X-ray action on polymeric membrane surfaces: a chemical and morphological characterization

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INTRODUCTION

Polymeric membranes are of great interest in many industrial processes and their performances depend, to a large extent, on the membrane morphology and surface chemistry. The morphology (roughness and porosity) is commonly studied using an advanced technique such as atomic force microscopy (AFM), where a high spatial resolution is attained, whereas the surface chemistry is usually characterized by X-ray photoelectron spectroscopy (XPS), where not only the chemical composition of the top surface is determined but also the chemical state of the elements forming part of the membrane. Atomic force microscopy has been used combined with XPS in the characterization of different polymeric membranes, where not only the chemical composition of the top surface is determined but also the chemical state of the elements forming part of the membrane. Atomic force microscopy has been used combined with XPS in the characterization of different polymeric membranes, where not only the chemical composition of the top surface is determined but also the chemical state of the elements forming part of the membrane.

X-ray photoelectron spectroscopy has been used not only for study of the membrane chemical composition but also for other chemical properties such as membrane hydration or chemical interactions between the polymeric matrix and some added functional groups in activated membranes and in hybrid membranes. All these examples show that XPS is a powerful technique for characterizing membranes; however, it is well known that X-rays may damage organic materials. Degradation of organic polymers occurs at different rates, depending on each polymer and also on additives to the polymer. Because membranes can be modified polymers or even organic composites, the influence of x-ray radiation should be studied in order to determine the optimum recording time for each type of polymeric membrane. Polyamides and polyamides are polymers widely used in membrane manufacture owing to their high thermal, chemical and mechanical stability. Polyamide asymmetric membranes find applications as ultrafiltration membranes in different industries. In order to improve membrane resistance to fouling and water flux, the hydrophobic character of polyamides can be decreased by the addition of hydrophilic polymers, grafting of hydrophilic groups or the introduction of ionic groups. These modified polyamide membranes are also used as supports for a polyamide thin layer in reverse-osmosis and nanofiltration membranes. In this case, the polyamide layer is usually made by interfacial polycondensation to obtain a three-dimensional network of aromatic polyamide with different cross-linkings. The porosity of the polyamide layer is so low that it is considered a dense layer. On the other hand, organic acids can be introduced in the polyamide layer to make activated membrane carriers, respectively — have been characterized before and after irradiation with an x-ray source, both chemically and topographically by XPS and atomic force microscopy (AFM), respectively. Changes in atomic concentrations of the characteristic elements of the membranes and in the shape of XPS spectra as a function of irradiation time can be related to chemical modifications on the membrane surface. The most significant changes have been observed for polysulphone, which is reduced by x-ray action; this fact also shows the inhomogeneity of the surface of the di-2-ethylhexylphosphoric-acid-activated membrane. In contrast, polyamide top layers of composite membranes have been shown to be the most stable. Chemical modifications are not related directly to changes in membrane roughness because for all membranes only small changes have been observed for AFM images recorded before and after membrane irradiation. Moreover, the roughness of both polysulphone membranes decreases slightly due to x-ray radiation but increases slightly for all polyamide-containing membranes (composite and activated membranes).
membranes, which are being developed for their application in the separation of metal ions from hydrometallurgical effluents.\textsuperscript{25–31} Di-2-ethylhexylphosphoric acid (DEHPA) and di-2-ethylhexylidithiophosphoric acid (DTPA) are two organic acids with high selectivity to metal ions, and they have been used as carriers in experimental activated membranes.\textsuperscript{26,27} Resistance to x-rays of some type of polysulphone and polyamides has been studied previously.\textsuperscript{24,25} In the case of aromatic polysulphones, irradiation with x-rays causes the reduction of $\text{-SO}_2$ – groups to sulphur linkages and the reattachment of oxygen species to carbon sites in the chain,\textsuperscript{21–25} whereas polyamides are more resistant to x-rays.\textsuperscript{16} Because the carriers of activated membranes are also organic materials, x-rays could affect their chemical composition as well as the composition of the polymeric matrix.

The aim of the present work is to study possible morphological and chemical modifications on the surface of several polymeric membranes after x-ray irradiation. Membranes were selected among those covering different kinds of materials (polysulphone and polyamide), obtained both commercially and experimentally, as well as activated membranes having organic acids in polyamide top layers.

**EXPERIMENTAL**

**Materials**

Three different types of membrane were studied: two polysulphone membranes, one being a supported ultrafiltration commercial membrane\textsuperscript{32} (PSF) supplied by PRLDESA (Spain) and the other being a symmetric experimental membrane (PSC),\textsuperscript{33} two composite polyamide/polysulphone membranes, one commercial\textsuperscript{15} (NF45) from FilmTec and one experimental\textsuperscript{29} (B0), both having polyamide as the active layer; and two experimental activated membranes (DPA-2 and DTA-2)\textsuperscript{9,10} obtained by adding a given amount of di-2-ethylhexylphosphoric acid (DEHPA) and di-2-ethylhexylidithiophosphoric acid (DTPA), respectively, to B0. Membrane PSC was prepared by Instituto de Polímeros (CSIC, Madrid) and supplied by Professor J. de Abajo. Membranes B0, DPA-2 and DTA-2 were made at Departamento de Química Analítica, Universidad Autónoma de Barcelona (Bellaterra, Spain) and kindly supplied by Dr M. Valiente and Dr M. Muñoz.

**Membrane irradiation**

Non-monochromatic Mg Kz x-rays (300 W, 15 kV, 1253.6 eV) were used for irradiating the membranes. Membranes were studied after different irradiation times (15 $\leq t$ (min) $\leq 180$). Consecutive XPS spectra were recorded after each 15 min, which was considered the minimum time necessary for obtaining good-quality XPS multi-region spectra, including the characteristic element of each type of membrane. At least 12 of these spectra were recorded for each sample, which means that membranes were under the x-ray flux for 3 h.

**Surface chemical and morphological characterization**

High-resolution XPS spectra were recorded at a 45$^\circ$ take-off angle using a Physical Electronics PHI 5700 spectrometer with a concentric hemispherical electron analyser operating in constant pass mode at 29.35 eV. The spectrometer energy scale was calibrated using Cu 2p$_{3/2}$, Ag 3d$_{5/2}$ and Au 4f$_{7/2}$ photoelectron lines at 923.2, 368.3 and 84.0 eV, respectively. Working under such conditions, the full width at half-maximum (FWHM) of the Au 4f$_{7/2}$ line was 1.16 eV. The analysed area was 720 $\mu$m in diameter. The electrostatic charge effect was not corrected during XPS measurements and spectral charge referencing was done against aromatic carbon at 285.0 eV.\textsuperscript{34} Membranes were fixed to the sample holder without adhesive tape and kept overnight at high vacuum in the preparation chamber before they were transferred to the analysis chamber. Residual pressure was always $<5 \times 10^{-6}$ Pa. Short ($<2$ min) survey spectra in the range 0–1200 eV were recorded at 187.85 eV pass energy in order to select the regions of interest. The PHI ACCESS ESCA-V6.0 F software package was used for acquisition and data analysis. A Shirley-type background was subtracted from the signals before determining atomic concentrations using the corresponding area sensitivity factors for each spectral region.\textsuperscript{35} Curve fitting was performed using Gaussian–Lorentzian curves.\textsuperscript{9,10,36} The homogeneity of the surface (between 2 and 9 nm) has been determined previously by measurements at different take-off angles.\textsuperscript{15}

The AFM images were obtained with a Nanoscope Multimode IIIa microscope (Digital Instruments) in tapping mode under room temperature conditions. This method maintains the high resolution achieved in contact mode but minimizes the surface damage, because it eliminates the lateral friction forces. Common silicon NanoprobeTM tapping tips with a high aspect ratio were used, which allow us to minimize the convolution of the tip shape by the membrane surface. A vertical scanner (AS-130V) with a maximum scan size of 130 $\mu$m$^2$ was used. Several images of increasing size resolution from 15 $\mu$m to 1 $\mu$m were recorded for each fresh and 180-min-irradiated membranes. To obtain good-quality images, a scanning speed as low as possible (0.8 Hz) was used. NanoScope v4.23 software was used for recording and analysing the AFM topographic and phase contrast images. The average roughness ($R_a$), which is defined as\textsuperscript{37}

$$R_a = \frac{1}{n} \sum_{i=0}^{n} |Z_i - Z_m|$$  

where $Z_m$ is the mean value of the tip height in each point of the image ($Z_i$) over a reference baseline ($Z$), was determined from 15 $\mu$m AFM topographic images. This value was chosen because a constant value for surface roughness was achieved for the interval between 10 and 18 $\mu$m.

**RESULTS AND DISCUSSION**

**Polysulphone membranes**

Relative atomic concentrations of elements found on the surface of PSF and PSC membranes after different irradiation times are listed in Table 1. Although nitrogen is not a characteristic polysulphone element, it is commonly observed on the surface of polysulphone membranes\textsuperscript{8,32} and it has been attributed to chemical products used in membrane
Table 1. Relative atomic concentrations (%), the S(IV) percentage with respect to total sulphur and the sulphur to oxygen ratio (S/O) for PSF and PSC after different irradiation times $t_i$

<table>
<thead>
<tr>
<th>$t_i$ (min)</th>
<th>PSF</th>
<th>PSC</th>
<th>PSF</th>
<th>PSC</th>
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</thead>
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<tr>
<td></td>
<td>%C</td>
<td>%O</td>
<td>%N</td>
<td>%S</td>
</tr>
<tr>
<td>15</td>
<td>75.3</td>
<td>19.1</td>
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<td>30</td>
<td>76.6</td>
<td>17.9</td>
<td>3.7</td>
<td>1.9</td>
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<td>60</td>
<td>77.6</td>
<td>16.9</td>
<td>3.6</td>
<td>1.9</td>
</tr>
<tr>
<td>105</td>
<td>78.8</td>
<td>15.6</td>
<td>3.4</td>
<td>1.9</td>
</tr>
<tr>
<td>180</td>
<td>80.6</td>
<td>14.4</td>
<td>3.1</td>
<td>1.9</td>
</tr>
</tbody>
</table>

$^a$ Error <2%.
$^b$ Error <4%.
$^c$ Error <2%.
$^d$ Error <6%.

manufacture or added to decrease the polysulphone’s hydrophobic character. The percentage of nitrogen in PSC is lower than in PSF because no additives have been used in the experimental membrane, but silicon impurities were also detected in this case. For both membranes, the percentage of oxygen decreases and the percentage of sulphur slightly increases or remains constant with increasing irradiation times. In the commercial PSF membrane the nitrogen percentage decreases but the percentages of both impurities do not change in the experimental membrane. It should be noticed that sulphur concentration with respect to carbon is higher in the experimental membrane, which suggests that the nitrogen-containing additive is also an organic compound.

For both polysulphone membranes, O 1s spectra only decrease in intensity and increase in breadth due to x-ray action, but S 2p core-level spectra present the more significant changes, as can be observed in Fig. 1 for PSF. After only 15 min of irradiation this signal shows a maximum containing the doublet S 2p$_{3/2}$ and S 2p$_{1/2}$ at 168.2 eV that corresponds to the existence of S(VI) and is assigned to –SO$_2$– (sulphonyl) species.$^{38}$ With increasing irradiation times, the intensity of this band decreases and a new peak at lower binding energy (163.8 eV) appears. For samples irradiated for 15 min a small shoulder (~4% of the total S 2p signal area) can be observed at this position, but after 180 min of irradiation this peak represents 32% of the total area. The area of the new peak increases exponentially with irradiation time. The binding energy of the new peak indicates the presence of S(IV) and it is assigned to –SO– (sulphoxy) groups, which can be formed by reduction of sulphonyl groups. Table 1 also shows the percentages of S(IV) after different irradiation times. This reduction process is accompanied by a loss of oxygen, which agrees with the observed increase of S/O atomic ratio. Reduction of –SO$_2$– groups to sulphur groups has not been observed within the irradiation times used and C–S bonds should not be broken because the total sulphur percentage does not decrease upon irradiation. Therefore, for performing experiments involving x-rays, the measuring time should be minimized to prevent chemical degradation of polysulphone membranes.

Figure 2 shows 1 µm AFM images of fresh and irradiated polysulphone membranes, and the roughness data are listed in Table 2. The morphology of both membranes is different, because a granular surface structure with an average size of 40 nm is observed in PSF but the PSC does not show a well-defined structure. However, no significant differences can be appreciated between fresh and 180-min-irradiated membranes, and only a very slight decrease of roughness occurs, despite the significant chemical modifications.

Polyamide membranes
Atomic concentrations of the polyamide characteristic elements found on NF45 and B0 after different irradiation times are listed in Table 3. As can be seen, in this kind of membrane the experimental sample also presents more impurities than...
the commercial one, but elements other than those characteristics of polyamide were not found in relative concentrations of >1%: sulphur (<0.5%), phosphorus (<0.5%) and chloride (<1%) were found in B0, and only a small amount of sulphur was detected in NF45. Also, an excess of nitrogen (N/O>1) with respect to the polyamide ratio was observed in B0, which also shows the presence of a small amount of nitrogen-containing impurities, although any additional peak appears in the N 1s signals, which are very similar for both membranes. With increasing irradiation time, the oxygen percentage decreases and the nitrogen percentage increases for both membranes, although the variation in NF45 was higher than in B0. The shapes of the multi-region spectra present only very small changes, as can be seen in Fig. 3 for the NF45 membrane. The shoulder of the O 1s signal at high binding energy decreases slightly, which could be due to a slight loss of water owing to both the low pressure in the analysis chamber and the heating induced by the x-ray flux. For membrane B0 the shapes of the C 1s, N 1s and O 1s core-level spectra were almost unaffected by irradiation.

Table 3. Atomic concentrations (%) and N/O ratio for NF45 and B0 after different irradiation times $t_i$

<table>
<thead>
<tr>
<th>$t_i$ (min)</th>
<th>NF45</th>
<th></th>
<th>B0</th>
<th></th>
</tr>
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<tr>
<td></td>
<td>%C</td>
<td>%O</td>
<td>%N</td>
<td>N/O</td>
</tr>
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<td>7.2</td>
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</tr>
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<td>7.6</td>
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<tr>
<td>165</td>
<td>77.7</td>
<td>13.8</td>
<td>8.5</td>
<td>0.616</td>
</tr>
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</table>

$^a$ Error ~1%.
$^b$ Error <4%.
$^c$ Error <3%.
$^d$ Error <1%.
Figure 3. Comparison of $C\, 1s$, $O\, 1s$ and $N\, 1s$ core-level spectra for NF45 after 15 and 180 min of irradiation.

Figure 4. The AFM 1 $\mu$m images of the commercial polyamide membrane NF45, both fresh (left) and after 180 min of irradiation (right).

Morphology does not change significantly, as can be seen in Fig. 4 for NF45, although a very slight increase in the roughness of both composite membranes is observed after 180 min of Mg $K\alpha$ radiation (Table 2). Similar to the polysulphone membranes, the commercial polyamide membrane presents a granular surface with 125 nm average size but an ill-defined structure is observed in the experimental membrane. Both experimental and commercial polyamide membranes have a higher roughness than polysulphone membranes, which has been attributed to fluctuations at the interface between aqueous and organic phases during the interfacial polycondensation of the polyamide thin layer. As expected, polyamide surfaces are more stable against x-ray irradiation because only the hydration state of the membrane seems to be altered.

Activated membranes

Table 4 shows the evolution of atomic concentrations with irradiation time for membranes DPA-2 and DTA-2. For both membranes the phosphorus and oxygen percentages increase slightly, but for the DTA-2 sample the percentage of sulphur also increases; then, the concentration of organic acid characteristic elements increases on the surface of both membranes. The shapes of photoelectronic signals for both...
Table 4. Atomic concentrations (%) and N/P ratio for both activated membranes (DPA-2 and DTA-2) at different irradiation times $t_i$

<table>
<thead>
<tr>
<th>$t_i$ (min)</th>
<th>DPA-2</th>
<th></th>
<th>DTA-2</th>
<th></th>
<th></th>
<th></th>
</tr>
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<tbody>
<tr>
<td></td>
<td>%C&lt;sup&gt;a&lt;/sup&gt;</td>
<td>%O&lt;sup&gt;b&lt;/sup&gt;</td>
<td>%N&lt;sup&gt;c&lt;/sup&gt;</td>
<td>%P&lt;sup&gt;d&lt;/sup&gt;</td>
<td>N/P</td>
<td>%C&lt;sup&gt;e&lt;/sup&gt;</td>
</tr>
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<td>76.5</td>
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<td>0.690</td>
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<tr>
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<td>0.636</td>
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</tr>
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<td>4.5</td>
<td>0.622</td>
<td>74.8</td>
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<td>4.6</td>
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<tr>
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</tr>
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<td>2.7</td>
<td>5.3</td>
<td>0.509</td>
<td>73.5</td>
</tr>
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</table>

<sup>a</sup> Error <0.5%.  
<sup>b</sup> Error <4%.  
<sup>c</sup> Error <10%.  
<sup>d</sup> Error <6%.  
<sup>e</sup> Error <1%.  
<sup>f</sup> Error <5%.  
<sup>g</sup> Error <3%.  
<sup>h</sup> Error <8%.

Figure 5. Comparison of C 1s, O 1s, N 1s and P 2p core-level spectra recorded on DPA-2 after 15 and 180 min of irradiation.

activated membranes are modified upon irradiation, as can be seen in Figs 5 and 6 for DPA-2 and DTA-2, respectively. In the case of DTA-2, the percentage of nitrogen atoms with lower electronic density (peak at higher binding energy) increases for the 180-min-irradiated membranes and the maximum of the P 2p signal shifts slightly to a higher binding energy. Because the polyamide matrix is not greatly modified, as shown previously, these results suggest that x-ray radiation is able to modify the amount of carrier molecules ionically interacting with the polyamide matrix. No other significant changes are observed in the P 2p or N 1s spectra that could clearly indicate degradation of DEHPA molecules. For membrane DTA-2, a notorious modification of the S 2p core-level spectrum after 180 min...
of irradiation can be observed in Fig. 6. The S 2p signal of the 15-min-irradiated membrane shows three peaks (see Fig. 6(b)): a peak at 162.3 eV that can be assigned to sulphur as S(-II) of carrier molecules ionically bonded to the polyamide and sulphur double-bonded to phosphorus in the free acid; a peak at 163.6 eV assigned to S(IV); and a peak at 168.2 eV that corresponds to S(VI), which indicates the existence of sulphur in a high oxygen environment, such as sulphate or sulphonate groups. The latter types of sulphur would be associated with impurities or to the support of

Figure 6. (a) The S 2p, O 1s, N 1s and P 2p core-level spectra for DTA-2 after 15 and 180 min of irradiation. (b) Curve-fit analysis for the S 2p spectra.
polysulphone. After 180 min of irradiation the intensity of the peak at low binding energy, i.e. S(-II), remains almost constant but the intensity of the S(VI) peak decreases with a concomitant increase in the intensity of the S(IV) peak. These results seem to indicate a photodegradation of the impurities or of the polysulphone of the support. The x-ray irradiation provokes a reduction of the sulphonyl groups to sulphoxyl groups.

Roughness data in Table 2 show that both activated membranes are less rough than membrane B0, which indicates the influence of the addition of the carrier in the miscibility between aqueous and organic phases during the polymerization process. The DPA-2 membrane is less rough than the DTA-2 membrane, but any well-defined structure can be distinguished on the surface of both membranes, as can be seen in Fig. 7. Upon irradiation the average roughness of both membranes increases, therefore both morphological and chemical changes occur on the surface of activated membranes due to long-term x-ray irradiation.

CONCLUSIONS

The effect of x-ray flux on the chemical and structural stability of the top layer of three types of polymeric membranes (polysulphone, composite polyamide/polysulphone and activated with organic carriers) has been studied by XPS and AFM. Polyamide membranes are resistant to irradiation, but polysulphone and activated membranes are not chemically stable because long-term Mg Kα x-ray irradiation modifies their chemical surfaces. In fact, x-ray irradiation of polysulphone membranes causes a reduction of sulphonyl groups (–SO₂–) to sulphoxyl groups (–SO–). Therefore, irradiation times must be minimized for performing XPS in these types of membranes. Recording times of 15–20 minutes have been found to be a good compromise between good-quality XPS spectra and x-ray-induced damage. The study of fresh and 180-min-irradiated membranes by AFM reveals that chemical degradation of polysulphone membranes does not affect their surface morphology but the average roughness of activated membranes increases, probably due to photodegradation of their surfaces.

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REFERENCES