

Surface Modification of a Polyurethane Film by Low Pressure Glow Discharge Oxygen Plasma Treatment

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ABSTRACT: Low pressure oxygen plasma has been used to improve the surface wettability of a polyurethane film. The modifications induced by the plasma treatment in the material were analyzed using contact angle measurements. X-ray photoelectron spectroscopy technique was used for surface characterization of the plasma-treated films. Atomic force microscopy and scanning electron microscopy were used to analyze topography changes due to the plasma-etching mechanism. The results show a much better surface wettability of the film even for short exposure times, with a considerable increase in the surface energy values. As expected, functionalization with oxygen

plasma is mainly because of surface oxidation with species like (C—O, C=O, OH, etc). An aging process with regard to polar groups rearrangement has been observed, thus promoting a partial hydrophobic recovery. Besides functionalization, the surface wettability of the material improves as a consequence of a slight increase in surface roughness because of the etching effect of oxygen plasma. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 105: 1077–1085, 2007

Key words: surfaces; polyurethanes; films; aging; cold plasma

INTRODUCTION

Among the wide variety of technical and high-performance plastics used in industry, thermoplastic polyurethane-based polymers find growing use in technological applications because of an excellent balance between mechanical, thermal, and chemical properties together with high biocompatibility and excellent flow properties.^{1–3} All this has favored the growing use of polyurethanes in the automotive industry, as this sector requires materials with high mechanical performance, excellent thermal stability, and good barrier response against chemical agents and aggressive conditions (mainly temperature and humidity).^{4–6} Some of such applications include back-support systems, headliners, rear parcel shelves, molded floor carpets, etc. Polyurethane films are also used laminated with other materials to obtain the required properties. Laminate manufacturing requires good adhesive properties of the bonding materials. Polymeric materials present low surface energy, which negatively affects their adhesive properties; as a result these polymers present poor adhesive properties. For use in industrial applications, the surface

properties of these materials have to be improved by different treatments (chemical, thermal, electrical) or additives.^{7–9} These treatments improve surface wettability by increasing the hydrophilic nature of the film surface. Some of the advantages resulting from this improved hydrophilic behavior of the material are better biocompatibility and much better adhesive properties because of an increase in the surface activity of the polymer.^{10–13}

In the past decades, plasma treatments have been successfully used to modify surface wettability in polymers,^{14,15} with the additional advantage of being environmental-friendly and easy to implement. The use of low pressure conditions allows the application of plasma treatments at low or moderate temperatures. It is possible to promote glow discharge by either radio frequency (RF) or microwave, but at industrial level RF excitation is preferred for surface modification.^{16–19} The different species present in the plasma induce the formation of free radicals on the polymeric chains, and in this way it is possible to interlock certain functional groups on the polymeric surface depending on the gas used and on the general conditions of the treatment, and this will have a positive effect on the functionalization/activation of the polymer surface.

The objective of this work is to improve surface wettability in a polyurethane film for industrial applications. Surface functionalization was analyzed

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using X-ray photoelectron spectroscopy (XPS), and surface topography was analyzed using scanning electron microscopy (SEM) and atomic force microscopy (AFM) techniques. In addition, the aging of the plasma-treated samples was analyzed to assess the durability of the treatment by contact angle measurements.

EXPERIMENTAL

Materials and sample preparation

The film used for the study was a transparent ester type polyurethane film Walopur 2102 AK 050, supplied by Epurex Films (Epurex Films GmbH and Co, Walsrode, Germany) which is suitable for automotive applications with a density $\rho = 1.21 \text{ g cm}^{-3}$. Double distilled water and glycerol with AR grade were used as test liquids for contact angle measurements. Samples of $20 \times 20 \text{ cm}^2$ in size were prepared for the plasma treatment and after this, samples of different dimensions were cut for the different measurements.

Low pressure RF plasma treatment

Polyurethane films were exposed to a RF low pressure oxygen plasma to change wettability properties. It was used a glow discharge RF generator (operating at 13.56 MHz with a maximum power of 600 W) type CD 400 MC option PC (Europlasma, Oudenaarde, Belgium), which is specially appropriate for surface modification of small size technical parts; the plasma chamber consists of a four aluminum shelves for sample holders and a volume of 64 L. The gas used for the plasma generation was oxygen, and the working power was fixed to 300 W since higher power values promote important overheating that can perform changes in structure and unnecessary surface degradation. All samples were placed on the upper shelf to obtain comparative results, since some differences were observed regarding sample position. Samples were exposed to O_2 low pressure plasma for different times ranging from 1 to 30 min. It was used an oxygen flow rate of $100 \text{ cm}^3 \text{ min}^{-1}$ and the working pressure varied in the 31–32 Pa range. All posterior measurements were carried as soon as possible to avoid aging processes.

XPS surface analysis

The XPS spectra were obtained with a VG-Microtech Multilab electron spectrometer (Thermo Fisher Scientific, Waltham) by using the Mg K_α (1253.6 eV) radiation of twin anode in the constant analyzer energy mode with pass energy of 50 eV. Pressure of the analysis chamber was maintained at $5 \times 10^{-8} \text{ Pa}$.

The binding energy (BE) scale was regulated by setting the C1s transition at 285.0 eV. The accuracy of BE values was $\pm 0.2 \text{ eV}$. The BE values were obtained by using the Peak-fit Program implemented in the control software of the spectrometer.

Contact angle measurements and surface energies estimation

Static contact angle measurements of the plasma-treated samples were carried out at room temperature on a KSV CAM 200 goniometer (KSV Instruments, Helsinki, Finland) using two different test liquids: water and glycerol. At least six different measurements on the plasma treated surfaces were obtained and the average values for contact angles were calculated. The maximum error in the contact angle measurement did not exceed $\pm 3\%$.

Surface energies were calculated using the Owens–Wend method derived from the general theory of adhesion work (W_{sl}) among solid and liquid phases on which polar and nonpolar (dispersive) contributions are considered to explain interactions among the two phases.²⁰ In this method, it is possible to determine the solid surface energy (γ) as the sum of polar (γ^p) and dispersive (γ^d) contribution using at least two different test liquids. The relationship between the equilibrium contact angle of the liquid phase deposited onto a solid phase is derived from the general Fowkes expression, which considers the polar and dispersive contributions for both solid and liquid designed as γ_l and γ_s with a superscript “d” or “p” for the dispersive and polar contributions, respectively.^{21,22}

$$W_{sl} = \gamma_l(1 + \cos \theta) = 2(\gamma_l^d \gamma_s^d)^{1/2} + 2(\gamma_l^p \gamma_s^p)^{1/2} \quad (1)$$

Constant values for the two test liquids used for contact angle measurements are as follows:

$$\begin{aligned} \text{Water: } \gamma_l &= 72.8 \text{ mJ m}^{-2}, \gamma_l^d = 21.8 \text{ mJ m}^{-2}, \gamma_l^p \\ &= 51.0 \text{ mJ m}^{-2} \\ \text{Glycerol: } \gamma_l &= 64.0 \text{ mJ m}^{-2}, \gamma_l^d = 34.0 \text{ mJ m}^{-2}, \gamma_l^p \\ &= 30.0 \text{ mJ m}^{-2} \end{aligned}$$

Surface morphology study

Morphology analysis of the plasma treated surfaces for different exposure times was carried out by means of a scanning electron microscope Jeol JSM-6300 (Jeol USA, Peabody) using secondary electrons. Samples were covered with a 5–7 nm Au layer in vacuum conditions prior to each measurement. AFM was used to determine surface topography and roughness of the plasma-treated samples. AFM analysis was performed on a Multimode AFM micro-

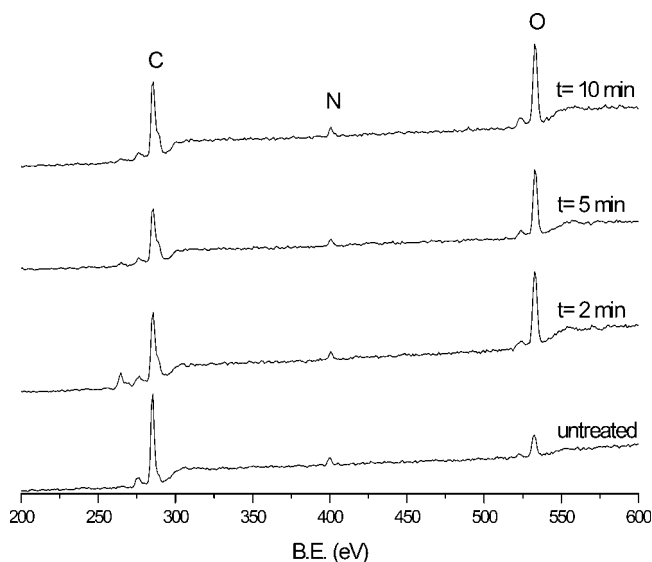


Figure 1 Survey (low resolution) XPS scans of polyurethane with different exposure times to oxygen plasma.

scope with a Nanoscope IIIa AD/CS controller (Veeco Metrology Group, Cambridge, United Kingdom). A monolithic silicon cantilever (NanoWorld Pointprobe[®] NCH) with a force constant of 42 N m^{-1} , and a resonance frequency of 320 kHz was used to work on tapping mode. From the analysis of the images, the root-mean-squared roughness (R_{rms}) for the topographic profiles measured on $5 \mu\text{m} \times 5 \mu\text{m}$ images were evaluated.

RESULTS AND DISCUSSION

Characterization of chemical surface changes

O_2 plasma treatment induces surface functionalization as a consequence of the interlock of oxygen-based polar species resulting from the interaction of the film surface with the species present in the oxygen plasma gas. Some of these species promote polymer chain scission thus promoting the formation of free radicals, highly instable, that act as insertion points of polar species since they have a tendency to react with oxygen.²³ The low-resolution XPS scans (Fig. 1) show the peaks corresponding to carbon (C 1s), oxygen (O 1s) and nitrogen (N 1s). It is easy to observe some differences between the untreated film and the plasma-treated films for different exposure times. Plasma-treated samples present a considerable increase in the O 1s transition regarding C 1s, whereas the peak corresponding to N 1s is almost independent of the exposure time to O_2 plasma. This fact corroborates the assumption that functionalization is caused by the interlock of oxygen-based species on the surface of the plasma-treated samples.

The main oxygen-based species achieved by the plasma treatment are $(-\text{C}-\text{O}-\text{C})$ and $(-\text{C}=\text{O})$ groups, as XPS analysis reveals.^{24,25} The C 1s spectrum of untreated polyurethane can be resolved into four contributions [Fig. 2(a)].^{1,26-29} The peak corresponding to the lowest BE (285.0 eV) corresponds to $(-\text{C}-\text{C}-)$ and $(-\text{C}-\text{H})$ species; the peak located at 286.3 eV corresponds to carbon atoms single-bonded to oxygen atoms $(-\text{C}-\text{O}-\text{C}-)$; the peak

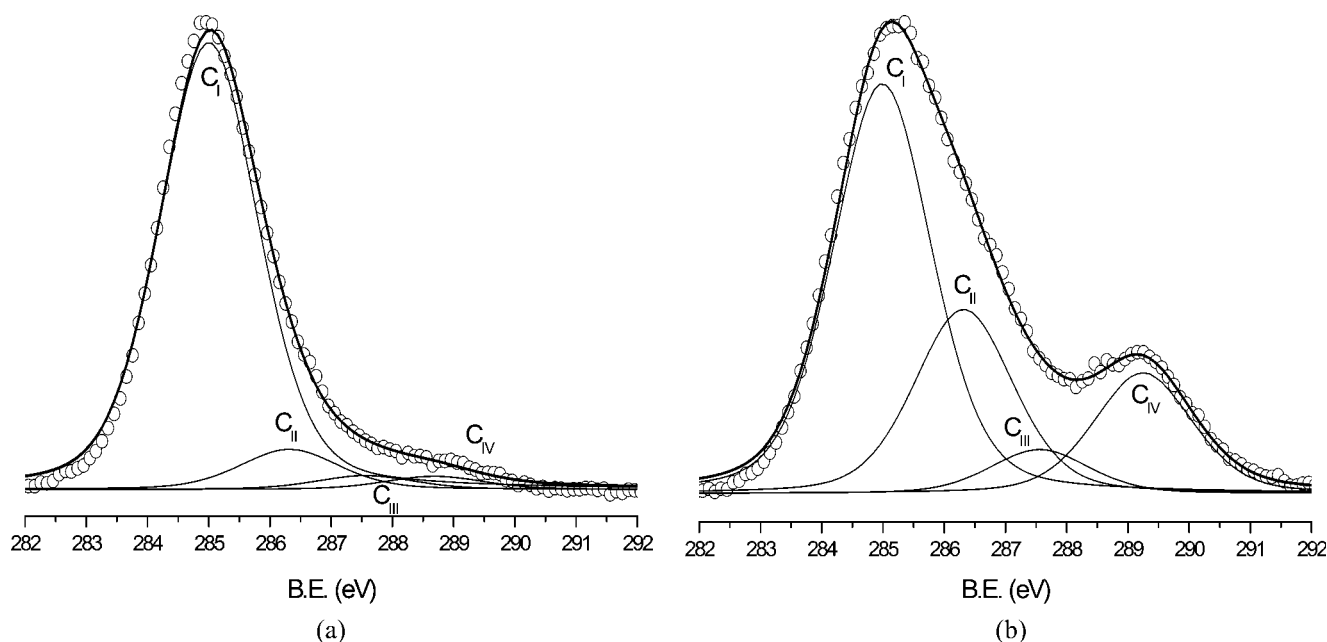


Figure 2 High resolution XPS spectra showing the deconvoluted C 1s envelope for: (a) untreated polyurethane, (b) 5 min oxygen plasma exposure.

TABLE I
Surface Composition (Atomic %) of Oxygen Plasma Treated Polyurethane for Different Exposure Times Obtained by XPS Analysis

Exposure time (min)	C	O	N	O/C ratio
0	86.4	9.5	4.1	0.11
2	68.7	27.1	4.2	0.39
5	68.8	27.0	4.2	0.39
10	70.4	25.6	3.9	0.36

located at 289.2 eV corresponds to carbon atoms of carbamate groups ($-\text{N}-\text{CO}-\text{O}-$); and a small peak around 287.6 eV can be assigned to some urea groups ($-\text{N}-\text{CO}-\text{N}-$). The C 1s spectrum of plasma-treated polyurethane clearly illustrates the oxygen-based functionalization of the material after O_2 plasma treatment. As illustrated in [Fig. 2(b)], the peaks corresponding to the oxygen-containing carbon atoms (single or double bonded) are much higher in the treated samples than in the untreated material, while the contribution of the nitrogen-containing carbon atoms remains practically constant, as expected. The surface atomic composition of the polyurethane for different exposure times to oxygen plasma is listed in Table I. Surface functionalization is practically independent of exposure time to oxygen plasma, with almost constant oxygen contents (26–27 atomic %) in all the plasma-treated samples. The global oxidation can be observed following the evolution of the O/C ratio since together with oxygen insertion, some carbon atoms are removed with the plasma action. The initial oxidation ratio, close to 0.11 reaches values up to 0.39 for relative short exposure times. In this sense it is convenient to note that long exposure times do not result in a higher surface activation by interlock of polar groups.

It is important to note that this oxidation process promoted by the plasma treatment is, in part, similar to that obtained as a result of photo-degradation processes, which also contribute to the addition of oxygen-based species.³⁰

Changes in surface wettability

Oxygen-plasma treatment improves surface wettability by the interlock of hydrophilic species on the surface (oxygen-containing species). This improvement in surface wettability can be observed by analyzing the variation of the contact angles versus plasma exposure times (Fig. 3). The different test liquids showed a similar behavior. The initial contact angles, 87.0° and 91.9° , for water and glycerol respectively, significantly decrease for short exposure times (35° and 45° for water and glycerol respectively) and remain constant for long exposure times. This behavior is similar to other polymer films.^{27,31,32}

These results are consistent with those obtained by XPS, since long exposure times do not lead to higher oxidation ratios (which remains almost constant), thus we can observe a rapid increase in wettability (decrease in contact angle values) for short exposure times while no significant changes are observed for longer times.

It is also important to emphasize that in plasma-treated films, the contact angles of both test liquids are higher than those corresponding to a situation of total wettability with contact angle values near 0° ; this indicates that oxygen plasma promotes the formation of polar species on the polyurethane surface. The surface energy of the untreated polyurethane surface is about 26 mJ m^{-2} with low polar contribution. Oxygen plasma treatment increases surface energies up to 70 mJ m^{-2} with a remarkable increase in polar contribution, while the dispersive contribution represents low values as it can be observed in Table II.³³

Bearing in mind that the main acting mechanism of plasma is surface functionalization, it is important to determine the durability of the treatment and to analyze the changes in surface wettability by aging. The aging process of the plasma-treated surfaces is closely related to the rearrangement of the different polar groups interlocked on the film surface because of their instability. With time, the different dipoles rearrange towards the bulk material until they reach a more stable structure, thus reducing the wettability of the plasma-treated surface.^{12,34,35} This in turn reduces the hydrophilic nature of the plasma-treated surface, and that is why this process is known as "hydrophobic recovery." Figures 4 and 5 show the hydrophobic recovery of the plasma-treated polyur-

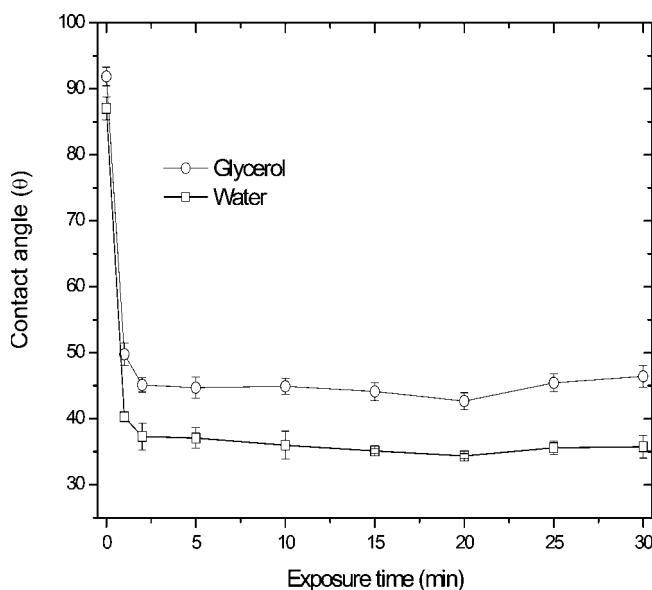


Figure 3 Variation of the static contact angle of polyurethane surface versus exposure time to oxygen plasma.

TABLE II
Surface Energies (Polar and Nonpolar Contributions) of a Plasma-Treated Polyurethane Film in Terms of the Exposure Time to Oxygen Plasma

Exposure time (min)	γ_s (mJ m^{-2})	γ_s^p (mJ m^{-2})	γ_s^d (mJ m^{-2})
0	25.6	25.1	0.5
1	68.2	66.3	1.9
2	67.6	64.2	3.4
5	67.3	63.8	3.5
10	69.7	66.8	2.9
15	70.1	67.1	3.0
20	69.6	66.1	3.5
25	71.0	68.6	2.4
30	72.1	70.2	1.9

ethane surfaces for different test liquids. In both cases, i.e., water and glycerol, a similar behavior was observed. Hydrophobic recovery is a diffusion controlled process^{23,36–38}; aging occurs in the following days after plasma treatment, reaching an asymptotic value after one week. It is important to note that the surface of the material does not completely lose the hydrophilic nature gained during the plasma treatment mainly because of the fact that oxygen plasma also causes surface etching, which allows the surface to maintain certain wettability with time.

Changes in surface topography

One plasma-acting mechanism is material removing or etching.^{12,39} Oxidizing plasmas are characterized

by significant surface etching, which causes changes in surface roughness and contributes to improve surface wettability.

As exposure time increases, the etching effect of the plasma increases in an exponential form. This situation induces changes in surface roughness that can be appreciated by observing SEM images for different oxygen plasma-treated polyurethane films (Fig. 6). SEM micrographs show a small variation in surface roughness and appearance of microcracks for high exposure times,^{26,40} although the data available is not enough for quantitative analysis.

However, oxygen plasma treatment induced changes in the surface roughness of the plasma-treated samples for short and medium exposure times. On the other hand, the samples exposed to oxygen plasma for longer times (30 min) showed a surface morphology different to that of the samples treated for shorter times. These effects are evident from the observation of weight loss as a function of the exposure time. The aggressiveness of oxygen plasma causes important surface etching. Surface roughness in untreated polyurethane is about 2.0 nm (R_{rms} values taken from a $5 \times 5 \mu\text{m}^2$ section); the 10 min-exposure sample shows surface roughness values of about 2.7 nm; however the samples exposed to longer times present much higher surface roughness values (13.5 and 21.6 nm for 20 and 30 min exposure, respectively). These results agree with the exponential weight loss values observed in Figure 7.

The 3D AFM representations of the surfaces of the different plasma-treated polyurethanes for different exposure times (Fig. 8) clearly show the changes in

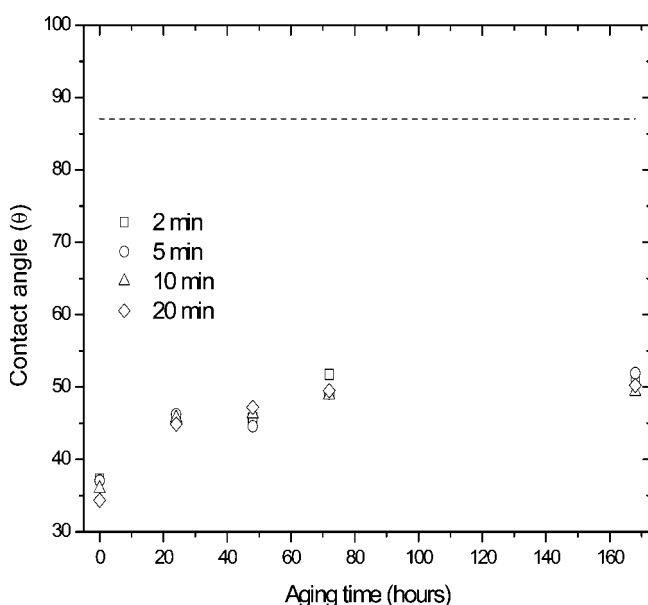


Figure 4 Variation of the water static contact angle values versus aging time for polyurethane film with different exposure times to oxygen plasma.

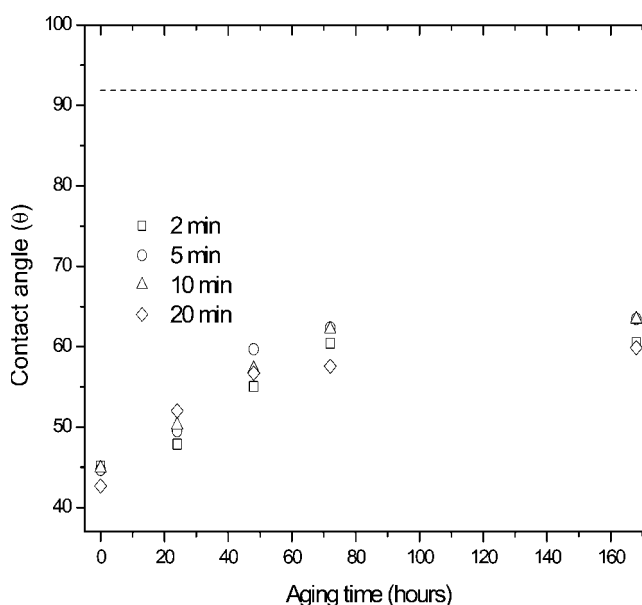


Figure 5 Variation of the glycerol static contact angle values versus aging time for polyurethane films with different exposure times to oxygen plasma.

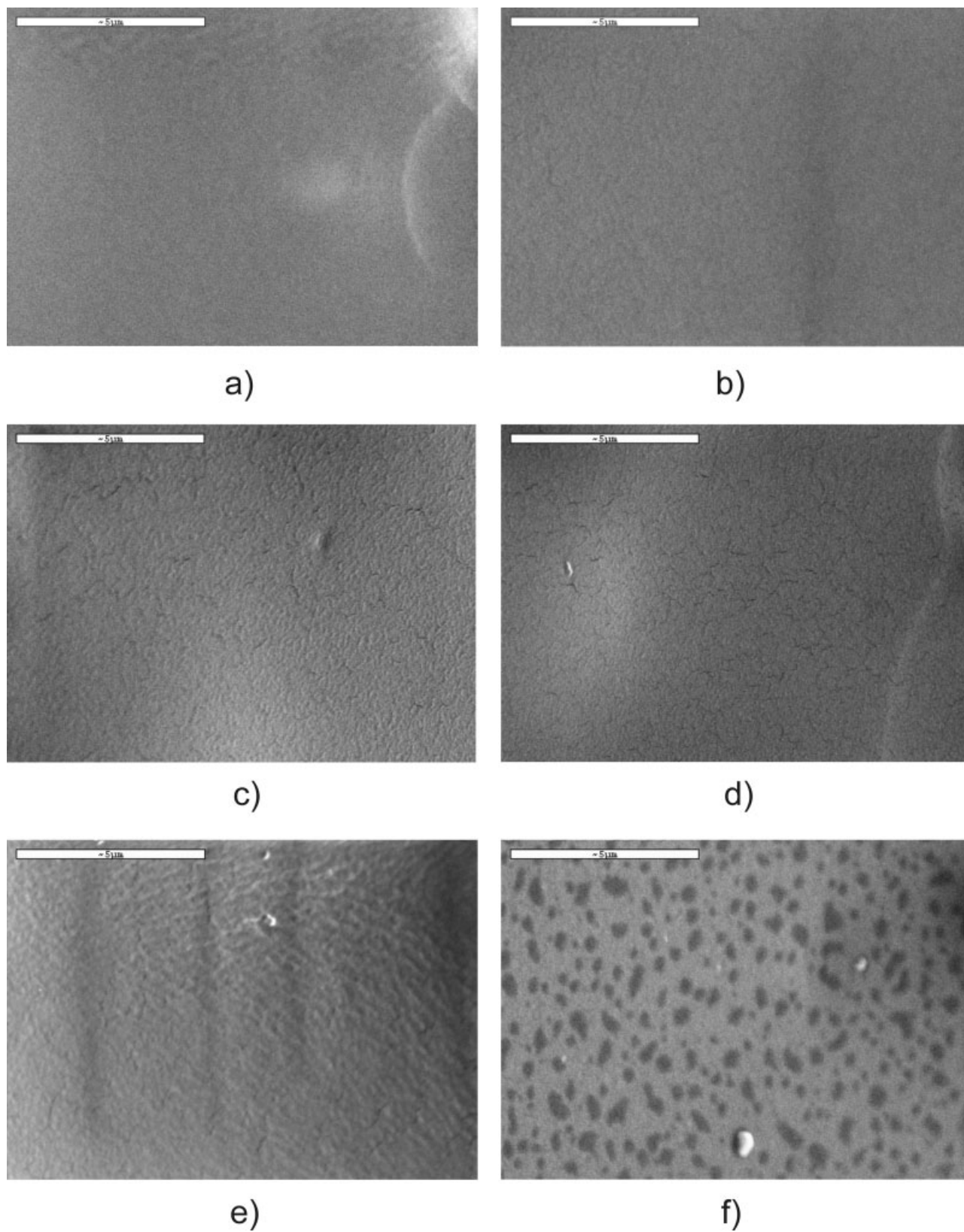


Figure 6 SEM micrographs of polyurethane film with different exposure times to oxygen plasma ($\times 10,000$); (a) untreated; (b) 1 min; (c) 2 min; (d) 10 min; (e) 20 min; (f) 30 min.

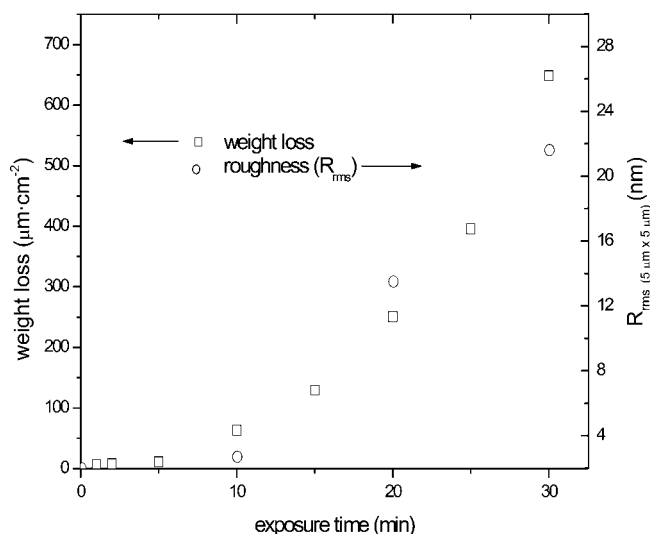


Figure 7 Plot of the evolution of the polyurethane weight loss and surface roughness (R_{rms}) versus exposure time to oxygen plasma.

surface topography as a result of the etching process induced by the oxygen plasma. It can be noted that the samples treated for shorter times present

changes in surface roughness, which improves the wettability properties of the material as observed in other polymer films.^{2,41} However, as O_2 plasma exposure time increases, there is an exponential increase of surface etching, which increases surface degradation.

Figure 9 compares the changes in surface roughness of a polyurethane film at different exposure times to oxygen plasma. Surface roughness increases as exposure time increases. In addition, longer exposure times (more than 20 min) cause important changes in the surface topography of the sample, reaching roughness values much higher than for shorter exposure times.

CONCLUSIONS

Oxygen plasma notably improves surface wettability even for short exposure times, which in turn results in a significant increase in surface energy. The high contribution of the polar component indicates that the main plasma-acting mechanism of the oxygen plasma is surface functionalization by the interlock of polar species since a great increase in wettability is obtained even for short exposure times.

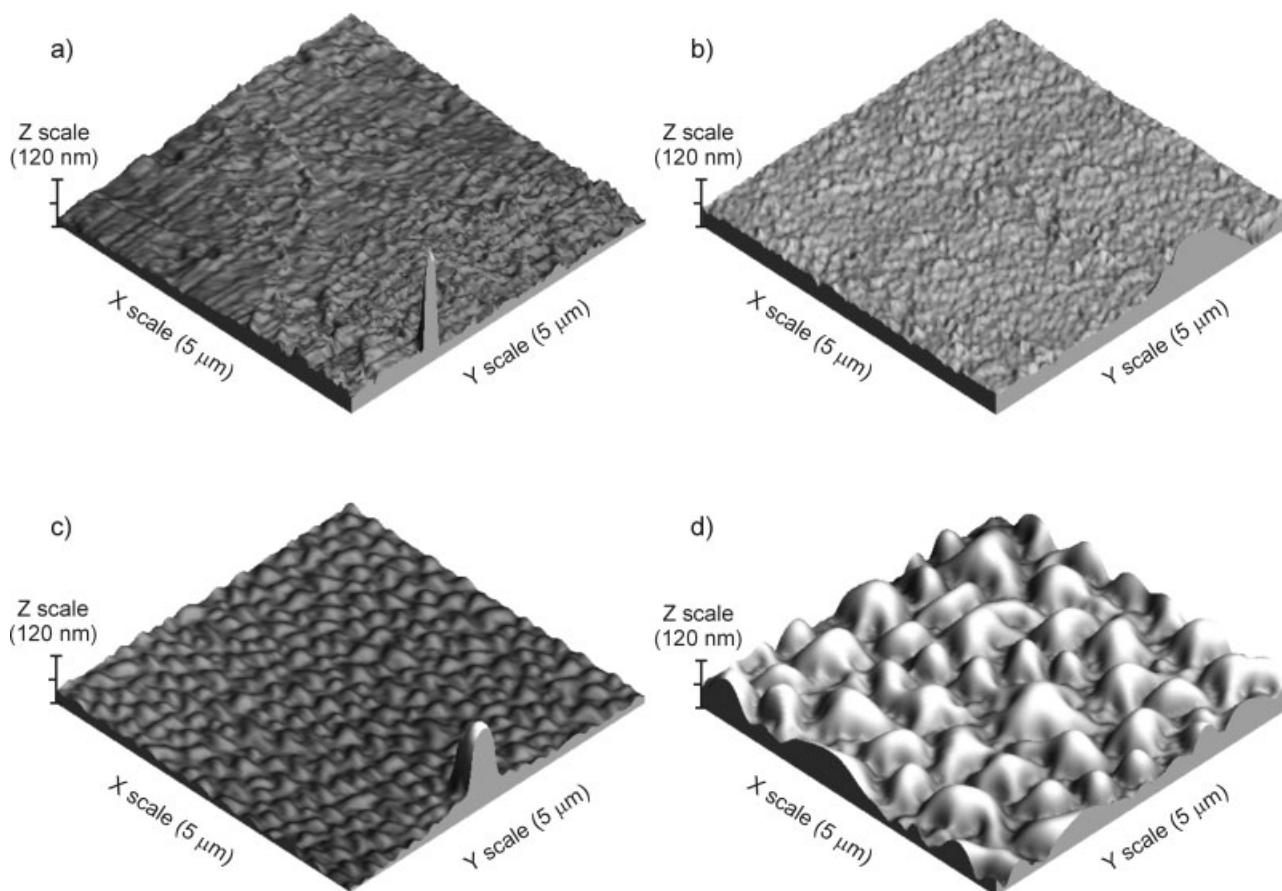


Figure 8 AFM 3D-topographic images of polyurethane film with different exposure times to oxygen plasma; (a) untreated; (b) 10 min; (c) 20 min; (d) 30 min.

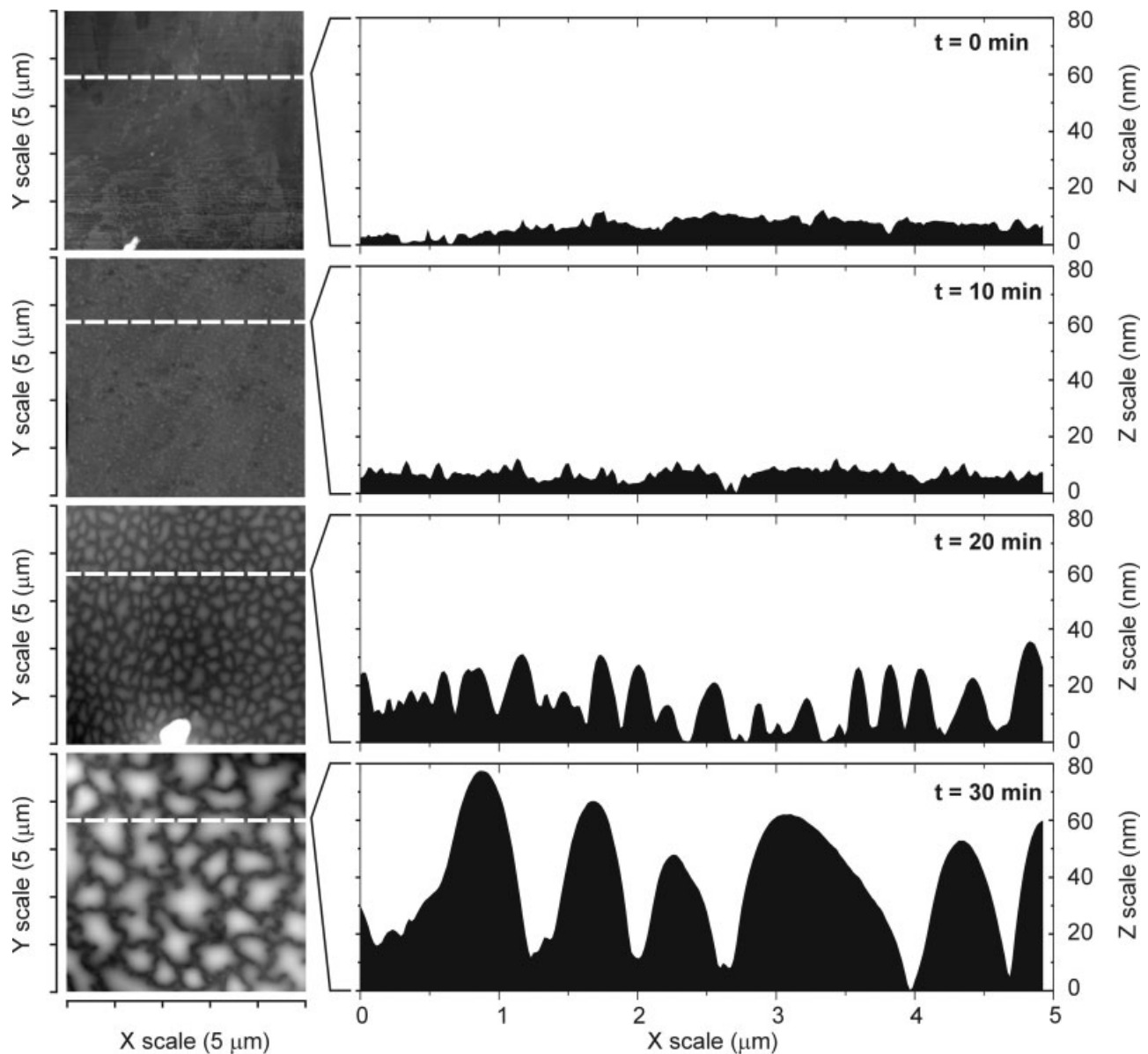


Figure 9 Roughness profiles of polyurethane surface with different exposure times to oxygen plasma.

Together with surface functionalization, some roughness changes can be observed but do not contribute in a significant way to improve wettability properties. Another aspect to take into account is that plasma treatment is not permanent; with time, hydrophobic recovery occurs and this has to be taken into account for the optimization of the adhesive properties of polyurethane films. We can conclude that low pressure glow discharge oxygen plasma treatment is an efficient method from a technical point of view for the modification of the surface properties of polyurethane films since produces an important increase in surface wettability. Furthermore, oxygen plasma treatment is an environmentally friendly process since waste generation is almost reduced to minimum.

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