Information</th>
<th>Drawbacks</th>
</tr>
</thead>
<tbody>
<tr>
<td>WCA(^a)</td>
<td>Surface energy, polar and dispersive components</td>
<td>Possible modification of the surface by water. No chemical information. Mix of polarity and roughness.</td>
</tr>
<tr>
<td>XPS(^b)</td>
<td>Composition, functionalities</td>
<td>Not totally surface specific; X-ray degradation; hydrogen not detected; limited energy resolution.</td>
</tr>
<tr>
<td>(S)SIMS(^c)</td>
<td>Functionalities</td>
<td>Fragmentation, complex data analysis.</td>
</tr>
<tr>
<td>SEM(^d)</td>
<td>Topographic information</td>
<td>Surface must be conducting.</td>
</tr>
<tr>
<td>AFM(^e)</td>
<td>Topographic information</td>
<td>No chemical information.</td>
</tr>
<tr>
<td>ATR FTIR(^f)</td>
<td>Functionalities</td>
<td>No chemical information.</td>
</tr>
</tbody>
</table>

\(^a\) Water contact angle.
\(^b\) X-ray photoelectron spectroscopy.
\(^c\) (Static) secondary ion mass spectrometry.
\(^d\) Secondary electron microscopy.
\(^e\) Atomic force microscopy.
\(^f\) Attenuated total reflectance Fourier transform infrared spectroscopy.
better signal/noise ratio. That favored the use of monochromators which are often necessary to unambiguously identify functionalities grafted onto a polymer surface. A recent review about the improvements in XPS can be found in Ref. [19].

3. Section 2: Analytical considerations for the use of XPS in the characterization of plasma treated polymers and plasma polymers

3.1. Charging and energy scale calibration

Most of the time, polymers are non-conductive. Due to the X-ray excitation mechanism, and to the ejection of the (photo) electrons from the sample, a positive charge spontaneously appears on the surface. Because of this surface charging, spectra are shifted of a few eV towards higher binding energies (lower kinetic energies). Although in non-monochromatized XPS the X-ray gun also generates some electrons that can reach the surface and that can partly compensate for the positive charging, this is not the case anymore with monochromatized XPS. For plasma treated samples, this is dramatic, as one of the main uses of XPS is the identification by peak fitting of the chemicals functionalities grafted. To compensate for this charging effect some authors use an electron flood gun [20–27] or a magnetic lens [28].

If no flood gun is used, the spectra are shifted by the user, with the software, using internal references. Most of the time the internal reference used is the C1s peak of CC/CH bonds coming from the polymer itself or the CC signal coming from small contaminations by adventitious carbon. Depending on the authors, this reference value is 284.6 eV [21, 24, 25, 29–36] or 285.0 eV [37–50]. There is therefore already a 0.4 eV difference between the references used. Consequently, as some components are separated by less than 0.4 eV it is not easy to have an unambiguous identification of the functionalities. Although most of the papers in the literature use now this approach (energy calibration on the C1s peak), this is not in perfect agreement with the usually accepted good practices in analysis: the C1s peak is usually the one which is strongly modified due to the change in chemical environment. On fluorinated samples some authors use the F1s signal [51–54] instead of the C1s one. The F1s peak is very symmetrical and can be fit with just one component, even for copolymer having fluorine atoms with different neighborhoods [52]. The only difference between the different neighborhoods is the position of the F1s peak (Table 2). Ferraria et al. [52] propose the following equation (Eq. (4)) to estimate the position of the F1s peak. This equation was determined from experimental data of PVF, PVdF and PTFE. BE stands for binding energy, \( F/C \) is the atomic ratio of fluorine over carbon:

\[
\text{BE}_{(\text{F1s})} = -0.6 \left( \frac{F}{C} \right)^2 + 3.32 \left( \frac{F}{C} \right) + 685.43
\]  

As it can be seen in Fig. 6, the position of the F1s peak in the copolymer named Viton fits very well with the proposed equation.

![Fig. 4. Typical experimental strategy to study plasma-modified polymers.](image)

![Fig. 5. # of reference containing both the concept “XPS” and “plasma” (SciFinder, March 2009).](image)

<table>
<thead>
<tr>
<th>Table 2</th>
<th>F1s binding energy as a function of the F/C ratio. From Ref. [70].</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polymer</td>
<td>F/C ratio</td>
</tr>
<tr>
<td>PVF (-CHF–CH2–)</td>
<td>0.5</td>
</tr>
<tr>
<td>PVdF (-CH2–CF2–)</td>
<td>1</td>
</tr>
<tr>
<td>PTFE (-CF2–CF2–)</td>
<td>2</td>
</tr>
<tr>
<td>Viton</td>
<td>8/5</td>
</tr>
</tbody>
</table>
According to this, if one would use the F1s peak as an internal reference, its binding energy should be set in accordance with the expected F/C ratio.

3.2. Peak fitting

As one of the major applications of the plasma treatment of polymers is to chemically modify their surface, the analysis of the high-resolution C1s peak (HRC1s) shape with peak fitting is a powerful tool to identify the functionalities grafted on the sample. Depending on the chemical environment of the carbon atom, the C1s peak can present high chemical shifts making it relatively easy to identify its main components. Fig. 7 presents the HRC1s spectrum of a modified polyimide sample. The addition of O, N and F substituent results in strong changes in the C1s envelope due to the various chemical environments of the carbon atoms (chemical shifts). The peak fitting can help to identify the grafted components.

However, it is not always as straightforward, as various species present chemical shifts very similar to one and other (Table 3).

In some cases the difference in binding energy between two species is smaller than the resolution of the apparatus, even with a monochromator. In this case the two species cannot be distinguished from each other.

3.3. Derivatization

For some components, like C–N and C–O (see Table 3), the binding energies of the C1s peak are very close, making it almost impossible to identify unambiguously the components. In such cases, a chemical derivatization may help to identify specific

![Fig. 7. C1s spectra from modified polyimides used as liquid crystal alignment layers. Sample contains a side-chain which includes both an amide and –CF3. This results in increased nearest-neighbor (beta-C) effects as well as the addition of the peak at \(\sim 292 \text{ eV}\) [137].](image)

### Table 3

<table>
<thead>
<tr>
<th>Chemical function</th>
<th>C1s B.E., eV</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>C–C</td>
<td>284.6</td>
<td>[138]</td>
</tr>
<tr>
<td>C=O</td>
<td>284.7</td>
<td>[70]</td>
</tr>
<tr>
<td>(CH2)n</td>
<td>285.0</td>
<td>[70,138,139]</td>
</tr>
<tr>
<td>CHF–CH2</td>
<td>285.7</td>
<td>[70]</td>
</tr>
<tr>
<td>CHF–CF2</td>
<td>285.9</td>
<td>[140]</td>
</tr>
<tr>
<td>C–N</td>
<td>286.3</td>
<td>[141]</td>
</tr>
<tr>
<td>–(CF2–CH2)–n</td>
<td>286.4</td>
<td>[70,139]</td>
</tr>
<tr>
<td>C–O–C</td>
<td>286.45</td>
<td>[139]</td>
</tr>
<tr>
<td>C–O or C–CF</td>
<td>286.5</td>
<td>[142]</td>
</tr>
<tr>
<td>CHF–CH2</td>
<td>286.9</td>
<td>[143]</td>
</tr>
<tr>
<td>CHF–NH2F</td>
<td>287.4</td>
<td>[141]</td>
</tr>
<tr>
<td>CH2–CHF–CH2</td>
<td>287.7</td>
<td>[139]</td>
</tr>
<tr>
<td>C=O or CHF–CH2</td>
<td>287.9</td>
<td>[70,139]</td>
</tr>
<tr>
<td>C=O or CHF or N–C=O</td>
<td>288.0</td>
<td>[142,143]</td>
</tr>
<tr>
<td>CHF–CH2</td>
<td>288.1</td>
<td>[140]</td>
</tr>
<tr>
<td>EF</td>
<td>288.3</td>
<td>[139]</td>
</tr>
<tr>
<td>CHF–CO</td>
<td>288.4</td>
<td>[140]</td>
</tr>
<tr>
<td>C=O or CHF–CF2 or CF–CF2</td>
<td>289.2</td>
<td>[142]</td>
</tr>
<tr>
<td>CHF–CO–CF2</td>
<td>289.8</td>
<td>[145]</td>
</tr>
<tr>
<td>–(CHF–CF2)–n</td>
<td>290.9</td>
<td>[70]</td>
</tr>
<tr>
<td>–(CHF–CF2)–n</td>
<td>291.6</td>
<td>[139]</td>
</tr>
<tr>
<td>CHF–CF3</td>
<td>292.2</td>
<td>[144]</td>
</tr>
<tr>
<td>–(CF2–CF2)–n</td>
<td>292.5</td>
<td>[70,139,140]</td>
</tr>
<tr>
<td>CHF–CF2–O</td>
<td>294.1</td>
<td>[144]</td>
</tr>
<tr>
<td>CHF–CF2</td>
<td>294.6</td>
<td>[139]</td>
</tr>
</tbody>
</table>

![Fig. 6. F1s binding energy as a function of the atomic ratio F/C for PVF, PVdF and PTFE. The squares represent experimental data points. The line corresponds to the empirical equation (Eq. (4)). The full square is the point corresponding to Viton. From Ref. [52].](image)
species. The basic principle is to have a very specific reaction between the target functionalities to be studied and a special marker molecule. The marker molecule usually contains fluorine atoms because of the very large chemical shift it induces in the C1s binding energy. More generally the marker must have at least one element not present in the original sample. Therefore the target functionality can be detected unambiguously by the new element present in the spectra. Careful calculations, taking into account the stoichiometry of the reaction, may allow to quantify the target functionalities probed. Fig. 8 shows some examples of derivatization reactions. After the reaction, new components appear on the HRC1s spectra. Those new components are the signature of the targeted functionalities that have reacted with marker molecule. Fig. 9 presents the HRC1s spectra of O2 plasma treated polypropylene.
sample, before and after derivatization of the hydroxyl groups by trifluoroacetic anhydride (TFAA).

We emphasize here that derivatization is a very powerful technique, but the overall analysis procedure is delicate, and not trivial [55,56]. Those derivatization reactions are of great interest for surfaces containing both nitrogen and oxygen. The most common groups to be derivatized are carboxyl [44,57–62], hydroxyl [57–59,61,63,64], carbonyl [57,58,61] and amine [34,61,64–67].

3.4. Angle-resolved XPS (ARXPS)

In-depth information in XPS is usually obtained by means of ion etching (“depth profiling”). However, this approach is mostly prohibited for polymers, as the information about the chemical bonds and the chemical environment will be lost by the sputtering [68].

During angle-resolved XPS measurements the angle between the sample surface and the entrance of the analyzer is changed, this allows to analyze different depth. When the photoemission angle is set to 0° the sampling depth is maximum, when the angle is set to 90° the sampling depth is minimum (Fig. 10).

More specifically, when it comes to plasma-treated polymers, only the very first atomic layers will be chemically modified by the treatment. As during XPS measurements, the information is averaged out over a depth of 3–6 nm, depending on the attenuation of...
Fig. 15. The XPS wide scan spectra of the delaminated PTFE and Cu surfaces of the Cu/pp-GMA-PTFE assemblies: (a) having a 180°-peel strength of about 0.5 N/cm and prepared in the absence of H2 plasma pre-activation and (b) having a 180°-peel strength of about 5 N/cm and prepared in the presence of H2 plasma pre-activation. From Ref. [111].

Fig. 16. A plasma polymerized film examined by XPS. Points are experimental data fitted with seven contributions in the C1s region. A precisely resolved C–Ni peak at 283.6 eV permits the identification of direct carbon–nickel bonds at the film/substrate interface, which account for the good adhesion of the film to the substrate. From Ref. [113].

the emergent electrons [69], the entire useful in-depth information can therefore be obtained by ARXPS. It allows to discriminate between the compositions of the top layers (those modified by plasma) and the averaged out surface. For example during the expo-

Fig. 17. Wetting properties of CO2 plasma-treated PTFE foils depending on the ambient conditions. From Ref. [114].

Fig. 18. Surface composition variation as a function of time storage in ambient air. aPS: atactic polystyrene, iPS: isotactic polystyrene From Ref. [20].

Fig. 19. Relative contact angle variation as a function of time storage in ambient air. aPS: atactic polystyrene, iPS: isotactic polystyrene From Ref. [20].

sure of a polystyrene sample to an oxygen/helium plasma, the O at.% decreases while the sampling depth increases (decreasing photoemission angles), Fig. 11. The shape of the HRC1s also changes with the depth of analysis. The HRC1s peak has more oxygenated component (C–O, C=O...) at the surface, showing that the plasma treatment only affects the top layers of the sample (Fig. 12).

3.5. X-ray degradation

One of the big issues in XPS analysis of polymers is sample degradation. It is indeed well known that some polymers are degraded

Fig. 20. The ARXPS data for the O–CO–O component in the C1s envelope, obtained in Al (close symbols) or Mg (open symbols) radiation: square = 0°, circle = 15°, up triangle = 30°, down triangle = 45°, diamond = 60°, star = 75°. From Ref. [71].
by X-ray exposure [69–72]. In fact this degradation comes from the secondary electrons emitted during the X-ray exposure. In most of the cases this degradation is slow enough not to change the composition of the sample during the analysis. However, this can be a problem while performing ARXPS, often used to characterize plasma-treated samples. The X-ray exposure time is much longer, as several spectra of the same region have to be recorded at different angles [73]. The exposure time is therefore multiplied by the number of angles at which the measurements have to be done. To avoid X-ray damage on the samples some authors use a reduced X-ray power (150 W instead of the usual 300 W power) [21,30,52,74–86].

4. Section 3: Applications of XPS for selected “materials–plasma” applications

4.1. Modification of polymers by plasma–adhesion

Fig. 13 [87] shows the correlation between the surface energy and the surface composition for PTFE samples treated by a low pressure radio frequency (r.f.) N2 plasma. The surface energy is represented by the cosine of the contact angle (Eq. (2)). It can be seen that an increase in the nitrogen content and a decrease in the fluorine content are correlated to an increase in the surface energy.

XPS is used to quantify the amount of polar species grafted and their nature. One of the most common and efficient treat-
Adhesion of metal on polymers with low-k dielectric constant is an important matter for the microelectronics industry. The Cu/PTFE system is of particular importance because of the excellent thermal and dielectric properties of PTFE as well as the low resistance of aluminum for integrated circuits [26]. As polymers tend to have a low surface energy, their adhesion to metals is weak. As already shown, plasma treatments are very efficient to increase the surface energy of polymers, therefore they are used to increase the adhesion between metal and polymers. Fig. 14 [111] presents the increase in adhesion strength between the are used to increase the adhesion between metal and polymers. This increase in the adhesion strength is correlated with the increase in the [O]/[C] and with the decrease in the [F]/[C] atomic ratio on the PTFE surface.

The study of both the polymer and the metal surface after delamination gives information about the type of bond between the two surfaces. If metal is still detected on the metallic surface, the adhesion was not good; the metal is totally delaminated from the polymer. On the other hand if the surface analysis of the metal side only shows polymer signal it means that adhesion was good and the sample have delaminated by cohesive failure. Fig. 15 [111] shows an example of both cases.

The adhesion between metals and polymers is also important for micro- and nano-technologies. Ultra-thin fluorinated films are used as anti-adhesive layer in the replication of micro- and nanostructures by hot embossing, where a controlled interface is desired between the hard master and the thermoplastic [113]. The hard master is the mould used to replicate the nanostructure on the thermoplastic material. The fluorinated films were deposited on the Ni master by r.f. plasma sputtering of a PTFE target. HRC1s spectrum allows the author to have information on the adhesion of the film on the metallic master. The C–Ni bond detected in the HRC1s peak (Fig. 16), accounts for the good adhesion of the film to the substrate.

4.2. Study of the ageing of plasma-modified polymers by XPS:

Plasma treatments are often used to increase the hydrophilicity (increase of the surface energy) of the sample. However, due to the rotation and the movement of the polymer chains, this modification is not permanent. This is referred to as the ageing phenomenon. When the samples are stored in a hydrophobic environment such as air, a hydrophobic recovery occurs, which is not happening when the samples are stored in a hydrophilic environment like water. Fig. 17 shows the contact angle results for a PTFE surface treated by a CO2 plasma (MW–ECR, microwave electron cyclotron resonance, p = 2 × 10−3 mbar, P = 300 W, Pulsed Mode Duty Cycle = 50%, treatment time = 4 min). Storage in water causes a significant improvement in wettability. However, when the sample is removed from the water, a fast hydrophobic recovery was observed [114].

This hydrophobic recovery can be explained by a change in the surface composition of the samples during the ageing. When the samples are stored in air, the polar functionalities present at the surface (–OH, –COOH . . .), slowly disappear in the bulk of the sample. Fig. 18 [20] presents the O/C ratio of isotatic and atactic polystyrene sample treated by an oxygen plasma (p(O2) = 4 mbar, P = 6 W, t = 60 s Duty Cycle = 1%). A few days after the treatment the O/C ratio at the surface is already decreasing [20,71,72] as the polar functionalities are buried in the bulk of the polymer, too deep to be detected by XPS. This change in the surface composition is very well correlated with the change of the surface energy (Figs. 18 and 19).

These changes in surface composition are also correlated to changes in the envelope of the HRC1s peak. Fig. 20 [71] presents the % of the C1s envelope attributed to O–CO–O component for a polystyrene sample treated by a 10% oxygen–90% helium plasma. The plasma parameters were: r.f. power = 15 W at 13.56 MHz, p = 13.3 Pa, gas flow = 0.169 Pa m3 s−1). The high energy component, coming from polar functionalities (e.g., C–OH, C=O, COOH . . .) slowly disappears with time. This example also underlines the power of ARXPS to study the ageing of plasma-treated polymer surfaces.

4.3. XPS to study plasma polymerized films

XPS is also used to characterize plasma polymerized films (pp-film). It is one of the few techniques that give access to the atomic composition of the films. Indeed, one of the advantages of XPS (over SIMS for example) is the relatively easy and robust atomic quantification. This can also give information about the degradation of the monomer in the plasma, and therefore provide information about the mechanism of reaction. Indeed, if the ratios of the peaks of the elements are the same in the pp-film and in the monomer one can conclude that there was not much degradation of the monomer functionalities by the plasma.

![Fig. 23. Comparison of valence band (VB) spectra of pulsed plasma polymerized PS and commercial PS. From Ref. [116].](image)
Fig. 24. Comparison of VB spectra from pulsed plasma polymerized ethylene, acetylene and butadiene with commercial poly(butadiene) and poly(propylene). From Ref. [116].

The HRC1s peak could also be used to study fragmentation and/or damage of the monomer during the polymerization process. Fig. 21 shows the HRC1s spectra of the monomer, 4,4′-hexafluoroisopropylidene diphthalic anhydride (6FDA) before plasma polymerization and of the plasma polymer film. The strong decrease of the (CO)–O– component (±288 eV) in the pp-6FDA film clearly evidences damage to the monomer with the lost of CO/CO2 groups from the anhydride ring [76].

For aromatic monomers, the π–π* shake-up can be used to study if the aromatic structure of the monomer was preserved in the polymerized film. Fig. 22 compares the HRC1s spectra for commercially available polystyrene (PS) (Fig. 22a and b) and plasma polymerized PS (pp-PS). The pp-PS where synthesized with a dielectric barrier discharge (DBD) in He (Fig. 22d) or Ar (Fig. 22e) and with a commercially available r.f. plasma torch (Atomflo 250 D SurfX Technologies) (Fig. 22f). It can be seen that the aromaticity is conserved for both films synthesized by DBD as the π–π* shake-up is present in the spectra. On the other hand, the film prepared with the atmospheric plasma torch has lost his aromaticity as no π–π* shake-up is detected in the spectrum anymore [13].

Touzin et al. [115] studied the stability of plasma polymerized fluorocarbon on stainless steel substrates. The survey spectra never show any metallic element, even after ageing. Therefore they concluded that there is no delamination or cracks of the film even after ageing.

Some authors use the valence band (VB) analysis to study their plasma polymerized films [15,116]. Although usually, XPS deals with core electrons (C1s, N1s, O1s, etc.), there is also significant information at low binding energies representative from electrons originating from the valence band of the sample. Those authors compare the VB spectra of plasma polymerized polystyrene (pp-PS), polyethylene (pp-PE), poly(acetylene) and poly(butadiene) with those of commercial PS, PE, polypropylene (PP) and poly(butadiene) [116]. For the pp-PS the VB spectra are very similar for both samples (Fig. 23). Comparison between commercial poly(butadiene) and pp ethylene, acetylene and buta-
diene reveal a good correspondence of the overall shape. However higher densities of state at around 16 eV in the pp spectra (like in polypropylene) suggest that the pp-films are more branched and crosslinked (Fig. 24) than the traditional polymers. This is usually expected for plasma polymers.

However, most of the time, XPS analysis alone is not sufficient to obtain a correct chemical characterization of plasma polymerized films. This requires a multitechnique approach [117]. Indeed during the plasma polymerization a lot of fragmentation from the monomer could happen, which result in very complex chemistry. Amongst the other techniques, ToF-SSIMS, nuclear magnetic resonance and infrared spectroscopy are the most powerful and complementary to XPS.

### 4.4. XPS for plasma-modified membranes

Membranes are used in a wide variety of applications: ultrafiltration [118], fuel cells [119], and gas separation [120]. Usually they are made of porous thermoplastic polymers, such as polysulfone and fluoropolymers, because of their good mechanical and chemical resistance. As the majority of those polymers are hydrophobic, before they can be used to filtrate aqueous solutions they must be rendered hydrophilic by the addition of a wetting agent and/or a surface chemical modification [121]. As already shown plasmas are very efficient for increasing the hydrophilicity of polymers. They involve clean and rapid reactions that graft new functionalities and crosslink the surface, without altering the bulk properties for which the polymer was originally selected [122]. However, for the specific case of membranes it is important that the modification penetrates through the membrane so even the inside of the pores are treated. XPS has been used to check for this. If the concentration of the grafted groups is the same on both sides of the membrane, the one facing the plasma and the other one, it can be concluded that the plasma has effectively penetrated through the entire membrane [121]. Table 4 shows results of polysulfone (PSf), polyethersulfone (PES) and polyethylene (PE) membranes treated by plasma. For both PSf and PES membrane the oxygen concentration is the same on each side of the membrane indicating a penetration of the plasma through the membrane. However for the PE membrane the oxygen concentration is lower on the side not facing the plasma, indicating that in this case the plasma has not fully penetrated the membrane.

In the plasma treatment of membranes, acrylic acid is often a molecule of choice [122–130], as this allows to graft carboxylic acid groups on the membrane. Indeed, those groups are suitable for biotechnological applications such as covalent binding of enzymes [123]. XPS is used to determine the concentration of carboxylic groups grafted on the sample (Fig. 25). Derivatization reactions (described in Section 3.3) can be used to have a better estimation of the carboxylic group content.

#### 4.5. XPS for the detection of biofouling properties of plasma-treated polymers

Plasma treatments are also used to obtain protein resistant surfaces (i.e. surfaces which do not adsorb proteins). Polyethylene glycol [131] surfaces are amongst the most used but other exist, such as ultra-hydrophobic PTFE [86] which also present good resistance to protein adsorption. XPS is used to detect the presence or the absence of the protein on the surface of the sample. Usually the N1s signal coming from the protein is used to detect it. Some authors use plasma treatment to decrease the adsorption of pro-

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**Table 4**

<table>
<thead>
<tr>
<th>Material</th>
<th>XPS (at.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Carbon</td>
</tr>
<tr>
<td>Stoichiometric PSf</td>
<td>84.3</td>
</tr>
<tr>
<td>Stoichiometric PES</td>
<td>75</td>
</tr>
<tr>
<td>Stoichiometric PE</td>
<td>100</td>
</tr>
<tr>
<td>Untreated PSf (both side)</td>
<td>84.5 ± 0.5</td>
</tr>
<tr>
<td>Treated PSf (open)</td>
<td>74.4 ± 0.2</td>
</tr>
<tr>
<td>Treated PSf (right)</td>
<td>73.7 ± 0.6</td>
</tr>
<tr>
<td>Untreated PES (both sides)</td>
<td>75.5 ± 0.9</td>
</tr>
<tr>
<td>Treated PES (both sides)</td>
<td>67.9 ± 1.1</td>
</tr>
<tr>
<td>Untreated PE (both sides)</td>
<td>100</td>
</tr>
<tr>
<td>Treated PE (A)</td>
<td>72.3 ± 3.5</td>
</tr>
<tr>
<td>Treated PE (B)</td>
<td>84.4 ± 2.3</td>
</tr>
</tbody>
</table>

* Trace impurities (<2%) of atomic silicon also detected.
* Trace impurities (<2%) of atomic sodium also detected.
* Trace impurities (<2%) of atomic chlorine also detected.
* Side A is facing the coil and side B is the downstream side during plasma treatment.

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**Fig. 25.** High-resolution XPS spectra of the C1s peak of an untreated polyurethane (PU) membrane, acrylic acid (AA) plasma-treated PUs at several plasma treatment times and synthesized poly(acrylic acid). Plasma power: 5 W. The ≡C and COO groups are shown in different spectra for better presentation. From Ref. [122].
tein on membranes. The adsorption of proteins on the membrane causes a strong decrease of the permeate flux [118,132]. Wang et al. [132] used the N1s signal from the peptide bond of the protein to detect the adsorption of protein onto their plasma-treated membranes. The presence of the protein can also be seen on the HRC1s peak shape. Fig. 26 [86] shows the HRC1s spectra of PTFE samples treated by various O2 plasma before and after exposure to a protein (bovine serum albumin, BSA) solution. Samples that do not resist the protein adsorption exhibit new components coming from the protein itself. Those new components are C–C at 285.0 eV, C–N or C–O between 285.7 and 286.5 eV and N–C=O at 288.2 eV [133].

Plasma treatments are used to immobilize biomolecules on surfaces. This is of great importance in tissue engineering research [134,135]. The following example shows the plasma treatment (radio frequency glow discharge) of expended PTFE (ePTFE) with oligopeptides, known for their role in mediating the adhesion of cells to the extracellular matrix [136]. As shown in Fig. 27 the XPS measurements allow to follow the grafting of the species on the sample.

5. Conclusions

X-ray photoelectron spectroscopy is, without any doubt, one of the most useful tools to characterize plasma-treated polymers.

The control of the plasma modification of surfaces is closely related to the development of surface analytical techniques, able to characterize the resulting surface.

XPS is an essential tool to probe the physical and chemical properties of the plasma-treated polymers: adhesion, biocompatibility, ageing are today studied using XPS, in conjunction with other techniques. XPS is mostly used to probe for the identification of chemical groups grafted, through the compositional analysis and the peak fitting (mostly of the C1s peak). With the help of derivatization and ARXPS, a decent characterization of the plasma-treated surface can now be achieved.

Finally, plasma polymerization, which is taking more and more importance since a few years, also needs XPS to probe for the conservation of the monomer chemistry and to better understand the polymerization mechanism.
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