Surface Characterization of Hydrophilic Coating Obtained by Low-Pressure CH$_4$—O$_2$ Plasma Treatment on a Polypropylene Film

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ABSTRACT: The use of surface treatments at industrial level is generalized as they allow obtaining a wide variety of properties such as soft in the touch, hydrophilic behavior, and biocompatibility. The use of low-pressure plasma techniques with organic gases or organic mixtures is an easy way to obtain surface coatings very small in depth through plasma-polymerization processes that can be assimilated to a plasma-enhanced chemical vapor deposition (PECVD) process. In this work, we have carried out a plasma-polymerization process on a polypropylene (PP) film to obtain a hydrophilic coating. To obtain this, the film surface has been treated on a low-pressure plasma reactor with a methane–oxygen mixture gas with a volume ratio of 80 : 20, respectively. The chemistry changes in the outermost layers of the deposited coating have been investigated with X-ray photoelectron spectroscopy (XPS). The different processes that take part as a consequence of the interaction between the plasma gas species and the PP film surface mainly drive to the deposition of an organic layer, which is functionalized with oxygen-based species as XPS study reveals. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 111: 2992–2997, 2009

Key words: coatings; cold plasma; ESCA/XPS; films; polyolefins

INTRODUCTION

In the last years, surface treatments have acquired a remarkable significance because they allow optimizing the external properties by modifying a small part of the material structure.[1,2] Many of these surface treatments are focused on the improvement of wettability, biocompatibility, adhesive properties, hydrophilic or hydrophobic properties, etc. for different technical and high-performance applications.[3–6]

Traditional coatings and surface treatments allow obtaining many of the aforementioned properties, but the increasing growth of nanotechnology offers new possibilities for surface finishing and coatings because it is possible to change the topmost layer properties without affecting the bulk material properties.[7–9] Low-pressure plasma techniques have been used to obtain surface coatings with different properties (wettability enhancement, biocompatibility, surface energy increase, etc.) through a plasma-polymerization process, which is similar to a plasma-enhanced chemical vapor deposition (PECVD).[10,11] The plasma-acting mechanisms depend on many factors but it is important to remark the nature of the gas used for the plasma generation; so that, the use of conventional gases such as oxygen, nitrogen, and argon drives to an increase in surface functionalization as the species present in the plasma gas promote chain scission and subsequent free radicals formation, which act as interlock points for polar groups[12]; furthermore, some surface abrasion occurs as a consequence of the chain scission and formation of low-molecular weight species that are easily removed, thus promoting surface topography changes.[13–15]

Nevertheless, when the gas used for the plasma formation is an organic gas or a gas mixture with some organic component, the plasma-acting mechanisms are completely different. When the plasma is formed after the glow discharge is generated, multiple reactions occur and these drive to the construction of polymeric structures with different nature depending on the gas and composition; these organic structures are deposited on the treated material surface, and thus allowing the formation of a coating very small in depth with specific properties.[16]

Depending of the organic gas type and/or mixture composition, the plasma-polymerized coating will possesses specific properties such as hydrophility, hydrophobicity, and biocompatibility. There are many techniques to characterize surfaces but if we take into account that many of the surface treatments are carried out by plasma-polymerization processes with very small thickness (in the nanoscale range or even lower), a suitable technique to obtain useful and reliable information is X-ray photoelectron spectroscopy (XPS).[4]

The main aim of this work is to improve the wetting properties of a polypropylene (PP) film using a low-pressure plasma treatment. As the effects of low-pressure plasma treatments with conventional gases (such as oxygen, air, and argon) are not permanent, we have used a methane–oxygen mixture (with a 80 : 20 volume ratio) to promote plasma polymerization of a functionalized-organic layer to ensure both functionalization and durability. The overall effects of the plasma treatment have been followed by contact angle measurements and weight changes and the surface chemistry changes have been studied by XPS.

EXPERIMENTAL

Materials and sample preparation

The film used in this study was a transparent PP film supplied by Logoplast (Logoplast, S.L, Alicante, Spain) of 50 µm thickness. Samples of 20×20 cm^2 in size were prepared for the plasma treatment and then followed by a cleaning process in an acetone bath for 9 min and then dried in air prior to plasma treatment. After the plasma treatment, samples of different dimensions were cut for measurements.

Plasma surface treatment

PP films were exposed to radio frequency (RF) low-pressure glow discharge plasma with a methane–oxygen mixture gas. It was used a glow discharge RF generator (operating at 13.56 MHz) type CD 400 MC option PC (Europlasma, Oudenaarde, Belgium). The plasma chamber consisted of four aluminum shelves for sample holders and a total volume of 64 l. The gas used for the plasma generation was a mixture of CH_4–O_2 with a volume ratio of 80 : 20. It was used a gas flow rate of 100 cm^3 min^{-1} and the working pressure varied in the range of 31–32 Pa. The working power was fixed to 150 W.

Surface wettability and weight changes characterization

Changes in surface wettability were determined by contact angle measurements. Static contact angle of the plasma-treated samples were measured at room

TABLE I
Variation of Static Contact Angle Values and Weight on Polypropylene Film with Different Exposure Times to Low-Pressure CH_4–O_2 Plasma

Exposure time (s)	Contact angle		Δ weight·cm^{-2} (µg $\times$ cm^{-2})
	θ	Standard deviation	
0	99.3	1.5	–
15	76.3	1.6	61
30	74.5	1.1	154
60	51.5	0.7	245
120	47.8	1.2	380

temperature on a KSV CAM 200 goniometer (KSV Instruments, Helsinki, Finland) using double distilled water as test liquid. At least six different measurements were obtained on the plasma-treated surfaces, and the average values for contact angles were calculated. The maximum error in the contact angle measurement did not exceed ±3%.

Weight changes because of plasma modification were determined using a Mettler-Toledo AL-104 balance (Mettler-Toledo, Schwerzenbach, Switzerland). The films were weighed before and after exposure to plasma, and an average of five readings was taken for each sample.

XPS surface analysis

The XPS spectra were obtained with a VG-Microtech Multilab (Thermo Fisher Scientific, Waltham, MA) electron spectrometer, by using the Mg Kα (1253.6 eV) radiation of a twin anode X-ray tube operating at 15 kV and 20 mA, respectively, working in constant analyzer energy mode with a pass energy of 50 eV. Pressure of the analysis chamber was maintained at 5×10^{-8} Pa. The binding energy (BE) scale was regulated by setting the C1s transition at 285.0 eV. The accuracy of BE values was ±0.4 eV. BE values were obtained using the Peak-fit program installed in the XPS spectrometer control software. The baseline used for peak fitting was the Shirley type and all peaks were fitted with Lorentzian-Gaussian (30–70%, respectively) lineshapes.

RESULTS AND DISCUSSION

Effects of low-pressure CH_4–O_2 plasma on PP substrate

The most important effect of the low-pressure plasma with CH_4–O_2 mixture gas is a remarkable improvement on wettability and consequently hydrophilic properties of the PP film. This situation can be observed in Table I, which shows static contact angle values of the PP surface in terms of the exposure time to low-pressure plasma. The decrease in contact

angle is directly related to a wettability improvement. We can observe a remarkable decrease from values close to 100° for the untreated material up to 50° for the plasma-treated material for 60 s. It is important to note that higher exposure times do not lead to a significant increase in wetting properties, since contact angles remain in the 48°–50° range.

In a first approach, similar effects are obtained with the use of conventional gases such as oxygen or nitrogen, so we could think that the plasma-acting mechanisms are similar; nevertheless, the real situation is clearly different. When using gases such as oxygen or nitrogen, the main plasma-acting mechanism is surface functionalization by insertion of polar groups. Together with this mechanism, some etching occurs and this leads to slight changes in surface topography.[17,18] On the other hand, the presence of an organic component in the mixture (methane) drives to a polymer synthesis process on the PP surface through a plasma-polymerization process or PECVD. Additionally, the presence of a highly reactive gas (oxygen) in the plasma mixture gas leads to surface functionalization by inserting polar groups in the plasma-polymerized layer. Some previous works have demonstrated that the use of methane plasmas leads to a PECVD of organic layers very small in depth (in the nanoscale range or even lower).[19–22] The effects of this deposition process can be observed in Table I, which shows weight variation in terms of the exposure time to low-pressure plasma. Although the plasma processes and reactions are very complex and difficult to analyze, abrasion and deposition occur simultaneously but when using a mixture gas (CH_4–O_2), the neat effect is a mass deposition of an organic layer that leads to a neat weight. It is important to note that the semicrystalline nature of PP could lead to a selective abrasion process as crystalline zones are less sensitive to plasma abrasion than amorphous zones, but in this case, the absence of any etching pattern is indicative that very small abrasion occurs so the neat effect is deposition, which is confirmed by the weight increase.[23]

XPS characterization of polypropylene surface

XPS represents an important tool to evaluate changes in the surface chemistry (in the outer most layers) obtained by the plasma treatment with CH_4–O_2 mixture gas. As we have observed earlier, a remarkable increase in surface wettability is obtained with the plasma treatment with 60-s exposure time by decreasing contact angles from 100° up to 50° (or lower).

XPS results confirm the formation of an oxygen-functionalized nanolayer. Figure 1 shows in a comparative way the low-resolution (survey scans) XPS spectra for PP film with different exposure times to
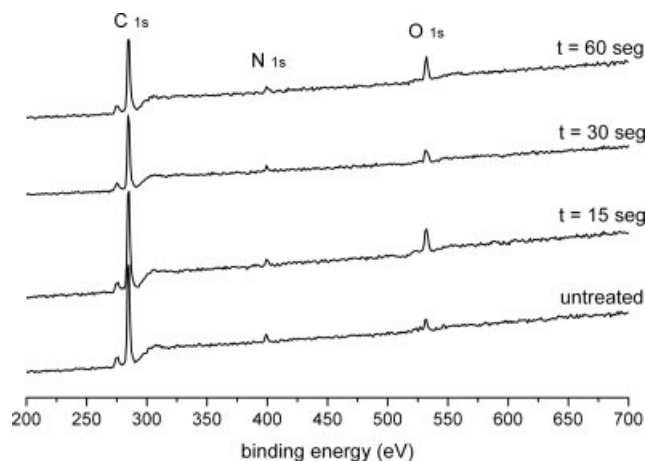

Figure 1 Low resolution (survey scans) of polypropylene film with different exposure times to low-pressure CH_4–O_2 plasma.

low-pressure CH_4–O_2 plasma. We can clearly observe the presence of the peak corresponding to carbon (C 1s at a BE of 285 eV), oxygen (O 1s at a BE of 533 eV), and nitrogen (at a BE of 399 eV).

If we observe the XPS spectrum for the untreated substrate, we can clearly distinguish the contribution of the carbon (C 1s) and small contributions of oxygen (O 1s) and nitrogen (N 1s). As the exposure time to low-pressure CH_4–O_2 plasma increases, the peak corresponding to oxygen (O 1s) increases considerably, whereas the nitrogen contribution (N 1s) remains almost constant. The presence of nitrogen could be attributable to the presence of some additives because we are working with a commercial grade for technological applications, but as we have described, nitrogen does not take part in the functionalization process and the total amount of atomic nitrogen does not change.

Changes in chemical composition of surface are representative of the functionalization process achieved with the plasma treatment (Fig. 2). We can see an increasing tendency regarding the oxygen content, from values close to 4.0% for the untreated substrate (as a consequence of some surface oxidation or presence of adsorbed species or additives) up to values close to 11.1% for 60-s exposure time; for 15-s exposure time to plasma, the oxygen atomic content is higher than the 30 s exposed sample and this situation could be due to the consequence of the measurement error and some heterogeneity in sample functionalization. We can also observe that nitrogen surface content remains almost constant with values around 3.8% for both untreated and plasma-treated samples susbtrates. These results show that the deposited plasma-polymerized organic nanolayer is functionalized with oxygen-based species because of the presence of oxygen in the mixture gas for the plasma generation.[22,24] Nevertheless, the real
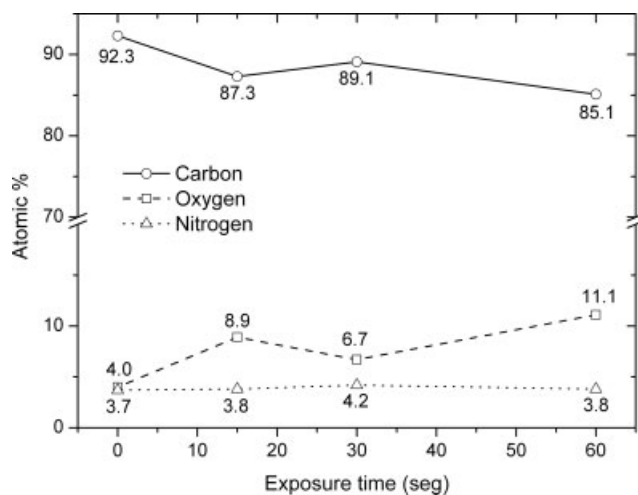
Figure 2 Plot of the evolution of the polypropylene film surface composition in terms of the exposure time to low-pressure CH_4—O_2 plasma.

oxidation level of the outermost layers must be expressed not only in terms of the oxygen atomic percentage (%) but also through the use of the O/C ratio, which is much representative of the oxidation state of the plasma-polymerized layer.

The O/C ratio for the untreated material is about 0.04 and this value is considerably increased up to values close to 0.13, which indicates high oxidation levels while the N/C ratio remains almost constant, thus indicating that nitrogen does not takes part in a significant way in the plasma polymerization–functionalization process.

As we can observe in Figure 3(a,b), the high-resolution spectrum corresponding to N 1s can be resolved in two contributions: a first peak $[N_I]$ (which represents the main contribution around 80–90% for all samples) with a BE of 399.7 eV can be assigned to species with a nitrogen atom single-bonded to carbon or hydrogen atoms; the second contribution $[N_{II}]$ (smaller than the first one) with a BE of 401.4 eV can be attributed oxidized nitrogen.[25–27] Despite this analysis, we must remark that we do not observe important changes for these contributions in all samples (untreated and plasma-treated for different exposure times). As we have described previously, the nitrogen surface content remains almost constant and the total atomic nitrogen amount is independent of the exposure time to low-pressure CH_4—O_2 plasma. As we have seen, slight variations can be observed after the plasma exposure as a consequence of oxidation of some nitrogen atoms, but do not introduce remarkable changes in surface activity. It is important to notice that the vacuum conditions do not ensure total absence of nitrogen in the plasma chamber so that, some nitrogen atoms could participate in certain reactions and this could be responsible for the small changes in the peaks as observed.

The high-resolution spectrum corresponding to O 1s can be deconvoluted in two main contributions (Fig. 4): the first one $[O_I]$ with a BE close to 532.0 eV, which includes contributions like [—C=$\underline{O}$], [—C—$\underline{O}$—C] and the second peak, with higher BE, around 533.3 eV can be assigned to more polar species such as [—(C≡$\underline{O}$)—O—] and [—C—$\underline{O}$H].[27,28] Therefore, it is very difficult to quantify the presence and variation of each of these species because their peaks are overlapped, but as a general overview, we can observe an increase in oxidized species as the exposure time to low-pressure CH_4—O_2 plasma increases.

Figure 5 shows graphical deconvolution of the high-resolution spectra for the C 1s peak. The untreated film clearly shows a main contribution regarding [—$\underline{C}$—C—] y [—$\underline{C}H_2$—] species and a small contribution attributed to impurities and/or additives (oxygen and nitrogen-based species). As the exposure time to CH_4—O_2 plasma increases, etching and deposition (plasma polymerization) mechanisms occur simultaneously and consequently, the two processes compete, but the global effect is deposition of an
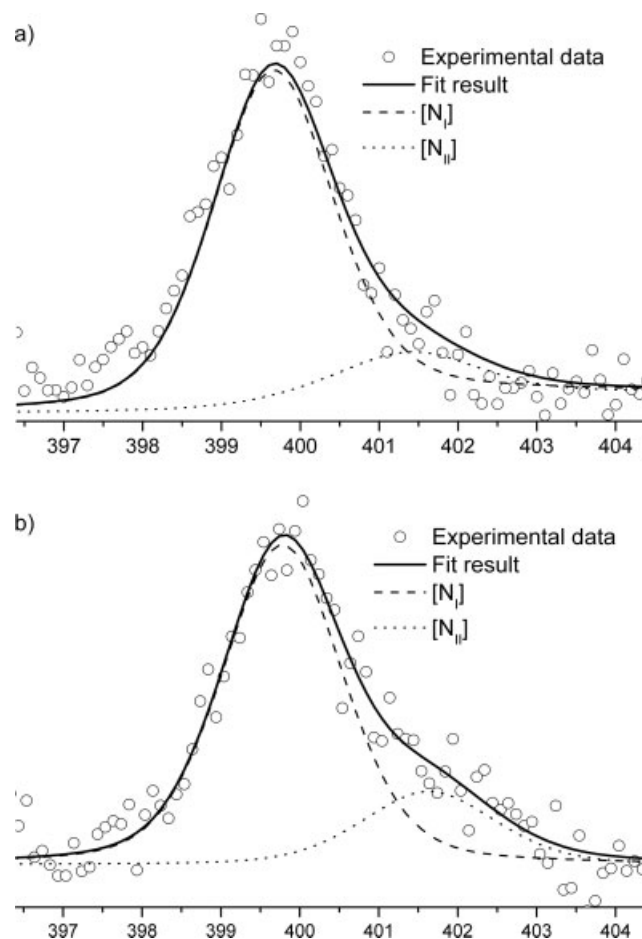

Figure 3 Deconvolution of the high-resolution spectra corresponding to N 1s peak for polypropylene surface: (a) untreated PP film and (b) plasma-treated PP film with 60-s exposure time.

Figure 4 Deconvolution of the high-resolution spectra corresponding to O 1s peak for polypropylene surface: (a) untreated PP film and (b) plasma-treated PP film with 60-s exposure time.
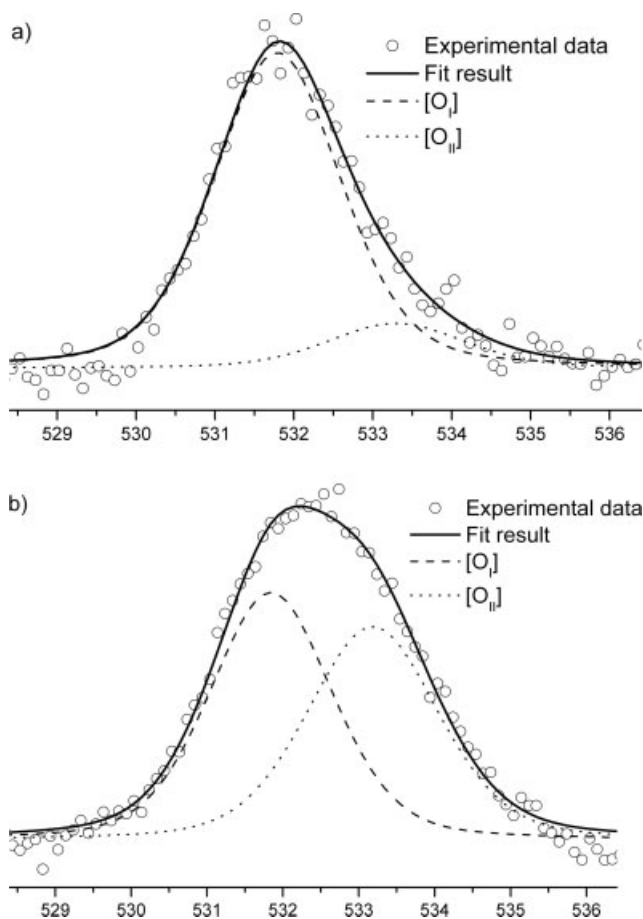
oxygen-functionalized organic layer.[29,30] This layer is functionalized with new oxygen-based functionalities as a consequence of the presence of O_2 in the mixture gas. For long exposure times (60 s), we can clearly observe the formation of great amounts of oxidized species: with single bonds (hydroxyl and ether) and double bonds (mainly aldehyde and ketone groups).

As we have seen, deconvolution of N 1s and O 1s peaks gives some qualitative information of the functionalization process, but the global effects of the plasma can be analyzed by observing the high-resolution spectra of the C 1s contribution. The C 1s peak can be resolved in three main contributions [Fig. 5(b)]; the BE values and geometry (FWHM-full width at half maximum) are summarized in Table II. The first peak [C_I] with a BE of 285.0 eV is assigned to [—C—C—] y [—CH$_2$—] species and, obviously, it represents the main contribution although the percentage decreases as the exposure time to CH$_4$—O$_2$ plasma increases because of the formation of oxidized species.[31,32]

We can also observe a second peak [C_{II}] with a BE of 286.4 eV that can be assigned to carbon atoms sin-

gle-bonded to oxygen atoms [—C—O]; but this peak also contains contribution of amine groups [—C—N] with a BE of 286.2 eV, which is very similar to that of the [—C—O] groups, so the contributions are overlapped; nevertheless, as we have seen previously, the global contribution of nitrogen remains constant and with very low values, so the deconvoluted peak would be very small and would not give significant information, so that it is included in the [C_{II}] contribution.

Also, we can observe a third contribution [C_{III}] with a BE slightly higher, around 288.1 eV that can be assigned to carbon atoms double-bonded to oxygen atoms [—C=O]; in a similar way, this peak would also contain the contribution of some oxidized nitrogen atoms with binding energies in the same range (close to 288.0 eV) but in this case, the contribution is even lower than amine groups, so it is preferable to include it in the carbonyl contribution.

We can clearly observe that as the exposure time to CH$_4$—O$_2$ plasma increases, the total amount of more
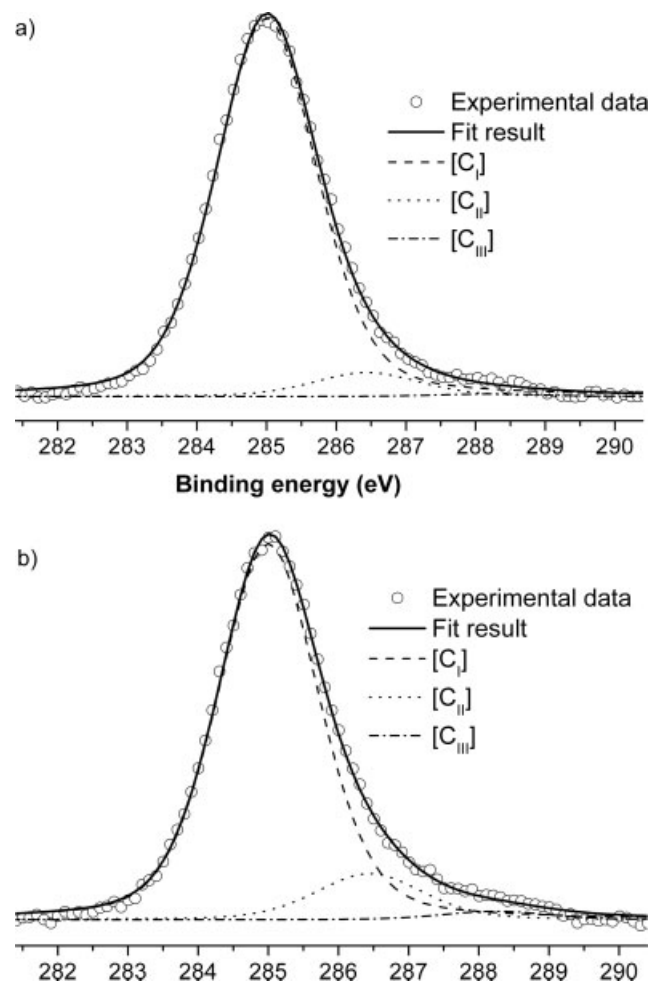

Figure 5 Deconvolution of the high-resolution spectra corresponding to C 1s peak for polypropylene surface: (a) untreated PP film and (b) plasma-treated PP film with 60-s exposure time.

TABLE II
Characteristics of the Deconvolution of C 1s Peak in Terms of the Exposure Time to Low-Pressure CH$_4$—O$_2$ Plasma Obtained by XPS Analysis

Exposure time (s)	[C$_I$] [—C—C—], [—CH$_2$—]			[C$_{II}$] [—C—O]			[C$_{III}$] [—C=O]		
	B.E. (eV)	FWHM (eV)	%	B.E. (eV)	FWHM (eV)	%	B.E. (eV)	FWHM (eV)	%
0	285.0	1.7	91.7	286.4	1.8	6.5	288.2	1.8	1.9
15	285.0	1.7	86.6	286.4	1.8	11.3	288.2	1.8	2.1
30	285.0	1.7	90.9	286.4	1.8	7.5	288.0	1.8	1.6
60	285.0	1.7	83.5	286.4	1.8	12.3	288.1	1.8	4.2

oxidized species increases. It is difficult to form carboxylic acids and esters with the use of these particular conditions because they require high oxidation levels that are difficult to reach with these particular plasma process conditions: plasma mixture gas, treatment power, and exposure times. If these species would have been formed, an additional contribution could be observed at 288.6 eV or higher.

CONCLUSIONS

As a general conclusion, we can say that low-pressure plasma with a CH$_4$—O$_2$ mixture gas in a 80 : 20 volume ratio is an appropriate process to obtain functionalized coatings on PP film surface, and thus increasing in a remarkable way the hydrophilic properties. The action of the plasma gas promotes etching and plasma polymerization but the neat effect is deposition of an organic layer with hydrophilic properties. The presence of an organic gas in the mixture gas promotes a PECVD or plasma polymerization; on the other hand, the presence of oxygen induces the formation of oxidized species that are interlocked in the deposited nanolayer, thus contributing to a remarkable increase in wettability.

XPS results reveal formation of an oxidized layer on PP substrate. Functionalization depends on the exposure time; the contact angle study reveals that the most appropriate exposure time is about 60 s by using a power of 150 W. As the exposure time increases, the oxidation ratio (O/C) ratio changes from 0.04 for the untreated material up to values close to 0.13, thus indicating a remarkable increase in surface functionalization that contributes to increase wetting properties.

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