

Surface Modification of a Thermoplastic Polyurethane by Low-Pressure Plasma Treatment to Improve Hydrophilicity

Patrícia Alves, Susana Pinto, Hermínio C. de Sousa, Maria Helena Gil

Department of Chemical Engineering, University of Coimbra, Rua Sílvio Lima, Polo II, 3030-790, Coimbra, Portugal

Received 17 November 2010; accepted 14 February 2011

DOI 10.1002/app.34348

Published online 16 June 2011 in Wiley Online Library (wileyonlinelibrary.com).

ABSTRACT: The performance of a material in a biological environment is mainly mediated by its surface properties and the combination of chemical, physical, biological, and mechanical properties required for a specific application. In this study, the surface of a thermoplastic polyurethane (TPU) material (Elastollan®1180A50) was successfully modified by plasma treatment. Two different working gases were studied: argon and oxygen, which promoted the incorporation of oxygen-containing groups on the surface. The optimal plasma parameters were investigated by evaluating the wettability of the surfaces. Changes in the surface functional groups chemistry were studied using X-ray photoelec-

tron spectroscopy (XPS). The obtained results showed that the plasma treatment process caused surface modifications that, in all cases, increased the polar nature of the surface. In terms of the desirable properties, it was found that the best operational conditions were: 100 W gas plasma, under a pressure of 60 Pa for 3 min. Argon seems to be more efficient than oxygen, because lower water contact angle results were obtained. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 122: 2302–2308, 2011

Key words: thermoplastic polyurethanes; surface modification; contact angle; argon plasma; oxygen plasma

INTRODUCTION

In the last few years, polymeric materials have been widely used as biomaterials. However, only a few commercial materials exhibit, as a bulk material, the optimal characteristics for some specific biomedical applications.¹ When implanted in biological environment, these materials might be covered by proteins or colonized by cells or microorganisms (biofouling) depending on the environment.^{2,3} Surface modification is a way to overcome this problem. Although, on surfaces with higher or lower wettabilities, cell adhesion decrease.^{4,5}

For biomedical applications, the most important surface properties include the chemical structure (hydrophilicity and presence of groups that could initiate reaction in biological systems) and the morphology (the distribution and abundance of hydrophilic/hydrophobic and crystalline/amorphous phases and surface topography).⁵ Biomaterial surface hydrophilicity (or hydrophobicity) influences biocompatibility.⁶ Hydrophilicity may be the initial parameter affecting protein adsorption. It is well known that hydrophobic surfaces thermodynamically favor the adsorption of proteins from aqueous solutions, but

may induce strongly irreversible adsorption and also denature the protein native conformation and its bioactivity. On the other hand, a highly hydrophilic surface may repulse any protein molecules and thus inhibits protein adsorption. It is known that cell adhesion increase by decreasing the water contact angle of the material surface to around 70°. ^{4,7–9} Maximal cell adhesion occurs on surfaces with moderated water contact angle. Due to their physical, chemical, and degradation properties, polyurethanes are seen as being potential, optimal materials for various implant applications (e.g., endoprostheses, cardiac valves, and/or regenerative membranes for damaged internal organs). They do not induce any inflammatory condition of tissues, and in some cases, they do not suffer any kind of degradation by body fluids.^{10–12}

In this work, a commercial preprocessed polyurethane—Elastollan®1180A50 [polyether-based thermoplastic polyurethane (TPU)]—was used as support for the modifications. TPU are currently used in several industrial branches in particular as coating, adhesives, engineering materials, and films.¹³ They have excellent mechanical properties, chemical stability, easy processing and can be used in biomedical application (e.g., as catheters and artificial vein).¹⁴ This material was chosen not only due to its high mechanical flexibility but also due to its properties (free from plasticizers and good heat resistance). Elastollan®1180A50 exhibits excellent abrasion

Correspondence to: P. Alves (palves@eq.uc.pt).

resistance, toughness, transparency, hydrolytic stability, and fungus resistance.¹⁵

Plasma treatment is able to change the surface energy of polymers, by changing their wettability and polarity.¹⁶ In plasma treatments, the exact control of the process conditions, such as plasma working gas, time of reaction, and pressure in the plasma chamber, allow high surface homogeneity. Due to the plasma nature, its mechanism is very complex, but the main effects achieved are surface cleaning, activation, crosslinking, etching, or, in most cases, combined effects.¹⁷ Plasma irradiation promotes the formation of free radicals that can act as interlock points for active species (polar groups).¹⁸

According to the gas used in the plasma treatment, plasma can by itself introduce groups at the surface or can be used to activate surface for subsequent linkage of water soluble polymer chains that are known to suppress biofouling. In this work, a commercial polyurethane was studied, this is a material of easy access with controlled bulk properties and which could be easily used in several applications if this surface could be adapted (or modified). Therefore, the aim of the present study was to evaluate the influence of argon and oxygen plasma parameters on the hydrophilicity of TPU film, and to study the functionalization/activation phenomena with the intent of improving hydrophilicity to enlarge the application of this material mainly in the biomedical field but also, for example, in automotive and shoe industry. In addition, the durability of the plasma treatment as a consequence of the hydrophobic recovery due to the rearrangement of the polar groups generated during and after the plasma treatment was also evaluated.

EXPERIMENTAL

Materials

The solvents, isopropyl alcohol and dimethylformamide (DMF), were obtained from José Vaz Pereira, S.A, Portugal. Elastollan[®]1180A50 was obtained from BASF (Germany). All of the chemicals were used as received.

Methods

Films preparation

Elastollan[®]1180A50 films were prepared by solvent evaporation. Elastollan[®]1180A50 was dissolved in DMF to a 10% (w/v) solution. This solution was poured into glass Petri plates. Then, the Petri dishes were stored in an oven, at 60°C for 24 h. Afterwards, films were removed from the dishes.

Elastollan[®]1180A50 films were ultrasonically cleaned with isopropyl alcohol for 15 min, prior to surface grafting experiments.

Plasma surface modification

A laboratory and small-scale production plasma system FEMTO (low-pressure plasma), manufactured by Diener Electronics (Germany), with a stainless steel plasma chamber of 100 mm diameter and 270 mm length, was used for the plasma surface modification experiments. The TPU films were placed 80 mm from the electrode. Various parameters were analyzed to evaluate the effects of plasma treatment, namely working gas (oxygen and argon), chamber pressure (40–200 Pa), time of irradiation (1–5 min), and power of plasma (from 0 to 100 W).

Characterization techniques

The contact or wetting angle tests were performed on air-facing surfaces of samples using the sessile drop method^{19,20} at room temperature in an OCA 20 contact angle measurement unit from Dataphysics. Nine measurements on different points were performed on each sample (three distinct films for each treatment conditions) from which the mean static contact angle and its standard deviation were determined. In the study of the different parameter of the plasma activation, the measurement of water contact angle was performed immediately after the treatment.

X-ray photoelectron spectroscopy (XPS) measurements were performed on a VGS ESCALAB 200A spectrometer with an Al K α X-ray source. The operation conditions were set to 15 kV. The binding energy scale was fixed by assigning a binding energy of 285.0 eV to the $-\text{CH}_2-$ carbon (1s) peak. The samples were analyzed at a take-off angle of 0° relative to the normal of the surface. The C1s, O1s, and N1s envelopes were analyzed and peak-fitted using a combination of Gaussian and Lorentzian peak shapes obtained from the XPSPEAK 4.1 software.

Atomic force microscopy (AFM) was performed in a Nanoscope IVa Veeco Metrology using the tapping mode (scan size 4.0 μm and scan rate 1.0 Hz). The average roughness (R_a) was calculated directly from the AFM images.

RESULTS AND DISCUSSION

Influence of the plasma parameters on the surface hydrophilicity

To modify the surface of the studied TPU without affecting its bulk properties, a low-pressure plasma treatment was performed. In the following figures (Figs. 1–3), the zero time, pressure, or power are related with the untreated TPU.

To evaluate the variations of argon (Ar) and oxygen (O₂) plasma treatment with time, the pressure in the chamber and the power were kept constant. Figure 1 shows the results obtained for water contact

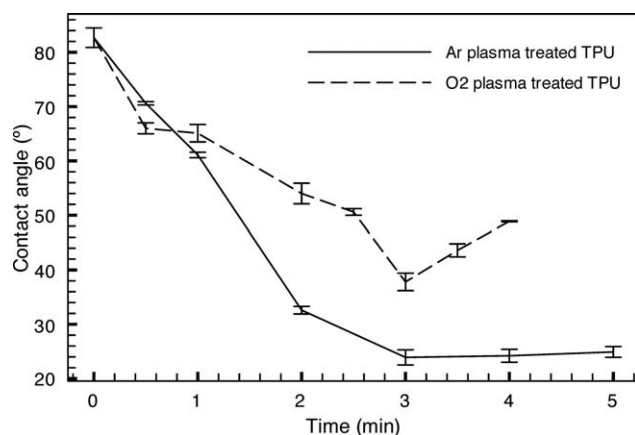


Figure 1 Contact angle variation along different processing times for a constant chamber pressure of 60 Pa and power of 100 W. The 0 min point is related to the untreated TPU surface.

angle determinations. When Ar was used, the water contact angle significantly decreases along the time from 61.1° (after 1 min) to 32.6° (after 2 min). After 3 min of plasma treatment, water contact angle reaches a constant value of about 24° . When O_2 was used, the behavior was much more irregular, and a minimum value of water contact angle was obtained for 3 min of processing time. After this time, the water contact angle starts to increase probably due to the etching effect of the plasma treatment.²¹

The results presented in Figure 2 show the influence of operational pressure inside the chamber, with a constant power of 100 W and the processing time of 3 min. Water contact angle significantly decreases from the result obtained for the unmodified film to when a chamber pressure of 40 Pa was employed. The minimal value is obtained for a chamber pressure of 60 Pa and then, for higher

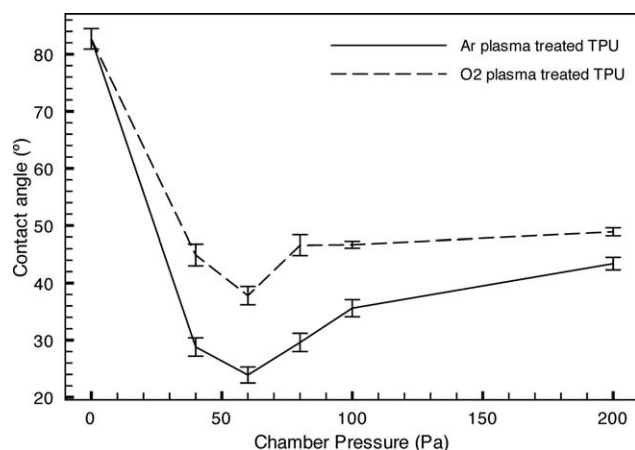


Figure 2 Contact angle variation with different pressure inside the chamber for a constant power of 100 W and processing time of 3 min. The 0 Pa point is related to the untreated TPU surface.

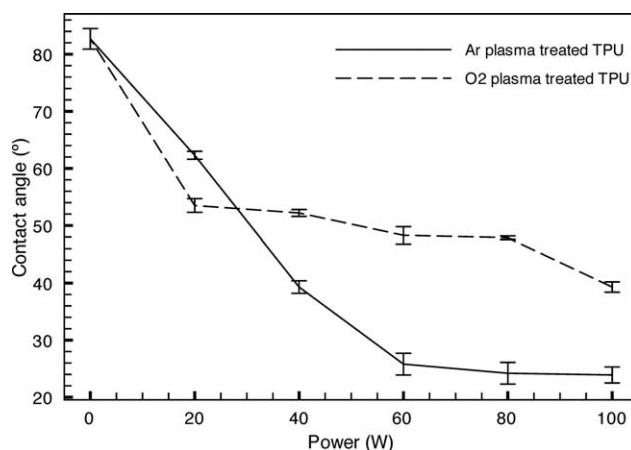


Figure 3 Variation of the water contact angle along different power of plasma, with constant processing time of 3 min and chamber pressure of 60 Pa.

chamber pressure values, the water contact angle starts to increase. This effect could be probably due to not only etching,²¹ but also the fact that the plasma state can only be achieved at low pressures from about 1 to 100 Pa, which could reduced plasma activity at the surface. Once again, when Ar is used as the working gas, the decrease in the water contact angle is more significant.

In another experiment, the power employed in the plasma treatment was evaluated. The chamber pressure (60 Pa) and the time of reaction (3 min) were kept constant. The results shown in Figure 3 show the obtained water contact angle results. These results suggest that water contact angle decreases with the increasing of the power input, because higher power leads to higher ionization of atoms and molecules that induce surface modification of the films.²¹ When Ar is used, the contact angle decreases from 82.7° down to 23.9° , at a power input from 0 W to 100 W, respectively. When O_2 was used, the water contact angle decreases from 82.7° down to 37.8° . Therefore, from all the obtained results, hydrophilicity increased when the working conditions for the TPU surface activation are: 100 W gas plasma, under a chamber pressure of 60 Pa, for 3 min, for both working gases (Ar and O_2). However, Ar seems to be more efficient than O_2 because lower water contact angle results are always obtained at the same conditions.

The results presented in Figure 4 show the variation in contact angle after the plasma treatment (at a power of 100 W and a pressure of 60 Pa for 3 min) with the two different gases: oxygen (O_2) and argon (Ar).

Hydrophilicity was highly improved in both cases. The water contact angle decreased from 82.7° in the untreated TPU to 37.8° and 23.9° after treatment with O_2 and Ar, respectively. As stated by several authors,^{12,21–23} different gases used in the plasma

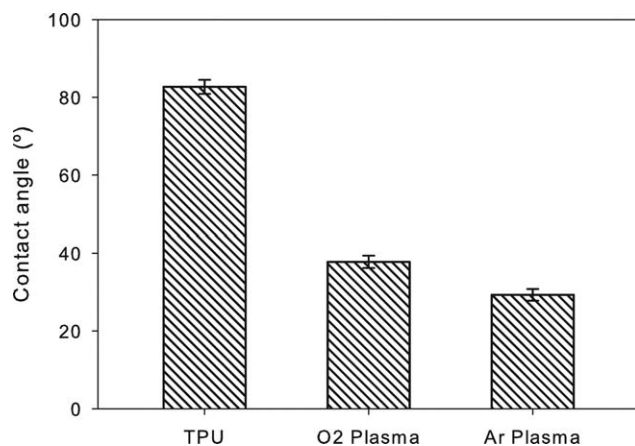


Figure 4 Variations of the contact angle of the untreated TPU and of the plasma-treated TPU with the different working gases, under a chamber pressure of 60 Pa and 100 W power, for 3 min.

treatment can modify the surface of polymeric materials by forming different active groups, according to the working gas used. Thus, oxygen plasma might induce the formation of C=O and OH groups on the surface. On the other hand, when inert gases like argon are used, plasma treatment cannot, by itself introduce functional groups on the polymer surface. It has been predicted that noble gases such as Ar can be used to generate free radicals at the polymer surface, by breaking C–C or C–H bonds in the polymer substrate. Subsequent exposure of Ar-treated samples to air may also result in formation of new functional groups, as the reactive radical species combine with oxygen and other components present in the atmosphere. For the studied TPU, as shown in Figure 4, better hydrophilicity was obtained when Ar was used as working gas. This could be due to the fact that in the plasma process, radicals will be first created by hydrogen abstraction from polymer chains, then, polymer radicals will combine with

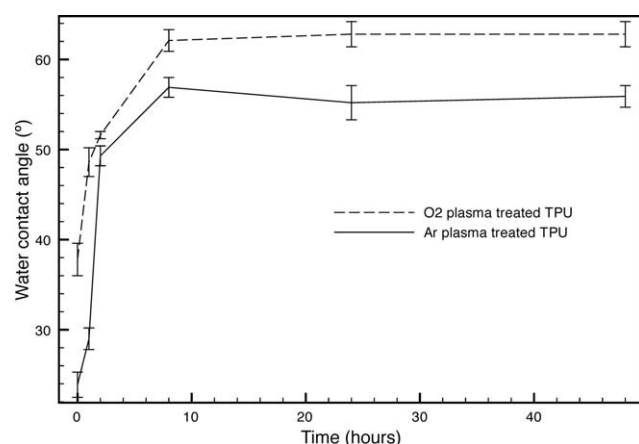


Figure 5 Water contact angle of the Ar plasma-activated surface and O₂ plasma-activated surface along time (plasma treatment conditions: 60 Pa and 100 W, for 3 min).

radicals created from the gas used to form functional groups. When oxygen is used, oxygen radicals are created and oxygen functionalities, such as hydroxyl, carbonyl, or carboxyl groups, are obtained in the plasma treatment process. When argon is used as the working gas, no gas radicals are formed once argon is a noble gas, thus it can only create polymer radicals. However, few oxygen functionalities might be found in Ar-treated surfaces due to water molecules absorbed at the surface of the reaction chamber wall. Water will be evaporated and fragmented onto hydroxyl, oxygen, and hydrogen radicals by plasma irradiation, and these radicals will react with the film to create oxygen functionalities. Still, this assumption does not exclude the postreactions of radicals with air after finishing the plasma treatment.

It is known that plasma-treated surfaces are not stable along the time.²³ A process named “hydrophobic recovery” occurs, meaning that the original hydrophobic polymer surface is partially recovered. Thus, to evaluate this phenomenon, water contact angle was measured for several days. Figure 5 shows the obtained results for the Ar plasma-activated surface and the O₂ plasma-activated surface. The starting point, at 0 h, represents the value of the water contact angle directly after plasma treatment (0 h = 37.8° and 23.9° for O₂ and Ar). It can be observed that in both cases, the plasma-treated surface partially recovered its hydrophobicity along time. However, when O₂ was used as working gas, the recovery of hydrophobicity is more significant than when Ar was used. Water contact angle increased mainly in the first 8 h. This can be explained by air contamination or even by surface rearrangements.^{23–25} These phenomena can decrease the active sites induced to the surface by the plasma, and therefore, the water contact angle increases.

Chemical analysis of the TPU surface after plasma treatment

Widescan and high-resolution XPS spectra were recorded for the TPU materials to determine the existing functionality present in the surface and to show any subsequent changes in surface introduced by each gas treatment.

TABLE I
Surface Elemental Composition Determined from XPS

	Atomic percentage (%)			Atomic ratio	
	C1s	N1s	O1s	O1s/C1s	N1s/O1s
Untreated TPU	75.56	2.93	21.41	0.28	0.14
Ar activated	67.26	3.09	29.48	0.44	0.10
O ₂ activated	65.10	2.74	31.92	0.49	0.09

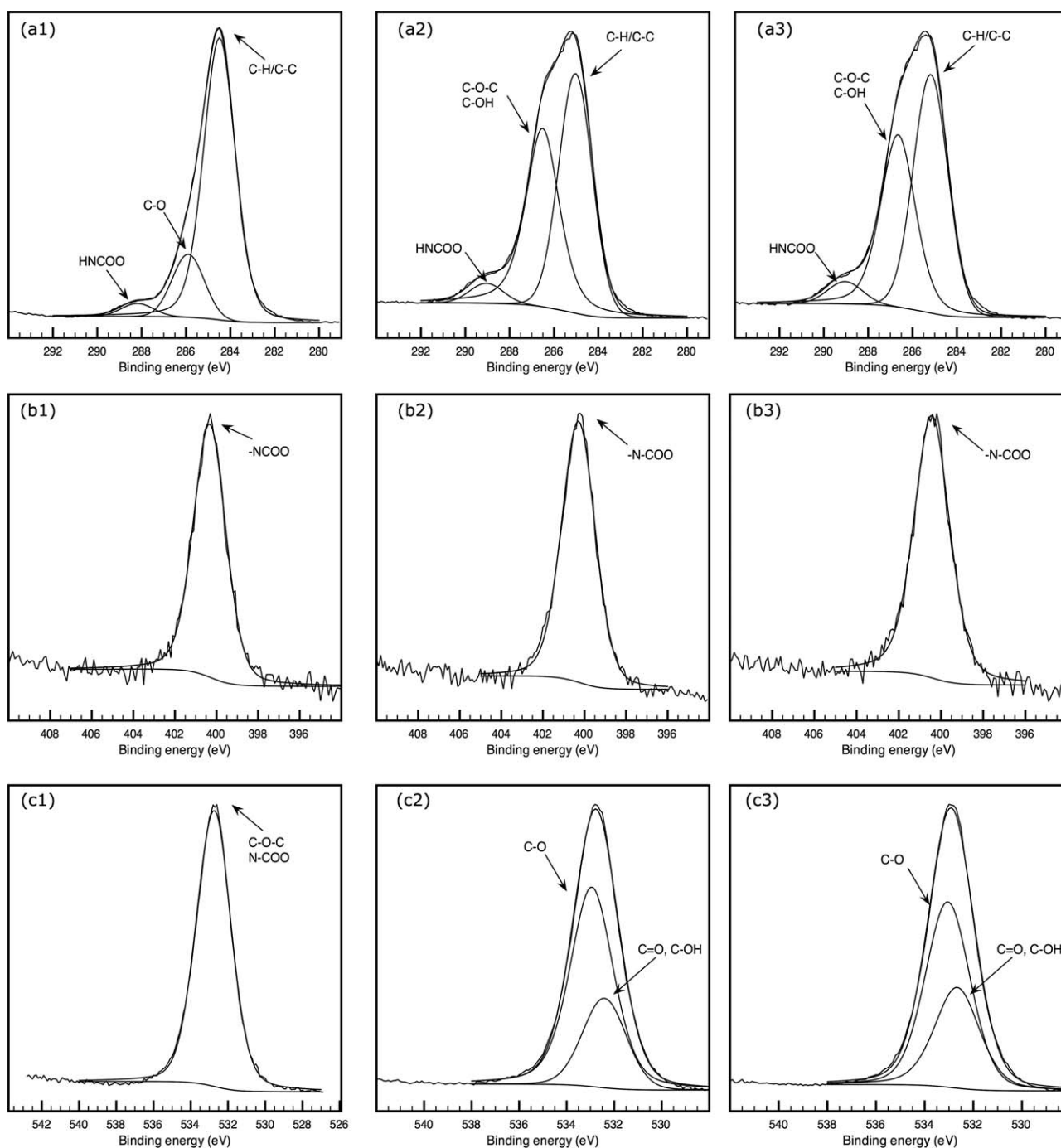


Figure 6 XPS spectra of (a) C1s, (b) N1s, and (c) O1s for the untreated TPU (1), the Ar activated (2), and the O₂ activated (3) surfaces (plasma treatment conditions: 60 Pa and 100 W, for 3 min).

Table I summarizes the atomic percentage of the elements present on these surfaces, measured by XPS. The elemental composition of the surfaces was calculated from the XPS spectra.

Figure 6 shows the different spectra obtained for the unmodified and the activated TPU. Their relative composition ratio based on the area is shown in Table II.

The C1s peak can be resolved in three components: the hydrocarbon peak (C=C and C=H) at 284.49 eV, the ether peak (C—O—C) at 285.90 eV, and the ure-

thane peak (NH—COO) at 288.19 eV. The latter two oxidative functionalities are an integral part of the repeat unit for soft and hard segments, respectively.²¹

In general terms, the effects of Ar and O₂ plasma activation on the surface of this TPU can be due to the decrease of the C1s and N1s with respect to the O1s signal, resulting from the incorporation of oxygen-containing groups.

After Ar plasma activation of the TPU surface, some changes on the symmetry of the C1s signal,

TABLE II
Binding Energy and Relative Composition Ratio Based on the Area (Data in Parenthesis) of each Peak for the Untreated TPU Surface, Ar Plasma-Activated Surface, and O₂ Plasma-Activated Surface

		Untreated TPU	Ar activated	O ₂ activated
C1s	HNCOO	2442.85 (3.4%)	3869.17 (4.1%)	3793.45 (4.8%)
	C—O—C/C—OH	11822.75 (16.3%)	42500.44 (45.5%)	33685.82 (42.8%)
	C—H/C—C	58415.52 (80.4%)	47114.21 (50.4%)	41186.90 (52.4%)
N1s	—NCOO	11552.81 (100.0%)	14801.21 (100.0%)	12572.56 (100.0%)
O1s	C—O/N—COO	67868.87 (100.0%)	88057.82 (71.5%)	74122.18 (63.5%)
	C=O/C—OH	—	35169.40 (28.5%)	42602.62 (36.5%)

shown in Figure 6(a2) can also be seen. These changes are very similar to those observed for the oxygen plasma, shown in Figure 6(a3). They include an increase of the component at 286.5 eV due to possible C—OH bonds.²⁶ However, this binding energy is indistinguishable from the ether functionality and cannot be separated, so, the increase of this peak suggests the surface enrichment with polyether soft segments, also confirmed by the results in Table II.

Changes in the O1s signal [Fig. 6(c2)] also fit this explanation, explaining the presence of the OH groups on the surface of the TPU after treatment. For the oxygen plasma treatment, a more significant increase in the intensity of the O1s signal relative to the untreated surface can be seen in Table I due to the immediate grafting of OH groups to the surface of the material in the plasma chamber. However, from Table II, a higher increase of the C—O peak is obtained for the argon plasma treatment. This might be due to the ability of the argon plasma to generate radicals, and also the reason for the achievement of lower water contact angles with this gas.

The intense peak shown in Figure 6(b) is attributed to the nitrogen (—NH—) present in urethane links (RNHCOOR'). This peak slightly increases after the treatment with both gases, which represent changes in the concentration of hard segment at the surface region compared with the untreated material, because the nitrogen-containing functionality is only present in the hard urethane blocks of the studied TPU.²⁷ Concomitantly, the N/O ratio decreases.

Atomic force microscopy

Surface topography was evaluated by AFM analysis. Figure 7 shows the three-dimensional AFM images of untreated TPU, and plasma-activated TPU with argon and oxygen. The plasma treatment changes the topography of the material leading to slightly smoother surfaces. To quantify this event, the roughness of each surface was evaluated. The average roughness (R_a) was calculated directly from the AFM images. It was determined in a 700×700 nm surface region. The results shown in Table III confirm the conclusion observed on the micrographs in Figure 7. These results also suggest that, for this material, the topography is not significantly compromised by either plasma treatment. Thus, the material surface was only activated, because an increase in surface roughness caused by plasma treatment demonstrates the existence of the surface etching process,²⁵ and that was not observed for the conditions selected for the plasma treatment for both gases.

CONCLUSIONS

The surface of Elastollan[®]1180A50 was modified by plasma treatment. For all the treated surfaces, the surface polar character was increased, and consequently, the wettability also increases. To activate the surface of this material, argon plasma activation seemed to be more efficient than oxygen plasma activation, because argon plasma activation led to a lower water

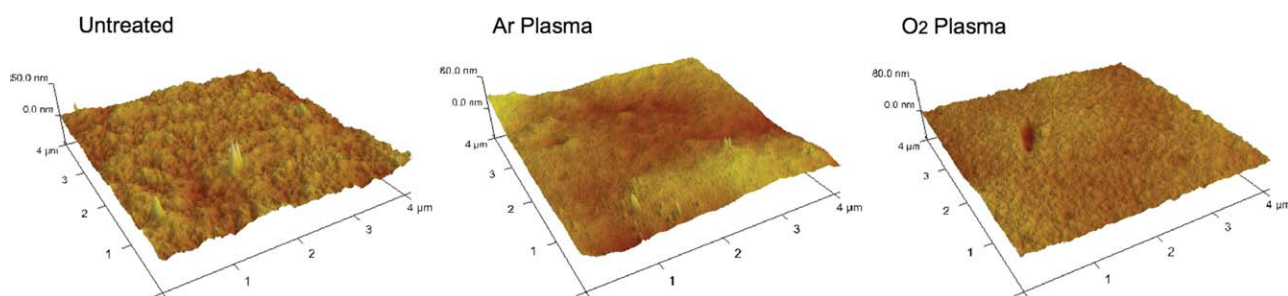


Figure 7 Atomic force micrographs of the untreated TPU surface, Ar plasma-activated surface, and O₂ plasma-activated surface. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

TABLE III
Surface Roughness, R_a (nm), of the Untreated TPU Surface, Ar Plasma-Activated Surface, and O₂ Plasma-Activated Surface

	R_a (nm)
Untreated TPU	2.57 ± 0.31
Ar activated	1.70 ± 0.19
O ₂ activated	1.82 ± 0.13

contact angle. Optimal plasma operational conditions were investigated. It was found that the best conditions were: 100 W argon plasma, under a vacuum of 60 Pa, and for 3 min.

Plasma-treated surface tends to partially (or totally) recover its hydrophobicity along time. However, when O₂ was used as the working gas, the recovery of hydrophobicity was more significant than when Ar was used. Surface hydrophobicity recovery can be explained by air contamination or even by surface rearrangements.^{23–25} These phenomena can decrease the active sites induced to the surface by the plasma, and therefore, the water contact angle increases. To overcome hydrophobicity recovery, the surface should be immediately grafted with a vinyl monomer or a polyfunctional polymer. This would allow the surface to maintain the hydrophilicity and at the same time improve the free functional groups available at its surface.^{28,29}

XPS spectra showed that the plasma treatment was successful in the formation of surface species that could not be seen in the untreated material, for example the increase of the O1s peak due to the appearance of the C—OH functionalities for both Ar and O₂ treatments. AFM analysis also demonstrated the activation of the surface for the selected plasma treatment conditions, for both gases studied, and that no etching process occurred because surface roughness did not increased significantly.²⁵

The present study was supported by the European Commission through the specific targeted research project CellForce of the 6th FP (Contract No. NMP4-CT-2005-016626).

References

- Xu, H.; Kaar, J. L.; Russel, A. J.; Wagner, W. R. *Biomaterials* 2006, 27, 3125.
- Horbett, T. J.; Brash, J. L. American Chem Society, Division of Colloid and Surface Chemistry, American Chem Society, Meeting, Washington, DC, 1995.
- Hylton, D. M.; Shalaby, S. W.; Latour, R. A. *J Biomed Mater Res* 2005, 73A, 349.
- Tamada, Y.; Ikada, Y. *J Colloid Interf Sci* 1993, 155, 334.
- Weightman, P.; Martin, D. S. In *Surfaces and Interfaces for Biomaterials*; Vadgama, P., Ed.; Woodhead Publishing Ltd: Queen Mary-University of London, UK, 2005; p 40.
- Volger, E. *Adv Colloid Interf* 1998, 74, 69.
- Arima, Y.; Iwata, H. *Biomaterials* 2007, 28, 3074.
- Tamada, Y.; Ikada, Y. *Polymer* 1993, 34, 2208.
- Takemoto, S.; Yamamoto, T.; Tsuru, K.; Hayakawa, S.; Osaka, A.; Takashima, S. *Biomaterials* 2004, 25, 3485.
- Poussard, L.; Burel, F.; Couvercelle, J. P.; Merhi, Y.; Tabrizian, M.; Bunel, C. *Biomaterials* 2004, 25, 3473.
- Krol, P. *Prog Mater Sci* 2007, 52, 915.
- Wang, J.-H.; Yao, C.-H.; Chuang, W.-Y.; Young, T.-H. *J Biomed Mater Res* 2000, 51, 761.
- Bajsic, E. G.; Smit, I.; Leskovic, M. *J Appl Polym Sci* 2007, 104, 3980.
- Su, C.-Y.; Lin, C.-K.; Lin, C.-R.; Lin, C.-H. *Surf Coat Technol* 2006, 200, 3380.
- Wang, X.; Luo, X.; Wang, X. *Polymer Test* 2005, 24, 18.
- Ozdemir, Y.; Hasirci, N. *J Mater Sci Mater Med* 2002, 13, 1147.
- Sanchis, M.; Calvo, O.; Fenollar, O.; Garcia, D.; Balart, R. *Polym Test* 2008, 27, 75.
- Molina, R.; Erra, P.; Julia, L.; Bertran, E. *Text Res J* 2003, 73, 955.
- Correia, N. T.; Ramos, J. J. M.; Saramago, B. J. V.; Calado, J. C. G. *J Colloid Interf Sci* 1997, 189, 361.
- Chibowski, E. *Adv Colloid Interf Sci* 2003, 103, 149.
- Inagaki, N. In *Plasma Surface Modification and Plasma Polymerization*; CRC Press; Technomic publishing Co., Inc.: USA, 1996.
- Wilson, D.; Rhodes, N.; Williams, R. *Biomaterials* 2003, 24, 5069.
- Lappan, U.; Buchhammer, H.-M.; Lunkwitz, K. *Polymer* 1999, 40, 4087.
- Wang, P.; Tan, K. L.; Ho, C. C.; Khew, M. C.; Kang, E. T. *Eur Polym Mater* 2000, 36, 1323.
- Qiu, Y. X.; Klee, D.; Plüster, W.; Severich, B.; Höcker, H. *J Appl Polym Sci* 1996, 62, 2373.
- Tieszer, C.; Reid, G.; Denstedt, J. *J Biomed Mater Res* 1998, 43, 321.
- Vargo, T.; Hook, D.; Gardella, J.; Eberhardt, M.; Baier, R. *Appl Spectrosc* 1991, 45, 448.
- Pinto, S.; Alves, P.; Matos, C. M.; Santos, A. C.; Rodrigues, L. R.; Teixeira, J. A.; Gil, M. H. *Colloids Surf B* 2010, 81, 20.
- Alves, P.; Pinto, S.; kaiser, J.-P.; Bruinink, A.; Sousa, H. C.; Gil, M. H. *Colloids Surf B* 2011, 82, 371.